

**Structure-Performance Relationships
in Ionic Liquid-Coated Supported Iridium Catalysts:
Effects of Metal Nuclearity, Support Type, and Ionic Liquid
Structure on Catalytic Performance**

by



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Abstract

This dissertation is a report of synthesis of ionic liquid (IL) coated atomically dispersed iridium species and iridium nanoparticles supported on various metal oxides, their characterization, and investigation of their structure-performance relationship at fundamental level.

Determination of the thermal stability limits of ILs immobilized on supports is important since in catalysis, ILs are used at high temperatures that may cause their degradation. Structurally different 33 imidazolium ILs were supported on SiO₂, γ -Al₂O₃, and MgO. Thermal stability tests indicate that as the bonding strength of the most acidic proton in the imidazolium ring ($\nu(\text{C2H})$, representing the interionic interaction energy of the ILs) increases, supported ILs becomes thermally more stable. Other systematic structural changes in the ILs also have a strong influence on the stability limits. Surface electron donor character of the supports probed by point of zero charge (PZC) values also influence the stability such that as the metal oxide becomes more electron-donor, the stability limits of supported ILs decrease. In the scope of understanding further the reasons behind the variations in stability limits of IL/support systems, interactions between one of the common used ILs, 1-*n*-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF₄]), and metal oxides, SiO₂, TiO₂, Fe₂O₃, ZnO, γ -Al₂O₃, CeO₂, MgO, and La₂O₃ covering a wide range of PZC from pH = 2 to 11 were elucidated. Infrared (IR) fingerprints of the IL and density functional theory (DFT) calculations were probed to understand the interactions and consequent short- and long-term thermal stability limits, and activation energy for decomposition calculations. Results indicate that PZC of metal oxides is one of the key factors influencing the direct interactions between ILs and supports. The elucidation of thermal stability limits creates opportunities for utilization of ILs in catalysis systems.

Controlling the catalytic performance of the active species can be achieved by regulating the electronic environment of the catalysts. The influence of the following variables on the electronic structure of supported iridium catalysts was investigated: the electron-donating/withdrawing properties of a) the supports and b) IL coating layers, and c) the metal nuclearity from single-site to several.

To investigate the support effect on catalysis, atomically dispersed $\text{Ir}(\text{CO})_2$ catalysts were synthesized by the reaction of $\text{Ir}(\text{CO})_2(\text{acac})$ (acac is acetylacetonato) with high-surface-area SiO_2 , TiO_2 , Fe_2O_3 , $\gamma\text{-Al}_2\text{O}_3$, CeO_2 , MgO , and La_2O_3 . The uncoated catalyst structures characterized by extended X-ray absorption fine structure (EXAFS) spectroscopy indicate that iridium species are site-isolated on each support, giving no Ir–Ir contribution, and are bonded to two carbon atoms of the carbonyl ligands and two oxygen atoms of the support. IR spectra confirm the presence of iridium *gem*-dicarbonyls. Electronic environment of the active sites were probed with X-ray absorption near edge structure at the Ir L_{III} edge and IR fingerprint of carbonyl ligands ($\nu(\text{CO})$). Results indicate that when the electron donor character of the metal oxide increases probed with a higher PZC, the Ir L_{III} edge energy and ($\nu(\text{CO})$) positions of the corresponding supported iridium complexes decrease, indicating that iridium sites become electron-rich. Furthermore, electron-rich iridium sites become more selective for partial hydrogenation of 1,3-butadiene, giving a strong correlation between the electron donor character of the support and selectivity for butenes of corresponding supported catalysts.

The influence of the ILs on the performance of the catalysts was investigated based on the structure of the ILs by coating the atomically dispersed supported iridium with imidazolium ILs. High-energy resolution fluorescence detection X-ray absorption near edge structure (HERFD XANES) at Ir L_{III} edge measurements quantify the electron donation to active sites upon IL coating, and are correlated with the $\nu(\text{C}_2\text{H})$ of the ILs. 1,3-butadiene hydrogenation tests of the IL-coated supported catalysts demonstrate the ligand effect of the

IL such that ILs electron donation from IL to active sites favor the partial hydrogenation with providing tunable selectivity for the production of *n*-butenes rather than butane.

Elucidation of the synergistic effects of supports and ILs as ligands is also one of the aims of this research since the behavior of each ligand would be different on the active sites. For this purpose, three ILs having different electron donating/withdrawing properties were coated on single-site iridium supported on SiO₂, TiO₂, Fe₂O₃, CeO₂, MgO, and La₂O₃. The results indicate that when the IL has electron withdrawing character probed by the interionic interactions of the ILs, the selectivity performance of the catalysts for partial hydrogenation decreases, and vice versa. The results also resolve the combined effects of the IL and support; for example, effect of the IL on the electronic environment and performance of the catalyst becomes dominant when the support has a weak electron-donor character.

The other design variable that may have an impact on the catalytic performance along with the support and IL effect is the metal nuclearity. To investigate it, atomically dispersed iridium species supported on SiO₂, γ -Al₂O₃, and MgO were converted to small iridium nanoparticles by treatment at 673 K in flowing H₂. High angle angular dark field scanning transmission electron microscopy (HAADF-STEM) demonstrated that the average nanoparticle size was approximately 1.2 nm on each support. Each sample was coated with ILs and tested as catalyst for partial hydrogenation of 1,3-butadiene. Results illustrate that the effect of IL coatings becomes dominant on iridium nanoparticles, whereas the electron donor character of the support is the major structural parameter controlling the catalytic performance when the active species were site-isolated.

The dependency on the performance of IL-coated supported nanoparticles were studied on the structural factors on ILs was investigated by considering the change in the size of anion/cation, the methylation on C2 site of the imidazolium ring, and the substitution of

alkyl groups on the imidazolium ring with various functional groups. Results demonstrated that selectivity and activity of the catalysts change as electron donating/withdrawing properties of the ILs change with a high dependency of the interionic interactions of the ILs.

The results presented in this research indicate that it is possible to have an ultimate control over tuning the performance of the catalysts by regulating the local electronic environment of the active sites by changing the metal nuclearity and support type and by coating the catalysts with IL layers with almost infinite number of combinations.



Özet

Bu tez çalışması, çeşitli metal oksitler üzerine desteklenmiş iyonik sıvı (İS) kaplı atomik dağılımlı iridyum aktif merkezlerinin ve iridyum nanoparçacıklarının sentezlenmesini, karakterizasyonunu ve temel düzeyde yapı-performans ilişkilerini araştıran bir rapordur.

Kataliz alanında iyonik sıvılar, yapılarında bozunmalara sebep olabilecek yüksek sıcaklıklarda maruz kaldıklarından, destek malzemeleri üzerine kaplanmış İS'lerin termal kararlılık limitlerinin belirlenmesi önemlidir. Yapısal olarak farklı 33 imidazolyum-türü İS, elektron verme özellikleri farklı olan yüksek yüzey alanına sahip SiO_2 , $\gamma\text{-Al}_2\text{O}_3$ ve MgO üzerine kaplanmıştır. Termal kararlılık testleri, imidazolyum halkasında bulunan en asidik bağın ($\nu(\text{C}_2\text{H})$), İS'lerin iyonları arası etkileşim enerjisini temsil eden bağ) kuvveti arttıkça, destekli İS'lerin termal dayanıklılıklarını arttığını göstermiştir. Ayrıca İS yapısındaki sistematik yapısal değişiklikler, kararlılık limitlerinde önemli etkiye sahiptir. Destek malzemelerinin sıfır yük noktası (SYN) ile belirlenen yüzey elektron verici özelliği kararlılığı etkilemektedir. Buna göre, metal oksitin elektron verici özelliği arttıkça, destekli İS'lerin kararlılık limitleri düşmektedir. İS'ler ile destek malzemeleri arasındaki etkileşimi incelemek ve bu etkileşimin termal dayanıklılığına etkisini araştırmak amacı ile yaygın olarak kullanılan iyonik sıvılardan biri olan 1-*n*-butil-3-metilimidazolyum tetrafloroborat ([BMIM][BF₄]) İS'si, sıfır yük noktası pH=2'den 11'e kadar değişen meal oksitler üzerine (SiO_2 , TiO_2 , Fe_2O_3 , ZnO , $\gamma\text{-Al}_2\text{O}_3$, CeO_2 , MgO ve La_2O_3) kaplanmıştır. İS ile destek malzemeleri arasındaki etkileşimlerin belirlenmesinde, destek malzemesine bağlı olarak İS'nin kızılötesi band pozisyonlarındaki değişimler ve yoğunluk fonksiyon teorisi (DFT hesaplamaları kullanılmıştır. Sonuçlara göre, metal oksitlerin SYN'si İS ile etkileşimleri belirlemede önemli rol oynamaktadır. İS/deste malzemesi sistemlerinde termal dayanıklılık limitlerinin belirlenmesi, İS'erin katalizör sistemlerinde kullanım alanlarının artmasını sağlamaktadır.

Katalizörlerin performanslarını kontrol edebilmek için aktif metal merkezlerinin elektronik yapılarının düzenlenmesi gerekmektedir. Bu sebeple bu araştırmada destekli iridyum katalizörlerinin elektronik yapısında etkiye sahip değişkenler araştırılmıştır. Bu etkenler: a) aktif metal merkezlerinin boyutu b) destek malzemelerinin ve c) İS kaplamalarının tabakalarının elektron verme/çekme özellikleridir.

Destek malzemelerinin katalizör üzerindeki etkisini araştırmak amacıyla, yüksek yüzey alanına sahip SiO_2 , TiO_2 , Fe_2O_3 , $\gamma\text{-Al}_2\text{O}_3$, CeO_2 , MgO , and La_2O_3 destek malzemelerinin, $\text{Ir}(\text{CO})_2(\text{acac})$ (acac: asetilasetonat) ile reaksiyonu sonucunda atomik dağılımlı destekli $\text{Ir}(\text{CO})_2$ katalizörleri sentezlenmiştir. İS kaplanmamış katalizörlerin X-ray absorpsiyon ince yapı spektroskopisi (EXAFS) karakterizasyon sonuçları, iridyum atomlarının destek malzemesi üzerinde bölgesel olarak izole olduklarını, diğer iridyum atomlarıyla bağlanmayıp herhangi bir Ir-Ir bağı olmadığını ve her bir iridyum atomunun karbonil ligandlarının iki karbon atomu ve destek malzemesinin 2 oksijen atomuna bağlı olduğunu göstermektedir. Kızılötesi spektrum sonuçları atomik dağılımlı iridyum *gem*-karbonillerin varlığını doğrulamaktadır. Aktif merkezlerin elektronik yapıları, Ir L_{III} eşik (edge) enerjisinde X-ray absorpsiyon yakın kenar yapısı (XANES) ve karbonil ligandlarının kızılötesi bandları ($\nu(\text{CO})$) ile araştırılmıştır. Sonuçlar, metal oksitlerin SYN'si ile ölçülen elektron verici özelliklerinin artmasıyla, iridyum komplekslerinin L_{III} eşik enerjilerinin ve ($\nu(\text{CO})$) pozisyonlarının düştüğünü, bu durumda iridyum aktif merkezlerinin elektronca zengin hale geldiğini göstermektedir. Bunlara ek olarak, elektronca zengin iridyum merkezleri, 1,3-bütadien kısmi hidrojenasyon reaksiyonları için daha seçici olmaktadır. Ayrıca bütünler olan seçicilik ile destek malzemesinin elektron verme özellikleri arasında güçlü bir korelasyon gözlemlenmiştir.

İS'lerin katalizörlerin performansları üzerindeki etkisini anlamak amacıyla, atomik dağılımlı destekli iridyumlar imidazolyum İS'leri kaplanarak yapısal olarak incelenmiştir.

Yüksek enerji çözünürlüklü flüoresans tayin X-ray absorpsiyon yakın kenar yapı (HERFD XANES) Ir L_{III} eşi enerjisi iyonik sıvı kaplama durumundan aktif merkezlere olan elektron verme durumunu kantitatif olarak ölçmektedir. Sonuçlara göre, İS'lerin $\nu(\text{C}_2\text{H})$ bandları ile İS-kaplı destekli iridyumların eşik enerjisi arasında güçlü bir korelasyon bulunmaktadır. İS kaplı destekli katalizörlerin 1,3-butadien hidrojenasyon testleri, İS'lerin ligand etkilerini kanıtlamaktadır. Buna göre İS'lerden aktif merkezlere olan elektron aktarımı sayesinde iridyum aktif merkezleri kısmi hidrojenasyonu tercih etmekte ve bütünler olan seçicilik artmaktadır.

Destek malzemelerinin ve iyonik sıvıların ligand özelliklerinin sinerjistik etkisini araştırmak da her bir ligandın aktif merkezlere etkisi farklı olacağından ötürü önemlidir. Bu amaçla, elektron verme/alma eğilimi farklı olan üç farklı İS, SiO₂, TiO₂, Fe₂O₃, CeO₂, MgO, ve La₂O₃ destekli tek atomlu iridyumlar üzerine kaplanmıştır. Sonuçlara göre, destek malzemesinin elektron verme özelliği arttıkça, İS'lerin katalizörün performansına olan etkisi azalmaktadır. Bununla birlikte İS'nin etkisi, daha az elektron verme özelliğine metal oksit ile destekli olan katalizörlerde daha fazladır.

Katalizörlerin performansını, destek malzemesi ve İS ligand etkisi ile birlikte etkileyen başka bir dizayn parametresi de katalizörlerin boyutudur. Bu sebeple, tek atomlu SiO₂-, γ -Al₂O₃- ve MgO-destekli iridyum katalizörü, 673 K'de hidrojen akışı altında küçük iridyum nanoparçacıklarına dönüştürülmüştür. Üst açılı karanlık alan taramalı transmisyon mikroskopu (HAADF-STEM) sonuçlarına göre iridyum katalizörleri her bir destek malzemesi üzerine eşit aralıklarla dağılmıştır ve nanoparçacık boyutu yaklaşık 1.2 nm'dir. Destekli nanoparçacıklar İS'ler ile kaplanmış ve 1,3-bütadien hidrojenasyonu için test edilmiştir. İS'lerin katalitik performansa olan etkisi nanoparçacıklar üzerinde önemli bir ölçüde fazladır. Bununla birlikte destek malzemelerinin ligand etkisi ile iridyum aktif merkezi tek atomlu olarak dağıldığında, daha fazladır.

İS'lerin yapılarındaki deęişimlerin, kaplandıkları destekli iridyum nanoparçacıklara etkisini anlamak amacıyla İS'nin yapısı sistematik olarak deęiştirilmiştir. Bu deęişimler anyon ve katyon boyutu, imidazolyu halkasındaki C2 bölgesinin metillenmesi ve katyona farklı fonksiyonel gruplar eklenmesidir. Sonuçlar, İS'lerin elektron alma/verme özelliklerinin ve interiyonik etkileşim enerjilerinin, destekli iridyum nanoparçacıkların performansı üzerinde çok büyük etkiler olduğunu göstermektedir.

Bu araştırmada sunulan sonuçlar, İS kaplı destekli tek atom dağılımlı katalizörlerin elektronik yapısı ve buna baęlı olan performansını kontrol edebilmenin mümkün olduğunu göstermektedir.





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List of Publications

1. M. Babucci, C.-Y. Fang, J. E. Perez-Aguilar, A. S. Hoffman, A. Boubnov, E. Guan, S.R. Bare, B. C. Gates, A. Uzun "Controlling catalytic activity and selectivity for partial hydrogenation by tuning environment around active sites in iridium complexes bonded to supports", 2019, Chemical Science, accepted for publication.
2. M. Babucci, C.-Y. Fang, A.S. Hoffman, S.R. Bare, B.C. Gates, A. Uzun "Tuning the selectivity of single-site supported metal catalysts with ionic liquids" ACS Catalysis, 2017, 7 6969 (highlighted in C&E News).
3. M. Babucci, A. Uzun "Effects of interionic interactions in 1,3-dialkylimidazolium ionic liquids on the electronic structure of metal sites in solid catalysts with ionic liquid layer (SCILL)" Journal of Molecular Liquids, 2016, 216, 293.
4. M. Babucci, V. Balci, A. Akçay, A. Uzun "Interactions of [BMIM][BF₄] with metal oxides and their consequences on stability limits" Journal of Physical Chemistry C, 2016, 120, 20089.
5. M. Babucci, A. Akçay, V. Balci, A. Uzun "Thermal stability limits of imidazolium ionic liquids immobilized on metal-oxides" Langmuir, 2015, 31, 9163.
6. A. Akçay, M. Babucci, V. Balci, A. Uzun "A model to predict maximum tolerable temperatures of metal-oxide-supported 1-*n*-butyl-3-methylimidazolium based ionic liquids" Chemical Engineering Science, 2015, 123, 588 (featured in Advances in Engineering).
7. M. Babucci, Ozce Durak, A. Uzun "Tailoring Performance of Supported Metal Nanoparticles by Ligand Modification", in preparation.
8. M. Babucci, L. Debeve, S.R. Bare, B. C. Gates, A. Uzun "Elucidating the Relative Strengths of Individual Structural Factors Controlling the Partial Hydrogenation Performance of Supported Iridium Catalysts", in preparation.
9. L. Debeve, M. Babucci, F. E. Oztuna, B. C. Gates, A. Uzun "HAADF-STEM evidence of site-isolated high loading of iridium on graphene aerogel", in preparation.

Chapter 1

An Introduction



The motivation to design high performance catalysts has been raised due to increasing demands in industrial innovations that require conversion of any material to valuable products.¹ The development of these catalysts can be assessed by optimizing the geometric or electronic properties of the active sites.² The two types of catalysts are heterogeneous catalysts where phase of the catalyst differs from the reactants and homogeneous catalysts that have the same phase. Large-scale industrial processes mostly favor the heterogeneous catalysts due to their robustness and easy separation from the reactants. The catalysis occurs on the surface of the metals, thus, reactant molecules are required to be accessible to the metal atoms. Metals are synthesized on high surface area supports to have higher dispersion and better accessibility; however, they have complex structures that complicate the understanding of the structure-performance relationship.

Atomically dispersed supported metals provide connections between homogeneous and heterogeneous catalysts: the active sites are uniform and simple, simplifying the characterization and they offer new activity and selectivity performance for many reactions.³ When the active species are site-isolated, the drawbacks coming from the geometric properties of the catalysts are ruled out, thus, the control over the performance can be reached by adjusting the electronic environment of the active sites which is possible by controlling the supports⁴⁻⁸ and ligands^{1,9} bound to active sites. However, the number of available supports and ligands is limited. One of the alternative approaches is the utilization of ionic liquids (ILs) with tunable physicochemical properties.¹⁰⁻¹¹ ILs are coated on supported metals and they enhance the performance of the catalysts,¹²⁻¹⁴ however, the knowledge of ILs' influence on atomically dispersed active sites is lacking.

The main objective of this research is to synthesize atomically dispersed metal species supported on high surface area metal oxides and to coat these catalysts with ILs having various structures and electron donating/withdrawing properties. The aim was to elucidate the changes in the electronic structure of the active sites and to assess the consequent influence on the catalytic performance for a simple and industrially important reaction, partial hydrogenation of 1,3-butadiene.

The structural information and electronic environment of the active sites were elucidated using were probed by many spectroscopic techniques, such as infrared (IR), extended X-ray absorption fine structure (EXAFS), and X-ray absorption near edge structure (XANES). Scanning transmission electron microscopy (STEM) imaging also provided information about the atomic scale structure of the catalysts.

The research presented in this dissertation consists of following chapters that are independent from each other. The first part of the present thesis (Chapter 2 and 3) aims to elucidate the interactions between imidazolium ionic liquids (ILs) and metal oxides. Then the consequent influence of the interactions on the short- and long-term thermal stability limits of supported ILs was studied. The second part of this thesis (Chapter 4, 5, 6, 7, and 8) was performed in the aim of the investigation of the effects of metal nuclearity, support type, and IL structure on the electron density and partial hydrogenation performance of atomically dispersed supported iridium species.

In IL-assisted supported catalysts, the determination of the thermal stability limits is required since ILs may decompose easily on supports. In Chapter 2, stability limits of 33 different imidazolium ILs supported on high surface area metal oxides, SiO₂, γ -Al₂O₃, and MgO, were investigated. The focus of this chapter is the stability limits within the scope of the structural factors of the ILs and the surface properties of the metal oxides.

In Chapter 3, the investigation of the interactions between one of the most commonly used ILs, 1-*n*-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF₄]), and various metal oxides, SiO₂, TiO₂, Fe₂O₃, ZnO, γ -Al₂O₃, CeO₂, MgO, and La₂O₃, was aimed. Based on the findings on the interactions, the short- and long-term thermal stability limits and activation energy for thermal decomposition of the supported IL were assessed. The results were further complimented with density functional theory (DFT) calculations and a simple model to estimate decomposition temperatures of the supported ILs was obtained.

After determination of the stability limits of ILs between metal oxide surfaces, atomically dispersed Ir(CO)₂ complexes were synthesized on γ -Al₂O₃- and coated with various 1,3-dialkylimidazolium ILs. In Chapter 4, the ligand effects of the ILs were elucidated based on the variations in electron density of iridium sites upon IL coating, probed by IR fingerprints of carbonyl ligands.

Chapter 5 focuses on quantifying the electron density on atomically dispersed supported iridium complexes upon IL coating by X-ray absorption spectroscopy. The variations in the electron density on iridium sites and consequent influence on the activity and selectivity performance of each IL-coated catalyst for partial hydrogenation of 1,3-butadiene were investigated. ILs act as ligands to modify the performance of the supported iridium sites, given in Figure 1-1. To provide a complimentary perspective in influence of the ILs and supports together on the performance of the active sites, in Chapter 6, atomically dispersed Ir(CO)₂ complexes were synthesized on SiO₂, TiO₂, Fe₂O₃, CeO₂, MgO, and La₂O₃ and coated with three different ILs. The supports and ILs were chosen to have different electron-donor/acceptor tendencies. The partial hydrogenation of 1,3-butadiene performance of the catalysts are dependent on the surface properties of the supports and the structure of ILs.

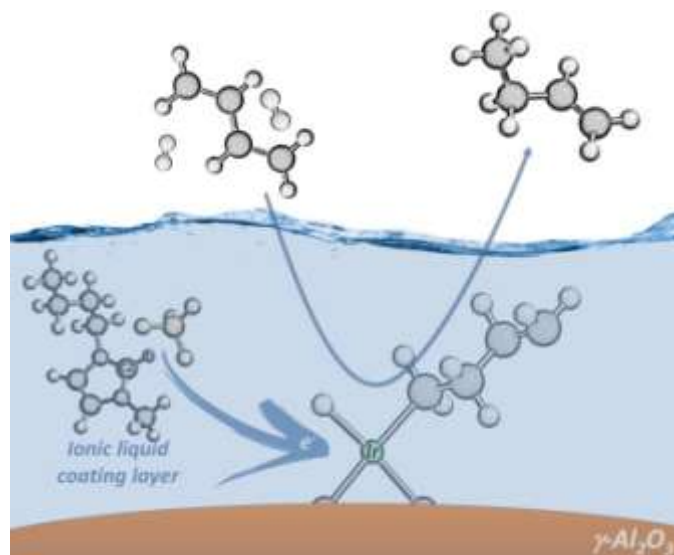


Figure 1-1. A representative picture showing the approach in this present thesis: the electron donation from ILs to atomically dispersed $\gamma\text{-Al}_2\text{O}_3$ -supported iridium sites influences the performance of the catalysts for partial hydrogenation of 1,3-butadiene.

Particle size of the metals dispersed on the surfaces is one of the other factors influencing the performance of the catalysts. When the metals are present in large particles, the character of the metal becomes bulk-like. However, in the range of nano-size, nonmetallic character increases.³ Chapter 7 demonstrates the conversion of the atomically dispersed supported iridium complexes into small nanoparticles, dispersed nearly uniformly on the supports with an average particle size of 1.2 nm. The aim of this chapter is to understand the influence of the metal nuclearity, support type and the IL structure on the performance of catalyst for partial hydrogenation of 1,3-butadiene. The SiO_2 -, $\gamma\text{-Al}_2\text{O}_3$ -, and MgO -supported catalysts were coated with 7 ILs. IL's ligand effect significantly influences the nanoparticles, whereas support type more dominant in influencing the atomically dispersed species.

To further evaluate how IL structure influences the supported metal nanoparticles, nanoparticles prepared in Chapter 8, were coated with 23 different ILs. IL structures are systematically changed, such as change in size of anion/cation, methylation on C2 site, and

substitution of functional groups to imidazolium ring and partial hydrogenation performance of each catalyst as a function of IL structure are investigated.

This present thesis provides information on the synthesis, characterization and performance of a new family of catalysts, IL-coated supported metal catalysts with varying nuclearity from single-site to small nanoparticles.

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Chapter 2

Thermal Stability Limits of Imidazolium Ionic Liquids

Immobilized on Metal Oxides*

*This chapter has been published in *Langmuir* **2015**, 31, 9163 by authors M. Babucci, A. Akcay, V. Balci, and A. Uzun. The original manuscript has been rearranged to conform to the format requirements of the dissertation.

2-1. Abstract

Thermal stability limits of 33 imidazolium ionic liquids (ILs) immobilized on three of the most commonly used high surface area metal oxides, SiO_2 , $\gamma\text{-Al}_2\text{O}_3$, and MgO , were investigated. ILs were chosen from a family of 13 cations and 18 anions. Results show that the acidity of C2H of imidazolium ring is one of the key factors controlling the thermal stability. An increase in C2H bonding strength of ILs leads to an increase in their stability limits accompanied by a decrease in inter-ionic energy. Systematic changes in IL structure, such as changes in electronic structure and size of anion/cation, methylation on C2 site, and substitution of alkyl groups on the imidazolium ring with functional groups have significant effects on thermal stability limits. Furthermore, thermal stability limits of ILs are influenced strongly by acidic character of the metal oxide surface. Generally, as point of zero charge (PZC) of the metal oxide increases from SiO_2 to MgO , the interactions of IL and metal oxide dominate over inter-ionic interactions, and metal oxide becomes the significant factor controlling the stability limits. However, thermal stability limits of some ILs show opposite trend as the chemical activities of the cation functional group or the electron donating properties of the anion alters IL/metal oxide interactions. Results presented here can help to pick the most suitable ILs for materials involving ILs supported on metal oxides, such as for supported ionic liquid membranes (SILM) in separation applications or for solid catalyst with ionic liquid layer (SCILL) and supported ionic liquid phase (SILP) catalysts in catalysis.

2-2. Introduction

Ionic liquids (ILs) are comprised of almost infinite number of anion-cation combinations with tunable physicochemical properties, such as viscosity, melting point, solubility, density and thermal stability.¹ These combinations offer new opportunities for applications in separation,^{2,3} electrochemistry,⁴ synthesis,⁵ oil and gas industry (flow assurance)⁶ and

catalysis.⁷ In catalysis, for example, they are either utilized as a selective layer over metal oxide-supported metal catalysts, as in the case of solid catalysts with ionic liquid layer (SCILL),⁸ or used to immobilize metal complexes on high area metal oxides, as supported ionic liquid phase (SILP) catalysts.⁹ In these applications, they work as a semipermeable coating layer, controlling the electronic structure of active sites and effective concentrations of reactants and intermediates. ILs are also utilized in supported ionic liquid membranes (SILM) to be used for separation applications. In these systems, they are supported on polymeric or inorganic^{10,11} supports and used as separation materials by crystallization, fractional distillation, solvent extraction and chromatographic techniques.¹² For gas separation, they provide a weak Lewis acid-base interaction between one of the gases and IL anions, and the gas forms a “tangent line” configuration of anion that maximizes favorable interactions.¹³ In these applications, ILs might be exposed to high temperatures, which results in IL degradation via decomposition,¹⁴ leaching out¹⁵ or evaporation¹⁶ resulting in the loss of structural integrity of the system. Thus, picking a proper IL that can withstand the application conditions is crucial.¹⁷

To date, thermal stability limits of bulk ILs have been studied extensively.¹⁸ Gharagheizi et. al.¹⁹ analyzed the available literature data on thermal stability limits of 586 ILs by using quantitative structure-property, QSPR, method. Adamova et. al.²⁰ investigated thermal and physical properties of 14 ILs by systematic changes on their structures. And recently, Cao et. al.¹⁸ analyzed thermal stability limits of 66 different bulk ILs. In addition to these, there are several thorough review articles summarizing the results on the thermal stability limits of bulk ILs.^{15,21,22}

Unlike bulk ILs, thermal stability limits of ILs immobilized on metal oxides have not been investigated much. Since interactions between ILs and metal oxides influence the thermal decomposition mechanisms, elucidation of the effect of these interactions on thermal

stability limits is important. Kosmulski et al.²³ performed short-term thermogravimetric analysis (TGA) and stated that for ILs including hexafluorophosphate anion, $[\text{PF}_6]^-$, thermal stability limit was reduced when crucible type was changed from aluminum oxide to aluminum because of the reactivity and surface acidity differences. Rodriguez-Perez et al.²⁴ performed short-term analysis on both bulk and metal oxide supported ILs. They indicated that bulk 1-butyl-3-methylimidazolium hexafluorophosphate, $[\text{BMIM}][\text{PF}_6]$, had a thermal stability limit of 698 K; however, when it was supported on SiO_2 , stability limit decreased to 588 K. Moreover, Lemus et al.²⁵ showed that the presence of metal oxide reduces the thermal stability limits of ILs significantly. For instance, bulk 1-methyl-3-octylimidazolium hexafluorophosphate, $[\text{OMIM}][\text{PF}_6]$, decomposed at 623 K; however, its decomposition was observed at 583, 488, and 368 K upon coating on SiO_2 , TiO_2 , and $\gamma\text{-Al}_2\text{O}_3$, respectively. Apparently, the interactions between ILs and metal oxides, as well as the solidification of ILs on metal oxides,²⁶⁻²⁷ play an important role in determining the stability limits of ILs on metal oxides. Very recently, we illustrated a direct dependence of the thermal stability limit of the metal oxide supported $[\text{BMIM}]^+$ -based ILs on surface acidity of the metal oxide and inter-ionic interactions in ILs.^{28,29} Based on these relations, we proposed a simple mathematical model as a function of acidity of the imidazolium ring and point of zero charge (PZC) of the metal oxide to predict the temperature limits that such $[\text{BMIM}]^+$ -based IL/metal oxide systems can tolerate for short-time periods.^{28,29}

Here, we extend this approach into a wider range of ILs of different cation/anion combination summarized in Figure 2-1. 33 different imidazolium ILs immobilized on three of the most commonly used metal oxides, SiO_2 , $\gamma\text{-Al}_2\text{O}_3$, and MgO , were investigated and structural factors controlling the stability limits were discussed. Results presented here can serve as a guideline to pick a suitable IL that can tolerate the operating conditions of materials

in which there is direct interactions between ILs and metal oxides, as in SILM, SCILL, and SILP concepts.

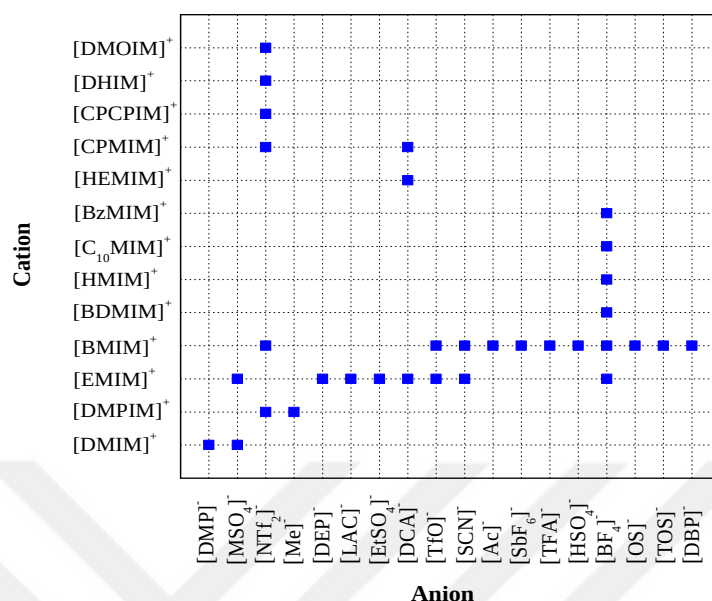


Figure 2-1. Cation-anion pairs of the ILs used in this study. Open names and structures are given below.

2-3. Materials & Methods

2-3.1. Materials

ILs, solvents, and metal oxides, SiO₂, γ-Al₂O₃, and MgO, were purchased from Sigma-Aldrich at the highest available purity level. SiO₂, γ-Al₂O₃, and MgO were calcined at 793, 773 and 973 K, respectively, in flowing O₂ for 5 h with temperature ramp of 10 K/min. ILs, either in freshly opened new bottles or bottles stored in a vacuum desiccator, were dried at 353 K in a vacuum oven for overnight before use. 200 mg of IL was first dissolved in 4 g of acetone or methanol; and 1 g of metal oxide was immersed in the IL-solvent mixture. After mixing gently for 1 h, resulting mixture was dried in vacuum oven for one day at 343 K. Infrared (IR) spectra of the dried samples show none to almost negligible solvent/water peaks confirming the performance of the drying process. Metal oxide supported IL samples were obtained in powder form with an IL loading of approximately 16.7 wt %. This loading amount

corresponds to single to a few layers of ILs on each metal oxide, as discussed below. Some of these samples were prepared using different solvents, such as ethanol, methanol, and acetonitrile; thermal stability limits measured for these samples confirmed that the type of solvent used for sample preparation does not have any detectable effect on the stability limits within the error range of our measurements.

2-3.2. Point of Zero Charge (PZC) Determination

Zetasizer Nanoseries instrument coupled with Malvern Multipurpose titrator were used to measure PZC and particle size of metal oxides. As described elsewhere,³⁰ 4 mg of metal oxide sample was dispersed in 20 mL of 0.1 M KNO₃ solution and the solution was ultrasonicated for approximately 5 min. Resulting solution was titrated with 0.25 M NaOH and HNO₃. Instrument pH increment was set to 0.2 for measurements in SiO₂ and γ -Al₂O₃, and that for backwards measurements was 0.1 for MgO. Tolerance was set to 0.2 for SiO₂, to 0.05 for γ -Al₂O₃, and MgO. Refractive indexes used during measurements are 1.46, 1.76 and 1.74 for SiO₂, γ -Al₂O₃, and MgO, respectively. Absorbance values used during measurements were 0.01, 0.01, and 0.1 for SiO₂, γ -Al₂O₃, and MgO, respectively.

2-3.3. Thermogravimetric Analysis (TGA)

For the determination of short-term thermal stability limits, TGA measurements were performed on a TA Instruments TGA Q500 model instrument from 298 to 1073 K with a heating rates of 2 K/min and 10 K/min, and in purge gas flow of 3 ml/min. Approximately 15 mg of samples in powder form were placed in an open platinum pan and purged with nitrogen at 353 K for 1 h to evaporate water content. Using the thermal analysis software “Measure”, temperature limits, (T_{onset}), were obtained from the interception of two straight lines one originating from the zero weight loss level and the other one tangential to the declining portion

of the weight change line. However, some experimental conditions, such as high heating rate and sample amount may cause T_{onset} to overestimate the thermal stability limits.¹⁶ Thus, to obtain more accurate and conservative results, thermal stability limits of ILs were determined from the onsets of derivative weight % change vs. temperature line, T'_{onset} . Reproducibility measurements, performed three times under identical conditions, showed that the results are reproducible within an error range of ± 3 K.

2-3.4. Fourier Transform IR (FTIR) Spectroscopy

A Thermo Scientific Nicolet iS10 model spectrometer and a Bruker Vertex 80v spectrometer with an attenuated total reflection (ATR) cell were used to collect IR spectra. Each IR spectrum was collected in air at room temperature with an average of 256 scans and a resolution of 4 cm^{-1} . 32 scans were collected as background before each measurement. Peak assignments were done according to literature.³¹ Relative ATR shifts were corrected according to the wavelength dependent factor-penetration depth of the IR beam of the spectrometer to adjust the relative peak intensities. Peak assignments were done according to literature.³¹

2-3.5. Scanning Electron Microscopy coupled with Energy-Dispersive X-Ray Spectroscopy (SEM/EDX)

A Zeiss Ultra Plus (FEG-SEM) scanning electron microscope with a SE detector was used to collect SEM images. Charging effect of supports were preventing by applying samples on a carbon tape. Images were collected at the magnifications of 30K $\times$ and 100K $\times$ with an accelerating voltage (EHT) of 5 kV for $\gamma\text{-Al}_2\text{O}_3$, of 1 kV for SiO_2 and MgO . Working distance for SiO_2 and MgO supported samples was within the range of 3.1-3.4 mm, while it was 5.3 mm for $\gamma\text{-Al}_2\text{O}_3$ supported samples. All EDX images were collected at a magnification of

100K $\times\times$ with an EHT of 5 kV and working distance of 6.7 mm for ILs on γ -Al₂O₃, EHT of 10 kV and a working distance in the range of 5.0-5.7 mm for ILs on SiO₂ and on MgO.

2-4. Results and Discussion

Distribution and loading of IL on metal oxide surface can alter the IL/metal oxide interactions. Thus, uniformity of the IL dispersion on metal oxides was confirmed by SEM imaging complemented by EDX mapping at different locations of the samples, as before,²⁸ given in Appendix A2. Relative areas under individual peaks in EDX atomic density distribution diagrams confirm the stoichiometric IL loading within 5% error in each sample. ILs become bulk-like when the thickness of the IL layer on metal oxide exceeds tens of nanometers.³² For such cases, it is expected to have a little influence of metal oxide on thermal stability, as most of the IL in the layer exists without interfacial interactions with the surface. Therefore, we calculated the thickness of IL layer according to surface area of metal oxides, density of ILs and the corresponding IL-loading to confirm the presence of sufficiently thin coating layer. The calculations indicate single to a few molecular layers of IL on metal oxides (surface areas are 212, 209, and 99 m²/g for SiO₂, Al₂O₃, and MgO, respectively) on each sample, confirming the presence of direct interactions between ILs and metal oxides.³² Aiming at elucidating the interactions between metal oxides and ILs, we have measured the IR spectra of the metal oxide-supported IL samples. Each of the spectra was compared with that of the corresponding bulk IL to check whether there is any changes in either positions of the IL fingerprints or their relative intensities upon loading on the metal oxide. Figure 2-2 shows a representative data set for [BMIM][NTf₂] on SiO₂, γ -Al₂O₃, and MgO in two different regions: 1000-1600 cm⁻¹ and 2750-3250 cm⁻¹. In these two regions, the low frequency region represents the fingerprints of mostly anion of the IL molecule, whereas the one in the higher frequency region represents the IR fingerprints of the cation.³³

Accordingly, bands at 3155, 3121, 3101, 2964, 2940, and 2880 cm^{-1} in Figure 2-2A represent $\nu_s(\text{HC4-C5H})_s$, $\nu_{as}(\text{HC4-C5H})_s$, $\nu(\text{C2H})_s$, $\nu_{as}(\text{CH})_s$, and $\nu_{as}(\text{CH}_2)_s$ of the IL's cation, respectively, while those of the bands at 1572, 1346, 1329, 1226, 1176, 1131, and 1050 cm^{-1} in Figure 2-2B, represent $\nu(\text{C=C/NCN})_s$, $\nu_s(\text{SO}_2)_s$, $\nu_{as}(\text{SO}_2)_s$, $\nu_{as}(\text{CF}_3)_m$, $\nu(\text{N-Me})_s$, $\nu_s(\text{SO}_2)_s$, and $\nu_{as}(\text{SNS})_s$ cm^{-1} of the IL's anion, respectively.^{24,34-37} When this IL is supported on SiO_2 , we observed that the bands at the higher and lower frequency region blue shifted to 3157, 3124, 3104, 2971, 2945, and 2885 cm^{-1} and 1572, 1348, 1328, 1227, 1194, 1131, and 1052 cm^{-1} , respectively. Similarly, when the same IL is supported on $\gamma\text{-Al}_2\text{O}_3$ and MgO , the bands specifically in the higher frequency region shift to 3157, 3123, 3102, 2970, 2942, and 2882 cm^{-1} and 3157, 3121, 3101, 2968, 2941, and 2882 cm^{-1} , respectively. Besides these changes in the position of IL fingerprints, data also illustrate changes in the relative intensities of these bands. As discussed by Steinrück et al.³³ and Sobota et al.,^{33,38} these results illustrate that there is direct interactions between $[\text{BMIM}][\text{NTf}_2]$ and the metal oxides and these interactions differ significantly when the same IL is supported on different metal oxides. Similar to these results presented in Figure 2-2, data for all other ILs both in bulk and supported on metal oxides (presented in Appendix A2 through Figures A2-102 to A2-134) illustrate that the fingerprint positions shift significantly, either blue or red, accompanied by changes in relative intensities, when the corresponding IL is supported on different metal oxides. Furthermore, data also show that these shifts are either in the lower or in the higher frequency region or in both. This variation in the region in which the shift/intensity variation occur indicates that there is strong interactions between the IL and the metal oxides and these interactions depend on both the type of the metal oxide and the structure of the IL. We infer that such interactions should strongly influence the thermal stability behavior of the IL on metal oxides. Thus, we focus on elucidating, such factors controlling the thermal stability of ILs on different metal oxides, SiO_2 , $\gamma\text{-Al}_2\text{O}_3$, and MgO .

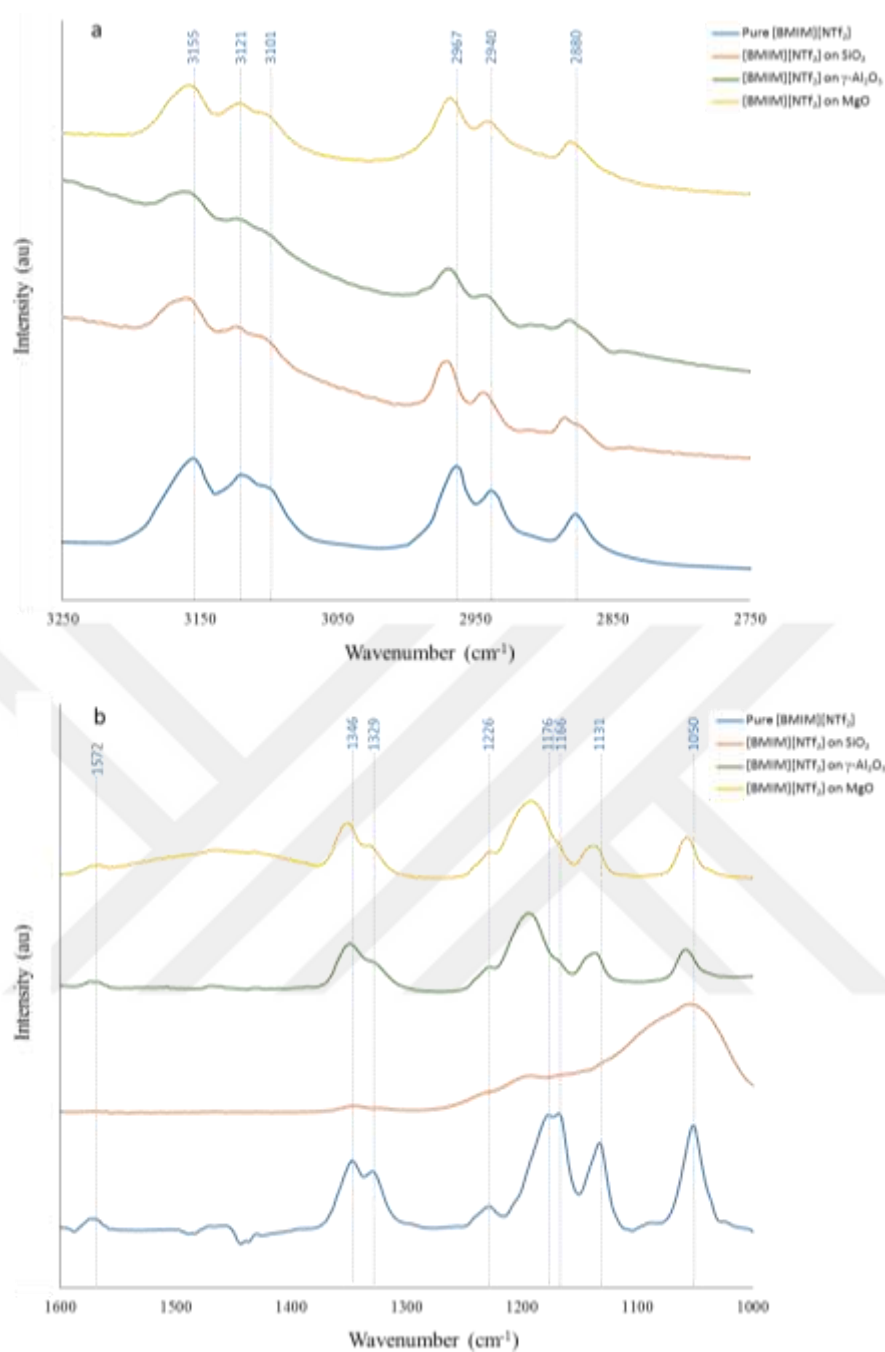


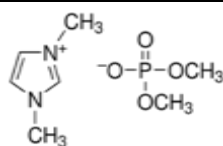
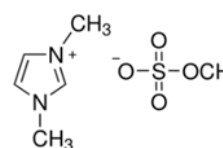
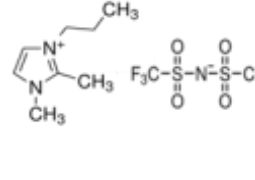
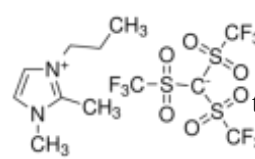
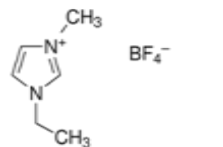
Figure 2-2. IR spectra of bulk and metal oxide-supported [BMIM][NTf₂]: bulk (—); SiO₂-supported (—); γ-Al₂O₃-supported (—); MgO-supported (—) in the region of A) 2750-3250 cm⁻¹; B) 1000-1600 cm⁻¹.

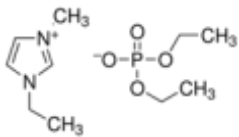
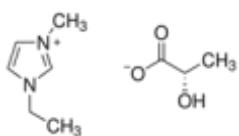
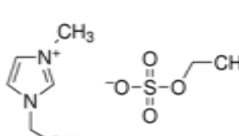
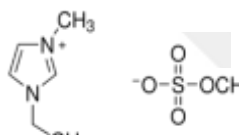
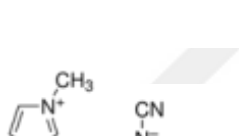
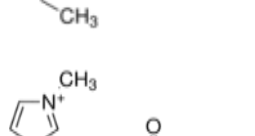
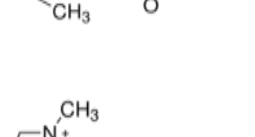
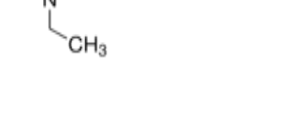
T'_{onset} values of metal oxide supported ILs were measured by using fast-scan temperature ramp method. Temperature ramp in TGA measurements causes mass loss resulting from either thermal decomposition or evaporation of ILs.³⁹ In either case, the structural integrity of the IL/metal oxide system is lost. Here, the temperature profile depends

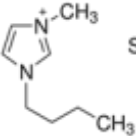
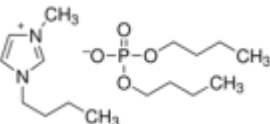
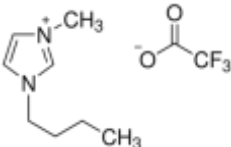
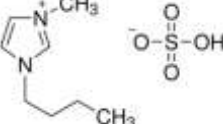
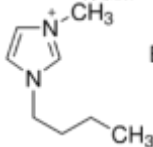
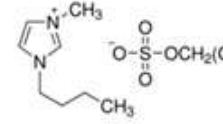
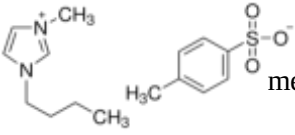
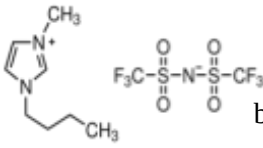
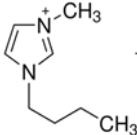
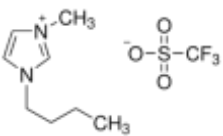
on some operating factors, such as heating rate, instrumentation, type of carrier gas, and sample amount.^{15,40} An increase in sample amount by a factor of two can cause an overestimation of T'_{onset} as 323 K in bulk ILs.²³ Also, Salgado et. al.⁴¹ stated that T'_{onset} of bulk [BDMIM][NTf₂] was 285 K more stable under N₂ atmosphere than air. Likewise, impurity content, may cause a decreasing thermal stability limit.⁴² Such kind of differences in operating conditions complicates the comparison of data. Therefore, we performed TGA measurements under identical conditions to reach reproducible and consistent results for determining the relationship between structural parameters and thermal stability limits of ILs. At low heating rates, IL evaporation may dominate decomposition.¹⁶ Thus, we preferred a relatively high heating rate of 10 K/min to characterize the dynamic structural dependency, which otherwise would not be possible to distinguish by slow heating measurements or isothermal TGA.²⁸ It was illustrated that thermal stability limit measured for bulk 1-butyl-3-methylimidazolium methylsulfate, [BMIM][MSO₄], varies within approximately 323 K when the heating rate was increased from 2 to 16 K/min.⁴³ To elucidate the effect of heating rate, we performed measurements at a heating rate of 2 K/min on metal oxide-supported ILs and reproduced the same T'_{onset} results within ± 3 K measurement error with the ones measured with a heating rate of 10 K/min (as given in Appendix A2).²⁸ Thus, we infer that the artifacts of relatively high heating rate in our TGA measurements are less pronounced on these metal oxide supported samples with low IL loading than the case with bulk ILs, especially when considering T'_{onset} , which provides more conservative results than T_{onset} . However, we note that these values are rather short-term stability limits indicating the highest temperature that the IL/metal oxide systems can tolerate for short-time periods. A more detailed kinetics study, such as the study by Heym et al.⁴⁴ and Seeberger et al.,¹⁶ is required for long-term stability limits, such as temperature at which 1% or 10% mass loss per year or month occurs.

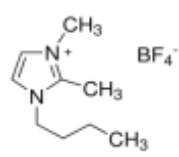
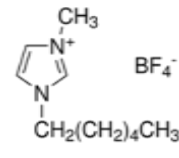
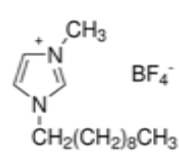
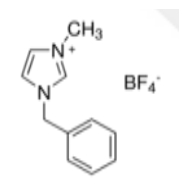
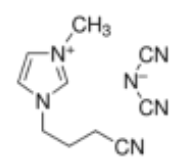
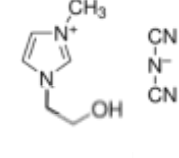
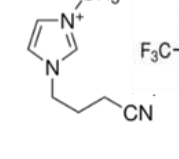
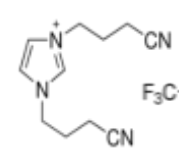
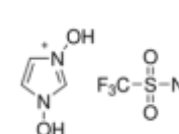
Table 2-1 summarizes T'_{onset} values of individual ILs immobilized on SiO_2 , $\gamma\text{-Al}_2\text{O}_3$, and MgO . As discussed before, when ILs are immobilized on metal oxides, their T'_{onset} values decrease significantly.^{28,29} Among the data for metal oxide supported ILs, SiO_2 - and $\gamma\text{-Al}_2\text{O}_3$ -supported [DMPIM][NTf₂] has the highest short-term stability limits with T'_{onset} values of 657 and 585 K, respectively; and the least stable IL/metal oxide combinations are [EMIM][DCA] (394 K) and [DMIM][DMP] (408 K) on SiO_2 and $\gamma\text{-Al}_2\text{O}_3$, respectively. Moreover, on MgO , T'_{onset} ranges from 517 to 602 K for [BMIM][Ac] and [DHIM][NTf₂]. Since T'_{onset} of individual ILs change significantly by the changes in IL structure and by the presence of metal oxide, we focus on understanding the consequences of these effects on the thermal stability limits.

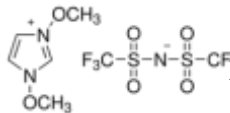
Table 2-1. TGA-determined thermal stability limits (T'_{onset}) of supported ILs.

Structure	Name of ILs	Abbreviation	SiO_2 $T'_{\text{onset}}/\text{K}$ PZC = 1.7	$\gamma\text{-Al}_2\text{O}_3$ $T'_{\text{onset}}/\text{K}$ PZC = 7.6	MgO $T'_{\text{onset}}/\text{K}$ PZC = 9.8
	1,3-Dimethylimidazolium dimethyl phosphate	[DMIM][DMP]	497	408	404
	1,3-Dimethylimidazolium methyl sulfate	[DMIM][MSO ₄]	615	501	444
	1,2-Dimethyl-3-propylimidazolium bis(trifluoromethylsulfonyl)imide	[DMPIM][NTf ₂]	657	585	494
	1,2-Dimethyl-3-propylimidazolium tris(trifluoromethylsulfonyl)methide	[DMPIM][Me]	653	557	497
	1-Ethyl-3-methylimidazolium tetrafluoroborate	[EMIM][BF ₄]	618	545	465

	1-Ethyl-3-methylimidazolium diethyl phosphate	[EMIM][DEP]	473	424	405
	1-Ethyl-3-methylimidazolium L-(+)-lactate	[EMIM][LAC]	474	430	419
	1-Ethyl-3-methylimidazolium ethyl sulfate-95%	[EMIM][EtSO ₄]	594	499	440
	1-Ethyl-3-methylimidazolium methyl sulfate	[EMIM][MSO ₄]	608	502	448
	1-Ethyl-3-methylimidazolium dicyanamide	[EMIM][DCA]	394	447	467
	1-Ethyl-3-methylimidazolium trifluoromethanesulfonate	[EMIM][TfO]	613	546	477
	1-Ethyl-3-methylimidazolium thiocyanate	[EMIM][SCN]	528	483	456
	1-Butyl-3-methylimidazolium acetate	[BMIM][Ac]	464	408	400

	1-Butyl-3-methylimidazolium hexafluoroantimonate	[BMIM][SbF ₆]	610	542	482
	1-Butyl-3-methylimidazolium dibutyl phosphate	[BMIM][DBP]	495	435	416
	1-Butyl-3-methylimidazolium trifluoroacetate	[BMIM][TFA]	434	440	434
	1-Butyl-3-methylimidazolium hydrogen sulfate	[BMIM][HSO ₄]	591	493	437
	1-Butyl-3-methylimidazolium tetrafluoroborate	[BMIM][BF ₄]	604	536	482
	1-Butyl-3-methylimidazolium octyl sulfate	[BMIM][OS]	544	443	438
	1-Butyl-3-methylimidazolium tosylate	[BMIM][TOS]	576	491	449
	1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	[BMIM][NTf ₂]	633	569	479
	1-Butyl-3-methylimidazolium thiocyanate	[BMIM][SCN]	524	484	463
	1-Butyl-3-methylimidazolium trifluoromethanesulfonate	[BMIM][TfO]	625	546	477

	1-Butyl-2,3-dimethylimidazolium tetrafluoroborate	[BDMIM][BF ₄]	643	536	453
	1-Hexyl-3-methylimidazolium tetrafluoroborate	[HMIM][BF ₄]	598	515	445
	1-Decyl-3-methylimidazolium tetrafluoroborate	[C ₁₀ MIM][BF ₄]	599	496	440
	1-Benzyl-3-methylimidazolium tetrafluoroborate	[BzMIM][BF ₄]	598	516	452
	1-(2-Hydroxyethyl)-3-methylimidazolium dicyanamide	[HEMIM][DCA]	471	481	485
	1-(3-Cyanopropyl)-3-methylimidazolium dicyanamide	[CPMIM][DCA]	396	411	450
	(3-Cyanopropyl)-1-methylimidazolium bis(trifluoromethylsulfonyl)imide	[CPMIM][NTf ₂]	628	565	473
	1,3-Bis(3-cyanopropyl)imidazolium bis(trifluoromethylsulfonyl)imide	[CPCPIM][NTf ₂]	625	559	469
	1,3-Dihydroxyimidazolium bis(trifluoromethylsulfonyl)imide	[DHIM][NTf ₂]	478	537	602

	1,3-Dimethoxyimidazolium bis(trifluoromethylsulfonyl)imide	[DMOIM][NTf ₂]	499	540	559

2-4.1. Dependency of Stability Limits on IL Structure

One of the simplest structural differences in ILs is the difference in chain lengths of the alkyl groups attached to the imidazolium ring. Alkyl chain length effect on thermal stability limits of bulk ILs was investigated in detail, and it was reported that, in general, as the alkyl chain length becomes longer, the thermal stability of ILs decreases.^{18,23,45,46-47} Cao et. al.¹⁸ showed that bulk [EMIM][BF₄] (686 K) has approximately 15 K higher thermal stability than bulk 1-octyl-3-methylimidazolium tetrafluoroborate, [OMIM][BF₄] (670 K). Moreover, Tokuda et. al.⁴⁵ reported that the difference was approximately 14 K between the thermal stability limits of bulk [EMIM][NTf₂] (712 K) and bulk 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [OMIM][NTf₂] (698 K). However, in some cases, alkyl chain length effect was negligible. Awad et. al.⁴⁸ showed that thermal stability of 1-butyl-2,3-dimethylimidazolium hexafluorophosphate, [BDMIM][PF₆] (698 K), and 1-decyl-2,3-dimethylimidazolium hexafluorophosphate, [C₁₀DMIM][PF₆] (693 K), are very close. Moreover, bulk [BMIM][Cl] and bulk [C₁₀MIM][Cl] started to decompose at 507 and 512 K, respectively.⁴⁸ Aiming to investigate the effect of alkyl chain length in metal oxide-supported imidazolium ILs, we considered a family of ILs with [BF₄]⁻ anion and with *ethyl*-, *butyl*-, and *decyl*- group attached to the imidazolium ring, [EMIM][BF₄], [BMIM][BF₄] and [C₁₀MIM][BF₄], respectively. As given in Figure 2-3, on SiO₂, T'_{onset} of [EMIM][BF₄] is 618 K, while that of [BMIM][BF₄] and [C₁₀MIM][BF₄] are 604 and 599 K, respectively. The trend is the same for these ILs on γ-Al₂O₃ and consistent with the previous reports on bulk

ILs.^{23,45,46} Similarly, on MgO, [C₁₀MIM][BF₄] has the lowest thermal stability among these ILs with [BF₄]⁻ anion. Here, as the alkyl chain length becomes longer, stability of both carbocation and free radicals increase, making them better leaving groups at high temperatures.⁴⁹ Moreover, at the same time, the number of bonds which can break during the decomposition reaction increases, making the IL more susceptible for decomposition.⁴⁹

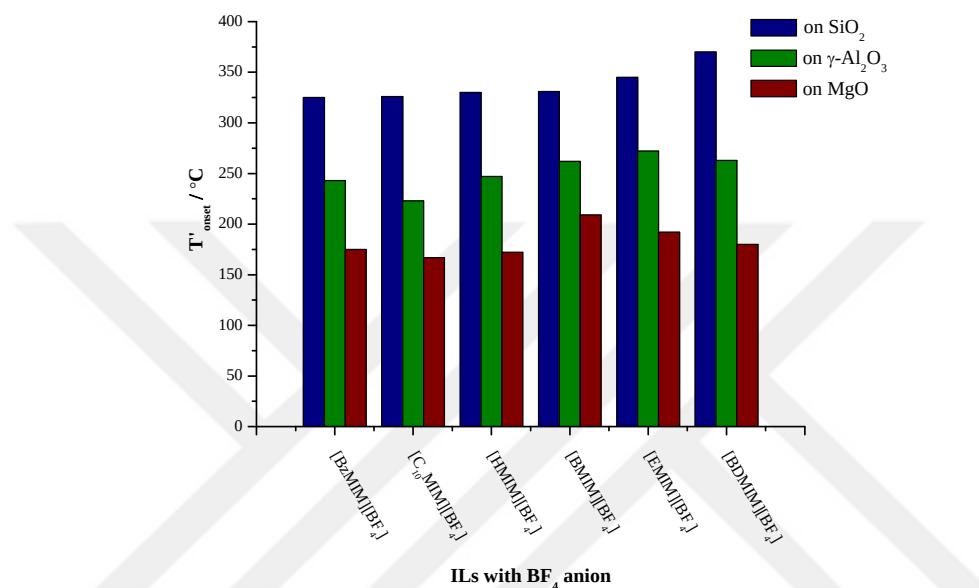


Figure 2-3. T'_{onset} of ILs with [BF₄]⁻ anion supported on SiO₂, γ-Al₂O₃, and MgO.

Another possible structural change in the cation of imidazolium ILs is the methylation on the C2 position. In a previous study, thermal stability limits of bulk ILs were investigated in the aspects of methyl substitution with the C2 proton. Data showed that methylation enhances the stability limits of bulk ILs.^{1,48} Noack et. al.³¹ found that thermal stability limit of bulk 1-ethyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide, [EDMIM][NTf₂], was 639 K, while that of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [EMIM][NTf₂], was 587 K. The proton located at C2 position is responsible for strong and directional hydrogen bonding between anion and cation.⁵⁰ These H-bonds cause damage on charge symmetry. Thus, Coulomb network of ILs are defected, resulting in increase in

dynamics of anion and cation.⁵¹ However, substitution of this proton with a methyl group provides steric hindrance and improves the Coulomb interaction by destroying H-bonds. This increase in Coulomb interaction leads to a decrease in the inter-ionic interactions.^{1,51} Such a decrease in inter-ionic interactions results in an increase in the thermal stability limits, as shown before.^{28,29} Here, thermal stability limits of metal oxide-supported [BMIM][BF₄] and [BDMIM][BF₄] were compared (Figure 2-3) to elucidate the effect of methylation on the thermal stability limits of the ILs immobilized on metal oxides. T'_{onset} of [BMIM][BF₄] on SiO₂ is 604 K and it increases to 643 K for the methyl substituted IL with the same cation on the same support. In the case of ILs supported on γ -Al₂O₃, methylation does not affect T'_{onset} . MgO-supported [BMIM][BF₄] and [BDMIM][BF₄], on the other hand, have T'_{onset} values of 482 and 453, respectively, indicating an opposite trend, which is most probably originated by the basic character of MgO. We infer that with a decrease in inter-ionic interactions, the hydrogen abstraction ability of MgO becomes the dominant factor leading to a decrease in thermal stability limit.

Another structural factor influencing the thermal stability limits of ILs on metal oxides is the functional group substitution on the alkyl chain of the imidazolium ring,⁵² such as substitution of nitrile, -CN, and hydroxyl, -OH, groups with the terminal methyl group of the alkyl chain. Here, the effect of -CN functional group substitution on T'_{onset} of ILs was investigated by comparing T'_{onset} of [BMIM][NTf₂], [CPMIM][NTf₂], and [CPCPIM][NTf₂] immobilized on metal oxides. Figure 2-4 shows that T'_{onset} of [BMIM][NTf₂] and [CPMIM][NTf₂] on SiO₂, γ -Al₂O₃, and MgO are 630, 569, and 476 K and 625, 559, and 746 K, respectively. Thus, we infer that nitrile group substitution results in a slight decrease in thermal stability limits on all metal oxides, although that on MgO was within the error range of our measurements. Also, when the methyl group at the N3 position of [CPMIM][NTf₂] is replaced by a second cyanopropyl group, thermal stability reduces further by 3-5 K (slightly

larger than the error range) on all metal oxides. The reason of such slight decrease may be attributed to the additional electron withdrawing character of the second cyanopropyl group. Interactions of nitrile with imidazolium and $[\text{NTf}_2]^-$ may cause conformational changes and destabilization of imidazolium ring.⁵³ Zhang et. al.⁵³ compared T'_{onset} of $[\text{BMIM}][\text{BF}_4]$ (676 K) and $[\text{CPMIM}][\text{BF}_4]$ (538 K) and stated that hydrogen-bonding interactions of ILs with $-\text{CN}$ group may result in a remarkable decrease in T'_{onset} of bulk ILs because of $-\text{CN}$ incorporation. Thus, as an unsaturated side chain on imidazolium ring, $-\text{CN}$ may reduce the thermal stability because of its rigidity, although our results on metal oxide supported ILs do not show any significant effect. We infer that for these ILs, the effect of metal oxide might be the dominant factor determining the stability limits, as discussed below.

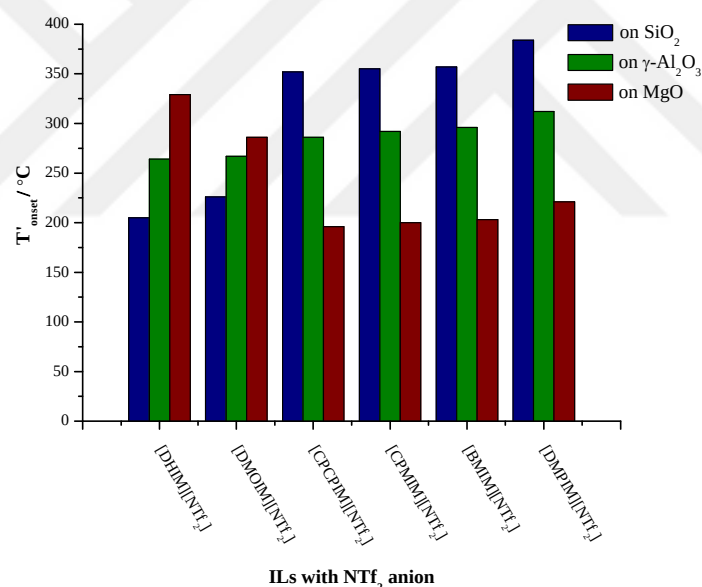


Figure 2-4. T'_{onset} of ILs with $[\text{NTf}_2]^-$ anion supported on SiO_2 , $\gamma\text{-Al}_2\text{O}_3$, and MgO .

Hydroxyl group substitution on the imidazolium ring may result in different changes in T'_{onset} dependent on the anion structure. In order to elucidate the effect of the presence of a $-\text{OH}$ group, first we compared T'_{onset} values of supported $[\text{BMIM}][\text{NTf}_2]$ with those of supported $[\text{DHIM}][\text{NTf}_2]$, as seen in Figure 2-4. Since ILs considered here are from a family

of the same anion, $[\text{NTf}_2]^-$, differences in T'_{onset} are attributed to the presence of the hydroxyl group. According to the literature, bulk ILs with $[\text{NTf}_2]^-$ anion and imidazolium ring with hydroxyl group may decompose at lower temperatures than their non-hydroxylated analogues, because of high chemical activity of hydroxyl group.⁵² Nevertheless, because of the size effect, one would expect to have a lower decomposition temperature for $[\text{BMIM}][\text{NTf}_2]$ as butyl group is longer than hydroxyl group. However, $[\text{BMIM}][\text{NTf}_2]$ (580 K) has a remarkably higher T'_{onset} than that of $[\text{DHIM}][\text{NTf}_2]$ (478 K) on acidic SiO_2 and on almost neutral $\gamma\text{-Al}_2\text{O}_3$. Here, nucleophilicity of $-\text{OH}$ group significantly affects the stability limits; it behaves as highly activating and electron donating group reducing the intramolecular bonding strength in imidazolium ring. However, on MgO , $[\text{DHIM}][\text{NTf}_2]$ becomes more stable than $[\text{BMIM}][\text{NTf}_2]$ by more than 20 K. Complementing these results, the IR fingerprints of $[\text{DHIM}][\text{NTf}_2]$ shows red-shift, whereas those for $[\text{BMIM}][\text{NTf}_2]$ presents blue-shifts in the lower frequency region when these ILs are supported on MgO (Figures A2-102 to A2-114, in Appendix A2). This opposite trend is discussed in terms of IL/metal oxide interactions in the following section. Moreover, the thermal stability of $[\text{EMIM}][\text{DCA}]$ and its hydroxylated counterpart, $[\text{HEMIM}][\text{DCA}]$, increase when metal oxide becomes basic and $[\text{HEMIM}][\text{DCA}]$ (471 K) has higher thermal stability than $[\text{EMIM}][\text{DCA}]$ (394 K) on SiO_2 . The trend is the same for ILs supported on $\gamma\text{-Al}_2\text{O}_3$ and MgO .

Furthermore, methoxylation effect was investigated by comparing T'_{onset} values of metal oxide-supported hydroxylated $[\text{DHIM}][\text{NTf}_2]$ and methoxylated $[\text{DMOIM}][\text{NTf}_2]$ ILs. T'_{onset} of $[\text{DMOIM}][\text{NTf}_2]$ (499 K) is greater than that of $[\text{DHIM}][\text{NTf}_2]$ (478 K) when they are supported on SiO_2 . However, T'_{onset} of $[\text{DMOIM}][\text{NTf}_2]$ becomes significantly lower than that of $[\text{DHIM}][\text{NTf}_2]$, when the support is MgO , (559 K for $[\text{DMOIM}][\text{NTf}_2]$ and 602 K for $[\text{DHIM}][\text{NTf}_2]$). Although both $-\text{OH}$ and $-\text{OCH}_3$ are electron donor groups, $-\text{OH}$ donates more of its electron density, providing high nucleophilicity and stronger chemical activity.

Thus, it is easier for ILs with –OH group to make interactions with acidic support, SiO₂, and initiate the decomposition reaction earlier during the temperature ramp. Our data confirm that initiation of the decomposition of [DHIM][NTf₂] on acidic SiO₂ is approximately 20 K earlier than that of [DMOIM][NTf₂]. On basic MgO, [DHIM][NTf₂] becomes thermally more stable than [DMOIM][NTf₂] by 45 K. We infer that, on MgO, interactions between –OH substituted IL and the metal oxide weaken, and the initiation of the decomposition reaction is delayed to some extent. Data show that on almost neutral environment, such as on γ -Al₂O₃, thermal decomposition temperatures of hydroxyl and methoxyl incorporated ILs with the same anion do not differ significantly.

Erdmenger et al.⁵⁴ reported that benzyl substitution on the alkyl chain of the imidazolium ring lowers the thermal stability of bulk IL with [BF₄][–] anion. Aiming to elucidate the effect of aromatic substitution on the imidazolium ring for the metal oxide-supported ILs, we compare T'_{onset} of supported [HMIM][BF₄] with those of supported [BzMIM][BF₄]. Our data illustrate that on SiO₂ and γ -Al₂O₃, benzyl substitution does not have any significant effect on T'_{onset} (Figure 2-3) within our error range. Although both of the ILs have bulky groups attached, their T'_{onset} values are not affected by the cation structure significantly. Moreover, the difference between T'_{onset} of these ILs is not influenced by the surface acidity of SiO₂, and γ -Al₂O₃. However, on MgO, benzyl substituted IL has 7 K higher thermal stability (slightly higher than the error range) than [HMIM][BF₄] does. Here, we predict that delocalization of aromatic ring slightly enhances the thermal stability on basic MgO.⁵⁵

Anion type is considered as the dominant factor for controlling the interactions between ions as well as between ILs and metal oxides.¹⁵ Coordinating nature, hydrophobicity and nucleophilicity of the anion are the key parameters taken into account as a measure of the H-bonding capacity.⁵⁶ In our previous study,²⁹ anion effect was quantified by comparing C2H

bonding strength of nine different bulk and SiO_2 -, TiO_2 -, $\gamma\text{-Al}_2\text{O}_3$ -, and MgO -supported ILs with $[\text{BMIM}]^+$ cation. Thermal stability limits of ILs decreased in the following order of anions: $[\text{NTf}_2]^- > [\text{TfO}]^- \sim [\text{SbF}_6]^- \sim [\text{BF}_4]^- > [\text{HSO}_4]^- > [\text{TOS}]^- > [\text{OS}]^- > [\text{DBP}]^- > [\text{Ac}]^-$, accompanied by a decrease in $\nu(\text{C}_2\text{H})$ frequency.²⁸ Here, we extend this study to metal oxide-supported ILs with cations other than $[\text{BMIM}]^+$ (Table 2-1 and Figure 2-1). $[\text{EMIM}]^+$ -based ILs were used to investigate the anion effect on T'_{onset} of ILs on metal oxides. T'_{onset} of SiO_2 -supported ILs decrease in the following order of anions: $[\text{BF}_4]^- \sim [\text{TfO}]^- \sim [\text{errMSO}_4]^- > [\text{EtSO}_4]^- > [\text{SCN}]^- > [\text{LAC}]^- \sim [\text{DEP}]^- > [\text{DCA}]^-$ (Figure 2-5). When these ILs are supported on $\gamma\text{-Al}_2\text{O}_3$, their T'_{onset} decreases in the order: $[\text{TfO}]^- \sim [\text{BF}_4]^- \sim [\text{MSO}_4]^- > [\text{EtSO}_4]^- > [\text{SCN}]^- > [\text{DCA}]^- > [\text{LAC}]^- \sim [\text{DEP}]^-$. Similarly, the thermal stability limits of MgO -supported ILs decreases in the following order: $[\text{TfO}]^- > [\text{BF}_4]^- \sim [\text{SCN}]^- > [\text{MSO}_4]^- > [\text{EtSO}_4]^- > [\text{LAC}]^- > [\text{DEP}]^-$ (Figure 2-5). Although there is not a remarkable change in the order, different anions cause varying interactions between IL and MgO , thus, the type of metal oxide becomes influential in controlling the thermal stability limits of ILs.

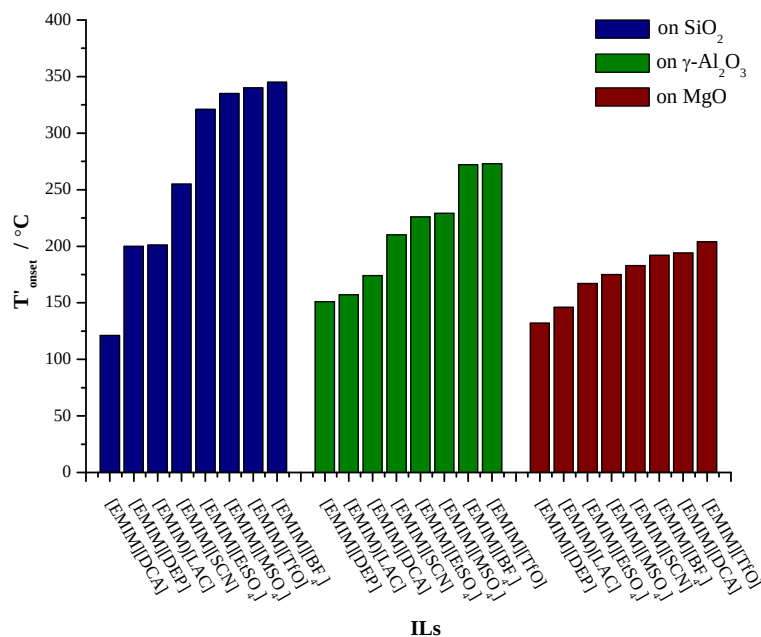
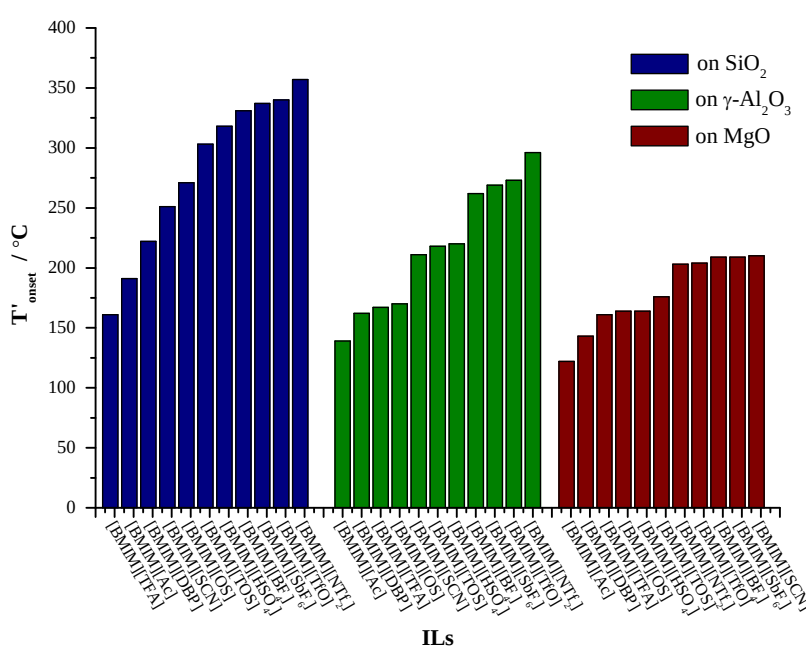


Figure 2-5. T'_{onset} of ILs with $[\text{EMIM}]^+$ cation supported on SiO_2 , $\gamma\text{-Al}_2\text{O}_3$, and MgO .

Electronic structure of anion has a significant effect on T'_{onset} of bulk ILs. Pringle et al.⁵⁷ investigated the effect of anion's electronic structure on stability limits. They showed that imidazolium ILs with fluorinated bis(trifluoromethylsulfonyl)imide anion, $[\text{NTf}_2]^-$, has 100 K higher thermal stability than that of non-fluorinated bis(methanesulfonyl)imide anion, $[\text{NMs}_2]^-$. Here, T'_{onset} of $[\text{BMIM}][\text{Ac}]$ and $[\text{BMIM}][\text{TFA}]$ were compared on three supports to investigate the effect of fluorination in the anion. Consistent with the case in bulk ILs, data show that IL with fluorinated anion, $[\text{BMIM}][\text{TFA}]$, has approximately 30 and 40 K higher thermal stability than $[\text{BMIM}][\text{Ac}]$ on almost neutral $\gamma\text{-Al}_2\text{O}_3$ and basic MgO , respectively (Figure 2-6). We predict that fluorination of anion decreases the nucleophilicity, resulting in a higher thermal stability. Pringle et al.⁵⁷ claimed that strength of the attractive forces between fluorinated molecules may increase the chemical stability of IL, which can be related to the thermal stability of IL. However, as seen in Figure 2-6, on acidic SiO_2 , non-fluorinated $[\text{BMIM}][\text{Ac}]$ has approximately 30 K higher T'_{onset} value than $[\text{BMIM}][\text{TFA}]$ does. This different behavior on acidic SiO_2 illustrates that the interactions between the IL and SiO_2 becomes the dominant factor in determining the thermal stability of these ILs when the support surface has acidic character.



T'_{onset} of ILs having [BMIM]⁺ cation with varying anion size were compared. T'_{onset} of [BMIM][HSO₄] are 591, 493, and 437 K on SiO₂, γ -Al₂O₃, and MgO, respectively. As the anion size increases from [HSO₄]⁻ to [OS]⁻, T'_{onset} of IL on SiO₂ and γ -Al₂O₃ is reduced (Figure 2-6). Accordingly, [BMIM][OS] has T'_{onset} of 544 and 443 K on SiO₂ and γ -Al₂O₃, respectively, which are dramatically lower than those of [BMIM][HSO₄] on the same metal oxides. This reduction in T'_{onset} of ILs is attributed to an increase in interactions of anion with cation or support; which initiates an early thermal degradation. Here, the effect of molecular size is considered. Accordingly, molar volumes of [BMIM][HSO₄] and [BMIM][OS] are approximated as 185 cm³/mol and 329 cm³/mol, respectively.⁵⁸ This difference in their molar volumes is compatible with our interpretations as [BMIM][OS] has considerably more sites for the decomposition reaction to start than [BMIM][HSO₄] does. Thus, its thermal stability limits on SiO₂ and γ -Al₂O₃ are significantly lower than those of [BMIM][HSO₄]. Here, we note that T'_{onset} values of these two ILs on MgO are exactly the same, 437 K, indicating that the anion size effect is not effective when these ILs are supported on MgO. Apparently, the interactions of these two ILs with MgO are significantly different than that with SiO₂ and γ -Al₂O₃. This difference indicates a possible change in the decomposition mechanism of the corresponding ILs when they are immobilized on a basic support, MgO, for which hydrogen abstraction ability might be playing a role.

Additionally, ILs with [EMIM]⁺ cation, and [MSO₄]⁻ and [EtSO₄]⁻ anions were analyzed to reinforce the anion size effect on T'_{onset} . Data demonstrate not so remarkable change in T'_{onset} of [EMIM][MSO₄] and [EMIM][EtSO₄] on all supports (Figure 2-5). T'_{onset} differences are approximately 10 K, [EMIM][MSO₄] being more stable than [EMIM][EtSO₄]. Molar volumes of those ILs are close to each other 179 and 191 cm³/mol for [EMIM][MSO₄]⁵⁹ and [EMIM][EtSO₄],⁶⁰ respectively. Data show that when the size of the chemically similar anions are comparable, their T'_{onset} values are close to each other. Thus, we

infer that the effect of anion size on the decomposition temperature becomes more significant as the difference in the size of anions becomes significantly large.

2-4.2. Dependency of Stability Limits on Metal oxide Type

Metal oxides can act as a catalyst to initiate the decomposition of ILs at a lower temperature than the thermal stability limit of bulk ILs. Their activity is controlled by their surface acidity and their interactions with ILs. As we discussed before, the IL loading in our samples were adjusted to have only single to a few molecular layers of ILs on metal oxides, ensuring the presence of direct interactions between ILs and metal oxides.

Figure 2-7 illustrates the differences between T'_{onset} values of ILs when they are supported on SiO_2 and when they are supported on $\gamma\text{-Al}_2\text{O}_3$ and MgO . Accordingly, the positive bar indicates that the corresponding IL has a higher thermal stability limit when it is supported on SiO_2 than its $\gamma\text{-Al}_2\text{O}_3$ or MgO -supported counterparts. Results demonstrate that among 33 ILs, 27 of them have higher thermal stability when they are immobilized on SiO_2 than those on $\gamma\text{-Al}_2\text{O}_3$ and MgO . For instance, one of the most stable ILs, bulk $[\text{BMIM}][\text{NTf}_2]$, has T'_{onset} value of 685 K;²⁸ however, when it is supported on SiO_2 , thermal stability limit decreases to 633 K. Its T'_{onset} values on $\gamma\text{-Al}_2\text{O}_3$ and MgO are 569 K and 479 K, respectively. These results implies that as the PZC of the metal oxide increases with decreasing surface acidity, thermal stability limits of supported ILs decrease. This decrease in T'_{onset} values shows that the metal oxide type becomes the dominant factor controlling the thermal stability with an increase in its surface basic character²⁸ accompanied by significant shifts in the lower frequency region of the IR spectra (Figure 2-2B) of the IL on MgO . Thus, we infer that interaction between the IL and MgO controlling the thermal stability can be mostly by the anion side of the IL. Whereas, when the same IL is supported on SiO_2 , the IR bands of the IL have the major changes in the higher frequency region mostly indicating the

fingerprints of the cation (Figure 2-2B). Apparently, such changes on SiO₂ do not influence the thermal stability of the IL as much as those in the anion fingerprints when the IL is supported on MgO.

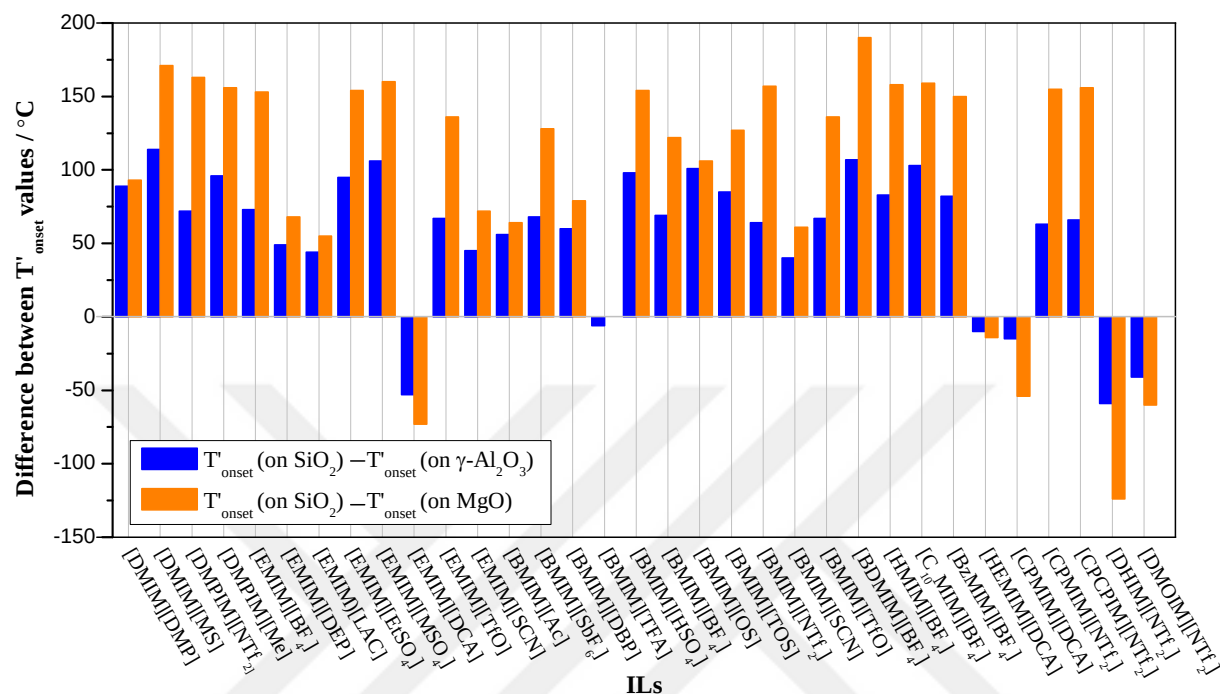


Figure 2-7. Differences between T'_{onset} of ILs when they are supported on SiO₂ and when they are supported on $\gamma\text{-Al}_2\text{O}_3$ (blue bars) and on MgO (orange bars).

In a previous work, the maximum tolerable temperatures of supported ILs with [BMIM]⁺ cation was analyzed in the aspects of anion effects. Data showed that the key factor controlling the thermal stability of ILs is the bonding strength of C2H proton. C2H is located between N1 and N3 atoms of the imidazolium cation. Imidazolium cation is a ring, which has a delocalized three-center (N1-C2-N3) and four-electron π -configuration across the N1-C2-N3 moiety.⁵⁰ Since N1 and N3 are highly electronegative, they carry the most of the negative charge, thus C2 proton has large partially positive charge because of the electron deficiency of the C–N bond and repulsive attractions in the C–C bond. Therefore, C2H is the most acidic proton in imidazolium, being responsible for directional hydrogen bonds between cation and anion, and the inter-ionic energy.⁵⁰ Wulf et. al.⁶¹ showed that as the anion structure changes,

C2H stretching vibration frequency of IL has either red- or blue-shift because of variations in anion-cation interactions. For instance, $\nu(\text{C2H})$ value of bulk [BMIM][BF₄] (3122 cm⁻¹) is higher than that of [BMIM][DBP] (3077 cm⁻¹), while their T'_{onset} values on SiO₂ are 331 and 495 K, respectively.²⁸ These results indicate that a high C2H bonding strength significantly reduces inter-ionic energies, resulting in a high thermal stability on SiO₂. We illustrated a direct dependence of the T'_{onset} of nine metal oxide-supported [BMIM]⁺-based ILs on $\nu(\text{C2H})$. Here, we extend this analysis to these 27 ILs, which have positive values in Figure 2-7, with decreasing T'_{onset} values from SiO₂ to MgO. Among these ILs, we excluded [BDMIM][BF₄], [DMPIM][NTf₂], and [DMIM][Me], as their cations are methyl substituted, and lack a C2 proton. Moreover, we also excluded [BMIM][OS], [HMIM][BF₄], [C₁₀MIM][BF₄], and [BzMIM][BF₄] from our analysis as their T'_{onset} values are significantly low because of their large anion or cation size. By using $\nu(\text{C2H})$ (FTIR spectra of individual bulk ILs are given in Appendix A2), C2H bonding strength of individual ILs were determined and correlations between $\nu(\text{C2H})$ and T'_{onset} supported-ILs were investigated. Figure 2-8 demonstrates a strong correlation between C2H stretching vibrations of individual ILs and their T'_{onset} values on metal oxides. In general, for supported ILs, increase in $\nu(\text{C2H})$ results in an increase in their thermal stability limits. Although the trend is the same for all of them, slopes of the plots for each metal oxide are different from each other as the variations in surface acidity of the metal oxide influence the IL-support interactions. The slopes of these correlations decrease in the following order: SiO₂ > γ -Al₂O₃ > MgO. A higher steepness of these slopes indicates that the inter-ionic energy becomes the dominant factor for determining the thermal stability limits. Accordingly, the dependency of the T'_{onset} on $\nu(\text{C2H})$ becomes the weakest for MgO-supported ILs (indicated by a slope of 1.24, compared to 2.76 and 2.48 for SiO₂ and γ -Al₂O₃, respectively). This weak dependence on the $\nu(\text{C2H})$ indicate that inter-ionic interactions

become less effective factor in controlling the thermal stability limits and the interactions between IL and the basic metal oxide becomes the dominant factor.

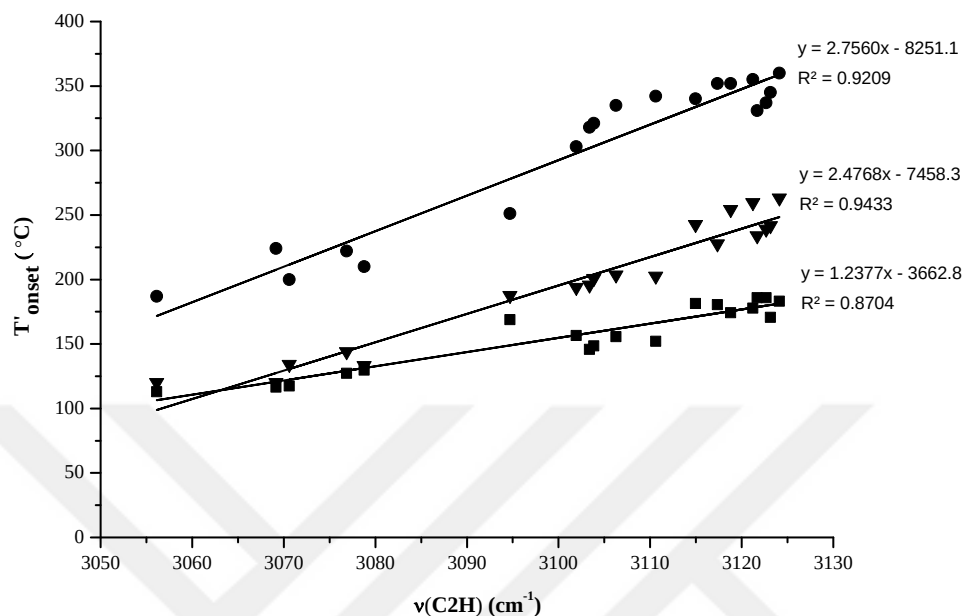


Figure 2-8. Variation of T'_{onset} values of metal oxide-supported ILs with increasing C2H acidity; SiO₂-supported ILs (●); γ -Al₂O₃-supported ILs (▼); MgO-supported ILs (■).

We have previously derived a simple model²⁸ to predict the thermal stability limits of metal oxide-supported [BMIM]⁺-based ILs as a function of $\nu(\text{C2H})$ and PZC. Here, we tested the performance of this model in predicting the T'_{onset} of these 27 ILs, with positive values in Figure 2-7, excluding those without C2H proton. Figure 2-9 illustrates that the model perfectly predicts the T'_{onset} of these metal oxide-supported ILs, except for those of [BMIM][OS], [HMIM][BF₄], [C₁₀MIM][BF₄], and [BzMIM][BF₄]. As discussed before, these exceptional ILs have significantly large cation or anion, which make them more susceptible for decomposition. Excluding these ILs, the model predicts the T'_{onset} values with an average relative error of 5.4%. We note that the values for SiO₂-supported [EMIM][LAC], [EMIM][SCN], and [BMIM][SCN] have the worst fit (shown in color in Figure 2-9). For

these ILs, the interactions with SiO₂ might be too strong, thus their T'_{onset} values are lower than the model-predicted values. The IR data given in Appendix A2 confirm this conclusion. Data show that the fingerprints of these ILs illustrate the highest amount of position shifts when they are supported on SiO₂, these changes occur mostly in the higher frequency region for the ILs with [SCN] anion (Figures A2-113 to A2-128, in Appendix A2), and they occur in both of the regions for [EMIM][LAC] (Figure A2-116 in Appendix A2). Excluding these ILs, the average relative error in the model predicted thermal stability temperatures becomes less than 5%.

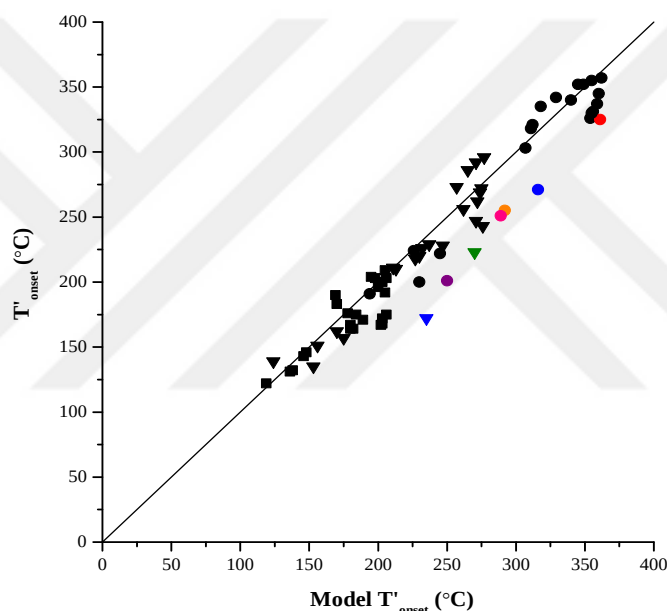


Figure 2-9. Comparison of model T'_{onset} values with experimental results: SiO₂-supported ILs (●); γ -Al₂O₃-supported ILs (▼); MgO-supported ILs (■), SiO₂-supported [BMIM][OS] (●); SiO₂-supported [BzMIM][BF₄] (●); SiO₂-supported [EMIM][LAC] (●); SiO₂-supported [EMIM][SCN] (●); SiO₂-supported [BMIM][SCN] (●); γ -Al₂O₃-supported [BMIM][OS] (▼); γ -Al₂O₃-supported [C₁₀MIM][BF₄] (▼). Solid line indicates the 45° line.

Besides the ILs with positive values in Figure 2-7, there are five ILs with negative values, indicating an opposite trend with respect to change in surface acidity of the metal oxide. T'_{onset} of these ILs increase with increasing surface basicity. These ILs are [EMIM][DCA], [CPMIM][DCA], [HEMIM][DCA], [DHIM][NTf₂], and [DMOIM][NTf₂].

Aiming to understand this opposite trend, we focused on their structures: [EMIM][DCA], [CPMIM][DCA], and [HEMIM][DCA] have [DCA]⁻ anion in common, so they are analyzed by considering a possible anion effect. [DCA]⁻ anion has high Lewis basic property, in contrast to the most commonly used anions, such as [PF₆]⁻, [BF₄]⁻, and [NTf₂]⁻.⁶² Also, charge delocalization is not apparent, producing high anion-cation interactions.⁶²⁻⁶³ Basicity of the anion influences the interactions between IL and metal oxide directly. These ILs demonstrate an increasing T'_{onset} trend with increasing basicity of the support; however, on SiO₂, the difference between T'_{onset} values of [EMIM][DCA] and [HEMIM][DCA] is 75 K, while on MgO it decreases to 35 K. It is easier for ILs including basic [DCA]⁻ anion to interact with acidic SiO₂ instead of almost neutral γ -Al₂O₃ and basic MgO, consistent with higher amount of changes in the positions of IR fingerprints of these ILs when they are supported on SiO₂ rather than their γ -Al₂O₃- and MgO-supported counterparts (data given in Appendix A2, Figures A2-118, A2-119, and A2-123). We predict that strong interactions between anion and acidic SiO₂ enable the initiation of decomposition reaction at an earlier temperature during the temperature ramp, resulting in a lower T'_{onset} value than that of these ILs on γ -Al₂O₃ and MgO. For other ILs with negative values in Figure 2-7, [DHIM][NTf₂] and [DMOIM][NTf₂], the opposite trend is clarified in aspects of cation/metal oxide interactions. Here, the key factor controlling the T'_{onset} of these supported ILs is the presence of functional groups on the imidazolium ring. Electron donating properties of -OH and -OCH₃ provide strong interactions with acidic SiO₂, causing an early thermal decomposition of IL. Conversely, in the case basic MgO, these ILs have difficulty to interact with the basic support, resulting in a higher thermal stability limit than its SiO₂- or γ -Al₂O₃-supported counterparts. However, we note that the IR data illustrate strong changes when these ILs are supported on metal oxides (Figure A2-114 to Figure A2-120 in Appendix A2). These changes might indicate that the structure of these ILs are not intact when supported. This might be the reason why they show

different decomposition temperatures when supported on different metal oxides because their initial structures on different metal oxides are not the same as a results of initial decomposition during the synthesis.

Among the ILs considered, T'_{onset} of [BMIM][TFA] does not show any significant change when supported on metal oxides. This result is because of the fluorination of anion, providing a reduction in nucleophilic character of anion, thus a higher stability of anion. Thus, we infer that the strong stability of anion-cation pair controls the decomposition mechanism when this IL is supported on the metal oxides.

2-5. Conclusions

Short-term thermal stability limits of 33 imidazolium ILs on metal oxides with varying surface acidities, SiO_2 , $\gamma\text{-Al}_2\text{O}_3$, and MgO were determined. Data show that stability limits are controlled directly by inter-ionic interactions quantified by FTIR fingerprints of $\text{C}2\text{H}$. Moreover, systematic changes in IL structures, such as changes in electronic structure and size of anion/cation, methylation on C2 site, and substitution of alkyl groups on the imidazolium ring with functional groups have significant effects. Also, an interaction between IL and metal oxide is another key factor. Commonly, supported ILs have lower thermal stability than their bulk case. This decrease in stability limits becomes significant as the surface acidity of metal oxide decreases. However, when the cation has an electron donating group, such as $-\text{OH}$ and $-\text{OCH}_3$, or when the IL has an anion with high Lewis basic character, such as $[\text{DCA}]^-$, the effect of IL/metal oxide interactions work in an opposite way and the stability limit increases with decreasing surface acidity. Results presented here can be utilized to choose proper ILs that can withstand the operating conditions of the materials, in which there is a direct interaction of IL with metal oxides, such as SCILL or SILP type catalysts or SILM.

2-6. Acknowledgement

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2-7. Supplementary Materials

All TGA data, FTIR spectra of bulk and metal oxide-supported ILs, individual percent error values of each model-predicted T'_{onset} value for each supported IL and a representative SEM/EDX image.

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Chapter 3

Interactions of [BMIM][BF₄] with Metal Oxides and Their Consequences on Stability Limits*



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3-1. Abstract

Interactions between 1-*n*-butyl-3-methylimidazolium tetrafluoroborate, [BMIM][BF₄], and high surface area metal oxides, SiO₂, TiO₂, Fe₂O₃, ZnO, γ -Al₂O₃, CeO₂, MgO, and La₂O₃, with a wide range of point of zero charges (PZC), from pH = 2 to 11, were investigated by combining infrared (IR) spectroscopy with density functional theory (DFT) calculations. The shifts in spectroscopic features of the ionic liquid (IL) upon coating different metal oxides were evaluated to elucidate the interactions between IL and metal oxides as a function of surface acidity. Consequences of these interactions on the short- and long-term thermal stability limits as well as the activation energy (E_a) and rate constant for thermal decomposition of the supported IL were evaluated. Results show that stability limits and E_a of the IL on each metal oxide significantly decrease with increasing PZC of the metal oxide. Results presented here indicate that the surface acidity strongly controls the IL–surface interactions, which determine the material properties, such as thermal stability. Elucidation of these effects offers opportunities for rational design of materials which include direct interactions of ILs with metal oxides, such as solid catalysts with ionic liquid layer (SCILL) and supported ionic liquid phase (SILP) catalysts for catalysis applications or supported ionic liquid membranes (SILM) for separation applications.

3-2. Introduction

Ionic liquids (ILs) have gained a great interest especially in the last decade because of their tunable properties¹ with an estimated 10^{18} different anion/cation combinations.² Each different ion pair combination results in a different set of physicochemical properties; thus, these salts are considered as “designer solvents”.³ With these tunable properties they can be utilized in electrolytes in electrochemical devices,⁴ lubricants,⁵ fuel cells,⁶ catalysts or catalyst activations,⁷ separation media,⁸⁻⁹ biomedical,¹⁰ and CO₂ capture applications.¹¹⁻¹² Among

these application areas, in catalysis, ILs enable immobilization of homogenous type catalysts on metal-oxides¹³ as in supported ionic liquid phase (SILP) catalyst¹⁴⁻¹⁶ or they can be utilized as a selective layer over the supported metal catalysts to increase selectivity as in solid catalysts with ionic liquid layer (SCILL)¹⁷⁻¹⁸. Although ILs offer many advantages in these IL-assisted systems,¹⁹ the interaction between IL/metal oxide strongly modifies some of their properties, such as thermal decomposition behavior,²⁰ as well as their leaching out²¹ or evaporation²²⁻²⁴ from the surface. The changes in these properties are generally influenced from nature and charge of the surface²⁵ and structure of the IL.²⁶ For instance, Kosmulski et al.²⁷ showed that the thermal decomposition temperature of IL, 1-*n*-butyl-3-methylimidazolium triflate, decreased significantly in the presence of acidic silica. Furthermore, Ngo et al.²⁸ illustrated that the thermal stability of ILs were significantly affected as the pan material used for thermogravimetric (TGA) measurements was changed from alumina to aluminum. Moreover, Tripathi et. al.²⁹ illustrated the strong interactions between 1-ethyl-3-methyl imidazolium tetrafluoroborate, [EMIM][BF₄], and mesoporous MCM-41. Accordingly, the interaction of cation is from oxygen of silica pore wall and they lead to a change in thermal stability and glass transition temperature of the IL as well. And very recently, we reported the short-term thermal stability limits of 33 different imidazolium ILs on various metal oxides, SiO₂, γ -Al₂O₃, and MgO.³⁰⁻³² Results of these studies illustrated that systematic changes in IL structure, such as those in anion/cation size, anion/cation interactions, C2 site methylation and changes in electronic structure, alter the interactions between IL/metal oxides. Moreover, surface acidity of metal oxide is another key factor in determining these interactions such that in general as the metal oxide surface basicity increases the thermal stability of IL on metal oxides decreases significantly, with a few exceptional ILs with functionalized groups on the cation. In the highlights of these previous studies, we predicted that metal oxides can work as a catalyst to initiate the thermal

decomposition reaction at lower temperatures than those of the bulk ILs. Apparently, the interactions between ILs and metal oxides strongly influence the system properties. Therefore, investigation of these interactions is required for a better control on the desired property of the IL/metal oxide systems. Surface science-based approaches have emerged to understand these interactions with well-defined metal oxides at the fundamental level.^{23-24,33-34} For instance, Schernich et. al.³⁴ investigated the effect of interactions between 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [HMIM][NTf₂], and well-defined CeO₂(111). They revealed that the reaction is between IL/surface via carbene of cation and this interaction results in a good thermal stability. However, when partially reduced CeO_{2-x} was used, surface mostly interacts with the anion resulting in a change in the thermal stability behavior. Moreover, Sobota et. al.²⁴ illustrated that the interactions between 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [BMIM][NTf₂] and well-ordered Al₂O₃ is via anion of the IL. Furthermore, Federov et al.,³⁵ studied the molecular modelling of the interfacial layer of dimethyl imidazolium chloride, [DMIM][Cl], at a cationic graphene layer. Accordingly, preferential adsorption of the imidazolium ring at the graphene surface and the anion result in a several distinct IL layer formation on the surface. As illustrated by these computational and surface science-based studies interactions of well-defined IL/oxides can be elucidated. However, in real systems, ILs are supported on high surface area metal oxides, leading to more complex interactions because of the complex nature of the metal oxide surface. Thus, such systems should also be investigated in detail in the light of valuable information that these computational and surface science studies provide.

Here, we report the results of our study on various IL/high surface area metal oxide combinations. The metal oxides were chosen in such a way that their surface acidity indicated by the point of zero charge (PZC) values were covering a wide range of pH values, from pH = 2 to 11. 1-*n*-butyl-3-methylimidazolium tetrafluoroborate, [BMIM][BF₄], was chosen as the

IL as it is one of the most commonly used and better understood ILs. The interactions of this IL on the following metal oxides: SiO₂, TiO₂, Fe₂O₃, ZnO, γ -Al₂O₃, CeO₂, MgO, and La₂O₃, were investigated spectroscopically to elucidate the influence of surface acidity on IL–metal oxide interactions. Experimental infrared (IR) spectroscopy features of the bulk IL was first fully assigned by the help of density functional theory (DFT) calculations performed at the B3LYP level with a basis set of 6-31+GD). Then the variations in the positions of these IR features upon coating metal oxides were determined to evaluate any changes in the positions as a result of the IL–metal oxide interactions. Then the consequences of these interactions on short- and long-term thermal stability limits of metal oxide-supported [BMIM][BF₄] were elucidated. These results illustrate that interactions with the surface play a crucial role in determining the properties of systems involving direct interactions of ILs with metal oxides,³⁶⁻³⁷ such as in the case of SCILL¹⁷ and SILP⁷ type catalysts and supported IL membranes, SILM.³⁸

3-3. Materials & Methods

3-3.1. Materials

[BMIM][BF₄], solvents, and metal oxides, SiO₂, TiO₂, Fe₂O₃, ZnO, γ -Al₂O₃, CeO₂, MgO, and La₂O₃, were purchased from Sigma-Aldrich at the highest available purity level. All metal oxides were calcined at appropriate temperatures (SiO₂ at 793 K; TiO₂ and CeO₂ at 673 K; ZnO, Fe₂O₃ and γ -Al₂O₃ at 773 K; La₂O₃ at 873 K and; MgO at 973 K) in air for 5 h with a temperature ramp of 3 K/min to the desired temperature. The IL was dried at 353 K in a vacuum oven for overnight then stored in an Ar-filled glove box, as reported before.³⁰ 200 mg of IL was first dissolved in 4 g of acetone or methanol; and 1 g of metal oxide was immersed in the IL-solvent mixture. Resulting mixture was mixed gently for 1 h and dried in vacuum oven for one day at 343 K. Performance of the drying process was confirmed by IR spectra of

the dried samples showing none to almost negligible solvent/water peaks. Metal oxide supported IL samples were obtained in powder form. Data presented in Appendix A3 confirm that use of different solvents does not have any detectable effect within the error range of our measurements.

3-3.2. Point of Zero Charge (PZC) Determination

PZC and particle size of metal oxides were determined by using Zetasizer Nanoseries Instrument coupled with Malvern Multipurpose titrator. As described elsewhere,³⁰ each metal oxide (4 mg) sample was dispersed in 0.1 M KNO₃ solution (20 mL) and the solution was ultrasonicated for approximately 5 min. Dispersed samples were titrated with 0.5 M NaOH and HNO₃ as described by Gulicovski et al. Instrument pH increment was set to 0.2 for measurements in SiO₂, TiO₂, and γ -Al₂O₃; that for backward measurements was 0.1 for MgO, CeO₂, and Fe₂O₃. Tolerance was set to 0.2 for SiO₂ and TiO₂; and to 0.05 for γ -Al₂O₃, MgO, CeO₂, and Fe₂O₃. Refractive indexes used during measurements are 1.46, 2.90, 1.76, 1.74, 2.20, and 2.94 for metal oxides SiO₂, TiO₂, γ -Al₂O₃, MgO, CeO₂, and Fe₂O₃, respectively. Absorbance values used during measurements are 0.01, 1.0, 0.01, 0.1, 0.01, and 0.1 for metal oxides SiO₂, TiO₂, γ -Al₂O₃, MgO, CeO₂, and Fe₂O₃, respectively. PZC of ZnO and La₂O₃ were used as 7 and 10.3, respectively, consistent with studies of Kosmulski et al.³⁹ Zetasizer Nanoseries instrument coupled with Malvern Multipurpose titrator were used to measure PZC and particle size of metal-oxides.

3-3.3. Thermogravimetric Analysis (TGA)

For the determination of short-term thermal stability limits, TGA measurements were performed and analyzed as described in Chapter 2, Section 2-2.3.

3-3.4. Fourier Transform IR (FTIR) Spectroscopy

FTIR spectra of each sample were collected and analyzed as described in Chapter 2, Section 2-3.4.

3-3.5. Scanning Electron Microscopy coupled with Energy-Dispersive X-Ray Spectroscopy (SEM/EDX)

SEM/EDX images and spectra were collected as described in Chapter 2, Section 2-3.5.

3-3.6. Brunauer-Emmett-Teller (BET) Surface Area Analysis and Barrett-Joyner-Halenda (BJH) Pore Size and Volume Analysis

BET analyses were performed on a Micromeritics ASAP 2020 HD Accelerated Surface Area and Porosimetry Analyzer model instrument. Approximate sample amount loaded into the instrument was 250 mg for metal-oxides and 90 mg for [BMIM][BF₄] coated metal-oxides. Metal-oxides and supported IL samples were degassed for 10 h at 573 and 353 K, respectively. 9 mm-small bulbs were used in analysis. Each measurement was repeated at 10 different pressure points in between 0.05–0.3 P/P₀.

3-3.7. Karl Fischer Titration for Water Content Determination

Karl Fischer titration measurements were carried out with a Titroline 7500 KF trace titrator at 294 K. [BMIM][BF₄] was dried at 343 K for 12 h before the measurement. Titration graph is given in Figure A3-1 in Appendix.

3-3.8. Computational Details-Density Functional Theory Calculations

DFT calculations were performed on Gaussian 09 software.⁴⁰ Different possible conformer geometries for [BMIM][BF₄] were fully optimized at the Becke's three parameter hybrid

exchange functional⁴¹ and the Lee-Yang-Parr correlation functional⁴² (B3LYP) method together with the 6-31+GD) basis set. In order to improve numerical accuracy and reliability, a “tight” convergence criteria (i.e., 10^{-8} on root mean square (RMS) density matrix, 10^{-6} on maximum density matrix and energy) and “ultrafine” numerical integration grid (i.e., 99 radial shells and 590 angular points per shell) were applied to all calculations. Possible geometries of [BMIM]⁺ were first optimized to acquire the most-stable conformer geometry. Subsequently, a full conformer search was performed to obtain the lowest-energy equilibrium geometry of [BMIM][BF₄] by rotating the position of [BF₄]⁻ around the most-stable conformer of [BMIM]⁺. Vibration frequencies were also calculated at the same level of theory, and there were no imaginary frequencies confirming that all optimized geometries corresponded to true minima on the potential energy surface.

Moreover, binding energies, ΔE_B , between anions and cations were calculated at the same level of theory using following formula:⁴³⁻⁴⁴

$$\Delta E_B = E_{IP} - E_C - E_A + \Delta ZPVE \quad (1)$$

$$\Delta ZPVE = ZPVE_{IP} - ZPVE_C - ZPVE_A \quad (2)$$

where E_{IP} , E_C , and E_A are the energies of ion pair, cation and anion, respectively. Similarly, $ZPVE_{IP}$, $ZPVE_C$, and $ZPVE_A$ are the zero-point vibrational energies of ion pair, cation and anion, respectively. All ZPVEs were scaled for B3LYP/6-31+GD) level of theory by using a scaling factor of 0.9829.⁴⁵

3-4. Results and Discussion

As a first step in understanding the interactions of [BMIM][BF₄] with metal oxides, IR fingerprints of the IL both in bulk and supported form should be identified precisely. In order to acquire a thorough peak assignment for the experimental IR spectrum of [BMIM][BF₄], we

performed a conformation search at 6-31+GD) level of theory to obtain the most stable equilibrium geometry that satisfactorily represents the dynamic structure. The conformation search of [BMIM][BF₄] yielded seven different stable conformer geometries (given in Figure A3-2 to Figure A3-7) and their ZPVE-corrected relative energies and ZPVE-corrected binding energies were provided in Table 3-1. Among these conformers, Conf-1, structure given in Figure 3-1, was selected as the lowest-energy equilibrium geometry. The relative energy, ΔE (kJ mol⁻¹), of each conformer was calculated by subtracting ZPVE-corrected energy of the corresponding conformer from that of the lowest-energy equilibrium geometry (i.e., Conf-1). Although the first three conformers (i.e., Conf-1, Conf-2, and Conf-3) are energetically quite similar, their ion-pair conformations differ considerably from each other. For the lowest energy conformer (Conf-1), the [BF₄]⁻ anion is located below the plane of imidazolium ring. For Conf-2 and Conf-3, however, the [BF₄]⁻ anion is located above the imidazolium ring plane. Detailed comparison of the conformer geometries can be found in Appendix A3, where corresponding xyz coordinates are also provided for each conformer.

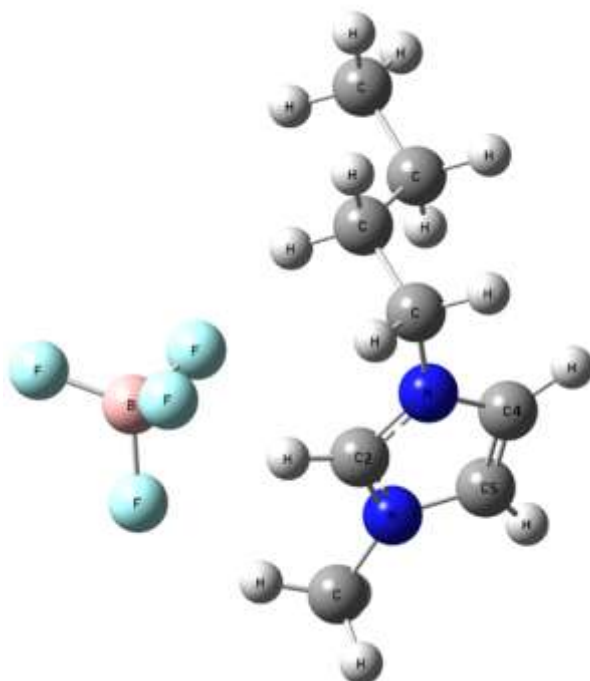


Figure 3-1. Structure of the most stable conformer (Conf-1) in DFT.

For each conformer obtained, computational FTIR values were obtained and scaled with a scaling factor of 0.9686.⁴⁶⁻⁴⁸ Table 3-2 presents a comparison of experimental, computational and scaled FTIR bands of bulk [BMIM][BF₄] and their corresponding assignments, consistent with literature values given in Appendix A3, Table A3-2.⁴⁶⁻⁴⁷ Moreover, Figure 3-2 shows there is a high consistency ($R^2 = 0.998$) between the experimental IR bands and their corresponding values calculated on Conf-1 geometry, confirming that this conformer can successfully represent the [BMIM][BF₄] structure. Conf-2 and Conf-3, on the other hand, do not provide such a good representation of the experimental IR bands (their corresponding R^2 values are usually below 0.85), even though their ZPVE-corrected energies are not significantly different from that of Conf-1 (Table 3-1). We note that it is possible to have more than one conformer for an IL as reported by Holomb et. al.⁴⁹ and Katsyuba et. al.⁴⁶ However, our data suggest that only the Conf-1 can satisfactorily represent the experimental IR features. Thus, we infer that it is the major contributor to the features observed in the experimental spectrum, even though Conf-2 and Conf-3 might be other possible conformers with minor contribution.

Table 3-1. ZPVE-corrected relative energies (ΔE) and ZPVE-corrected binding energies (ΔE_B) of all [BMIM][BF₄] conformers.

Conformer ID	ΔE (kJ mol ⁻¹)	ΔE_B (kJ mol ⁻¹)
Conf-1	0.00	-338.86
Conf-2	0.54	-338.32
Conf-3	0.87	-337.98
Conf-4	3.12	-335.74
Conf-5	31.48	-307.37
Conf-6	32.02	-306.84
Conf-7	38.32	-300.54

Table 3-2. Experimental and computational FT-IR bands of bulk [BMIM][BF₄] and their assignments. Literature comparison is given in Table A3-2.

IR assignments	Experimental IR bands (cm ⁻¹)	Conf-1 IR bands (cm ⁻¹)	Scaled IR bands (cm ⁻¹)
Higher frequency region			
Ring $\nu(\text{C4-C5H})_{\text{asym}}$ (s)	3162	3300	3196
Ring $\nu(\text{C2H})_{\text{sym}}$ (s)	3121	3224	3123
Ring $\nu(\text{CH}_3)_{\text{asym}}$ (vs)	3113	3181	3081
Butyl $\nu(\text{HC1HH})_{\text{sym}}$ (s), $\nu(\text{HC2H})_{\text{asym}}$ (w)	2964	3081	2984
Ring $\nu(\text{CH}_3)_{\text{sym}}$ (vs)	2939	3076	2979
Butyl $\nu(\text{HC1H})_{\text{sym}}$, $\nu(\text{HC2H})_{\text{sym}}$, $\nu(\text{HC3H})_{\text{asym}}$, $\nu(\text{HC4HH})_{\text{sym}}$	2876	3040	2945
Lower frequency region			
Ring in plane asym stretch (vs), Ring $\delta(\text{C2H})$ (vs), Ring CH_3 $\delta(\text{HCH})$ scissoring (s), Ring $\nu(\text{C2-N})$ (s)	1574	1615	1564
Ring $\delta(\text{CH}_3)$ wagging (vs),	1467	1480	1434
Butyl $\delta(\text{HC1H})$ scissoring (w)			
Ring in plane asym stretch (vs), Butyl $\delta(\text{HC1H})$ twisting (vs),	1433	1462	1416
Ring in plane sym stretch (s),	1385	1415	1371
Butyl $\delta(\text{C1H})$, $\delta(\text{C2H})$, $\delta(\text{C3H})$ (s),			

Ring $\delta(\text{CH}_3)$ wagging (s)				
Butyl $\delta(\text{C1H})$, $\delta(\text{C2H})$, $\delta(\text{C3H})$ (s), Ring $\nu(\text{N-Bu})$ (m),	1340	1367	1324	
Ring $\delta(\text{C2H})$, $\delta(\text{C4H})$, $\delta(\text{C5H})$ (vs) Ring in plane asym stretch (s), Ring $\nu(\text{C-N})$ $\nu(\text{BF}_4)$ (vw)	1170	1192	1155	
$\nu(\text{BF}_4)$ (vs), Ring CH_3 $\delta(\text{CH})$ wagging (s),	1119	1172	1135	
Ring $\delta(\text{C2H})$, $\delta(\text{C4H})$, $\delta(\text{C5H})$ (m)				
Ring $\delta(\text{HC4C5H})$ scissoring (vs), Ring CH_3 $\delta(\text{CH})$ (s), Butyl $\nu(\text{CCCC})_{\text{asym}}$ (m)	1091	1127	1092	
$\nu(\text{BF}_4)_{\text{asym}}$ (vs), Ring in plane sym stretch (w),	1046	1015	983	
Ring $\delta(\text{C4H-C5H})$ (w) Butyl $\delta(\text{HC1H})$ wagging (s), $\delta(\text{HC2H})$ twisting (s),	1034	998	967	
$\delta(\text{HC3H})$ twisting (s), $\delta(\text{HC4H})$ (m), Ring in plane sym stretch (w),				
$\nu(\text{BF}_4)_{\text{asym}}$ (vw) $\nu(\text{BF}_4)_{\text{asym}}$ (vs),	1017	979	948	
Ring $\delta(\text{C2H})$ (vs), Butyl $\delta(\text{HC4H})$ (m)				
$\nu(\text{BF}_4)_{\text{asym}}$ (vs), Butyl $\delta(\text{HC1H})$ rocking (vs),	987	966	936	

Note that ν : stretching, δ : bending, vs: very strong, s: strong, m: medium, w: weak, vw: very weak. Literature reference values were taken from references 48 and 49.

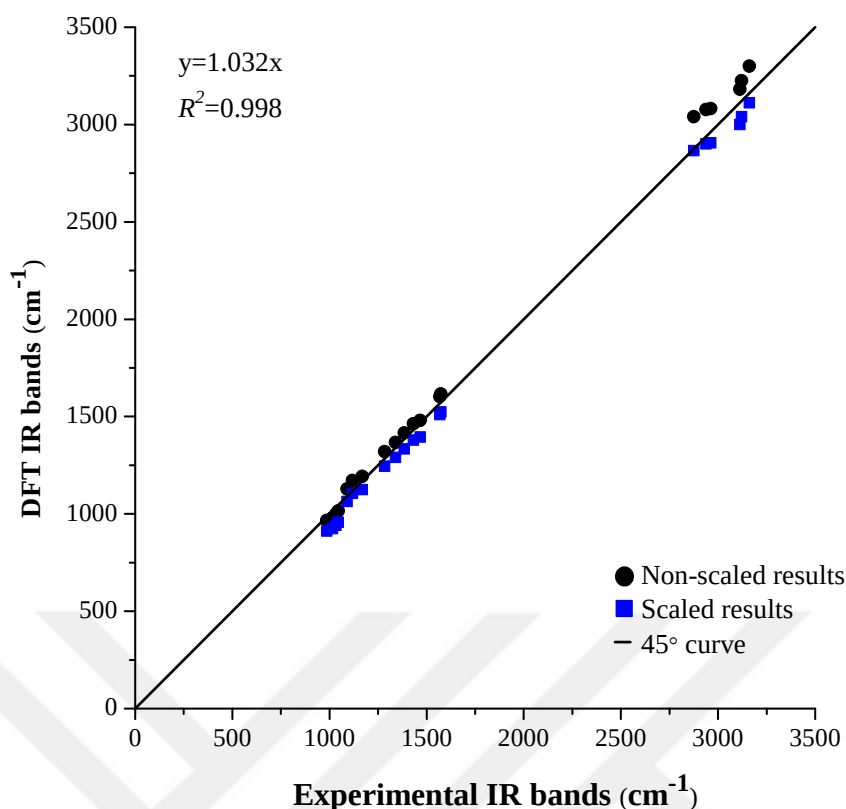


Figure 3-2. Correlation between experimental and computational (calculated for Conf-1 geometry) FT-IR fingerprint of [BMIM][BF₄].

After assigning the FT-IR fingerprints of bulk [BMIM][BF₄] by DFT calculations, corresponding positions of these fingerprints upon coating various metal oxides with this IL were identified. For this purpose, [BMIM][BF₄] was dried until the water content decreases below 1000 ppm and then impregnated on calcined metal oxides: SiO₂, TiO₂, Fe₂O₃, ZnO, γ -Al₂O₃, CeO₂, MgO, and La₂O₃.

Uniformity of distribution and layer thickness of ILs on metal oxides is important to understand the interactions between ILs and metal oxides and compare each supported IL. Therefore, we collected SEM imaging complemented by EDX mapping at different locations of supported ILs (Figure 3-3) and observed uniform distribution of IL on each metal oxide, as before.³⁰ Calculated IL loading amounts based on EDX spectra given in Appendix A3, Table A3-3 confirm that except for CeO₂-supported [BMIM][BF₄], all samples were prepared with

an IL loading around 11-16 %. Furthermore, for a direct contact of ILs and metal oxides, IL thickness layer on metal oxides should not exceed tens of nanometers. Otherwise, the effect of metal oxide on physicochemical properties of the IL becomes negligible and ILs behave as bulk-like.⁵⁰ Therefore, thickness of IL layer was calculated by dividing the difference in total pore volume of uncoated and IL-coated metal oxide over the BET surface area of the uncoated metal oxide (BET results of uncoated and IL-coated samples were given in Appendix A3, Section A3-4). Results given in Table 3-3 indicate an IL thickness of less than 2 nm on all metal oxides. This thickness value indicates only single to a few molecular layers of IL on metal oxides, ensuring direct interactions between the IL and metal oxides.⁵⁰ Moreover, pore filling degree (α) of supported [BMIM][BF₄] samples were also calculated as reported by Kernchen et al.¹⁷ Results of the calculations indicate that except from SiO₂-supported IL, volume content of the IL in pores of all metal-oxides are similar to each other with an α value higher than 0.85 (Table 3-3).

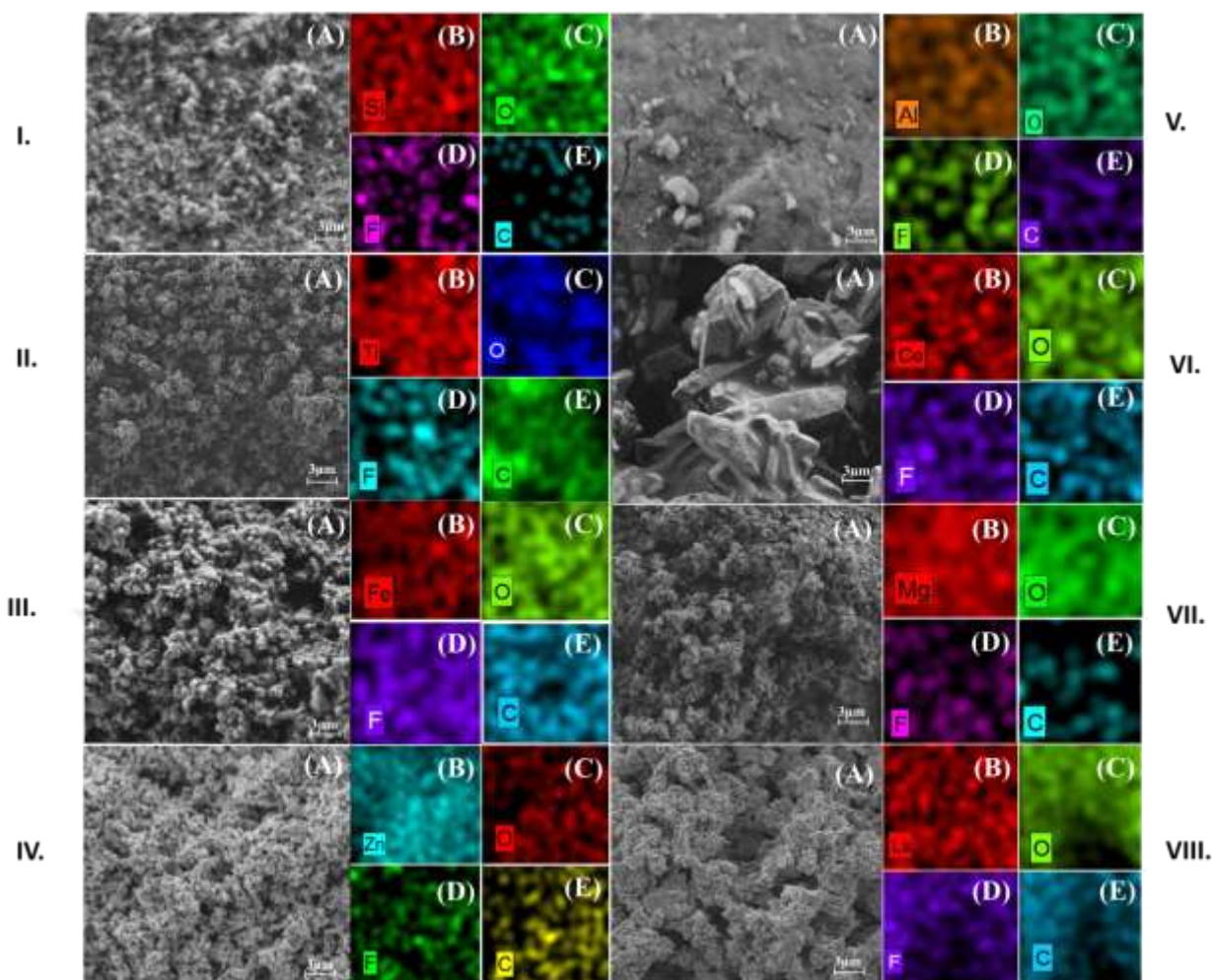


Figure 3-3. Representative SEM images characterizing the IL [BMIM][BF₄] on different metal oxides: SiO₂ (IA), TiO₂ (IIA), Fe₂O₃ (IIIA), ZnO (IVA), γ -Al₂O₃ (VA), CeO₂ (VIA), MgO (VIIA), La₂O₃ (VIII A); and EDX map showing the distribution of individual atoms (IB): silica, (IIB): titanium; (IIIB): iron; (IVB): zinc; (VB): aluminum; (VIB): cerium; (VIIB): lanthanum; (VIIIB): magnesium. (IC, IIC, IIIC, IVC, VC, VIC, VIIC, VIIIC): oxygen; (ID, IID, IID, IVD, VD, VID, VIID, VIIID): fluorine; (IE, IIE, IIIE, IVE, VE, VIE, VIIIE, VIIIE): carbon. EDX spectra of supported IL samples are given in Figures A3-8 to A3-15.

After confirmation of the uniform dispersion of IL on each metal oxide, IR spectra of bulk and metal oxide-supported [BMIM][BF₄] samples were measured and compared with each other. IR features of the IL molecules adsorbed on the metal oxide surface indicate some changes in terms of their positions and relative intensities as compared to their counterparts in bulk IL. Steinrück et al.²³ and Sobota et al.²⁴ discussed such changes and concluded that there are direct interactions between IL and surface. Here, we present our data in Figure 3-4 for

[BMIM][BF₄] on SiO₂, TiO₂, Fe₂O₃, ZnO, γ -Al₂O₃, CeO₂, MgO, and La₂O₃ in two different regions: 950-1600 cm⁻¹, representing the fingerprints of mostly anion of the IL, and 2700-3300 cm⁻¹, representing the fingerprints of the cation of the IL.²³ In both of these high and low frequency regions of all supported ILs there exist some changes in the relative intensities of fingerprints accompanied by blue- or red-shifts from their corresponding positions in the IR spectrum of bulk [BMIM][BF₄]. The individual shift amounts at each peak on different metal oxides are listed in Table 3-4 and 3-5. These changes in both position and intensities of the fingerprints confirm that the IL has strong interactions with metal oxides in these regions and these interactions strongly depend on the type of the metal oxide.

Table 3-3. BET surface area, estimated IL layer thicknesses and pore filling degree of metal-oxides and supported ILs. BET results are provided in Appendix A3, Section A3-4.

Sample	BET surface area (m ² /g)	Pore volume (m ³ /g*10 ⁶)	IL loading, determined by ICP-MS (wt%)	IL layer thickness (nm)	Pore filling degree,* α
SiO ₂	331	1.2			
[BMIM][BF ₄]/SiO ₂	194	0.88	18.1	0.97	0.31
TiO ₂	11	0.013			
[BMIM][BF ₄]/TiO ₂	4	0.0022	18.2	0.98	1.03
Fe ₂ O ₃	6	0.0082			
[BMIM][BF ₄]/Fe ₂ O ₃	2	0.0013	16.5	1.15	1.05
ZnO	5	0.0067			
[BMIM][BF ₄]/ZnO	1	0.0005	15.6	1.24	1.10
γ -Al ₂ O ₃	185	0.26			
[BMIM][BF ₄]/ γ -Al ₂ O ₃	14	0.061	16.8	1.08	0.80
CeO ₂	10	0.032			
[BMIM][BF ₄]/CeO ₂	0.6	0.0098	15.2	2.22	0.71
MgO	33	0.069			
[BMIM][BF ₄]/MgO	5	0.0072	14.7	1.87	1.05
La ₂ O ₃	1	0.0016			
[BMIM][BF ₄]/La ₂ O ₃	1	0.00055	15.0	1.05	0.76

* $\alpha = (V_{\text{pore,0}} - V_{\text{pore,IL}}) / V_{\text{pore,0}}$, where $V_{\text{pore,0}}$ is the initial pore volume of the corresponding metal oxide and $V_{\text{pore,IL}}$ is the pore volume of the metal oxide supported IL samples.¹⁷

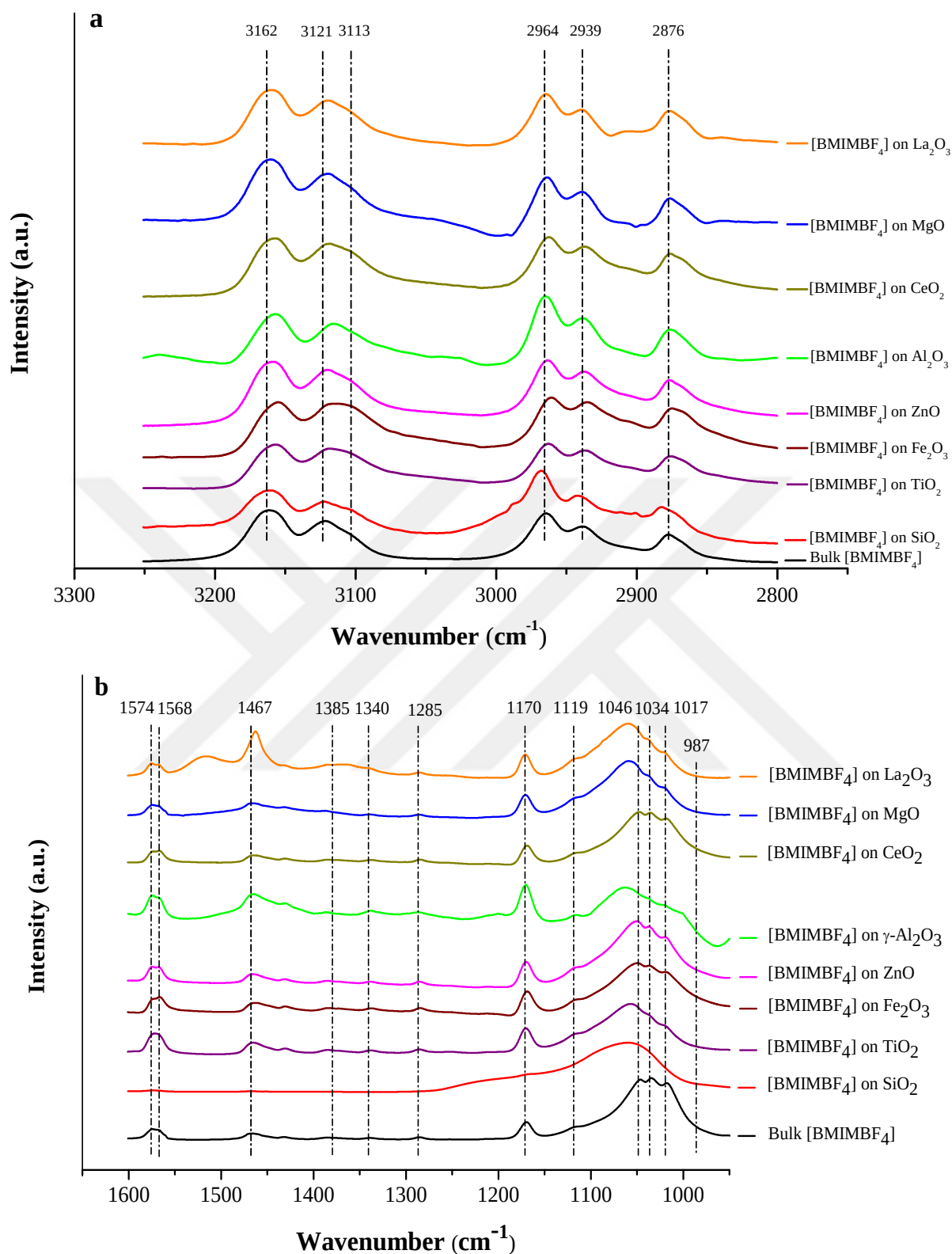


Figure 3-4. IR spectra of [BMIM][BF₄]: bulk (—); SiO₂-supported (—); TiO₂-supported (—); Fe₂O₃-supported (—); ZnO-supported (—); γ-Al₂O₃-supported (—); CeO₂-supported (—); MgO-supported (—); La₂O₃-supported (—) in the region of a) 2750-3300 cm⁻¹ b) 950-1600 cm⁻¹.

Table 3-4. Shifts in IR bands of bulk [BMIM][BF₄] upon coating on metal oxides in higher frequency region. Data was collected at spectral resolution of 4 cm⁻¹.

Supported ILs	IR bands of bulk [BMIM][BF ₄] in higher frequency region (cm ⁻¹)					
	2876	2939	2964	3113	3121	3162
[BMIM][BF ₄]/SiO ₂	7	-5	4	x	0	-3
[BMIM][BF ₄]/TiO ₂	-1	-9	-8	-6	1	-6
[BMIM][BF ₄]/Fe ₂ O ₃	-4	-5	-3	x	-8	-4
[BMIM][BF ₄]/ZnO	0	-4	-1	-2	-5	-3
[BMIM][BF ₄]/γ-Al ₂ O ₃	0	0	1	x	-4	-3
[BMIM][BF ₄]/CeO ₂	0	-3	-1	-2	-3	-3
[BMIM][BF ₄]/MgO	0	1	1	-2	0	-1
[BMIM][BF ₄]/La ₂ O ₃	0	-1	0	-2	0	-1

Table 3-5. Shifts in IR bands of bulk [BMIM][BF₄] when coated on metal oxides in lower frequency region. Data was collected at spectral resolution of 4 cm⁻¹.

Supported ILs	IR bands of bulk [BMIM][BF ₄] in lower frequency region (cm ⁻¹)											
	987	1017	1034	1046	1119	1170	1285	1340	1385	1467	1568	1574
[BMIM][BF ₄]/SiO ₂	-7	4	3	9	1	0	-1	x	x	-1	1	2
[BMIM][BF ₄]/TiO ₂	x	4	2	11	1	0	0	-2	0	-8	-1	0
[BMIM][BF ₄]/Fe ₂ O ₃	3	0	0	3	-2	-1	-1	-3	-5	-5	-1	2
[BMIM][BF ₄]/ZnO	6	-1	1	5	0	0	0	-2	-1	0	-2	1
[BMIM][BF ₄]/γ-Al ₂ O ₃	2	0	4	19	2	0	0	-1	0	-1	0	-2
[BMIM][BF ₄]/CeO ₂	1	-3	1	3	-5	-1	0	-3	-1	-3	-1	2
[BMIM][BF ₄]/MgO	5	2	3	13	-3	1	0	-2	0	-3	-2	1
[BMIM][BF ₄]/La ₂ O ₃	12	1	4	14	-2	0	0	-3	-14	-4	-1	2

As seen in Table 3-4 and 3-5, upon supporting [BMIM][BF₄] on SiO₂, the bands at 2939 and 987 cm⁻¹ red-shifted by approximately 5 and 7 cm⁻¹, respectively, excluding the shifts lower than the spectral resolution of 4 cm⁻¹. These bands correspond to imidazolium ring ν(CH₃)_{sym} and butyl δ(HC1H) rocking (or ν(BF₄)_{asym}) features, respectively. Together with these red-shifted features, bands at 2964, 2876, 1046, and 1017 cm⁻¹ indicate blue-shifts (4, 7, 9, and 4 cm⁻¹, respectively). Among these blue-shifted bands, those at 1046 and 1017 cm⁻¹ are directly attributed to ν(BF₄) and the remaining bands belong to the stretching of butyl

group of the imidazolium ring. Such small differences in the individual band positions and intensities might be interpreted in several different ways. Considering all of these changes together, our interpretation is that the IL interacts with SiO₂ surface through its imidazolium ring. Such interaction results in weakening of the interionic interaction of the IL. Thus, the B–F bonding gets stronger as confirmed by the blue-shifts at 1046 and 1017 cm⁻¹. Furthermore, because of the electron exchange between the surface and the imidazolium ring, the bonding between the ring and the butyl group also weakens, which leads to stronger C–H bonding in the butyl group as indicated by a blue-shift in 2964 and 2876 cm⁻¹. We note that such changes might indicate different kind of interactions. However, the interpretation provided above is consistent with the recent reports on the confinement of ILs in nano- and mesoporous SiO₂ illustrating that the C–H of the imidazolium ring interacts with the oxygen of the silica surface.^{29,51}

As given in Tables 3-4 and 3-5, the IR spectra of the TiO₂-supported [BMIM][BF₄] demonstrate red shifts at 3162, 3113, 2964, 2939, 1467, and 1385 cm⁻¹, indicating a decrease in C–H stretching or bending vibrations in butyl groups and imidazolium ring itself. Such changes in C–H stretching or bending vibrations in butyl groups might indicate possible immediate interactions of these CH moieties with the surface, or mutual disposition of cationic and anionic components of the IL. Besides these red shifts, data indicate a blue shift of approximately 11 cm⁻¹ on a band at 1046 cm⁻¹, and of 4 cm⁻¹ on that at 1017 cm⁻¹, corresponding to butyl $\nu(\text{BF}_4)_{\text{asym}}$. These changes might be as a result of the alterations in the interionic interactions originating from the presence of interactions with the surface. Previous reports illustrated a direct interaction of imidazolium ring with the TiO₂ surface.⁵²⁻⁵³ Accordingly, as the alkyl chain length increases, the alkyl group starts to play a role in the interactions between the IL and TiO₂ surface.⁵⁴ Consistent with these reports and based on the changes in the IR spectra, we infer that the IL interacts with the TiO₂ surface through its

cation. This interaction reduces the electron density available for internal bonding within the imidazolium ring, thus the corresponding IR bands shows red-shift, indicating that the C–H stretching weakens. Furthermore, as the interactions between the anion and cation weakens because of electron donation from cation to surface, the B–F bonding becomes stronger as confirmed by the presence of blue-shift on bands located at 1046 and 1017 cm⁻¹.

In higher frequency region of Fe₂O₃-supported IL (Table 3-5), the bands at 3162, 2939, and 2876 cm⁻¹, corresponding to ring $\nu(\text{C4-C5H})_{\text{asym}}$, ring $\nu(\text{CH}_3)_{\text{sym}}$, and butyl $\nu(\text{C1H1})_{\text{sym}}$ show similar red-shifts as observed in TiO₂-supported IL. In addition to them, the band at 3121 cm⁻¹ assigned to $\nu(\text{C2-H})$ also presents a strong red-shift of approximately 8 cm⁻¹. Besides these changes in the high frequency region, the bands at 1467 and 1385 cm⁻¹ also indicate red-shift of slightly higher than the resolution limit associated with weak blue-shifts at 1046 and 987 cm⁻¹, which might not be an actual shift as the shift amount is slightly less than our resolution limit. These results are very similar to the case in TiO₂-supported IL and indicate that the interaction of [BMIM][BF₄] with the Fe₂O₃ surface might be taking place through the imidazolium ring, specifically through the C2–H, resulting in slight increase in the internal bonding strength in the [BF₄]⁻ anion.

Wang et al.⁵⁵ illustrated that $\nu(\text{C2-H})$ bands of [EMIM][BF₄] weakens when the IL is in contact with ZnO. Such red-shift in $\nu(\text{C2-H})$ was interpreted as an indication of the presence of a hydrogen bonding between the C2–H of the imidazolium ring and the oxygen atoms of ZnO.⁵⁵ Consistent with this conclusion the IR spectra of the ZnO-supported [BMIM][BF₄] indicate a red-shift of 5 cm⁻¹ in the position of $\nu(\text{C2-H})$, indicating similar hydrogen bonding between the C2–H and the O²⁻ sites of ZnO surface. Associated with these changes, interactions between anion and cation weakens and the internal B–F bonding in the

anion becomes stronger as confirmed by blue-shifts observed on the band assigned to $\nu(\text{B-F})$ located at 1046 cm^{-1} .

When $\gamma\text{-Al}_2\text{O}_3$ -supported [BMIM][BF₄] is considered, only the band at 1046 cm^{-1} shows a significant shift, a blue-shift of approximately 19 cm^{-1} on $\nu(\text{B-F})$ (Table 3-5). This result is strongly consistent with the results of Sobota et al.²⁴ investigating the interactions of [BMIM][NTf₂] on well-ordered Al_2O_3 . They showed that upon supporting the IL with Al_2O_3 , IR bands of $[\text{SO}_2]^-$ groups of the anion have blue-shifts from their bulk counterpart, indicating that these groups are in contact with the surface. Moreover, our data further show that, on [BMIM][BF₄], the band at 3121 cm^{-1} has a 5 cm^{-1} red-shift, which probably results from the electron transfer from $\gamma\text{-Al}_2\text{O}_3$ to anion, leading a decrease in strength of C2H vibrations in cation. All the other shifts given in Table 3-4 and 3-5 for $\gamma\text{-Al}_2\text{O}_3$ -supported [BMIM][BF₄] are less than the spectral resolution of our measurements, thus we consider them as no change.

Changes in the positions of IR features of the bulk IL upon coating CeO_2 with [BMIM][BF₄] are mostly within our spectral resolution (4 cm^{-1}). Bands at 3162 , 2939 , 1467 , 1340 , and 1017 cm^{-1} corresponding to $\nu(\text{C4-C5H})_{\text{asym}}$, $\nu(\text{CH}_3)_{\text{sym}}$, $\delta(\text{CH}_3)$ wagging, $\nu(\text{N-Bu})$ of imidazolium ring, and $\nu(\text{BF}_4)_{\text{asym}}$, respectively, have a red-shift of approximately 3 cm^{-1} . Moreover, the band at 1119 cm^{-1} , attributed to ring CH_3 $\delta(\text{CH})$ wagging, has red shift of 5 cm^{-1} . We also observed blue-shift of 3 cm^{-1} at 1046 cm^{-1} , belonging to $\nu(\text{BF}_4)_{\text{asym}}$. These results indicate that both anion and cation of the IL may be in contact with CeO_2 . Schernich et al.³³ investigated that the reaction between $[\text{C}_6\text{MIM}][\text{NTf}_2]$ and well-ordered CeO_2 is from the most acidic proton in imidazolium ring, C2-H, and terminated oxygen of CeO_2 . However, when reduced CeO_2 is utilized as support material, reaction occurs between anion and the surface, instead of cation. Therefore, for CeO_2 -supported [BMIM][BF₄], both anion and

cation might have interactions with the metal-oxide depending on the local structure of CeO₂, our data do not provide sufficient evidence on elucidating these interactions.

When [BMIM][BF₄] was supported on MgO, we observed slight changes in the higher frequency region (in Table 3-4), these changes were lower than 4 cm⁻¹ so they are not considered as a significant shift. In the lower frequency region, however, bands at 1046, 1034, and 987 cm⁻¹, corresponding to $\nu(\text{BF}_4)_{\text{asym}}$ and butyl $\delta(\text{HC1H})$ wagging, indicate blue-shifts of 13, 3, and 5 cm⁻¹. MgO is a good electron-donor metal oxide, thus there might be an electron transfer from MgO to [BF₄]⁻ anion. The increasing electron density on [BF₄]⁻ anion might lead to an increase in B–F bond strength, resulting in a blue-shift. Therefore, we infer that MgO might be mostly interacting with the anion of the IL.

As in the case of MgO-supported IL, results in La₂O₃-supported [BMIM][BF₄] illustrate similar changes in the IR spectra. In lower frequency region, there are blue-shifts at 1046 and 987 cm⁻¹, corresponding to $\nu(\text{BF}_4)_{\text{asym}}$, because of strong interactions of La₂O₃, another basic support, with the anion. On top of these changes, data also indicate a red-shift of approximately 14 cm⁻¹ on a band at 1385 cm⁻¹, assigned to ring in plane symmetric stretching, ring $\delta(\text{CH}_3)$ and butyl $\delta(\text{C1H})$, $\delta(\text{C2H})$, and $\delta(\text{C3H})$. Here we interpret that with a strong electron donation from La₂O₃ to the anion, the interactions between the cation and the anion is also altered, most probably, the cation loses its flexibility, as indicated by such weakening of in these bending vibrations.

As we noted above, the interactions between ILs and metal oxides can be interpreted in different ways based on the changes in the positions and intensities of the IR bands of the bulk ILs observed upon coating the metal oxides. Here we attempted to develop our interpretations in such a way that i) they are broadly consistent with the literature; ii) they are self-consistent with each other as similar trend is expected on similar metal oxides (such as on

La₂O₃ and MgO with strong basic character). We suggest that detailed computational studies with proper treatment of the metal oxide surfaces and high level surface science studies on model surfaces can provide definitive elucidation of the interactions between the ILs and metal oxides.

3-4.1. Consequences of IL-Metal Oxide Interactions on Short-term Thermal Stability Limits

Recently, we have demonstrated that the maximum operating temperatures of ILs indicated by short-term stability limits deviate strongly to lower temperatures when the ILs are in contact with metal oxides.³⁰ For these systems, apparently, the metal oxide works as a catalyst for the decomposition reaction, reducing the temperature for decomposition significantly.³⁰⁻³² Thus, interactions between the metal oxides and ILs have a strong influence in determining these maximum operation temperatures. Here, we focused on elucidating the effects of interactions between the IL and metal oxides, as presented above, on the stability limits. The short-term thermal stability limits were determined as T'_{onset} values measured by TGA performed at a heating rate of 10 K (data are given in Appendix A3, Figure A3-16 to A3-23). The overall mass loss of an IL may be the result of both evaporation and/or thermal decomposition. Evaporation of IL was tested with thermal analysis carried out by using a different carrier gas (He) than N₂.¹⁷ Results of a representative run in He flow on Fe₂O₃-supported [BMIM][BF₄] sample provides a T'_{onset} value of 583 K, whereas the corresponding value in N₂ flow was 585 K. These values are almost the same within the error range of our measurements. Moreover, according to Krannich et al.,⁵⁶ bulk [BMIM][BF₄] has a very low vapor pressure of 1.5×10^{-8} Pa. Thus, we infer that evaporation of IL from the surface during the temperature ramp is rather negligible.

In Table 3-6, the measured T'_{onset} values of samples prepared by immobilizing [BMIM][BF₄] on SiO₂, TiO₂, Fe₂O₃, ZnO, γ -Al₂O₃, CeO₂, MgO, and La₂O₃ are given. Data show that the short-term stability limits of supported [BMIM][BF₄] decreases significantly as the basicity of the metal oxide increases from SiO₂ to La₂O₃. For instance, the T'_{onset} of SiO₂-supported sample was approximately 604 K, and that of La₂O₃-supported sample was approximately 451 K. These results suggest that interactions between metal oxide and the IL have a strong effect in determining the decomposition temperature. One reason for this decrease might be the fact that the surface areas of these metal oxides are not equal to each other, thus, the thickness of the IL layer might be varying. When the surface area of the IL is low, it might cause a very thick layer of IL, which behaves very similar to the bulk IL with a high T'_{onset} value. However, we ruled out this possibility because as we discussed above, we expect to have a single to only a few monolayers of ILs within the IL loading that we considered for this study (as shown in Table 3-3). Besides, although the surface areas of the metal oxides are significantly different from each other, among the metal oxides that we considered, SiO₂ is the one with one of the highest surface areas measured. Thus, we expect to have the thinnest IL layer on this metal oxide, resulting in a higher possibility for the IL to interact with the metal oxide. However, the T'_{onset} value determined for SiO₂-supported IL is one of the highest values among all samples that we considered. Therefore, we infer that difference in surface areas is not an important factor in determining the thermal stability of our samples. Surface acidity, on the other hand, has a more dominant effect on stability limits. Figure 3-5 shows the variation of T'_{onset} with respect to PZC (somehow an indicator of surface acidity⁵⁷) of the metal oxide. PZC (in pH) of metal-oxides increases in the following order: SiO₂ (1.7) < TiO₂ (4.5) < Fe₂O₃ (6.8) < ZnO (7) < γ -Al₂O₃ (7.6) < CeO₂ (8.7) < MgO (9.8) < La₂O₃ (10.3). Data illustrate that as the PZC of the metal oxide increases the short-term thermal stability limit decreases following a parabolic trend. This decrease in stability limits

indicates that decomposition reaction of [BMIM][BF₄] is easier when it is in contact with basic supports. As discussed above, on basic supports such as La₂O₃ and MgO, there is a strong electron donation from metal oxide to the IL. This high degree of electron donation should result in altering in the anion/cation interactions. Thus, we infer that such changes in the IL structure leads to thermal decomposition starting at earlier temperatures during the temperature ramp.

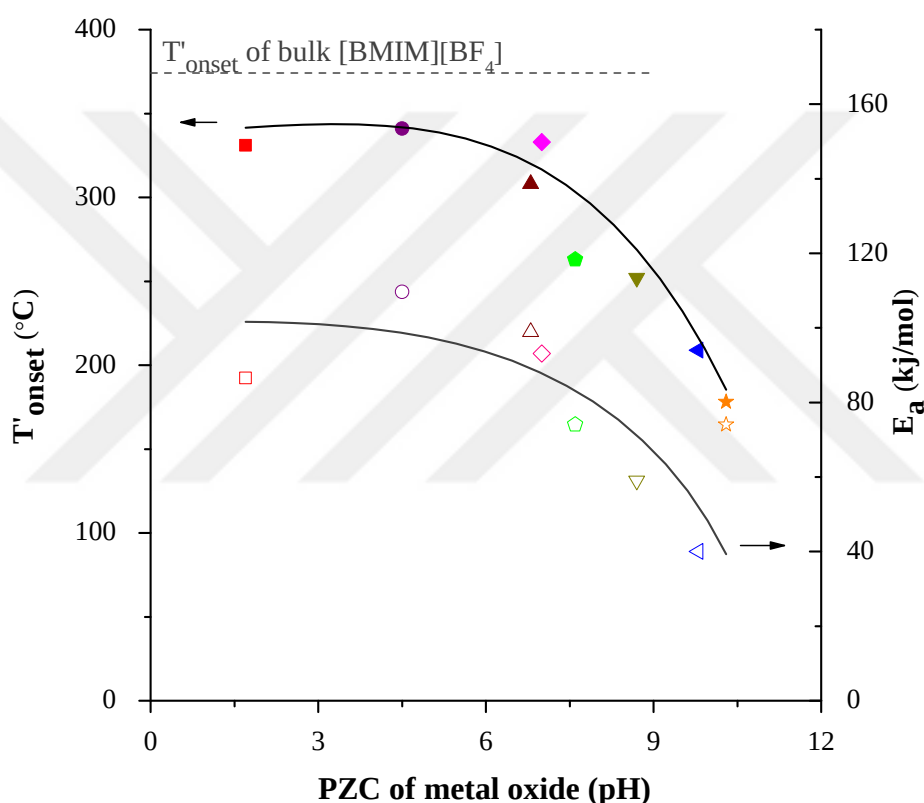


Figure 3-5. Variation of T'_{onset} of supported ILs with changing surface acidity (PZC): SiO₂-supported (■); TiO₂-supported (◆); Fe₂O₃-supported (▲); ZnO-supported (◆); γ-Al₂O₃-supported (◆); CeO₂-supported (▼); MgO-supported (▼); La₂O₃-supported (★). Secondary y-axis shows the variation of activation energy (E_a) with changing PZC. Open symbols indicate E_a values of supported ILs.

3-4.2. Long-term Stability Limits of Supported [BMIM][BF₄]

Fast-scan TGA provides rapid comparison of data and reproducible measurements for short-term stability measurements. The onset temperatures determined by these measurements are usually accepted as the highest temperature that the IL/metal oxide systems can tolerate for short-time periods. However, IL-assisted systems, such as those used for catalysis applications, might be subjected to elevated temperatures for long time periods. Therefore, isothermal TGA measurements conducted at high temperatures complemented by spectroscopy are required to determine whether there is any structural change taking place under harsh conditions for prolonged applications. Salgado et. al.⁵⁸ illustrated that the short-term stability of bulk 1-butyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide, [BDMIM][NTf₂], was 697 K; however, when it was subjected to isothermal heat treatments at 633 K for 100 min, IL structure showed 80 wt% loss in the structure. Similarly, Fox. al.⁵⁹ investigated that T'_{onset} of bulk 1,3-dialkylimidazolium ILs were generally above 623 K; however, under isothermal conditions, significant decomposition was observed at more than 373 K below these temperatures. Thus, aiming at overcoming the limitations of ramped temperature TGA method, we performed TGA in isothermal mode at five different temperature points for each supported IL sample for 10 h and investigated the long-term stability limits of the supported ILs. For such measurements, $T_{0.01/10h}$, the temperature at which supported ILs loses 1% of its weight in 10 h in isothermal TGA measurements, is very useful in evaluating the long-term thermal stability.⁶⁰ After measuring isothermal decomposition curves, $T_{0.01/10h}$ values for all metal oxide supported [BMIM][BF₄] samples were determined using the method of MacFarlane et. al.⁶¹ (given in Appendix A3 section A3-6). As discussed above, the short-term thermal stability limit of bulk [BMIM][BF₄] ranges from 633 to 708 K,^{32,62-64} and its $T_{0.01/10h}$ is reported in the range of 489 to 496 K.⁵⁶ $T_{0.01/10h}$ values of metal oxide supported [BMIM][BF₄] is given in Table 3-6. As in the case of bulk

IL, the long-term thermal stability limits of supported ILs are more than 373 K lower than those determined by quick temperature ramp measurements. For instance, T'_{onset} value of SiO₂-supported [BMIM][BF₄] was determined as 605 K. However, isothermal measurements indicate a $T_{0.01/10\text{h}}$ temperature of 473 K, slightly lower than its bulk counterpart reported in the literature.⁵⁶ Table 3-6 shows that in general the $T_{0.01/10\text{h}}$ values are approximately 473 K when [BMIM][BF₄] was supported on metal oxides with relatively low PZC values, however, as the surface basicity increases above 7.6, the $T_{0.01/10\text{h}}$ temperature decreases to first 393-413 K than down to approximately 373 K on basic supports. This result is very important as 373 K might be fairly low for many of the applications of IL/metal oxide systems. Thus, data suggests that the use of basic metal oxides would significantly limit the applicability of such materials.

Table 3-6. Short- and long term stability limits of metal-oxide supported [BMIM][BF₄].

Supported ILs	T'_{onset} (K)	$T_{0.01/10}$ (K)	6 h long- term stability (K)	10 h long- term stability (K)	24 h long- term stability (K)	Decomposition rate const, k , at 423 K (s ⁻¹)	Decomposition rate const, k , at 373 K (s ⁻¹)	E_a (kJ/mol)
[BMIM][BF ₄]/SiO ₂	473	746	< 473	< 423	< 373	1.6×10^{-6}	5.7×10^{-8}	87
[BMIM][BF ₄]/TiO ₂	476	749	< 523	< 523	< 423	4.8×10^{-7}	7.3×10^{-9}	110
[BMIM][BF ₄]/Fe ₂ O ₃	472	745	< 573	< 523	< 473	9.2×10^{-7}	2.1×10^{-8}	99
[BMIM][BF ₄]/ZnO	477	750	< 523	< 523	< 523	1.4×10^{-6}	3.8×10^{-8}	93
[BMIM][BF ₄]/ γ -Al ₂ O ₃	439	712	< 423	< 423	< 373	4.4×10^{-6}	2.1×10^{-7}	80
[BMIM][BF ₄]/CeO ₂	459	732	< 523	< 523	< 473	4.6×10^{-6}	4.8×10^{-7}	59
[BMIM][BF ₄]/MgO	374	647	< 423	< 373	< 373	2.9×10^{-4}	6.3×10^{-5}	40
[BMIM][BF ₄]/La ₂ O ₃	394	667	< 423	< 423	< 373	1.9×10^{-4}	5.7×10^{-4}	74

Assuming the decomposition reaction of the IL on metal oxides is pseudo-first order, the reaction rate and the apparent activation energy (E_a) for decomposition can be determined by using Arrhenius equation.⁶⁵ Accordingly, the decomposition rate can be expressed as the mass of decomposed IL in time, da/dt at different isothermal treatment temperatures (Eqn 1). A linear fit is then obtained by plotting $\ln(da/dt)$ against $1/T$, where T is the isothermal thermal treatment temperature and the slope of the curve gives $-E_a/R$.

$$d\alpha/dt = A \exp (-E_a/RT) \quad (1)$$

Previous kinetic studies performed on bulk [BMIM][BF₄] showed that the activation energy for decomposition ranges from 108.4 to 195 kJ/mol.⁶⁶⁻⁶⁷ As discussed above, the surface acidity of the metal oxide strongly affects the thermal stability limits (T'_{onset}) possibly altering the decomposition pathway, working as a catalyst. Thus, it is expected that such effects would affect the apparent activation energy barriers and decomposition rate constants as well. In Figure 3-5, apparent activation energy (E_a) values for supported [BMIM][BF₄] samples are given as a function of PZC of the metal oxide (E_a graphs are given in Appendix A3, Section A3-6). Results show that as the metal oxide becomes more basic, with an increase in PZC value from SiO₂ to MgO, E_a required for the decomposition of the IL on the corresponding metal oxide decreases from approximately 100 to less than 40 kJ/mol, following a similar parabolic trend with the decrease in short-term stability limits. Moreover, pseudo-first order decomposition rate constants (k) of supported [BMIM][BF₄] samples listed in Table 3-6 increase as the PZC of metal oxide increases. Such decrease in E_a values and increase in rate constants confirm that the metal oxide works as a catalyst to make the decomposition reaction easier to occur; thus, the decomposition starts at much lower temperatures when the IL was supported on basic metal oxides than the case where it was supported on metal oxides with lower PZC values. Results confirm that strong electron donation from the basic support to [BMIM][BF₄] is a crucial step for the initiation of the decomposition reaction.

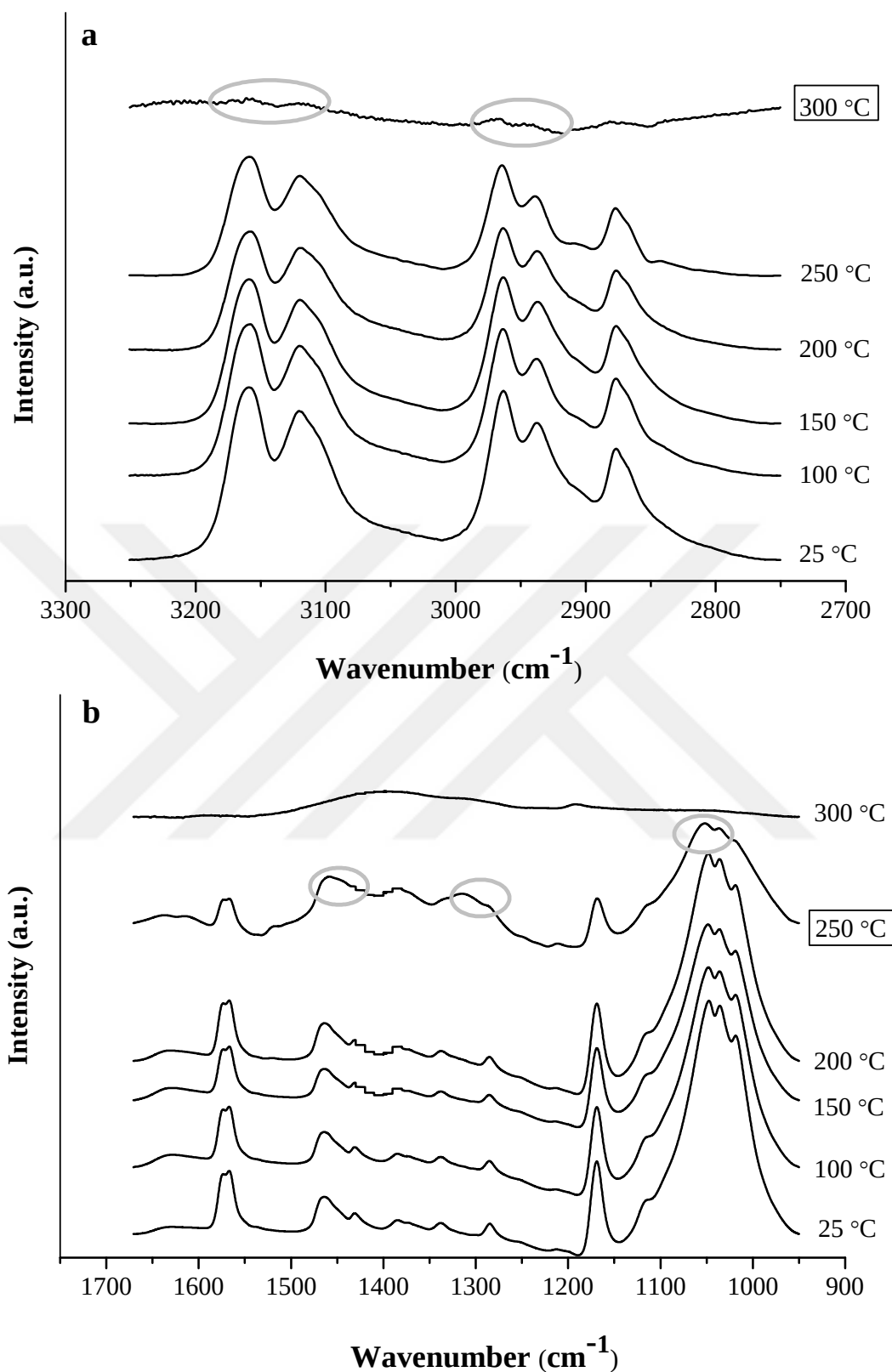


Figure 3-6. IR spectra of CeO₂-supported [BMIM][BF₄] after 6 h-treatments: room temperature, 373 K, 423 K, 473 K, 523 K and 573 K in the region of a) 2750-3250 cm⁻¹ b) 850-1750 cm⁻¹.

Table 3-7. The first degraded IR bands of metal-oxide supported [BMIM][BF₄].

Supported IL	Degraded IR bands after long-term treatments (cm ⁻¹)					
[BMIM][BF ₄]/SiO ₂	2968	2934	2883			
[BMIM][BF ₄]/TiO ₂	3107	1567	1459	1385	1338	
[BMIM][BF ₄]/Fe ₂ O ₃	3158	3113	1462	1337	1169	
[BMIM][BF ₄]/ZnO	3159	3116	1566	1467	1051	1035
[BMIM][BF ₄]/ γ -Al ₂ O ₃	3159	3117	1065	1017		
[BMIM][BF ₄]/CeO ₂	1464	1285	1049	1035		
[BMIM][BF ₄]/MgO	1116	1059	1037	1019		
[BMIM][BF ₄]/La ₂ O ₃	1463	1117	1060	1038		

We also analyzed the structures following isothermal treatments performed at different temperatures for prolonged time periods by IR spectroscopy. For this purpose of SiO₂-, γ -Al₂O₃-, MgO-, TiO₂-, ZnO-, CeO₂-, Fe₂O₃-, and La₂O₃-supported [BMIM][BF₄] samples were treated at 100, 150, 200, 250, and 573 K for 6, 10, and 24 hours. FTIR spectra of each treated sample was collected and compared with its untreated counterpart to elucidate any structural change occurred after these treatments, such as a representative data for CeO₂-supported IL in Figure 3-6. In Table 3-6 and 3-7, the results of these analyses are provided (related IR spectra are given in Appendix A3, in Figures A3-40 to A3-62). Accordingly, degradation of the peaks starts at 200, 150, and 373 K for isothermal treatment time periods of 6, 10, and 24 h, respectively, for SiO₂-supported [BMIM][BF₄]. These degraded peaks were identified as 2968, 2934, and 2883 cm⁻¹, associated with butyl $\nu(\text{HC1HH})_{\text{sym}}$, $\nu(\text{CH}_3)_{\text{sym}}$ of imidazolium ring and (CH) stretching butyl, respectively. As discussed above, upon supporting the bulk IL on SiO₂, these IR bands have either red- or blue-shifts, indicating that imidazolium ring of [BMIM][BF₄] have strong interactions with SiO₂ surface. Long-term stability data further confirms these interactions in such a way that during thermal treatments, SiO₂-supported sample started to degrade from the imidazolium ring. Accordingly, the decrease in anion-cation interactions as well as in the imidazolium ring-butyl group interaction strengths might lead to degradation of these peaks.

For TiO₂-supported [BMIM][BF₄], the first degradation was observed on bands at 3107, 1567, 1459, 1385, and 1338 cm⁻¹ (Table 3-7). Previously, we stated that the peaks of TiO₂-supported IL at 3107, 1459, and 1385 cm⁻¹ have high amount of shifts from its bulk counterpart, resulting from a high degree of interactions of the imidazolium ring with TiO₂ surface. When the sample was exposed to long-term treatments these interactions cause decomposition of the supported IL from imidazolium ring part of the cation, as expected. We report no observable changes in the peaks corresponding to anion at the initial stages of the decomposition. This case is similar for Fe₂O₃-supported [BMIM][BF₄] sample. Degraded IR peaks of Fe₂O₃-supported IL as a result of long-term treatments was observed at 3158, 3113, 1462, 1337, and 1169 cm⁻¹. In previous discussions, we attribute these IR bands to $\nu(\text{C-H})$ of imidazolium ring or the alkyl groups attached to the ring. The strong interactions between Fe₂O₃ and the imidazolium ring of the IL results in the loss of structural integrity starting from the imidazolium ring of the IL.

In IR spectrum of ZnO-supported [BMIM][BF₄], we observed that the first changes occur on the bands at 3159, 3116, 1566, 1467, 1051, and 1035 cm⁻¹ (Table 3-7). As discussed above, IR data of the sample before isothermal treatment indicated that C2-H of IL has interactions with O²⁻ of ZnO. Results of the long-term stability analysis is consistent with this interpretation such that the weakening of C2-H bond strength also influences other C-H bonds in imidazolium and leads to degradation of the related peaks. Moreover, unlike the other supported ILs mentioned above, in ZnO-supported IL, the effect of interactions between metal oxide and anion on decomposition of supported IL becomes apparent. Accordingly, the band at 1051 cm⁻¹, corresponding to $\nu(\text{B-F})$, also degraded because of changing interactions of anion and cation of IL in the presence of ZnO. Data summarized on Table 3-7 indicate that γ -Al₂O₃-supported [BMIM][BF₄] started to degrade from the peaks at 3158, 3116, 1065, and 1017 cm⁻¹. Among these peaks, those at 3158 and 3116 cm⁻¹ are associated with $\nu(\text{C4-C5H})$

and $\nu(\text{C}2\text{H})$, respectively.⁶⁸ As discussed above, red-shifts were detected on these bands upon supporting the bulk IL with $\gamma\text{-Al}_2\text{O}_3$. Results imply that C–H bond strength weakens in the presence of $\gamma\text{-Al}_2\text{O}_3$ and this weakening leads to the initiation of the decomposition reaction from the imidazolium ring. Moreover, the peaks at 1065 and 1017 cm^{-1} , corresponding to anion started to degrade during long-term thermal exposure. Here, similar to the case for ZnO-supported IL, there is strong interactions between $[\text{BF}_4]^-$ and $\gamma\text{-Al}_2\text{O}_3$ which influences the peaks related to anion and causes structural loss of IL from anion part.

Following the long-term thermal treatments at different temperatures, on CeO_2 -supported [BMIM][BF₄], we observed that the peaks at 1464, 1285 cm^{-1} , corresponding to $\delta(\text{C-H})$ of imidazolium ring, and 1049 and 1035 cm^{-1} , corresponding to $\nu(\text{BF}_4)$, were the first peaks degraded (Figure 3-6 and Table 3-7). In previous discussions we mentioned that both anion and cation are in contact with CeO_2 surface. Confirming our interpretations, interactions between metal-oxide and anion and cation cause degradation of the IR bands from the bands belonging to both anion and cation.

Long-term thermal treatment analysis of MgO-supported show that the degradation of the peaks started at 1116, 1059, 1037, and 1019 cm^{-1} which indicate the decomposition of ring $\delta(\text{C-H})$, $\nu(\text{BF}_4)_{\text{asym}}$, butyl $\delta(\text{C-H})$, and $\nu(\text{BF}_4)_{\text{asym}}$ in imidazolium ring. Previously, we mentioned that electron transfer from basic MgO to the anion changes the interactions between anion and cation as well. Confirming that interpretation, the decrease in bond strength of C–H of imidazolium ring might result in degradation of these peaks during thermal treatments. The very same changes were also observed in long-term thermal treatments of La_2O_3 -supported [BMIM][BF₄]. Accordingly, the degraded peaks at 1117, 1060, and 1038 cm^{-1} have the same assignments as in the case of MgO-supported IL. Here, highly basic character of La_2O_3 plays a role in the decomposition mechanism in a way similar to that of MgO does. As these metal oxides with highly basic characters strongly alter the thermal

stability limits of ILs on metal oxides, we infer that these interactions play a crucial role in determining the stability limits. We further suggest that these interactions might also alter other properties of these systems including direct interactions of ILs with metal oxides. Thus, they should be investigated in deep detail for the rational design of these materials for specific applications.

3-5. Conclusions

We have investigated the interactions of [BMIM][BF₄] with high surface area metal oxides, SiO₂, TiO₂, Fe₂O₃, ZnO, γ -Al₂O₃, CeO₂, MgO, and La₂O₃, with varying surface acidities. First, DFT calculations were performed on [BMIM][BF₄] to obtain the minimum energy conformer geometry and consequently to assign the IR fingerprints present in the experimental spectra of the bulk [BMIM][BF₄]. Then the changes in the positions of these spectroscopic features were analyzed to elucidate interactions between the IL and the metal oxides. Data show that type and nature of these interactions mostly depend on surface acidity of metal-oxide. Accordingly, when metal oxide surface is acidic, such as SiO₂, cation/metal oxide surface interactions are more apparent. However, with a more basic metal oxide, such as La₂O₃, both cation and anion of IL have significant interactions with surface. Consequently the thermal stability limit measurements indicate that these interactions between IL and metal oxide have a significant effect on short- and long-term stability limits of supported ILs. Generally, as the surface acidity decreases, the stability limits of supported IL decreases significantly. In decomposition reactions, the decrease in the apparent activation energy (E_a) of the supported IL samples with increasing PZC value confirms that metal oxides likely to catalyze the decomposition of supported ILs. Data illustrate that in IL-assisted systems, surface acidity of metal oxide is the key factor controlling the interactions between ILs and

metal oxides; and these interactions directly determine the physicochemical properties of these systems.

3-6. Acknowledgments

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3-7. Supplementary Materials

All BET surface areas and pore volume distributions of metal-oxides and supported [BMIM][BF₄] samples, calculated IL loading amounts (by EDX integration), cartesian coordinates of the most stable conformer structure of [BMIM][BF₄], structures of all conformers of [BMIM][BF₄], activation energy and T_{0.01/10} calculations, FTIR spectra of supported [BMIM][BF₄] after 6, 10, and 24 h-treatments at elevated temperatures, water content report of [BMIM][BF₄].

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Chapter 4

Effects of Interionic Interactions in 1,3-Dialkylimidazolium Ionic Liquids on the Electronic Structure of Metal Sites in Solid Catalysts with Ionic Liquid Layer (SCILL)*

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4-1. Abstract

Well-defined γ -Al₂O₃-supported Ir(CO)₂ complexes were coated with various 1,3-dialkylimidazolium ionic liquids (ILs) to elucidate the ligand effect of ILs. Variations in electron density of iridium sites when coated with ILs were probed by the infrared (IR) fingerprints of carbonyl ligands. Results presented here illustrate that IL layer strongly controls the electron density of metal sites; and there is a strong correlation between the interionic interactions in ILs and the amount of electron donation to the metal. These results create opportunities to tune the electronic structure of active metal sites by tailoring the structure of IL for optimum catalytic performance.

4-2. Introduction

Ionic liquids (ILs) have been generating great interest for the past decade. They are room temperature molten salts that are composed of almost infinite number of anion-cation combinations with a wide range of tunable physical and chemical characteristics. Some of the properties of ILs that make them interesting are nonvolatility, nonflammability, high chemical and mechanical resistance.¹ Due to their tunable properties, they offer advantages for a wide range of applications including separation,² electrochemistry,³ synthesis,⁴ and catalysis.⁵⁻⁶ One way of their utilization in the field of catalysis involves them as a thin film over the active sites of a supported metal catalyst. Such structural modification of supported metal catalysts by coating with ILs has been capturing attention specifically in the last decade.⁶ These “solid catalysts with IL layer” (SCILL) are interesting as they can alter the catalytic selectivity towards the desired products thanks to the tunable physicochemical properties of the ILs.^{5,7-8} However, as noted by Hallet and Welton,⁹ how exactly an IL layer influences the catalytic performance is not known. Such information is extremely crucial for tailoring the structural

properties for high performance. Recently, surface science-based model catalysts were utilized to solve this problem.¹⁰⁻¹² Results of these studies indicate that ILs not only act as a filter controlling the effective concentrations of reactants but also directly modify the metal centers via specific ligand effect. Other approaches to solve this problem with IL-coated metal catalysts supported on high-surface area supports are limited because of the complex nature of active sites in such conventional supported metal catalysts.^{7,13-14} This complexity in structure makes the understanding of how IL coating layer improves the catalytic performance a challenging task. Here, we utilized well-defined site-isolated Ir(CO)₂ complexes supported on a high-surface area metal-oxide, γ -Al₂O₃, and coated them with various 1,3-dialkylimidazolium ILs to elucidate the ligand effect of ILs on the metal sites in SCILL catalysts as a function of their structure. The variations in the electron density of iridium sites coated with ILs were probed by the infrared (IR) fingerprints of carbonyl ligands attached to the metal complexes.

4-3. Materials & Methods

4-3.1. Materials

All chemicals were purchased from Sigma-Aldrich with the highest available purity levels. All ILs were dried at 373 K for 6 h and kept under vacuum for 12 h before transferring into an argon-filled Labconco glove box. Supported molecular metal catalysts were prepared by the reaction of Ir(CO)₂(acac), where acac is acetylacetonate, (18 mg) with γ -Al₂O₃ (992 mg), which was calcined in flowing O₂ with a temperature ramp rate of 3 K/min from room temperature to 773 K and held for 5h, using air exclusion techniques. The precursor and support (with a catalyst loading of 1 wt.%) were slurried in *n*-pentane, which had been purified by an MBraun SBS solvent purifier system. The slurry was mixed for one day in a sealed round bottom flask, followed by evacuation for solvent removal. The resultant solid

catalyst was stored in an argon-filled glove box. IL-coated supported metal complex was prepared by immersing supported metal complex (200 mg) in IL (100 mg) and by adding an excess amount of calcined support (200 mg) to absorb remaining unabsorbed IL. The resultant sample has 20 wt% IL loading. For a different sample with a higher IL loading (40 wt% IL-loading), IL amount was increased to 200 mg. All IL-coated and uncoated samples were stored in the glove box under Ar atmosphere.

4-3.2. Fourier Transform IR (FTIR) Spectroscopy

A Bruker Vertex 80v spectrometer with a vacuum sample chamber was used in transmission mode to measure IR spectra with a spectral resolution of 2 cm^{-1} . IR spectra of samples were recorded with the exclusion of moisture and air at room temperature. Each sample was pressed between two KBr windows in the glove box, and transferred to the sample chamber of the spectrometer just before the measurement. Then, the sample chamber was evacuated quickly after the insertion of the sample. For each measurement 256 scans were averaged, and before each of these a background of 128 scans were collected.

4-3.3. Brunauer–Emmett–Teller (BET) Pore Volume and Surface Area Analysis

BET analyses were performed on a Micromeritics ASAP 2020 HD Accelerated Surface Area and Porosimetry Analyzer model instrument. Sample amount loaded into the instrument was approximately 250 mg for $\text{Ir}(\text{CO})_2/\gamma\text{-Al}_2\text{O}_3$ and 90 mg for $[\text{BMIM}][\text{BF}_4]$ coated $\text{Ir}(\text{CO})_2/\gamma\text{-Al}_2\text{O}_3$. Samples were degassed at 423 K for 10 h. Analyses were performed in 9 mm-small bulbs, measurements were repeated at 10 different pressure points for each sample in between 0.05–0.3 P/P_0 .

4-4. Results and Discussion

Elucidation of structural factors controlling the ligand effect of ILs in an IL coated supported metal catalysts is crucial in designing these materials for specific applications. These factors can alter the electronic structure of the active site resulting in significant changes in the catalytic performance specifically in terms of selectivity. However, because the structure of conventional supported metal catalysts is extremely complex, understanding of the ILs' ligand effects is challenging. Here, we utilized supported iridium *gem*-dicarbonyl complexes with simple and uniform structures so that their interactions with ILs can be probed.

Site-isolated mononuclear $\text{Ir}(\text{CO})_2$ complexes supported on $\gamma\text{-Al}_2\text{O}_3$ were prepared by the reaction of an organometallic precursor, $\text{Ir}(\text{CO})_2(\text{acac})$, with partially dehydroxylated $\gamma\text{-Al}_2\text{O}_3$ by air exclusion techniques, as reported before.¹⁵ Figure 4-1 compares the IR fingerprints of freshly calcined $\gamma\text{-Al}_2\text{O}_3$ and $\text{Ir}(\text{CO})_2(\text{acac})$ with those of the as-prepared sample. In Figure 4-1A, in the region of $3400\text{-}3800\text{ cm}^{-1}$, data show that the acidic hydroxyl groups of $\gamma\text{-Al}_2\text{O}_3$ at 3587 and 3693 cm^{-1} were consumed during the sample preparation suggesting the reaction of the precursor with these acidic hydroxyl groups. Furthermore, in Figure 4-1B, the presence of two distinct $\nu(\text{CO})$ bands at 1994 and 2074 cm^{-1} in as-prepared sample confirm the presence of iridium *gem*-dicarbonyl groups.¹⁶ We note that these fingerprints were shifted from those observed in $\text{Ir}(\text{CO})_2(\text{acac})$ mixed with KBr (1987 and 2049 cm^{-1}). Moreover, IR spectrum of the supported iridium complex in $1300\text{-}1700\text{ cm}^{-1}$ region (Figure 4-1C) shows the bands at 1365 , 1404 , 1460 , 1533 , and 1608 cm^{-1} , which are assigned to $\delta_s(\text{CH}_3)$, $\nu_{\text{as}}(\text{CO})_{\text{ring}}$, $\delta_{\text{as}}(\text{CH})$, $\nu_{\text{as}}(\text{CCC})_{\text{ring}}$, and $\nu_s(\text{CO})_{\text{ring}}$, respectively; resembling those characterizing Hacac adsorbed on $\gamma\text{-Al}_2\text{O}_3$ rather than those of the precursor (1365 , 1382 , and 1531 cm^{-1}).¹⁷⁻¹⁸ Thus, we infer that the (acac) ligand leaves $\text{Ir}(\text{CO})_2(\text{acac})$ and the remaining $\text{Ir}(\text{CO})_2$ complex chemisorbs onto the support forming site-isolated iridium *gem*-dicarbonyl complexes. These results are

broadly consistent with previous reports characterizing such metal-oxide-supported mononuclear iridium complexes by spectroscopy and electron microscopy.¹⁶⁻¹⁹

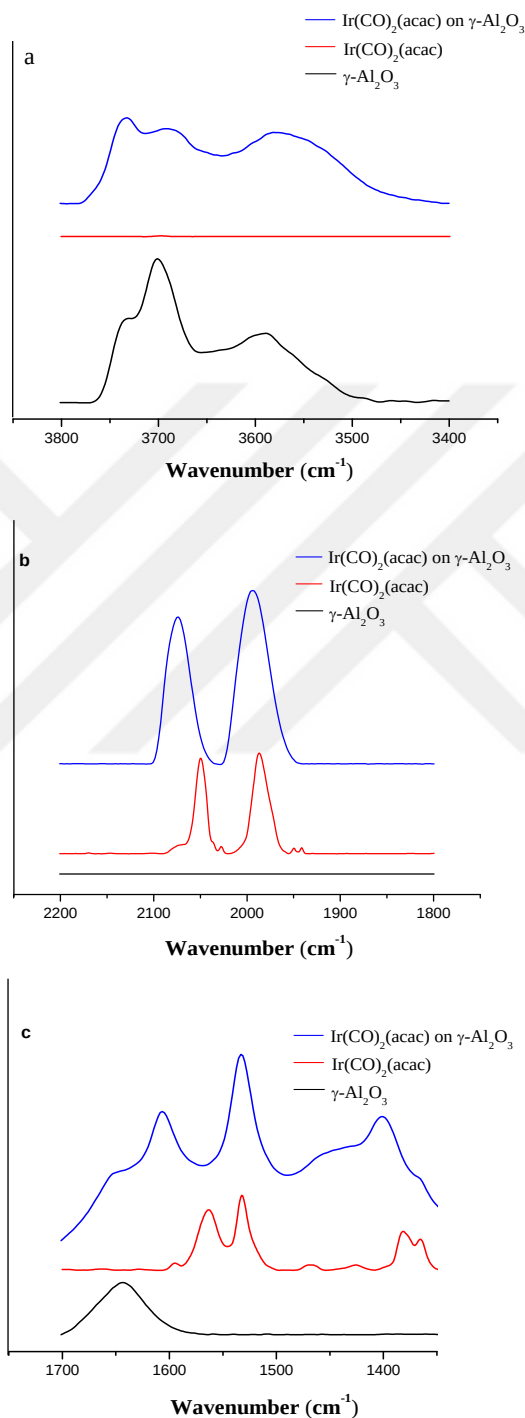
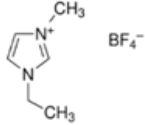


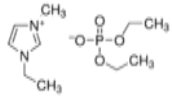
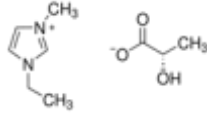
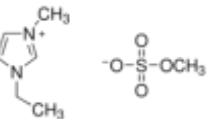
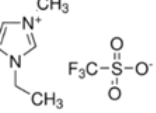
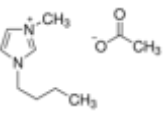
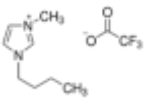
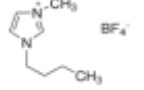
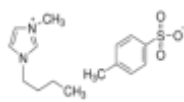
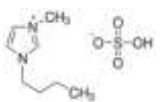
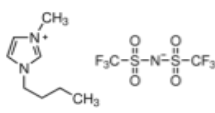
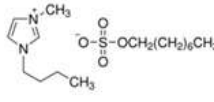
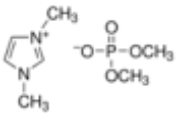
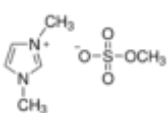
Figure 4-1. IR spectra of calcined $\gamma\text{-Al}_2\text{O}_3$ (black), precursor $\text{Ir}(\text{CO})_2(\text{acac})$ mixed with KBr (red) and the catalyst formed by reaction of $\gamma\text{-Al}_2\text{O}_3$ with $\text{Ir}(\text{CO})_2(\text{acac})$ (blue): A) in the region of 3400-3800 cm^{-1} ; B) in the region of 1800-2200 cm^{-1} ; C) in the region of 1300-1700 cm^{-1} .

Once the existence of site-isolated iridium *gem*-dicarbonyls on γ -Al₂O₃ is confirmed, they were coated with imidazolium ILs. For this purpose, ILs (listed in Table 4-1) were impregnated on as-prepared γ -Al₂O₃-supported iridium *gem*-dicarbonyls until obtaining wet samples. Then they were mixed with freshly calcined γ -Al₂O₃ to obtain dry samples adjusting IL loading. The corresponding IL loading was approximately 20 wt.%. Pore size distributions of samples before and after coating with ILs were measured by BET. Data (given in Appendix A4, Section A4.2) confirmed that ILs penetrate even into small pores, 2.8-5 nm. Thickness of IL layers on coated samples were estimated by dividing the difference in total pore volume of samples before and after coating with ILs over the surface area of the uncoated sample. Accordingly, IL-layer thickness ranges from 1 to 1.5 nm, corresponding to single to a few molecular layers of ILs. These values are also consistent with those calculated by dividing the total volume of IL loaded over BET-determined surface area. Here, we note that ILs are usually first dissolved in solvents such as acetone, ethanol, methanol or dichloromethane before impregnated on the supported metal catalysts. However, when we used such solvents we observed structural decomposition of the iridium carbonyls. Thus, instead of using these solvents, ILs were directly coated on the supported sample. Both IR and BET results confirm the success of sample preparation.

Table 4-1. Structures and abbreviations of the ILs.

Structure	Name of IL	Abbreviation
	1-Ethyl-3-methylimidazolium tetrafluoroborate	[EMIM][BF ₄]

Chapter 4: Effects of Interionic Interactions in 1,3-Dialkylimidazolium Ionic Liquids on the Electronic Structure of Metal Sites in Solid Catalysts with Ionic Liquid Layer (SCILL)

	1-Ethyl-3-methylimidazolium diethylphosphate	[EMIM][DEP]
	1-Ethyl-3-methylimidazolium L-(+)-lactate	[EMIM][LAC]
	1-Ethyl-3-methylimidazolium methylsulfate	[EMIM][MSO ₄]
	1-Ethyl-3-methylimidazolium trifluoromethanesulfonate	[EMIM][TfO]
	1-Butyl-3-methylimidazolium acetate	[BMIM][Ac]
	1-Butyl-3-methylimidazolium trifluoroacetate	[BMIM][TFA]
	1-Butyl-3-methylimidazolium tetrafluoroborate	[BMIM][BF ₄]
	1-Butyl-3-methylimidazolium tosylate	[BMIM][TOS]
	1-Butyl-3-methylimidazolium hydrogen sulfate	[BMIM][HSO ₄]
	1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	[BMIM][NTf ₂]
	1-Butyl-3-methylimidazolium octylsulfate	[BMIM][OS]
	1,3-Dimethylimidazolium dimethylphosphate	[DMIM][DMP]
	1,3-Dimethylimidazolium methylsulphate	[DMIM][MSO ₄]

FTIR characterization of IL-coated samples still show two distinct bands in C–O stretching region, confirming that iridium *gem*-dicarbonyls were intact after coating with ILs. However, these fingerprints shift upon coating with IL, and the absence of original $\nu(\text{CO})$ bands at 1994 and 2074 cm^{-1} observed on uncoated sample indicates that our coating procedure was successful. For instance, representative spectra for $\gamma\text{-Al}_2\text{O}_3$ -supported $\text{Ir}(\text{CO})_2$ complexes before and after coating with two representative ILs are illustrated in Figure 4-2. Upon coating $\text{Ir}(\text{CO})_2/\gamma\text{-Al}_2\text{O}_3$ with $[\text{EMIM}][\text{BF}_4]$ and $[\text{DMIM}][\text{DMP}]$, $\nu(\text{CO})$ frequencies shifted from 2074 to 2060 and 2049 cm^{-1} , and from 1994 to 1975 and 1962 cm^{-1} , respectively. These red shifts in $\nu(\text{CO})$ frequencies indicate a weaker C–O bonding in carbonyls in the presence of IL layer. We infer that these ILs have an electron-donor property, which makes the metal more electron-rich. The excess electron density is transferred from metal to the carbon atoms through π -back-donation leading a weaker C–O bond strength.²⁰ Thus, these results confirm that the ILs interact with the metal in such a way that they influence the electron density on the metal significantly as if they are a ligand themselves. Kizhakevariam et. al.²¹ studied solvent-induced surface potential profiles on Pt(111) by using (CO) groups as probe molecules in IR spectra. They investigated that larger solvent dosages may cause shifts in $\nu(\text{CO})$ shifts due to dipole-dipole coupling. However, this phenomenon is only applicable for multilayer solvent thicknesses. In our study, IL layer thickness is single to a few layers, indicating that dipole-dipole coupling effect is not applicable. The effect of IL loading was also checked by increasing the loading of $[\text{BMIM}][\text{BF}_4]$ to 40 wt%. Results show that the carbonyl peaks are nearly the same as 20 wt% IL loaded sample within the resolution-limits of our measurements (comparison is given in Appendix A4, Figure A4-12). These results are consistent with previous reports. For instance, Sobota et al.¹² reported similar shifts on (CO) covered-Pt/ Al_2O_3 /NiAl(110) nanoparticles upon coating with $[\text{BMIM}][\text{NTf}_2]$, $\nu(\text{CO})$ bands

are at 2066 and 2081 cm^{-1} shifted to 2030 and 2086 cm^{-1} , respectively. Similarly, Steinrück et al.¹⁰ illustrated that $\nu(\text{CO})$ positions of $\text{Pd}/\text{Al}_2\text{O}_3/\text{NiAl}(110)$ were shifted from 1999 to 1957 cm^{-1} and from 2109 to 2073 cm^{-1} for when coated with $[\text{BMIM}][\text{NTf}_2]$. Moreover, Arras et al. reported XPS analysis revealing a more oxidized Pd surface in Pd/SiO_2 when treated with ILs.¹⁴ However, the structural parameters of the ILs really controlling the electronic structure of the metal site has been unclear.

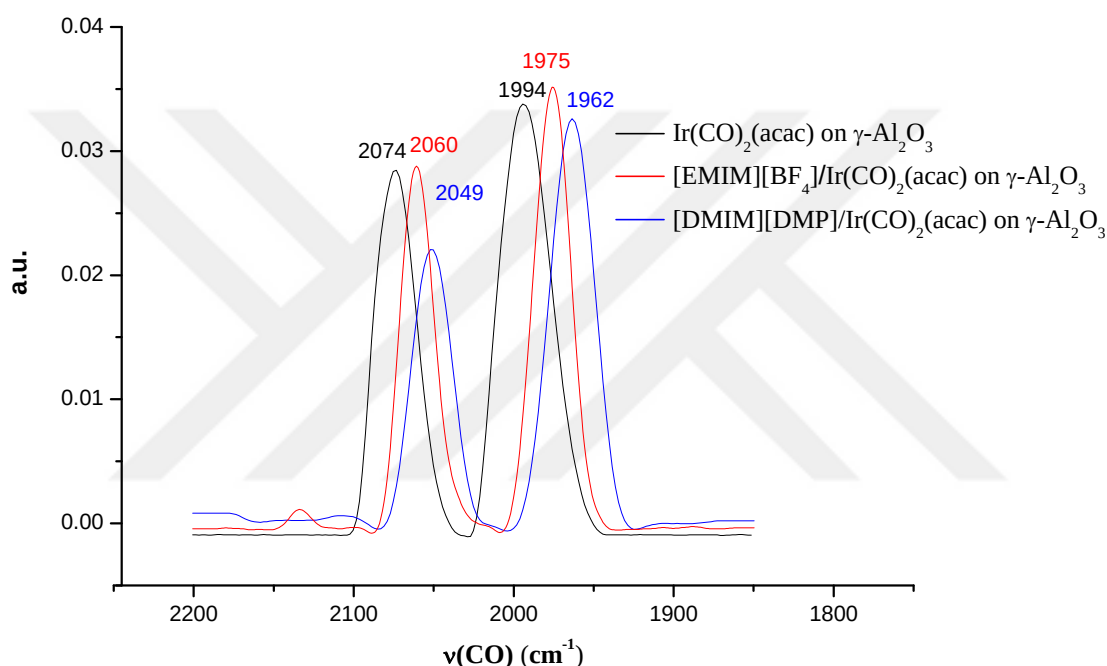


Figure 4-2. $\nu(\text{CO})$ of some of the representative samples: $\text{Ir}(\text{CO})_2/\gamma\text{-Al}_2\text{O}_3$ (black); $[\text{EMIM}][\text{BF}_4]$ coated $\text{Ir}(\text{CO})_2/\gamma\text{-Al}_2\text{O}_3$ (red), $[\text{DMIM}][\text{DMP}]$ coated $\text{Ir}(\text{CO})_2/\gamma\text{-Al}_2\text{O}_3$ (blue).

Figure 4-2 further indicates that the influence of IL on metal site changes depending on its structure. For instance, when $[\text{EMIM}][\text{BF}_4]$ and $[\text{DMIM}][\text{DMP}]$ are considered, $\nu(\text{CO})_{\text{sym}}$ of the supported iridium *gem*-dicarbonyl shifts from 2074 to 2049 cm^{-1} and 2060 cm^{-1} when the metal complex is coated with $[\text{DMIM}][\text{DMP}]$ and $[\text{EMIM}][\text{BF}_4]$, respectively. Thus, we infer that the effect of $[\text{DMIM}][\text{DMP}]$ on the electron density of metal site is more pronounced than that of $[\text{EMIM}][\text{BF}_4]$, as indicated by this higher red shift. As presented in

Table 4-2 and in the Appendix A4, the positions of the $\nu(\text{CO})$ features change significantly with changes in IL's structure. This change in $\nu(\text{CO})$ position with IL's structure indicates that the electronic structure on iridium sites changes when these complexes are coated with different ILs. Thus each IL has different ligand effect on the metal.

Aiming at elucidating the effects of IL structure on the electron density of metal sites, we consider the vibration frequency of the most acidic proton on imidazolium ring, $\nu(\text{C2H})$, given in Table 4-2. C2H is the proton that determines strongly localized hydrogen bonds between anion and cation, thus it is a measure of interionic energy, which decreases with an increase in C2–H bond strength (that is with higher $\nu(\text{C2H})$).²²⁻²⁷ Peak assignments of C2 proton of each IL was performed based on the assignments found in the literature.²⁸ Figure 4-3 shows the relation between $\nu(\text{C2H})$ of 14 different 1,3-dialkylimidazolium ILs (Tables 4-1 and 2) and the corresponding red shift amount in symmetric stretching vibration frequency of carbonyl groups of the coated iridium carbonyls from those of uncoated ones ($\Delta\nu(\text{CO})_{\text{sym}}$). Data demonstrate that there is a strong correlation between $\Delta\nu(\text{CO})_{\text{sym}}$ and $\nu(\text{C2H})$ fingerprints of bulk ILs ($R^2 = 0.9357$). A similar trend is also valid considering the antisymmetric stretching vibrations as presented in Appendix A4. Accordingly, a decrease in $\nu(\text{C2H})$ results in an increase in red shift amount. This increase in red shift with decreasing $\nu(\text{C2H})$ illustrates that as the interionic interaction energy increases, the electron density on iridium increases more because of a larger amount of electron donation to the metal site by the IL.

Electron donation from IL to metal is related to ligand-type behavior of ILs, thus the interactions of IL and supported metal catalyst. Sobota et. al.¹² studied the interaction of [BMIM][NTf₂] film with CO-covered Pd on model surface of Al₂O₃/NiAl(110). They used time-resolved infrared reflection absorption spectroscopy (TR-IRAS) to compare IL-coated and uncoated supported metal catalysts and investigated that only [NTf₂][−] anion interact with

Pd sites *via* the (SO₂) groups. In a similar way, in this study, we considered the changes in IR fingerprints of [BMIM][NTf₂]/ γ -Al₂O₃ upon addition of Ir(CO)₂ complex to elucidate the interactions between IL and Ir centers (given in Appendix A4). However, data illustrate that both anion and cation of the IL have interactions with metal sites, indicating that a more detailed study, such as a surface science-based model study, is needed for elucidation of direct interactions between anion/cation of IL and Ir sites.

Table 4-2. ν (C2H) fingerprints of bulk ILs, and the corresponding symmetric and antisymmetric ν (CO) of IL-coated metal complexes.

IL	ν (C2H), cm ⁻¹	When coated on Ir(CO) ₂ / γ -Al ₂ O ₃ , cm ⁻¹	
		ν (CO) _{sym}	ν (CO) _{asym}
[EMIM][BF ₄]	3123	2060	1975
[EMIM][DEP]	3071	2050	1962
[EMIM][LAC]	3079	2052	1964
[EMIM][MSO ₄]	3106	2055	1971
[EMIM][TfO]	3117	2061	1976
[BMIM][Ac]	3056	2046	1954
[BMIM][TFA]	3089	2053	1966
[BMIM][BF ₄]	3122	2060	1973
[BMIM][TOS]	3102	2054	1963
[BMIM][HSO ₄]	3103	2054	1967
[BMIM][NTf ₂]	3124	2063	1977
[BMIM][OS]	3105	2055	1968
[DMIM][DMP]	3069	2049	1962
[DMIM][MSO ₄]	3111	2057	1975

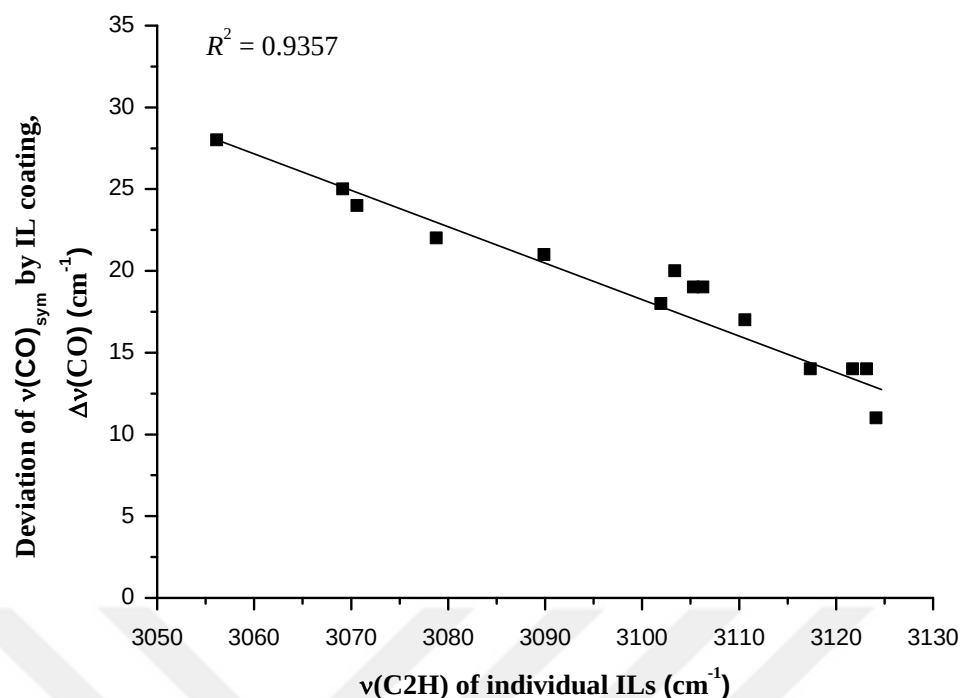


Figure 4-3. Variation of red shift amount in $\nu(\text{CO})_{\text{sym}}$ values when coated with IL as a function of $\nu(\text{C2H})$ of bulk 1,3-dialkylimidazolium ILs ($\nu(\text{C2H})$ values are provided in Appendix A4).

In summary, results presented here illustrate that IL coating layer strongly controls the electron density of the active metal sites. A stronger interionic interaction strength in 1,3-dialkylimidazolium ILs results in a higher electron donation to the metal. To the best of our knowledge, this is the first illustration of a correlation between an IL structural parameter and the electron density of metal sites in high-surface area metal-oxide-supported metal catalysts with an IL layer. These results create opportunities to tune the electronic structure of active metal sites by tailoring the structure of ILs for optimum performance. We suggest that the performance evaluation of such metal catalysts with different IL coating layer can exhibit a volcano plot type relation, a common phenomenon for transition metals for various reactions,²⁹⁻³⁰ as a consequence of this ligand effect of ILs. Thus, in a way, for instance, it would be possible to make an iridium-based catalysts act as a palladium- or ruthenium-based catalysts for partial hydrogenation of dienes by coating them with a proper IL to adjust its

electronic properties accordingly. Here, the selectivity towards olefins would also benefit from the relative solubility differences between olefins and paraffins in corresponding ILs, creating opportunities for rational design of catalyst. This work is being expanded on elucidating such kind of structure-performance relationships in these IL-coated single-site supported metal catalysts.

4-5. Conclusions

Structurally simple and well defined supported iridium *gem*-dicarbonyl complexes were utilized to elucidate the structural factors controlling the ligand effect of 1,3-dialkylimidazolium ionic liquids of metal sites in solid catalyst with ionic liquid layer (SCILL). Data illustrate a strong correlation between the interionic interactions in ILs and their corresponding ligand effect on a high-surface area metal-oxide supported metal catalyst.

4-6. Acknowledgments

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4-7. Supplementary Materials

All FT-IR data showing $\nu(\text{CO})_{\text{sym}}$ and $\nu(\text{CO})_{\text{asym}}$ of IL-coated $\text{Ir}(\text{CO})_2(\text{acac})$ on $\gamma\text{-Al}_2\text{O}_3$; comparison of 20 and 40 wt.% IL loaded samples; variation of red shift in $\nu(\text{CO})_{\text{asym}}$ when coated with IL as a function of $\nu(\text{C}_2\text{H})$ of bulk ILs.

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Chapter 5

Tuning the Selectivity of Single-Site Supported Metal Catalysts with Ionic Liquids*



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5-1. Abstract

1,3-Dialkylimidazolium ionic liquid coatings act as electron-donors increasing the selectivity for partial hydrogenation of 1,3-butadiene catalyzed by iridium complexes supported on high-surface-area γ -Al₂O₃. High-energy resolution fluorescence detection X-ray absorption near edge structure (HERFD XANES) measurements quantify the electron donation and are correlated with the catalytic activity and selectivity. The results demonstrate broad opportunities to tune electronic environments and catalytic properties of atomically dispersed supported metal catalysts.

5-2. Introduction

Atomically dispersed supported metals are an emerging class of catalyst. They offer opportunities for tuning their properties that make them comparable to ligated molecular metal complexes used in homogeneous catalysis.¹⁻³ The atomic dispersion offers advantages of A) the highest degree of utilization of metals, which are often expensive;³ B) new reactivities linked with the effects of supports as ligands;⁴ C) prospects of high selectivity associated with the structural uniformity of active sites;⁵⁻⁶ and D) opportunities for precise characterization to facilitate determination of atomic-level structure-performance relationships.⁷⁻⁸

The metal sites in these supported catalysts often require stabilizing ligands that intrinsically limit the catalytic performance,⁹ which is challenging to control. As the catalytic properties depend strongly on the electronic environment of the active site, researchers have attempted to tune these properties by modifying the ligands, as in homogeneous catalysis.¹⁰ However, this approach is limited by the available classes of ligands in the organometallic precursors.¹¹⁻¹² Promoters can also be used to modify the electronic environment of the metal,¹³⁻¹⁴ but

incorporation of promoters is often imprecise. An alternative approach is to modify the electron-donating/withdrawing properties of supports,^{12,15-16} but this approach is limited because the modified supports might fail to maintain the structural integrity of the catalyst.

Here, we illustrate an alternative strategy for tuning the properties of single-site supported metal catalysts—by using surface modifiers, as has been done before with conventional supported metal catalysts, to adjust the electronic environment of the active sites.¹⁷⁻²⁰ For example, Chen et al.¹³ showed that chelation of the surface of ultrathin Pt nanowires with electron-donating ethylenediamine induced high selectivity for the production of N-hydroxylanilines from nitrobenzene by favouring the adsorption of electron-deficient reactants over electron-rich intermediates to increase the selectivity for partial hydrogenation. Ionic liquids (ILs) offer especially good potential in this regard, offering an almost unlimited number of possible structures with physical and chemical properties tunable over wide ranges.²¹⁻²³ An example illustrating the benefits of an electron-donating IL, [BMIM][BF₄], was reported for a commercial nickel catalyst, giving >95% selectivity for butenes in the industrially important 1,3-butadiene (BD) hydrogenation, irrespective of conversion.²⁴

We report results characterizing the effects on catalyst performance of a family of ILs coating atomically dispersed supported iridium sites, having quantified the electron-donation effects by high-energy resolution fluorescence detection X-ray absorption near edge structure (HERFD XANES). HERFD XANES provides more detailed information than conventional XANES.^{7,25} Well-defined site-isolated iridium complexes were prepared on γ -Al₂O₃ and coated with 1,3-dialkylimidazolium ILs, chosen for their varied electron-donor strengths—which we have correlated with the stretching frequencies of the C–H groups on the imidazolium rings.^{21-23,26} The influence of the IL on catalyst performance was evaluated by the selectivity for partial hydrogenation of BD.

5-3. Materials & Methods

5-3.1. Materials

Uncoated and IL-coated site-isolated supported iridium complexes were prepared as described in Chapter 4, Section 4-3.1. Each IL-coated sample had approximately 20 and 0.4 wt% IL and iridium loadings, respectively. All the IL-coated and uncoated samples were stored in the glove box under argon.

5-3.2. Fourier Transform IR (FTIR) Spectroscopy

FTIR spectra of each sample were collected as described in Chapter 4, Section 4-3.2. Stretching vibrations of carbonyl groups, $\nu(\text{CO})$, of the metal oxide-supported $\text{Ir}(\text{CO})_2$ complexes were used to probe the electronic environment of the iridium centers.

5-3.3. High-Energy Resolution Fluorescence Detection X-Ray Absorption Near Edge Structure (HERFD XANES) Measurements

HERFD XANES measurements were collected at Beamline 6-2 at the Stanford Synchrotron Radiation Lightsource (SSRL). A liquid-nitrogen-cooled double-crystal $\text{Si}(311)$ monochromator was equipped to select the energy of the incident beam with a flux of 3×10^{12} photons $\times$ s $^{-1}$. A Rowland circle spectrometer (radius 1 m) equipped with three spherically bent $\text{Si}(800)$ analyzers and a silicon drift detector were used to select the Ir $L\alpha$ (9175 eV) emission line with a measured resolution of 1.3 eV. An iridium foil was scanned in the transmission mode for energy calibration. Each sample (less than 100 mg in mass) was loaded into a static cell, which was sealed in an argon-filled glovebox, preventing contamination by water and oxygen. The iridium loading of each sample was less than 0.5 wt% to minimize self-absorption, and all HERFD-XANES spectra were measured within 2 min with each

sample being scanned three to six times to improve signal-to-noise ratio. A reference material was not scanned simultaneously with the samples.

The analysis of the HERFD XANES data was carried out with the software ATHENA of the IFEFFIT package.²⁷⁻²⁸ The edge, determined by first inflection point of the absorption edge of the Ir foil, was calibrated to the reported Ir L_{III} energy, 11215 eV. This calibration was used to calibrate a known glitch in the monochromator observed in the I_0 signal of each scan. A least-squares Gaussian fit of the glitch, determined the error in the energy calibration of the samples to be 22 meV/0.022 eV. Energy calibration was achieved by aligning the glitch in each scan to the glitch in the Ir foil reference scans. Three to six scans per sample were averaged with the averaged spectra being used for deglitching and normalization. The averaged spectrum was processed by fitting a second-order polynomial to the pre-edge region and subtracting this from the entire spectrum. Edge energy was determined by the first derivative of the normalized absorbance. The data were normalized by dividing the absorption intensity by the height of the absorption edge.

5-3.4. Catalyst performance measurements

For catalyst performance measurements, uncoated and IL-coated supported iridium complexes (each including 250-350 mg of iridium dicarbonyl complexes) were placed into a ¼-in. stainless steel once-through tubular flow reactor. A three-zone resistively heated furnace (Thermcraft, model # XST-3-0-18-3V) equipped with PC-operated temperature controllers was utilized for temperature control in the reactor. Electronic mass flow controllers (Aalborg, model GFC17) were used to adjust the flow rates of gases. Before each measurement, samples were treated in flowing ethene (50 vol% in balance helium, Linde) at 373 K with a ramp rate of 3 K/min for 1 h to convert the almost inactive supported Ir(CO)₂ complexes into mixtures

of $\text{Ir}(\text{CO})_2(\text{C}_2\text{H}_4)$ and $\text{Ir}(\text{CO})_2(\text{C}_2\text{H}_4)_2$ complexes, as reported previously for HY-zeolite-supported complexes.²⁹

Following a cooling period to the reaction temperature (373 K) in flowing He, the feed was switched to a reaction gas mixture with a molar ratio of 1,3-butadiene (Linde, 99.6 vol%): H_2 (Linde, 99.99 vol%) = 1:2 with the reactor operated at atmospheric pressure and 373 K. Conversions of 1,3-butadiene were in the differential range, <2%. Product analysis was performed using an online gas chromatograph (Agilent GC 7890A) equipped with a GS-Alumina column (50 m $\times$ 530 μm) and a flame ionization detector. Reaction rates are reported per Ir atom in terms of turnover frequencies (TOFs), assuming that all the Ir atoms were accessible for reaction.

5-3.5. Conductor-Like Screening Model for Realistic Solvents (COSMO-RS) Calculations

COSMOTermX (version 1601) software with the Ionic Liquid Screening module was used to calculate the solubility of the reactants and products in each IL by setting the temperature to 333 K. Data were analyzed according to a previous study.²⁴ The capacity term is defined as the inverse of the activity coefficient at infinite dilution³⁰ for each component in each IL, considered as mole fraction in solution. The definition of capacity is as follows:

$$C_i^\infty = \frac{1}{\gamma_i^\infty} \sim x$$

Here, C_i^∞ is the solvent capacity at infinite dilution for components “i” being 1,3-butadiene (BD), butane (B), *trans*-2-butene (T2B), *cis*-2-butene (C2B), 1-butene (1B), and hydrogen (H_2) in each IL at 373 K and γ_i^∞ is the activity in each IL and x is the mole fraction of the gas components in solution.

5-4. Results and Discussion

Atomically dispersed supported iridium *gem*-dicarbonyl complexes were prepared by the reaction of Ir(CO)₂(acac) (acac = acetylacetonato), with partially dehydroxylated γ -Al₂O₃, as before, with characterization by X-ray absorption spectroscopy and atomic resolution aberration-corrected scanning transmission electron microscopy.³¹ IR spectra confirmed the removal of acac ligands from the precursor, and bands at 2074 and 1994 cm⁻¹ characterizing the initial sample (Figure A5-1, Appendix A5) indicate the terminal CO ligands of supported Ir(CO)₂.³¹ These isolated complexes were coated with ILs (Table 5-1 and Table A5-1 in Appendix A5) such that each resultant sample had approximately 20 and 0.4 wt% IL and iridium loadings, respectively. Pore size distributions of the catalysts before and after coating show that the ILs penetrated even into small pores, 2.8-5 nm in diameter.²³ The IL-coating layer thicknesses ranged from 1 to 1.5 nm, corresponding to a maximum of a few molecular layers of ILs.²³

Table 5-1. Names and abbreviations of IL coatings.

IL Name	Abbreviation
1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	[BMIM][NTf ₂]
1-Butyl-3-methylimidazolium tetrafluoroborate	[BMIM][BF ₄]
1,3-Dimethylimidazolium methyl sulfate	[DMIM][MSO ₄]
1-Butyl-3-methylimidazolium trifluoroacetate	[BMIM][TFA]
1-Ethyl-3-methylimidazolium diethyl phosphate	[EMIM][DEP]
1,3-Dimethylimidazolium dimethyl phosphate	[DMIM][DMP]
1-Butyl-3-methylimidazolium acetate	[BMIM][Ac]

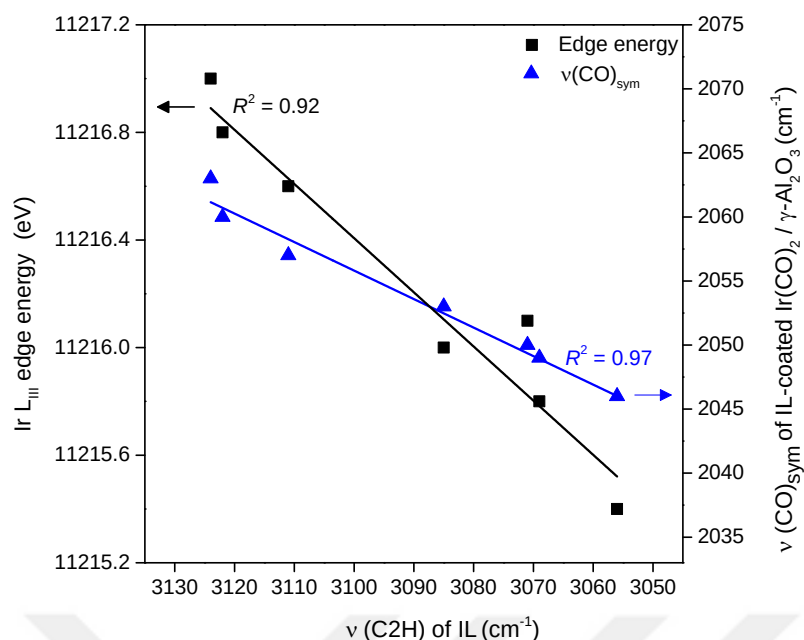


Figure 5-1. Variations of Ir L_{III} edge energy in $\gamma\text{-Al}_2\text{O}_3$ -supported $\text{Ir}(\text{CO})_2$ complexes resulting from coating with various 1,3-dialkylimidazolium ILs (left vertical axis) and the corresponding $\nu(\text{CO})_{\text{sym}}$ (right vertical axis) with $\nu(\text{C2H})$ of the coating IL.

The $\nu(\text{CO})_{\text{sym}}$ band shifted to lower wavenumbers upon coating of $\text{Ir}(\text{CO})_2/\gamma\text{-Al}_2\text{O}_3$ with various ILs (Figures A5-2 to A5-8, Table A5-2 in Appendix A5). For example, when the ILs were $[\text{BMIM}][\text{NTf}_2]$ and $[\text{BMIM}][\text{Ac}]$, the corresponding red shifts were 11 and 28 cm^{-1} , respectively, consistent with electron donation from each IL to the Ir.^{23-24,29} The degree of electron donation was quantified by HERFD XANES data recorded at the Ir L_{III} edge characterizing the uncoated and IL-coated $\text{Ir}(\text{CO})_2$ complexes, Figure A5-9 in Appendix A5. The edge energy of the uncoated $\text{Ir}(\text{CO})_2/\gamma\text{-Al}_2\text{O}_3$ was found to be 11217.8 eV, as expected.^{29,32-33} It shifted to lower values as a result of IL coating (Figure 5-1 and Table A5-2 in Appendix A5I). The results confirm that 1,3-dialkylimidazolium ILs donate electron density to Ir in the catalysts.

Figure 5-1 illustrates the variation of edge energy (and $\nu(\text{CO})_{\text{sym}}$) with the interionic interaction energy in ILs probed by the stretching frequency of the most acidic proton-donor

group on the imidazolium ring, $\nu(\text{C2H})$.²⁶ Accordingly, the edge energy decreased (almost linearly, $R^2 = 0.92$) from 11217.0 to 11215.4 eV (from [BMIM][NTf₂] to [BMIM][Ac]) with a decrease in $\nu(\text{C2H})$ of the IL from 3124 to 3056 cm^{-1} , related to an increase in the interionic interaction energy in the IL.²⁶ The results demonstrate that the 1,3-dialkylimidazolium IL layer strongly controls the electron density on Ir, with the strongest interionic interactions in the ion pairs corresponding to the greatest electron donation to the Ir sites.^{26,34}

We thus infer that ILs present in coatings can be used to tune the electronic properties of supported metals, and thereby influence their catalytic performance. To test this inference, we investigated the samples as catalysts for BD hydrogenation (at a BD:H₂ molar ratio of 1:2) at 333 K and 1 bar in a once-through flow reactor with differential conversions (<2%, the selectivities are constant within $\pm 0.5\%$ in this range as shown in Figure A5-10; the conversion values for each catalyst are listed in Table A5-3 in Appendix A5). Before each measurement, samples were treated in flowing ethene at 373 K with a ramp rate of 3 K/min for 1 h to convert the almost inactive supported Ir(CO)₂ complexes into active iridium complexes incorporating ethene ligands.³² IR spectra of the treated catalysts indicate that mixtures of Ir(CO)(C₂H₄) and Ir(CO)(C₂H₄)₂ were present (data in Appendix A5), as reported for HY-zeolite-supported complexes.³² Figures A5-11 to A5-18 confirm that the ligands hindered iridium cluster formation, evidenced by the lack of stretching vibrations of bridging CO ligands bonded to neighboring Ir sites, as expected.^{7,35}

The data of Figure 5-2 and Table A5-3 show that in catalysis with the uncoated γ -Al₂O₃-supported iridium complex the selectivity for butenes (sum of 1-butene (1B), *cis*-2-butene (C2B), and *trans*-2-butene (T2B)) was 51% with a turnover frequency (TOF) of 8.4×10^{-3} (molecules of 1,3-butadiene converted) $\times$ (Ir atom $\times$ s)⁻¹. On the other hand, when the supported iridium complex was coated with [BMIM][Ac], the selectivity to total butenes increased to 78% (Figure 5-2). The selectivity enhancement is attributed to the increased

electron density on iridium—evidenced by a decrease in the Ir edge energy from 11217.8 to 11215.4 eV resulting from coating with [BMIM][Ac]. Accordingly, the data show that Ir sites coated with more electron-donating ILs favor the adsorption of more electron-deficient BD over the less electron-deficient butenes and thereby favor the selective hydrogenation. This effect also leads to a decrease in TOF to 1.2×10^{-3} (molecules of 1,3-butadiene converted) $\times$ (Ir atom $\times$ s) $^{-1}$, consistent with previous reports.^{24,36} Extending these results to all our samples (Table A5-3 in Appendix A5), we demonstrate in Figure 5-2 a strong correlation between the edge energy and the selectivity for butenes ($R^2 = 0.90$). Accordingly, as the IL donates more electrons with an increase in its interionic interaction energy (indicated by a decrease in $\nu(\text{C2H})$ position), the edge energy shifts to lower values and the Ir sites become more selective for partial hydrogenation. The data also indicate that this effect is the strongest in influencing the formation of 1B. This behavior is consistent with the detection of 1B as the most abundant isomer formed on Rh species supported on the strongly electron-donating MgO.^[21]

Differences in relative solubility of reactants and intermediates in the IL layer might also be expected to lead to a filter effect controlling the selectivity.²⁴ However, data presented in Figure A5-19 in Appendix A5, illustrate that the solubility ratios of BD to 1B, T2B, and C2B in ILs estimated by COSMO-RS calculations at the reaction conditions remain in the range of 1.6-2.1 (Table A5-4). The absence of any trend in solubility ratios with $\nu(\text{C2H})$ of the IL rules out the possibility of a dominant filter effect.

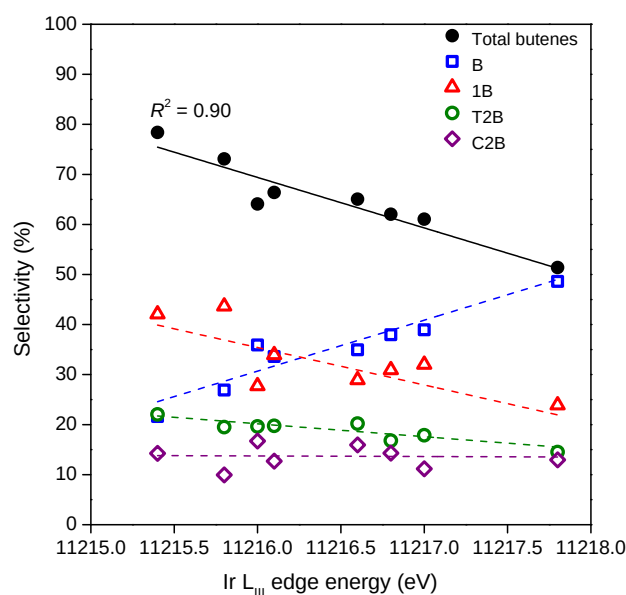


Figure 5-2. Control of selectivity in BD hydrogenation by electron donation from IL to the γ - Al_2O_3 -supported Ir complexes. Data demonstrate the variation of selectivity (B (blue $\square$), 1B (red $\triangle$), T2B (green $\circ$), C2B (purple $\diamond$), and total butenes (sum of 1B, C2B, and T2B) ($\bullet$)) with Ir L_{III} edge energy shifting from 11217.8 eV to lower energies upon coating the metal complexes with 1,3-dialkylimidazolium ILs.

5-5. Conclusions

In summary, we report a class of atomically dispersed supported metal catalysts with performance tuned by IL coatings. The coating layer controls the electron density of the active metal sites, and the data guide the choice of IL. Because there are so many possible ILs with various electron-donor properties, we envision a large class of tunable supported catalysts.

5-6. Acknowledgement

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5-7. Supplementary Materials

Synthesis methods of atomically dispersed supported metal complexes, names, abbreviations and structures of the ILs, characterization of the samples by IR, HERFD XANES, COSMO-RS, catalytic performance measurements and characterization before and after the reaction, selectivity, and TOF values.

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Chapter 6

Controlling Catalytic Activity and Selectivity for Partial Hydrogenation by Tuning Environment around Active Sites in Iridium Complexes Bonded To Supports*

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6-1. Abstract

Single-site Ir(CO)₂ complexes bonded to high-surface-area metal oxide supports, SiO₂, TiO₂, Fe₂O₃, CeO₂, MgO, and La₂O₃, were synthesized by chemisorption of Ir(CO)₂(acac) (acac = acetylacetonato) followed by coating with each of the following ionic liquids (ILs): 1-*n*-butyl-3-methylimidazolium tetrafluoroborate, [BMIM][BF₄], 1-*n*-butyl-3-methylimidazolium acetate, [BMIM][Ac], and 1-(3-cyanopropyl)-3-methylimidazolium dicyanamide, [CPMIM][DCA]. Extended X-ray absorption fine structure carbonyl infrared spectra show that the iridium was bonded to oxygen atoms of the support. Electron densities on the iridium enveloped by each IL sheath/support combination were characterized by carbonyl infrared spectra of the iridium *gem*-dicarbonyls and by X-ray absorption near-edge structure data. The electron-donor/acceptor tendencies of both the support and IL determine the activity and selectivity of the catalysts for the hydrogenation of 1,3-butadiene, with electron-rich iridium being selective for partial hydrogenation. The results resolve the effects of the IL and support as ligands; for example, effect of the IL becomes dominant when the support has a weak electron-donor character. The combined effects of supports and ILs as ligands offer broad opportunities for tuning catalytic properties of supported metal catalysts.

6-2. Introduction

Atomically dispersed metal catalysts on supports are drawing wide attention, because they offer new catalytic properties¹⁻⁵ and an efficient use of expensive transition metals. Notwithstanding numerous recent investigations of structure and novel performance of such catalysts on supports such as metal oxides,⁶⁻¹⁴ there is only limited insight into how to control their catalytic properties. Some researchers have tuned the catalytic properties by choice of ligands bonded to the metal,¹⁵⁻¹⁶ the supports

act as ligands as well.¹⁷⁻¹⁹ Electron-donor properties of supports are determined by the compositions and structures of the sites where the metals are bonded to the supports,²⁰⁻²¹ and they can be tuned by promoters nearby on the support.²²⁻²³ The effects of supports are sometimes pronounced, as illustrated by rhodium complexes on HY-zeolite and on MgO—the strong electron-donor MgO induces high selectivity for 1,3-butadiene hydrogenation to butenes, whereas the zeolite does not.²⁴

Molecules nearby metal centers on surfaces may also act as ligands,²⁵ as illustrated by electron-donor ethylenediamine coatings of platinum nanowires,²² which influence the selectivity of the platinum for catalytic hydrogenation of nitroaromatics. The class of coatings influencing catalytically active metals in supported catalysts has recently been extended to include ionic liquids (ILs), which have been shown to enhance catalytic selectivity in the hydrogenation of cyclooctadiene.²⁶ Many ILs are available, offering a wide range of electron-donor/acceptor properties. They can be quite stable on surfaces, and in addition to acting as ligands, they can also act as “molecular filters” controlling the active concentrations of reactants and intermediates.²⁶⁻²⁹

Early results show that 1,3-dialkylimidazolium-type IL coatings significantly influence the electronic properties of iridium carbonyls that are chemically bonded to alumina, $\text{Ir}(\text{CO})_2/\gamma\text{-Al}_2\text{O}_3$,³⁰ and they thereby influence the catalyst performance for partial hydrogenation of 1,3-butadiene.³¹ We posit that ILs, because they offer a wide range of electron-donor/acceptor properties, offer wide-ranging prospects for tuning supported catalysts. We posit that they can be tuned to work synergistically with supports to control the electronic environments and thereby the catalytic properties of essentially molecular species on supports.³⁰⁻³¹

Now we report such control for a family of site-isolated iridium complex catalysts by choice of the environment enveloping the metal—comprising both the support and a sheath of IL molecules—that regulate the chemical environment, and thereby the catalytic properties of the metal, while allowing the access of reactant molecules.

We assess the effects of the support and the IL in terms of their electron-donating/-withdrawing properties. Our data show how to dial-in the selectivity for partial hydrogenation of 1,3-butadiene to selectively give *n*-butenes. For example, the selectivity of these isolated Ir sites on porous silica incorporating the electron withdrawing IL 1-(3-cyanopropyl)-3-methylimidazolium dicyanamide ([CPMIM][DCA]) was only 22%, but this value increased to 93% when the IL was switched to the electron-donating 1-*n*-butyl-3-methylimidazolium acetate ([BMIM][Ac]). Supports separately affect the catalytic properties,^{3,32-38} and we demonstrate how to measure the essential electron donor/acceptor properties of the ILs and the supports acting in concert, by using infrared (IR) and X-ray absorption near-edge structure (XANES) spectroscopies. Because there is an extremely large set of available ILs, the approach can be generalized to a large class of supported metal catalysts ranging from atomically dispersed species to nanoparticles.

Our goals were to learn how to control the catalytic properties of our single-site iridium catalyst by investigating a family of supports offering a wide range of electron-donor/acceptor tendencies. The supports (SiO₂, TiO₂ (anatase), Fe₂O₃, CeO₂, MgO, and La₂O₃) and the ILs were chosen to offer a wide range of complementary electron donor/acceptor tendencies (the ILs were the strong electron-acceptor [CPMIM][DCA], the strong electron-donor [BMIM][Ac], and one with intermediate electron-donor character, 1-*n*-butyl-3-methylimidazolium tetrafluoroborate, [BMIM][BF₄]). We tested

the catalysts for partial hydrogenation of 1,3-butadiene because this reaction is industrially important³⁹⁻⁴¹ and because the selectivity of a supported nickel nanoparticle catalyst has been improved by an electron-donating IL.⁴² Our results show how the ILs and supports act synergistically as ligands to control the catalytic properties, and the spectroscopic data resolve the individual roles of each.

6-3. Materials & Methods

6-3.1. Materials

All sample handling and preparations were done with standard air-exclusion techniques. The chemicals were purchased from Sigma-Aldrich with the highest available purities. The metal oxide supports were calcined in flowing O₂ with the temperature ramped at a rate of 3 K/min from room temperature to a selected final temperature (K) for each support: 793 for SiO₂; 673 for TiO₂ and CeO₂; 773 for Fe₂O₃; 873 for La₂O₃; and 973 for MgO; thereafter, each sample was held at the final temperature for 5 h in flowing O₂. Each IL, [BMIM][BF₄], [BMIM][Ac], and [CPMIM][DCA], was dried at 353 K for 6 h and kept under vacuum for 12 h before being transferred into an argon-filled Labconco glove box. The supported catalysts were synthesized by the reaction of Ir(CO)₂(acac), where acac is acetylacetonato, (18 mg) with a sample of each metal oxide (982 mg) to give an iridium loading of 1 wt% in the final uncoated sample. The precursor and support were slurried in *n*-pentane, which had been purified in an MBraun SBS solvent purifier system. The slurry was mixed for one day in a sealed flask, followed by evacuation to remove the solvent and leave all the iridium on the support. Each of the resultant solid catalysts was stored in the argon-filled glove box. Coating of these samples with ILs involved impregnating the IL (100 mg) in the supported metal complex (200 mg) and then adding an excess of calcined support (200 mg) to absorb the remaining unabsorbed IL, with the handling done in the glove box. Each of the resultant IL-coated samples had an

iridium loading of 0.4 wt%. IL loading of each sample is approximately 20 wt%, as shown by energy-dispersive X-ray spectroscopy (EDX) measurements in Appendix A6. All of the samples were stored in the argon-filled glove box after synthesis.

6-3.2. Fourier Transform IR (FTIR) Spectroscopy

FTIR spectra of each sample were collected as described in Chapter 4, Section 4-3.2. X-Ray Absorption Spectroscopy

6-3.3. Extended X-ray Absorption Fine Structure (EXAFS) Measurements and Data Analysis

X-ray absorption spectroscopy (XAS) measurements were collected at beam line 9-3 at the Stanford Synchrotron Radiation Lightsource (SSRL). Beam line 9-3 is a columnating and focusing beam line with a 20 pole, 2 Tesla, wiggler insertion device, Rh-coated harmonic rejection mirrors, and a double-crystal, liquid-nitrogen cooled, Si (220) monochromator. Spectra were collected in fluorescence detection mode using N₂-filled ion chambers and a 30-element Ge detector to measure signal. An Ir black powder (Sigma-Aldrich) was scanned simultaneously with the sample for energy calibration. EXAFS spectra were measured from 200 eV below the Ir L_{III} edge (11215 eV) to $k = 15.3 \text{ \AA}^{-1}$ in 20 min, with three scans collected and averaged to improve the signal-to-noise ratio. Approximately 250 mg of a sample was pressed into an in-situ XAS cell⁴³ in an argon-filled glove box and handled in the absence of air at the beam line to prevent contamination.

ATHENA software, a part of the IFEFFIT package,⁴⁴ and the software XDAP⁴⁵ were used in the analysis of the EXAFS data. Data alignment, edge calibration, and deglitching were performed with Athena. The edge, determined by first inflection point

of the absorption edge of the iridium black powder, was calibrated to the reported Ir L_{III} energy, 11215.0 eV. XDAP was used for normalization, background subtraction, and conversion of the data into a chi file and data fitting,⁴⁵ which allows the efficient application of a difference-file technique⁴⁶ for the determination of optimized fit parameters and isolation of individual shells. Reference files, used in the data analysis, were calculated by using the code FEFF7.0.⁴⁷

The crystal structure of $Ir(CO)_2(acac)$ ⁴⁸ was used to calculate the phase shifts and backscattering amplitudes representing the Ir–C_{CO}, Ir–O_{CO}, and Ir–O shells, as it was foreseen that the structure of the supported iridium species would be similar to that of this precursor. The phase shifts and backscattering amplitudes representing Ir–Si, Ir–Ti, Ir–Ce, Ir–Fe and Ir–Mg shells were calculated from the structural parameters characterizing Ir–Si, Ir–Ti, Ir–Ce, Ir–Fe, and Ir–Mg alloys, respectively. The Ir–Si distance (3.42 Å) was found to be longer than typical Ir–Si (2.56 Å) distance whereas the Ir–Ti distance (2.56 Å) and the Ir–Ce distance (2.54 Å) were found to be shorter than typical the Ir–Ti (2.69 Å) typical Ir–Ce (3.05 Å) distances, respectively. These contributions might also represent Ir–O* contribution (where O* is oxygen at long distance), however, the data quality was not sufficient to identify the back-scatterer or even to determine this contribution with confidence.

Iterative fitting was carried out for various structural models until the best agreement was attained between the calculated k^0 , k^1 , and k^2 - weighted EXAFS data and the postulated model. Plots were made to show the residuals remaining after the fitting; representative results are shown in Appendix A6.

The fitting ranges in both k and r space, where k is the wave vector and r the distance from the absorbing Ir atom, in the analysis of the data characterizing the as-

prepared sample were determined by the data quality; the range in k was in general between 3.5 ± 0.4 and $12.0 \pm 0.6 \text{ \AA}^{-1}$, and the range in r was 0–3.5 $\text{\AA}$ for each sample. These values were used with the Nyquist theorem⁴⁹ to estimate the justified number of fitting parameters. The accuracies of the parameters are estimated to be as follows (except for Ir–Si, Ir–Ti, Ir–Ce, Ir–Fe and Ir–Mg contributions): coordination number N , $\pm 20\%$; distance R , $\pm 0.02 \text{ \AA}$; disorder term σ^2 , $\pm 20\%$; and inner potential correction E_0 , $\pm 20\%$.

Data analysis for XANES spectra was performed with ATHENA using standard procedures.⁴⁴ The data for each sample was first calibrated using a known glitch in the monochromator observed in the I_0 signal. A least-squares Gaussian fit of the glitch determined the error in the energy calibration of the samples to be 0.022 eV. The absorption edge energy was defined as the maximum of the first derivative of the normalized absorbance with respect to beam energy.

6-3.4. Point of Zero Charge (PZC) Determination

PZC of metal oxides were determined as described in Chapter 3, Section 3-3.2.

6-3.5. Scanning Electron Microscopy coupled with Energy-Dispersive X-Ray Spectroscopy

A Zeiss Ultra Plus scanning electron microscope (SEM) equipped with a field-emission gun was used to collect images of the catalyst samples in secondary-electron mode. Powder samples consisting of IL-coated supported iridium complexes on SiO_2 , TiO_2 , Fe_2O_3 , CeO_2 , MgO , and La_2O_3 were mounted on carbon tape to minimize support charging effects. Images were collected at magnifications of 20 k $\times$, 50 k $\times$, and 100 k $\times$ with an accelerating voltage

(electron high tension, EHT) of 3 kV for each sample. The working distances between the probe of the microscope and samples were in the range of 2.6–2.8 mm. Each EDX image was collected at a magnification in the range of (10–75) $\times$ with an EHT of 10 kV and a working distance in the range of 5.2–5.4 mm.

6-3.6. Catalytic Performance Measurements

To evaluate the performance of each catalyst, uncoated and IL-coated supported iridium complexes (each including 300–350 mg of the supported iridium *gem*-dicarbonyl complex, independent of whether an IL coating was present) were each placed in a 1/4-in. stainless-steel once-through tubular flow reactor. A Thermcraft three-zone resistively heated furnace (Model number XST-3-0-18-3V) equipped with PC-operated temperature controllers was used for temperature control of the reactor. Electronic mass flow controllers (Aalborg, Model GFC17) were used to control the flow rates of feed gases. Before each measurement, the catalysts were treated in flowing ethylene at 373 K for 1 h as the temperature was ramped at a rate of 3 K/min to convert the almost inactive supported $\text{Ir}(\text{CO})_2$ complexes into mixtures of $\text{Ir}(\text{CO})_2(\text{C}_2\text{H}_4)$ and $\text{Ir}(\text{CO})_2(\text{C}_2\text{H}_4)_2$ complexes, as reported for the isostructural HY-zeolite-supported iridium complexes.³⁷ Then, the flow of the reaction mixture with a molar ratio of H_2 (Linde, 99.99 vol%) to 1,3-butadiene (Linde, 99.6 vol%) of 2:1 was started through the catalyst bed, operated at atmospheric pressure and 333 K. Products were analysed with an online gas chromatograph (Agilent 7890A) equipped with a GS-alumina column (50 m $\times$ 530 μm) and a flame-ionization detector. Conversions of 1,3-butadiene were in the differential range, <2%. Reaction rates are reported per Ir atom in terms of turnover frequency (TOF), assuming that all of the Ir atoms were accessible

for reaction. Repeat measurements showed that the TOF values are reproducible within $\pm 2\%$.

6-4. Results

6-4.1. Atomically Dispersed Supported Iridium Complexes

Supported iridium complexes were synthesized by the reaction of $\text{Ir}(\text{CO})_2(\text{acac})$ (acac is acetylacetonato) with freshly calcined metal oxides. The samples incorporated 1 wt% Ir, giving an average distance between Ir atoms of at least 1 nm, depending on the support surface area, to assure site-isolation. Consistent with the atomic dispersion, Ir L_{III} -edge extended X-ray absorption fine structure (EXAFS) spectra of the samples (Table 6-1 and Table A6-1 and Figures A6-1 to A6-36 in Appendix A6) give no evidence of an Ir–Ir scattering path that would represent metal clusters/nanoparticles, consistent with atomically dispersed iridium in each catalyst.⁵⁰ The best-fit EXAFS model characterizing each sample includes an Ir–O_s scattering path (the subscript refers to the support) with a coordination number of 2.2 ± 0.2 (Table 6-1) and a bonding distance ranging from 2.01 to 2.07 Å, as expected for positively charged group-8 metals on metal oxides.⁴⁶ The data in Table 6-1 indicate that each Ir atom was bonded to approximately two carbon atoms (indicated by a coordination number of 2.1 ± 0.2) at a distance ranging from 1.90 to 2.02 Å, which is typical of Ir–C bonding in iridium dicarbonyl complexes.⁵¹

Table 6-1. Summary of EXAFS fit parameters characterizing samples prepared by adsorption of Ir(CO)₂(acac) on metal oxides having various electron-donor characteristics.

Sample	Shell ^a	N	R (Å)	$\Delta\sigma^2 \times 10^3$ (Å ²)	ΔE_0 (eV)	k range (Å ⁻¹)	R range (Å)
Ir(CO) ₂ /SiO ₂	Ir–O _s	2.25	2.07	3.46	-3.42	3.82 – 12.43	0.5 – 3.50
	Ir–C _{CO}	2.25	2.00	3.87	-1.61		
	Ir–O _{CO}	2.00	3.28	7.78	-5.12		
	Ir–Si	2.50	3.42	5.94	5.01		
Ir(CO) ₂ /TiO ₂	Ir–O _s	2.40	2.03	0.10	4.21	3.17 – 12.10	0.5 – 3.00
	Ir–C _{CO}	2.20	1.92	1.55	-0.64		
	Ir–O _{CO}	2.10	2.95	5.00	5.66		
	Ir–Ti	1.40	2.65	6.21	-8.00		
Ir(CO) ₂ /Fe ₂ O ₃	Ir–O _s	2.40	2.01	0.10	3.54	3.92 – 12.30	0.5 – 3.20
	Ir–C _{CO}	2.14	1.90	2.80	8.00		
	Ir–O _{CO}	1.90	2.91	6.89	-1.70		
	Ir–Fe	1.12	2.52	7.69	-5.48		
Ir(CO) ₂ /CeO ₂	Ir–O _s	2.30	2.02	0.10	-3.75	3.92 – 12.60	0.5 – 3.2
	Ir–C _{CO}	2.10	1.90	3.73	8.00		
	Ir–O _{CO}	1.90	2.83	6.54	-7.73		
	Ir–Ce	2.20	2.54	10.17	-8.00		
Ir(CO) ₂ /MgO	Ir–O _s	2.40	2.06	0.10	-6.98	4.02 – 11.30	0.5 – 3.40
	Ir–C _{CO}	2.20	2.02	0.62	0.29		
	Ir–O _{CO}	2.20	2.95	5.91	-8.00		
	Ir–Mg	1.45	2.76	0.10	7.36		
Ir(CO) ₂ /La ₂ O ₃	Ir–O _s	2.00	2.02	0.10	1.76	3.15 – 11.30	0.5 – 3.20
	Ir–C _{CO}	1.89	1.93	3.16	4.26		
	Ir–O _{CO}	2.14	2.92	5.98	8.00		
	Ir–O _l	2.10	2.46	0.10	0.21		

Notation: N, coordination number; R, distance between the absorber and backscatterer atoms; $\Delta\sigma^2$, mean square relative displacement; ΔE_0 , inner potential correction. Error bounds are estimated as follows: N, $\pm 20\%$; R, ± 0.02 Å; $\Delta\sigma^2$, $\pm 20\%$; ΔE_0 , 20%. ^aO_s and O_l denote surface oxygen atoms of supports; C_{CO} and O_{CO} denote carbon and oxygen atoms of carbonyl ligands bonded to iridium.

IR spectra (Figure A6-37A and B in Appendix A6) confirm the identification of iridium *gem*-dicarbonyls. We observed no bridging CO bands that would have indicated the presence of iridium clusters (details in Appendix A6, Section A6-2.1).⁵² A comparison of the IR spectra of the Ir(CO)₂(acac) precursor and the supported samples (Figures A6-37A and B, Tables 6-2 and A6-2) shows that when Ir(CO)₂(acac) was adsorbed, some bands shifted or were replaced, as expected,⁵¹ for the formation of the supported iridium *gem*-dicarbonyls (details in Appendix A6, Section A6-2.1).

Table 6-2. Ir L_{III} edge energies, $\nu_{\text{sym}}(\text{CO})$ and $\nu_{\text{asym}}(\text{CO})$ characterizing of Ir(CO)₂(acac) and uncoated and IL-coated metal-oxide-supported Ir(CO)₂ complexes.

Supported Ir(CO) ₂ complex	$\nu_{\text{sym}}(\text{CO}) (\text{cm}^{-1})$	$\nu_{\text{asym}}(\text{CO}) (\text{cm}^{-1})$
Ir(CO) ₂ (acac)	2049	1985
Ir(CO) ₂ (acac) in hexane ⁵¹	2074	2000
Ir(CO) ₂ /SiO ₂	2081	2008
Ir(CO) ₂ /TiO ₂	2076	1988
Ir(CO) ₂ /Fe ₂ O ₃	2073	1981
Ir(CO) ₂ /CeO ₂	2071	1982
Ir(CO) ₂ /MgO	2069	1985
Ir(CO) ₂ /La ₂ O ₃	2066	1977
[BMIM][BF ₄]-coated Ir(CO) ₂ /SiO ₂	2052	1981
[BMIM][BF ₄]-coated Ir(CO) ₂ /TiO ₂	2055	1971
[BMIM][BF ₄]-coated Ir(CO) ₂ /Fe ₂ O ₃	2056	1969
[BMIM][BF ₄]-coated Ir(CO) ₂ /CeO ₂	2057	1974
[BMIM][BF ₄]-coated Ir(CO) ₂ /MgO	2058	1960
[BMIM][BF ₄]-coated Ir(CO) ₂ /La ₂ O ₃	2055	1970
[BMIM][Ac]-coated Ir(CO) ₂ /SiO ₂	2049	1953
[BMIM][Ac]-coated Ir(CO) ₂ /TiO ₂	2052	1962
[BMIM][Ac]-coated Ir(CO) ₂ /Fe ₂ O ₃	2053	1947
[BMIM][Ac]-coated Ir(CO) ₂ /CeO ₂	2050	1966
[BMIM][Ac]-coated Ir(CO) ₂ /MgO	2056	1952
[BMIM][Ac]-coated Ir(CO) ₂ /La ₂ O ₃	2053	1970
[CPMIM][DCA]-coated Ir(CO) ₂ /SiO ₂	2098	1974
[CPMIM][DCA]-coated Ir(CO) ₂ /TiO ₂	2084	1956
[CPMIM][DCA]-coated Ir(CO) ₂ /Fe ₂ O ₃	2081	1973
[CPMIM][DCA]-coated Ir(CO) ₂ /CeO ₂	2074	1955
[CPMIM][DCA]-coated Ir(CO) ₂ /MgO	2064	1959
[CPMIM][DCA]-coated Ir(CO) ₂ /La ₂ O ₃	2061	1991

6-4.2. Supports as Ligands

The $\nu(\text{CO})$ positions (Table 6-2) distinguish one support from another as electron-donor/acceptor ligands. The major $\nu_{\text{sym}}(\text{CO})$ peaks indicate Ir(CO)₂ on the surface, and the shoulders at 2028 and 2036 cm⁻¹ in the spectra of the Fe₂O₃- and CeO₂-supported samples, respectively, indicate iridium carbonyls on minority surface sites.⁵¹

Electronic environments of the supported iridium were probed with XANES spectroscopy at the Ir L_{III} edge (Figures A6-38 to A6-44 in Appendix A6) Table A6-3 in Appendix A6 is a summary of the absorption edge energies of each uncoated sample. This energy decreased from 11,218.0 to 11,216.0 eV in the order SiO₂, TiO₂, Fe₂O₃, CeO₂, MgO, and La₂O₃ indicating the increasing electron density on iridium donated by the support.³⁷ This order is consistent with the PZC values characterizing the metal oxides (Figure 6-1A).⁵³⁻⁵⁴ The IR $\nu_{\text{sym}}(\text{CO})$ band positions of the iridium carbonyls provide still another, easily determined, measure of the electron-donor strengths of the supports, as confirmed by the strong correlation between the edge energies of the iridium carbonyls and their $\nu_{\text{sym}}(\text{CO})$ band positions as shown in Figure 6-1B (or between $\nu_{\text{sym}}(\text{CO})$ and PZC of the support (Figure 6-1C)). Thus, for example, a red shift in the $\nu_{\text{sym}}(\text{CO})$ band position indicates an increase in the electron density on the iridium sites.⁵⁵

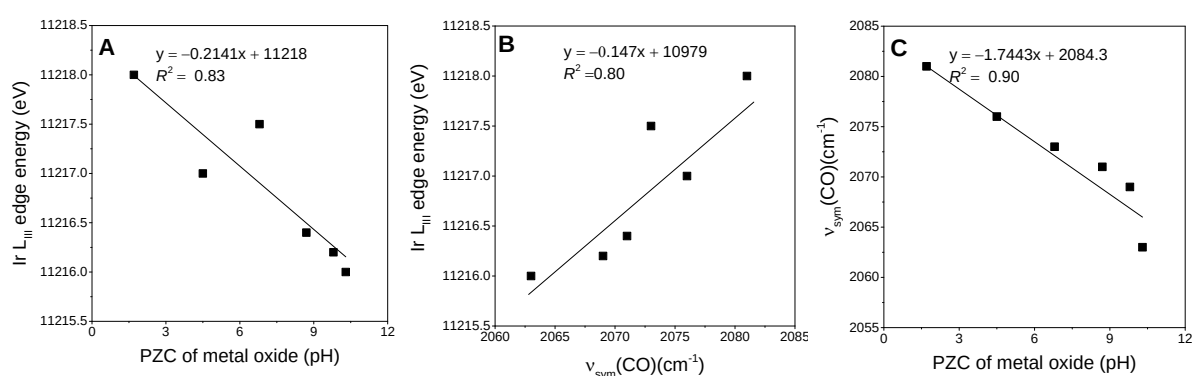


Figure 6-1. Measure of the electron-donor strengths of the supports: Variation of A) Ir L_{III} edge energy of the uncoated supported iridium carbonyls with PZC of the support; B) Ir L_{III} edge position with the corresponding $\nu_{\text{sym}}(\text{CO})$ band positions of uncoated supported iridium carbonyls; and C) $\nu_{\text{sym}}(\text{CO})$ band positions of uncoated supported iridium carbonyls with PZC of the support.

6-4.3. ILs Distributed Uniformly on Supports

Sample IL loadings were chosen to be 20 wt%, sufficient to provide a multilayer covering of all Ir sites in each sample but not so much as to present a significant transport limitation to the reactant molecules in catalysis. The loading corresponds to 45 ± 3 IL molecules per Ir site, on average. The IL was present in layers with a thickness on average of several molecules. On a macroscopic scale, at least, the ILs were uniformly distributed over the supported species, as shown by SEM/EDX images (Figures A6-45 to A6-51 and Table A6-4 in Appendix A6; details in Appendix A6).

6-4.4. ILs as Ligands

IR spectra of the various samples and the bulk ILs (Figures A6-37 and Figures A6-52 to A6-54 in Appendix A6) show that the supported complexes were still present as site-isolated iridium *gem*-dicarbonyls after addition of the IL, as shown by the two distinct carbonyl stretching bands of the iridium *gem*-dicarbonyls in each supported catalyst. The IL coatings shift these bands. For example (Figure 6-1B and Table 6-3) the $\nu_{\text{sym}}(\text{CO})$ and $\nu_{\text{asym}}(\text{CO})$ bands of $\text{Ir}(\text{CO})_2/\text{SiO}_2$, at 2081 and 2008 cm^{-1} , were shifted to 2052 and 1981 cm^{-1} , respectively, upon coating with [BMIM][BF₄]. Similarly, when the complexes were coated with [BMIM][Ac], the bands were red-shifted by 32 and 55 cm^{-1} , respectively. These shifts confirm^{28-29,56} that these ILs are electron-donor ligands. In contrast, the electron-withdrawing IL [CPMIM][DCA], with its cyano group on the cation, blue-shifted the corresponding bands to 2098 and 1974 cm^{-1} . Doubling the IL loadings led to no significant changes in the band shifts, demonstrating that ILs were present at saturation loadings in terms of their ligand effects.³⁰

To rule out the possibility that the iridium complex was removed from the surface and dissolved in the IL coating, we washed some IL-coated samples in methanol and checked the IR spectra of both the filtrates and the washed samples. No vibrational bands associated with iridium carbonyls were detected in the filtrates, and the spectra of the washed samples still indicated the presence of the iridium carbonyls (although the peak positions and shapes were changed by the treatments, as illustrated in Figure A6-55 in Appendix A6 for [BMIM][BF₄]-coated Ir(CO)₂/MgO). These results show that the iridium complexes remained bonded to the support even after the samples were coated with the ILs and did not dissolve in the IL.

6-4.5. Catalytic Hydrogenation of 1,3-Butadiene

The data presented above show that the electronic environments of the Ir centers are influenced both by the support and the IL. Thus, we tested the influence of each one on the catalytic properties for the hydrogenation of 1,3-butadiene. First, each catalyst was activated by removal of at least one of the CO ligands per Ir atoms by treatment in flowing ethylene at 373 K; this treatment incorporated ethylene ligands in place of CO, which is a strong catalytic reaction inhibitor,³¹ as reported for similar metal carbonyl complexes supported on metal oxides and zeolites. The relative concentrations of species and the IR spectra before and after ethylene exposure are provided in Table A6-5 and Figures A6-56 to A6-78 in Appendix A6. IR spectra recorded before and after ethylene exposure (Figures A6-56 to A6-78 in Appendix A6), indicate changes in the intensities and positions of the $\nu(\text{CO})$ bands as well as the formation of new bands, but none indicating the formation of carbonyls bonded to neighbouring iridium centres, which would have indicated iridium cluster formation.³¹ New bands located between the two carbonyl stretching bands are consistent with the partial replacement of CO

with ethylene.⁵⁷⁻⁵⁸ For example, in the spectrum of the TiO₂-supported iridium complex coated with [BMIM][BF₄], the intensity of the $\nu_{\text{asym}}(\text{CO})$ band at 1988 cm⁻¹ decreased slightly relative to that of the $\nu_{\text{sym}}(\text{CO})$ band, accompanied by the appearance of two new bands, at 2030 and 2048 cm⁻¹, assigned to Ir(CO)(C₂H₄) and Ir(CO)(C₂H₄)₂, respectively.³¹ The areas of the $\nu(\text{CO})$ bands indicate that the supported complexes were converted into mixtures of Ir(CO)₂ (~74%), Ir(CO)(C₂H₄) (~16%), and Ir(CO)(C₂H₄)₂ (~10%) on TiO₂. Data characterizing other samples indicate the presence of mixtures of Ir(CO)₂, Ir(CO)(C₂H₄), and Ir(CO)(C₂H₄)₂ in varying concentrations (Table A5 in Appendix A6). Following the activation of each supported iridium complex by reaction with ethylene, it was cooled to 333 K in flowing helium followed by the start of flow of the reactant stream consisting of H₂ + 1,3-butadiene in a molar ratio of 2:1 at a space velocity chosen to ensure differential conversions of the 1,3-butadiene (<2%). Typical data (Figure A6-79 in Appendix A6) characterizing [BMIM][BF₄]-coated iridium on SiO₂ for 3 h on stream show that the product distribution and 1,3-butadiene conversion of ca. 1.5% were essentially constant.

Table 6-3 is a summary of the TOF and selectivity data characterizing each catalyst, and Figure 6-2 illustrates the changes in total partial hydrogenation selectivity of the catalysts with changes in electron-donor/acceptor properties of the supports and the ILs; the catalyst performance data were measured at differential conversions, <2%. The data representing uncoated SiO₂-supported iridium complexes, for example, indicate a TOF of 9.6×10^{-3} (mol of 1,3-butadiene converted) $\times$ (Ir site $\times$ s)⁻¹ (Table 6-2) with a selectivity for butenes (sum of 1-butene (21%), *trans*-2-butene (11%), and *cis*-2-butene (10%)) of approximately 42% (Figure 6-2). Such a low selectivity for partial hydrogenation is typical of supported iridium complexes on supports such as SiO₂ that are not good electron-donor ligands. In contrast, when the iridium complexes were supported on good electron-donor supports such as La₂O₃,

the selectivity for butenes was approximately twice as high (81%) (Figure 6-2). For comparison,

Table 6-3. Selectivity and TOF values measured at steady-state and differential conversions (<2%) characterizing partial hydrogenation of 1,3-butadiene (BD) at an H₂/BD feed molar ratio of 2:1 at 333 K and 1 atm catalyzed by activated uncoated and IL-coated iridium complexes supported on metal oxides with various electron-donor characteristics.

Supported Ir(CO) ₂ complex	TOF × 10 ³ ((mole of BD converted) × (Ir site × s) ⁻¹)	Selectivity (%)			
		Butane	<i>trans</i> -2-butene	1-butene	<i>cis</i> -2-butene
Ir(CO) ₂ /SiO ₂	9.6	58	11	21	10
Ir(CO) ₂ /TiO ₂	4.8	51	15	25	8
Ir(CO) ₂ /Fe ₂ O ₃	4.7	30	24	30	15
Ir(CO) ₂ /CeO ₂	2.3	36	20	29	16
Ir(CO) ₂ /MgO	2.5	28	24	33	16
Ir(CO) ₂ /La ₂ O ₃	3.3	19	30	40	10
[BMIM][BF ₄]-coated Ir(CO) ₂ /SiO ₂	1.2	27	17	41	13
[BMIM][BF ₄]-coated Ir(CO) ₂ /TiO ₂	0.9	26	23	38	13
[BMIM][BF ₄]-coated Ir(CO) ₂ /Fe ₂ O ₃	1.4	21	26	33	20
[BMIM][BF ₄]-coated Ir(CO) ₂ /CeO ₂	0.8	16	22	47	15
[BMIM][BF ₄]-coated Ir(CO) ₂ /MgO	0.7	20	26	40	14
[BMIM][BF ₄]-coated Ir(CO) ₂ /La ₂ O ₃	1.8	16	24	46	15
[BMIM][Ac]-coated Ir(CO) ₂ /SiO ₂	0.5	7	45	18	31
[BMIM][Ac]-coated Ir(CO) ₂ /TiO ₂	1.8	5	36	38	21
[BMIM][Ac]-coated Ir(CO) ₂ /Fe ₂ O ₃	1.9	15	31	37	17
[BMIM][Ac]-coated Ir(CO) ₂ /CeO ₂	1.2	14	28	38	20
[BMIM][Ac]-coated Ir(CO) ₂ /MgO	0.9	16	27	39	18
[BMIM][Ac]-coated Ir(CO) ₂ /La ₂ O ₃	1.5	15	31	36	18
[CPMIM][DCA]-coated Ir(CO) ₂ /SiO ₂	9.3	78	6	12	4
[CPMIM][DCA]-coated Ir(CO) ₂ /TiO ₂	4.2	57	11	23	9
[CPMIM][DCA]-coated Ir(CO) ₂ /Fe ₂ O ₃	4.6	51	13	27	9
[CPMIM][DCA]-coated Ir(CO) ₂ /CeO ₂	2.2	46	17	26	11
[CPMIM][DCA]-coated Ir(CO) ₂ /MgO	1.6	36	24	31	10
[CPMIM][DCA]-coated Ir(CO) ₂ /La ₂ O ₃	1.2	23	29	36	12

Table 6-3 and Figure 6-2 also include the corresponding performance data characterizing the IL-coated catalysts—showing that the IL layer strongly influences the

catalytic performance. The TOF values characterizing the coated catalysts were lower than those characterizing the respective uncoated catalysts. The partial hydrogenation selectivity, on the other hand, increased when the ILs incorporated [BMIM]⁺-ions and decreased when the IL incorporated [CPMIM]⁺-ions (Figure 6-2). For example, under our conditions, the TOF characterizing the SiO₂-supported iridium complex decreased from 9.6×10^{-3} to 1.2×10^{-3} (mole of 1,3-butadiene converted) $\times$ (Ir site $\times$ s)⁻¹, whereas the partial hydrogenation selectivity increased from 42 to 73% as a result of the deposition of [BMIM][BF₄]. Data presented in Table 6-3 and Figure 6-2 also indicate that the effect of the IL coating on the catalytic performance depends strongly on the type of support.

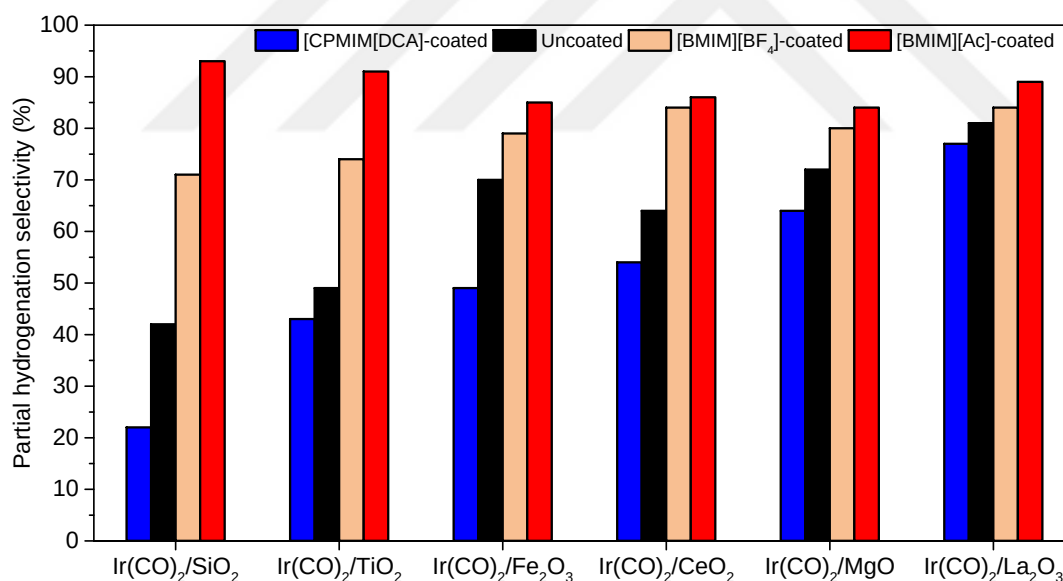


Figure 6-2. Partial hydrogenation selectivity (sum of all butene isomers: *trans*-2-butene, 1-butene and *cis*-2-butene) characterizing each catalyst, measured at steady state and under differential conversion conditions (<2%) at an H₂/BD feed molar ratio of 2:1 at 333 K and 1 atm catalyzed by activated uncoated and IL-coated iridium complexes supported on metal oxides with various electron-donor characteristics.

6-5. Discussion

The essential results are: A) that both the support and the IL act as ligands determining the electronic properties of the metal, which is represented simply by the $\nu_{\text{sym}}(\text{CO})$ band positions, and B) that the electronic properties control the catalytic selectivity and activity (TOF) for partial hydrogenation of 1,3-butadiene. All data are accounted for by the correlations of Figure 6-3. Thus, when the electron density on the iridium is the greatest, the selectivity for partial hydrogenation of 1,3-butadiene is maximized, and vice versa (Figure 6-3A). On the other hand, when the electron density on iridium is the greatest, the TOF is minimized, and vice versa (Figure 6-3B).

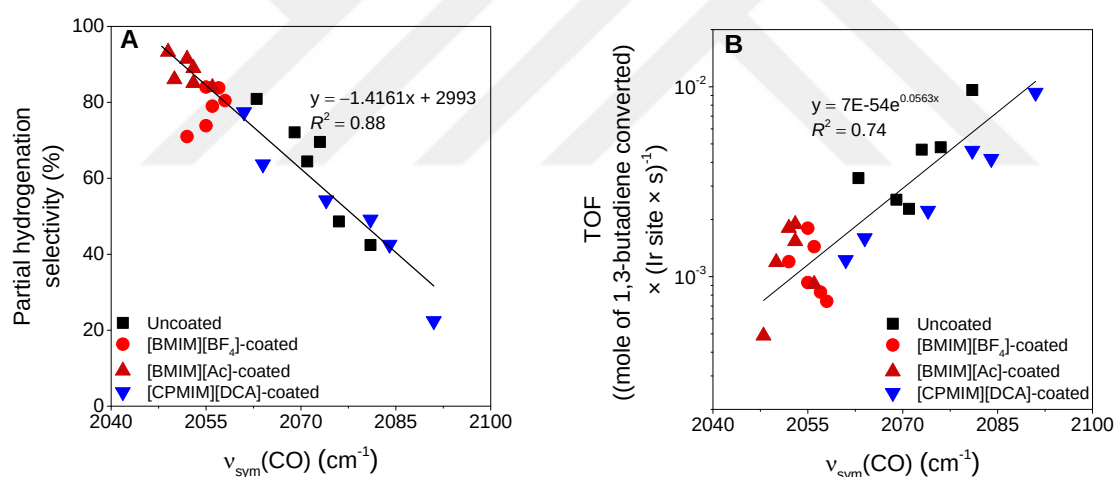


Figure 6-3. Variation of selectivity for partial hydrogenation (sum of all butene isomers) A) and TOF B) of 1,3-butadiene with the $\nu_{\text{sym}}(\text{CO})$ band position of the corresponding coated and uncoated iridium complexes supported on metal oxides, following activation. Black symbols indicate uncoated samples, while red, dark red, and blue symbols represent [BMIM][BF₄]-, [BMIM][Ac]-, and [CPMIM][DCA]-coated supported complexes, respectively.

The deviations from the trend lines in Figure 6-3 might originate from (i) non-uniformity of the active sites associated with the heterogeneity of the support surfaces and/or (ii) undetermined differences in the behavior of the ILs on various supports.

Presence of this second effect was illustrated in a report focusing on the interactions of [BMIM][BF₄] with various metal oxides in the absence of any active metal. These interactions vary considerably with the changes in the electron-donor character of the supports and lead to variations in the thermal stability of [BMIM][BF₄] on these metal oxides.⁵⁴ The interactions can also alter other physical and chemical characteristics of the IL when it is in contact with a metal oxide. Consequently, solubilities of guest molecules in a specific IL—thus, a filter effect²⁶—can vary significantly when an IL is dispersed on various supports. Because the IL filter effect controls the concentrations of the reactants and intermediates interacting with the active sites, it influences the catalytic performance, and this effect explains the deviations from a perfect correlation in Figure 6-3. Thus, we recognize the potential inclusion of an additional structural parameter that could be tuned to improve the catalytic performance.

The electronic effects shown in Figure 6-3 are substantial, but, on some supports the effects of the electron-donor/acceptor properties of the IL are small, whereas on others they are at least twice as large. For example, when the iridium complex is supported on the strongly electron-donating La₂O₃, the effect of the IL is indicated by shifts < 10 cm⁻¹ in the $\nu_{\text{sym}}(\text{CO})$ band position (Figure 6-4A). In contrast, when the support is the weak electron-donor SiO₂, the magnitude of the shift indicating the ligand effect of the IL exceeded 20 cm⁻¹ when the IL sheath contained the [BMIM]⁺ ion (a red shift) and the [CPMIM]⁺ ion (a blue shift). Figure 6-4A illustrates the magnitudes of these shifts, and thus the strength of the ILs' ligand effects compared with those of the supports.

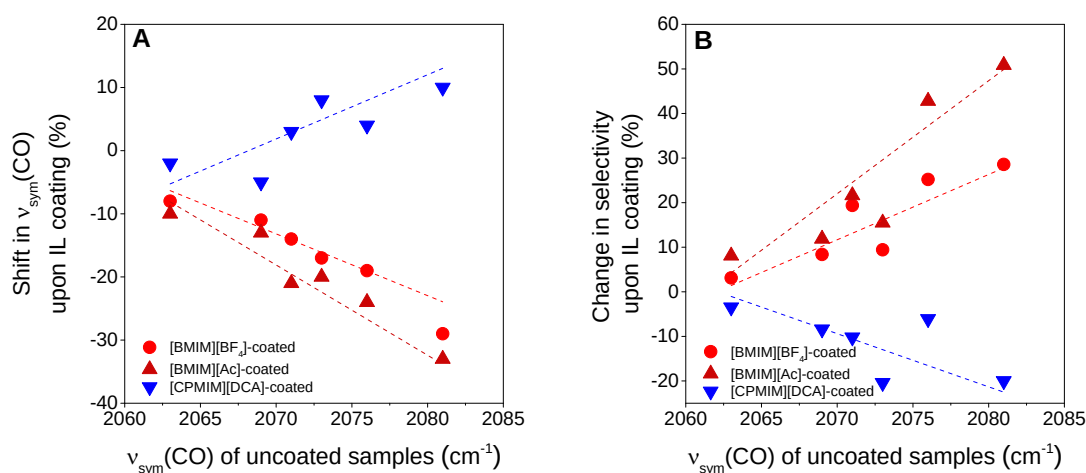


Figure 6-4. A) Variations in the magnitudes of $\nu_{\text{sym}}(\text{CO})$ band shifts observed upon coating the supported metal complexes with different ILs. The x-axis quantifies the electron-donor character of the supports, and the vertical axis represents the magnitude of the ligand effect of the IL; B) variation in the change of partial hydrogenation selectivity upon the deposition of various ILs, [BMIM][BF₄], [BMIM][Ac], and [CPMIM][DCA] with $\nu_{\text{sym}}(\text{CO})$ band positions on the corresponding uncoated supported iridium complexes, quantifying the electron-donor character of the support.

To further investigate the ligand effects on catalysis, we considered the change in catalytic selectivity for butenes as a function of the electron-donor character of the support. Figure 6-4B shows that the increase in partial hydrogenation selectivity upon the deposition of [BMIM]⁺-based IL sheaths becomes dominant when the support is a weak electron-donor, but when the IL incorporates a cyano group, the catalyst becomes less selective for partial hydrogenation, because (as illustrated in Figure 6-4A), this IL withdraws electrons from iridium. As shown in Figure 6-4B, this effect is dominant when the support is a weak electron-donor, as in the case of [BMIM]⁺-containing ILs, but presenting a correlation in the reverse direction.

Although there is more to learn about the interactions between the IL and the catalytic species, the correlations shown here make clear that the IL, like a support, acts as a ligand. Moreover, the data confirm that these ligand effects are additive,

providing a high degree of flexibility for controlling the electronic structures of catalytic sites with an enormous number of possible combinations presenting opportunities for tuning the electronic environments of supported metals over wide ranges. We posit that the opportunities offered by enveloping the catalytically active species with IL sheaths/supports for tuning the catalytic properties extend to many metals, supports, and ILs, and recent results characterizing nickel nanoparticles on supports incorporating ILs⁴² indicate that the opportunities extend beyond atomically dispersed metals to metal nanoparticles.

6-6. Conclusions

Atomically dispersed supported iridium complexes were synthesized on metal oxides having a wide range of surface electron-donor characteristics, SiO₂, TiO₂, Fe₂O₃, CeO₂, MgO, and La₂O₃, and coated with various ILs, [BMIM][BF₄], [BMIM][Ac], and [CPMIM][DCA]. The electron density on the iridium was probed with IR spectroscopy determining the $\nu(\text{CO})$ frequencies and with XANES determining the Ir L_{III} edge energies. The results show that the electron-donor/acceptor character of the support and that of the IL sheath together determine the electronic structure of the iridium complexes and their catalytic properties for hydrogenation of 1,3-butadiene, for which high selectivities for butenes were obtained.

6-7. Supplementary Materials

Plots of residuals and individual shells characterizing EXAFS data and fits, table summarizing goodness of fit parameters, characterization of the uncoated and IL-coated samples by XANES and by IR, SEM image and EDX spectra of IL-coated samples and calculated IL loadings, IR evidence of single-site iridium after IL coating,

characterization of the samples before and after 1,3-butadiene hydrogenation reaction and time on stream data.

6-8. Acknowledgments

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Chapter 7

Elucidating the Relative Strengths of Individual Structural Factors Controlling the Partial Hydrogenation Performance of Supported Iridium Catalysts: A Comparison of the Effects of Metal Nuclearity, and the Electron Donor Character of Supports and Ionic Liquid Coatings

7-1. Abstract

Controlling the catalytic performance of active species can be achieved by regulating the electronic structure by the choice of the metal nuclearity, support and the ligands attached to the active sites. Here, we resolve the individual strengths of these three structural variables. Atomically dispersed iridium species were synthesized on three different high-surface-area metal oxides, SiO₂, γ -Al₂O₃ and MgO, with various electron-donor characteristics. Extended X-ray absorption fine structure (EXAFS) and infrared spectroscopy confirmed that iridium was present as site-isolated complexes anchored on each support. Then these catalysts were treated in H₂ flow at 6733 K to convert the site-isolated complexes into small iridium nanoparticles. EXAFS and high angle angular dark field scanning transmission electron microscopy (HAADF-STEM) demonstrated that the average nanoparticle size was approximately 1.2 nm on each support. Then, each of these catalysts with single-sites and nanoparticles were coated with various 1,3-dialkylimidazolium ILs, having various interionic interaction energies, and thus various electron donating ability.

All of the coated and uncoated catalysts were tested for partial hydrogenation of 1,3-butadiene. Data illustrate that the influence of the electron donating abilities of IL coatings and supports is significantly different when the active sites are atomically dispersed or when they are present on nanoparticles. Accordingly, the effect of IL coatings becomes dominant on iridium nanoparticles, whereas the electron donor character of the support is the major structural parameter controlling the catalytic performance when the active species were site-isolated. The structure-performance relationships presented here offer opportunities for the rational design of highly selective supported metal catalysts by fine tuning of the structures of IL coatings and supports according to the metal nuclearity to optimize their synergistic effects on catalytic performance.

7-2. Introduction

Performance of a supported metal catalyst depends mostly on the electronic environment around the active metal sites. Approaches to tune the electronic environment over active sites in a supported metal catalyst involve i) varying the metal nanoparticle size¹⁻⁵ to control the fraction of active sites residing on terrace, corner or step sites with different bonding environments; ii) changing the support surface characteristics such that electronic interplay between the support and metal nanoparticles adjust the electron density over the active metal sites,⁶⁻⁸ or iii) incorporating promoter atoms,⁹ secondary/tertiary metal atoms or ligands that are directly or indirectly interacting with the metal sites to adjust the electron density.⁹⁻¹¹ As an example to the former of these approaches, Lykhach et al.¹² utilized a set of Pt/CeO₂(111) catalyst with various metal particle sizes to vary the metal/support interactions. Their results demonstrated the transfer of one electron per ten Pt atoms from the metal to the support when the nanoparticle size is set to 50 atoms, leading to a stronger adsorption of CO on the catalyst surface. Moreover, Aitbekova et al.⁵ demonstrated that by restructuring the CeO₂-supported Ru nanoparticles into atomically dispersed RuO_x species via oxidative treatment, the CO₂ reduction performance of the catalyst was switched from methanation to preferential CO formation with an exceptional selectivity.

Other than the effect of metal nuclearity, varying the surface properties of the supports also influences the catalytic performance. Electron-donor properties of supports are determined by their compositions and surface structures and can be tuned by incorporation of promoters⁶⁻⁹ and dopants to adjust the electron density at the surface metal center.⁹⁻¹¹

Molecules coating supported metals may also act as ligands,⁹ strongly influencing the hydrogenation selectivity. However, the structural variety of the coating materials is limited. As we illustrated in Chapter 5 and Chapter 6, ionic liquids (ILs), offer a broad prospect in this

respect, because ILs are available in a wide range of composition and structure—and thus offer tunable physical and chemical properties.¹³⁻¹⁵ ILs provide so called filter and ligand effects that enhance the catalytic performance of the active sites¹⁶⁻¹⁹, however, understanding of how an IL layer influences the active sites with varying nuclearity from one to several along with the various surface characteristics of the supports is largely lacking.

Here we aim at elucidating the individual strengths of the electron donor characters of IL coatings and supports on partial hydrogenation performance, and their dependence on the changes in metal nuclearity from single-sites to nanoparticles. Atomically dispersed iridium species were synthesized on three different metal oxides with varying electron-donor characters, SiO₂, γ -Al₂O₃, and MgO. Then they were converted into small iridium nanoparticles on supports. Each of the catalyst were then coated with seven different 1,3-dialkylimidazolium type ILs. We tested each catalyst for an industrially important, yet still a simple test reaction, 1,3-butadiene hydrogenation.²⁰⁻²¹ The catalyst performance results demonstrate remarkable variations in the selectivity and activity of the iridium catalysts depend strongly on the metal nuclearity, the type of supports and the structure of IL coatings. Accordingly, the effect of IL coatings becomes dominant on iridium nanoparticles, whereas the electron donor character of the support is the major structural parameter controlling the catalytic performance when the active species were site-isolated. Thus, the results presented here provide insights on the structure-performance relationships for the supported metal catalysts with IL coatings offering a broad prospect for rational design.

7-3. Experimental

7-3.1. Materials & Methods

All sample handling and preparations were done with standard air-exclusion techniques. The chemicals were purchased from Sigma-Aldrich with the highest available purities. The metal

oxide supports were calcined as described in Chapter 3, Section 3-3.1. Each IL was dried at 373 K for 6 h and kept under vacuum for 12 h before being transferred into an argon-filled Labconco glove box. The structures and the names of the ILs are provided in the Table A7-1 in Appendix A7. The atomically dispersed catalysts were synthesized as described in Chapter 4, Section 4-3.1. To synthesize supported iridium nanoparticles, the supported complexes were treated with H₂ up to 673 K with a ramp rate of 3 K/min and kept for 1 h. Then samples were cooled down to room temperature in flowing He and passivated in flowing 3 vol.% O₂ in balance He. Coating of all the supported catalysts with ILs was described in Chapter 4, Section 4-3.1. All of the samples were stored in the argon-filled glove box after synthesis.

7-3.2. X-Ray Absorption Spectroscopy

7-3.2.1. Extended X-ray Absorption Fine Structure (EXAFS) Measurements and Data Analysis

X-ray absorption spectroscopy (XAS) measurements were collected at beam line 9-3 at the Stanford Synchrotron Radiation Lightsource (SSRL). EXAFS and X-ray absorption near edge structure (XANES) data were collected and analysed as described in Chapter 6, Section 6-3.3.1.

For supported iridium nanoparticles, the crystal structure of iridium metal was used to calculate the phase shifts and backscattering amplitudes representing the Ir–Ir_{1st}, Ir–O_s, and Ir–Ir_{2nd} shells, as it was foreseen that the structure of the supported iridium species would be similar to that of this precursor.

Iterative fitting was carried out for various structural models until the best agreement was attained between the calculated k^0 -, k^1 -, and k^2 - weighted EXAFS data and the postulated model. Plots were made to show the residuals remaining after the fitting. The fitting ranges in both k and R space, where k is the wave vector and R the distance from the absorbing Ir atom,

in the analysis of the data characterizing the as-prepared sample were determined by the data quality; the range in k was in general between 3.5 ± 0.4 and $13.0 \pm 0.5 \text{ \AA}^{-1}$, and the range in r was 1–5 $\text{\AA}$ for each sample. These values were used with the Nyquist theorem²² to estimate the justified number of fitting parameters. The accuracies of the parameters are estimated to be as follows: coordination number N , $\pm 20\%$; distance R , $\pm 0.02 \text{ \AA}$; disorder term σ^2 , $\pm 20\%$; and inner potential correction E_0 , $\pm 20\%$. All the EXAFS fittings for supported nanoparticles are given in Appendix A7, Section A7-1 (Figures A7-1 to A7-17).

7-3.3. High Angle Angular Dark Field Scanning Transmission Electron Microscopy (HAADF-STEM)

HAADF-STEM images were obtained on a JEOL JEM-2100F electron microscope equipped with a CEOS hexapole probe aberration corrector. The microscope was equipped with a field emission gun and operated at 200 kV. Before each experiment, the microscope was aligned with a standard sample consisting of gold on holey carbon, until the expected lattice spacings for gold were resolved. The sample grids were prepared in an argon glovebox and loaded onto a vacuum transfer holder.

7-3.4. CO Pulse Chemisorption Analysis

CO chemisorption measurements were carried out in on a Micromeritics Auto-Chem II 2920 automated catalyst characterization system. A representative sample, $\gamma\text{-Al}_2\text{O}_3$ -supported iridium nanoparticles which was passivated before at room temperature in flowing 3 vol.% O_2 in balance He, was first heated to 373 K in H_2 -He flow for 1 h to reactivate. Then the sample was decreased to 303 K in He flow, followed by 30 injections of CO pulses. The outlet was monitored by TCD detector. CO chemisorption data is provided in Appendix A7, Figure A7-18.

7-3.5. Brunauer–Emmett–Teller (BET) Pore Volume and Surface Area Analysis

BET analysis were performed for uncoated SiO_2 , $\gamma\text{-Al}_2\text{O}_3$ and MgO-supported supported iridium nanoparticles and their [BMIM][BF₄]-coated counterparts. The analyses were performed as described in Chapter 4, Section 4-3.3.

7-3.6. Point of Zero Charge (PZC) Measurements

PZC of metal oxides were determined as described in Chapter 3, Section 3-3.2.

7-3.7. Scanning Electron Microscopy coupled with Energy-Dispersive X-Ray Spectroscopy (SEM/EDX)

SEM/EDX imaging of the samples were performed as described in Chapter 6, Section 6-3.5.

7-3.8. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for IL loading calculations

An Agilent 7700x ICP-MS (Agilent Technologies Inc., Tokyo, Japan) was used for the quantification of boron in each [BMIM][BF₄]-coated iridium nanoparticles supported on $\gamma\text{-Al}_2\text{O}_3$ and MgO. Samples for each measurement were prepared by dissolving 50 mg of IL-coated catalysts (including 20 mg of supported iridium nanoparticles, 10 mg of [BMIM][BF₄] and 20 mg of additional support) in 30 ml and 25 ml of 65 wt% HNO₃ for $\gamma\text{-Al}_2\text{O}_3$ and MgO-supported samples, respectively. The ICP-MS was operated with a PFA concentric nebulizer, an inert sample introduction kit with a sapphire injector (inner diameter 2.5 mm, for Agilent 7700 series, Agilent Technologies, Germany), and Ni sampler/skimmer cones. Spex Certiprep Multielement calibration standards were followed for the preparation of external calibration solutions. An amount of 1 $\mu\text{g/L}$ of tuning solution was used for instrumental optimizations. Calculations of the analytical results were performed by MassHunter software.

7-3.9. Catalyst Performance Measurements

To evaluate the performance of each catalyst, uncoated and IL-coated supported iridium nanoparticles (each including 300-350 mg of the supported iridium nanoparticle, independent of whether an IL coating was present) were each placed in a ¼-in. stainless-steel once-through tubular flow reactor. A Thermcraft three-zone resistively heated furnace (Model number XST-3-0-18-3V) equipped with PC-operated temperature controllers was used for temperature control of the reactor. Electronic mass flow controllers (Aalborg, Model GFC17) were used to control the flow rates of feed gases. The catalysts were activated before each performance measurements as follows: uncoated and IL-coated supported atomically dispersed Ir(CO)₂ catalysts were exposed to flowing ethylene at 373 K to be converted to catalytically active Ir(CO)(C₂H₄) and Ir(CO)(C₂H₄)₂ species. The IR data obtained before and after ethylene flow indicate that the supported iridium species are still in atomically dispersed form.²³ The activation of these samples are as reported for the isostructural HY-zeolite-supported iridium complexes.²⁴ For the supported iridium nanoparticles, which were previously passivated at 298 K with 3 vol% O₂ in balance with He, the activation was completed by treating the catalysts at 373 K with flowing H₂. After activation of the each catalyst, the flow of the reaction mixture with a molar ratio of H₂ (Linde, 99.99 vol%) to 1,3-butadiene (Linde, 99.6 vol%) of 2:1 was started through the catalyst bed, operated at atmospheric pressure and 333 K. Products were analyzed with an online gas chromatograph (Agilent 7890A) equipped with a GS-alumina column (50 m × 530 µm) and a flame-ionization detector. Conversions of 1,3-butadiene were in the differential range, <2%. Reaction rates are reported per Ir atom (i.e., as turnover frequencies, TOF), assuming that all the Ir atoms were accessible to the reactants in the atomically dispersed catalysts and estimating the accessible Ir atoms via dispersion of the atoms from average particle size analysis of the HAADF-STEM images in the iridium nanoparticles.

7-4. Results

7-4.1. Characterization of Atomically Dispersed Supported Iridium Species

Atomically dispersed supported iridium species were synthesized as before²⁵ by the reaction of Ir(CO)₂(acac) (acac is acetylacetonato) with freshly calcined SiO₂, γ -Al₂O₃, and MgO. The precursor and metal oxide amounts were adjusted to reach a metal loading of 1 wt%. Extended X-ray absorption fine structure (EXAFS) spectra of the samples characterized in our previous work²³ and given in Table 7-1 indicate no Ir–Ir contributions, consistent with the presence of site-isolated iridium species in each catalyst. High angle angular dark field scanning transmission electron microscopy (HAADF-STEM) images²⁶ also confirm that the iridium species are distributed atomically on the surfaces of the metal oxides, in an analogous sample prepared using the same procedure using Ir(C₂H₄)₂(acac) as precursor.

Table 7-1. Summary of EXAFS fit parameters characterizing the atomically dispersed iridium species and iridium nanoparticles supported on SiO₂, γ -Al₂O₃, and MgO. Supported iridium nanoparticles were prepared by treating the corresponding atomically dispersed supported iridium species in flowing H₂ at 673 K with a ramp rate of 3 K/min for 1h. Metal oxides are chosen to represent various electron-donor characteristics ranging from a PZC value of pH = 1.7 (SiO₂) to 9.8 (MgO).

Sample	Shell ^a	N	R (Å)	$\Delta\sigma^2 \times 10^3$ (Å ²)	ΔE_0 (eV)	k range (Å ⁻¹)	R range (Å)
Atomically dispersed iridium on SiO ₂	Ir–O _s	2.25	2.07	3.46	-3.42	3.82 – 12.43	0.5 – 3.50
	Ir–C _{CO}	2.25	2.00	3.87	-1.61		
	Ir–O _{CO}	2.00	3.28	7.78	-5.12		
	Ir–Si	2.50	3.42	5.94	5.01		
Atomically dispersed iridium on γ -Al ₂ O ₃	Ir–O _s	2.40	2.03	0.10	4.21	3.17 – 12.10	0– 3.00
	Ir–C _{CO}	2.20	1.92	1.55	-0.64		
	Ir–O _{CO}	2.10	2.95	5.00	5.66		
	Ir–Al	1.40	2.65	6.21	-8.00		
Atomically dispersed iridium on MgO	Ir–O _s	2.40	2.06	0.10	-6.98	4.02 – 11.30	0.5 – 3.40
	Ir–C _{CO}	2.20	2.02	0.62	0.29		
	Ir–O _{CO}	2.20	2.95	5.91	-8.00		
	Ir–Mg	1.45	2.76	0.10	7.36		
Ir nanoparticles on SiO ₂	Ir–Ir _{1st}	7.04	2.59	15.0	1.89	3.05 – 11.05	1.0 – 5.0
	Ir–O _s	0.75	2.02	7.98	-8.0		
	Ir–Ir _{2nd}	0.49	3.69	2.74	8.0		
Ir nanoparticles on γ -Al ₂ O ₃	Ir–Ir _{1st}	6.19	2.63	9.32	-4.74	3.05 – 13.8	1.0 – 5.0
	Ir–O _s	0.70	2.00	5.79	-1.40		
	Ir–Ir _{2nd}	2.52	3.81	15.0	-3.88		
Ir nanoparticles	Ir–Ir _{1st}	6.90	2.68	10.76	-8.00		

on MgO	Ir–O _s	0.96	1.99	8.43	-6.34	3.05 – 14.5	1.0 – 5.0
	Ir–Ir _{2nd}	4.06	3.78	15.0	-3.87		

Notation: N , coordination number; R , distance between the absorber and the backscatterer atoms; $\Delta\sigma^2$, mean square relative displacement; ΔE_0 , inner potential correction. Error bounds are estimated as follows: N , $\pm 20\%$; R , ± 0.02 Å; $\Delta\sigma^2$, $\pm 20\%$; ΔE_0 , 20%. ^aO_s denotes surface oxygen atoms of supports; Ir_{1st} and Ir_{2nd} denote first shell- and second shell iridium atoms, respectively.

IR spectra of supported iridium nanoparticles provided in Chapter 6 and Appendix A6, Figure A6-37A confirm the presence of iridium *gem*-dicarbonyls. The $\nu(\text{CO})$ band positions and Ir L_{III} edge energy values of each supported sample given in Chapter 6, Section 6-4.2 are different from each other. Details are provided in Chapter 6.

7-4.2. Characterization of Supported Iridium Nanoparticles

Treatment of the atomically dispersed supported iridium complexes in flowing H₂ at 673 K for 1 h leads to the formation of supported iridium nanoparticles. EXAFS data characterizing the treated samples, given in Table 7-1, demonstrate the average Ir–Ir coordination number is 6.5 ± 0.5 at a bonding distance of 2.63 ± 0.05 Å on each support. The best-fit EXAFS models also indicate the presence of a second Ir–Ir contribution shell with a coordination number of 0.5, 2.5 and 4.0 for SiO₂-, γ -Al₂O₃-, and MgO-supported nanoparticles and a distance ranging from 3.69 to 3.81 Å. Data further show that Ir–O_s contribution is at a coordination of 0.83 ± 0.15 at a distance of 2.01 ± 0.01 Å. The synthesized supported iridium nanoparticles were also characterized by HAADF-STEM images. The images in Figure 7-1 clearly indicate the predominance of small iridium nanoparticles. The size distribution diagrams presented in Figure 7-1 indicate that the supported iridium nanoparticles on each support are nearly uniform with an average diameter of 1.47 ± 0.39 nm, 1.17 ± 0.32 nm, and 1.10 ± 0.41 nm on SiO₂, γ -Al₂O₃, and MgO, respectively. Based on the experimental calculations that assumes

cubic structure of the nanoparticles,²⁷ we estimate that each nanoparticle consists of approximately 63 iridium atoms, consistent with EXAFS data.

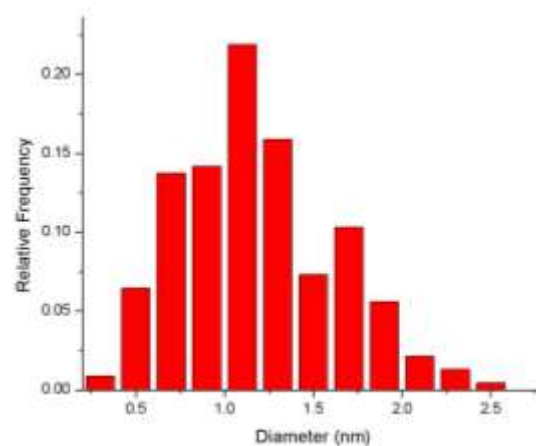
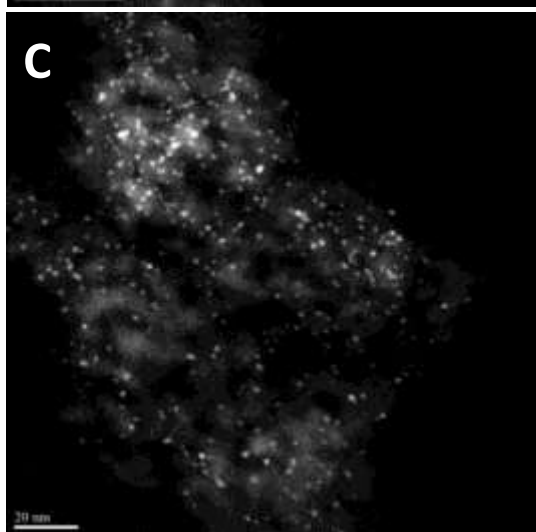
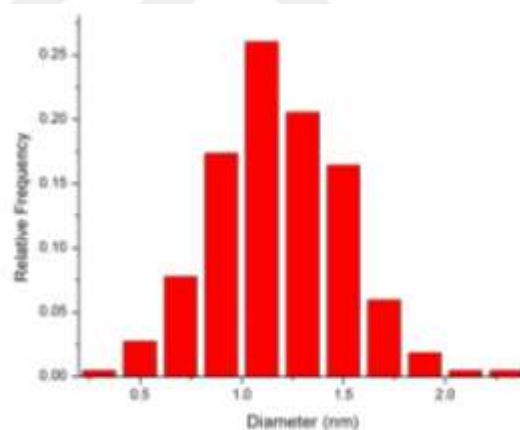
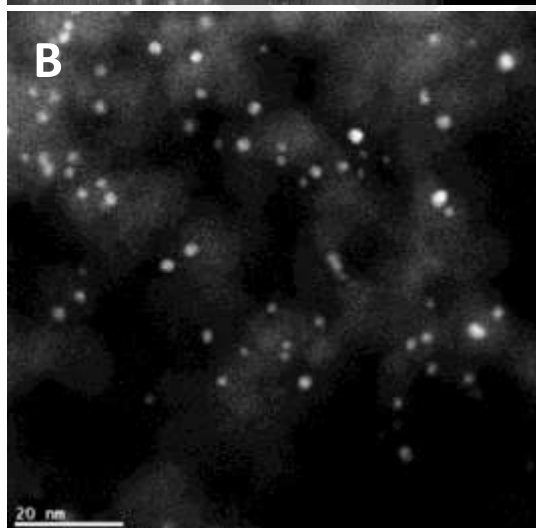
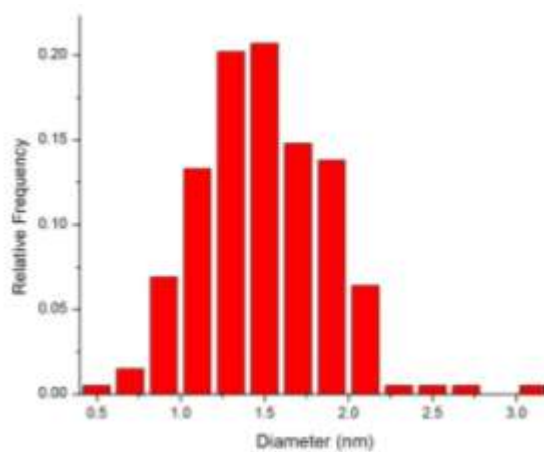
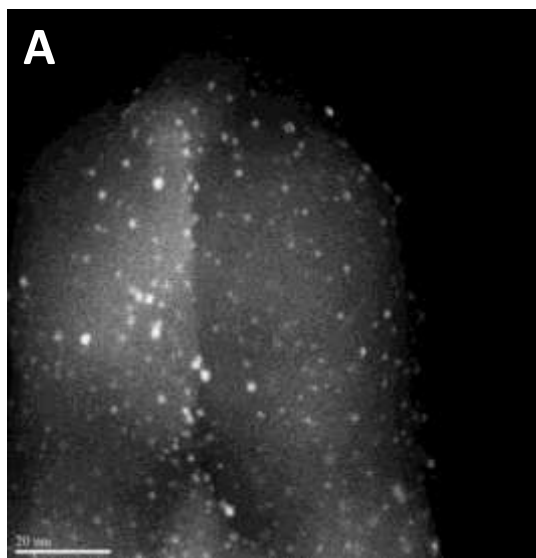


Figure 7-1. HAADF-STEM images and average particle size distributions characterizing the Ir nanoparticles supported on A) SiO₂, B) γ -Al₂O₃, and C) MgO.

Results of CO chemisorption (given in Appendix A7, Section A7-2) performed on γ -Al₂O₃-supported iridium nanoparticles indicate a metal dispersion of $76 \pm 4\%$, corresponding to nanoparticle size of approximately 1.20 nm on each support, consistent with the EXAFS and HAADF-STEM results. Powder X-ray Diffraction (XRD) spectra of the iridium nanoparticles supported on SiO₂, γ -Al₂O₃, and MgO given in Appendix A7, Figure A7-19 also confirm that the size of the iridium nanocrystallites are extremely small (less than 2 nm) that they are not in the detectable range of our XRD measurements.²⁸

The change in the electronic environment of the iridium sites upon supporting the nanoparticles on metal oxides with different electron-donor properties were probed by Ir L_{III} absorption edge energies of the supported iridium nanoparticles, characterized by (XANES) (given in Figure A7-20 in Appendix A7). The data demonstrate that Ir L_{III} edge energies of nanoparticles supported on SiO₂, γ -Al₂O₃, and MgO are 11216.3, 11216.0, and 11215.6 eV, respectively. The data further show that the white line intensities of the supported nanoparticles given in Figure A7-20A are different from that of bulk iridium, indicating that the electronic properties of the nanoparticles are not close to the bulk iridium.²⁵

7-4.3. Characterization of IL-Coated Atomically Dispersed Supported Iridium Species and Supported Iridium Nanoparticles

After confirming the proper preparation of atomically dispersed iridium species and nanoparticles on the supports, we coated each catalyst with 1,3-dialkylimidazolium ILs. The IL distribution on the atomically dispersed supported iridium species was shown previously²³ and on the supported iridium nanoparticles is shown by SEM/EDX images given in the Figure

A7-21 and 22 in Appendix A7. The images provide information on the presence of the fluorine atom of the representative IL, [BMIM][BF₄]. The IL loading of each sample was set to be 20 wt%. Inductively coupled plasma mass spectrometry (ICP-MS) measurements and the Brunauer–Emmett–Teller (BET) surface area analysis before and after IL-coating of the nanoparticles given in Appendix A7, Section A7-8 confirm that the IL loading is approximately 20 ± 1 wt%. IL loading calculations indicate that 45 ± 3 molecules of the IL is present per iridium site. Results demonstrate that IL coating layer does not limit the access of the reactants to be involved in the reaction. Moreover, pore size distributions of the samples given in the Figure A7-23 in Appendix A7 confirm that the ILs penetrate even into small pores of the supported nanoparticles.

7-4.4. Catalytic Performance Data of Uncoated and IL-Coated Supported Single-Site Iridium and Supported Ir Nanoparticles

The uncoated and IL-coated SiO₂-, γ -Al₂O₃-, and MgO-supported atomically dispersed iridium species and iridium nanoparticles were tested as catalysts for the hydrogenation of 1,3-butadiene .

Each catalyst was activated before catalytic performance measurements as described in the experimental section. Then each activated catalyst was cooled to 333 K in flowing helium. Partial hydrogenation of 1,3-butadiene was conducted by flowing of the reactant stream consisting of H₂ + 1,3-butadiene in a molar ratio of 2:1 at a space velocity chosen to ensure differential conversions (<2%). The catalyst performance data are summarized in Table 7-2, including the selectivity values (sum of butene isomers (1-butene, *trans*-2-butene, *cis*-2-butene) and activity (i.e., as turnover frequencies, TOF) values of the catalysts. Individual selectivity values for products on all catalysts are provided in Table A7-3 in Appendix A7. The IR spectra of the IL-coated supported nanoparticles before and after

activation indicate that during the activation, IL maintained its structure without any decomposition in the structure, given in Figure A7-24 in Appendix A7.

Table 7-2. Selectivity and TOF values measured at steady-state and differential conversions (below 2%) characterizing partial hydrogenation of 1,3-butadiene (BD) at an H₂/BD feed molar ratio of 2:1 at 373 K and 1 atm catalyzed by uncoated and IL-coated Ir nanoparticles supported on metal oxides with various electron-donor characteristics.

Catalysts	TOF × 10 ³ (mole of 1,3- butadiene converted) × (Ir site × s) ⁻¹			Selectivity for partial hydrogenation of 1,3-butadiene at 333 K (%)		
	Supported on			Supported on		
	SiO ₂	γ-Al ₂ O ₃	MgO	SiO ₂	γ-Al ₂ O ₃	MgO
Uncoated supported single-site iridium	9.6	8.4	2.5	42	51	72
[BMIM][NTf ₂]-coated supported single-site iridium	1.6	4.4	1.2	57	61	75
[BMIM][BF ₄]-coated supported single-site iridium	1.2	1.3	0.7	71	62	80
[DMIM][MSO ₄]-coated supported single-site iridium	1.1	1.3	1.1	65	65	77
[BMIM][TFA]-coated supported single-site iridium	1.1	0.9	1.0	75	64	79
[EMIM][DEP]-coated supported single-site iridium	0.6	1.5	0.9	80	66	84
[DMIM][DMP]-coated supported single-site iridium	0.5	2.1	1.0	82	73	85
[BMIM][Ac]-coated supported single-site iridium	0.5	1.2	0.9	93	78	84
Uncoated supported Ir nanoparticles	53.0	34.2	9.7	24	32	39
[BMIM][NTf ₂]-coated supported Ir nanoparticles	22.8	7.9	4.8	26	36	53
[BMIM][BF ₄]-coated supported Ir nanoparticles	23.6	9.6	2.9	26	39	54
[DMIM][MSO ₄]-coated supported Ir nanoparticles	20.9	9.0	2.6	32	47	61
[BMIM][TFA]-coated supported Ir nanoparticles	12.9	4.6	1.9	48	53	73
[EMIM][DEP]-coated supported Ir nanoparticles	8.4	4.0	1.7	57	66	82
[DMIM][DMP]-coated supported Ir nanoparticles	6.6	2.4	0.8	59	67	80
[BMIM][Ac]-coated supported Ir nanoparticles	5.1	0.8	0.2	65	77	90

The performance results of the catalysts provided in Table 7-2 demonstrate that the catalysts have varying TOFs when the active sites change from atomically dispersed species to nanoparticles. The results indicate that iridium nanoparticles on each support are more active than the atomically dispersed iridium complexes. The TOF of uncoated atomically dispersed iridium on SiO₂, γ-Al₂O₃, and MgO were 9.6×10^{-3} , 8.4×10^{-3} and 2.5×10^{-3} (mole of 1,3-butadiene converted) × (Ir site × s)⁻¹, respectively, while that of the iridium nanoparticles were 53.0×10^{-3} , 34.2×10^{-3} , and 9.7×10^{-3} (mole of 1,3-butadiene converted)

$\times (\text{Ir site} \times \text{s})^{-1}$), respectively. These results also indicate that both type of catalysts with atomically dispersed metal complexes and nanoparticles have a decreasing activity when the support changes in the following order: $\text{SiO}_2 > \gamma\text{-Al}_2\text{O}_3 > \text{MgO}$. Moreover, TOFs of the catalysts always decrease upon IL coating. For instance, the TOF of uncoated single-site $\gamma\text{-Al}_2\text{O}_3$ -supported iridium decrease by almost 6-fold upon [EMIM][DEP]-coating. The decreasing activity was also apparent for its nanoparticle counterpart with a TOF of uncoated and IL-coated samples of 34.2×10^{-3} and 4.0×10^{-3} (mole of 1,3-butadiene converted) $\times (\text{Ir site} \times \text{s})^{-1}$), respectively.

Catalyst performance measurements also show that the selectivity markedly depends on the changes in the nuclearity of the iridium species, the type of the support and the presence of ILs as ligands. The data led to the following comparison of the samples in terms of their hydrogenation selectivity: the iridium nanoparticles on each support were the less selective catalysts as compared to the atomically dispersed iridium complexes on each support. For instance, the selectivity of uncoated SiO_2 -supported single-site iridium catalysts was 42%, while that of its iridium nanoparticle counterpart was 24% selective for partial hydrogenation. The same trend was observed on $\gamma\text{-Al}_2\text{O}_3$ - and MgO -supported catalysts with 51 and 72% selectivity, respectively on single-site iridium and 32 and 39% selectivity, respectively on iridium nanoparticles. Data also indicate that catalysts have different selectivity performance when they are supported on metal oxides having different electron-donor characters. Accordingly, both of MgO -supported single-site and nanoparticles catalysts had more than 1.5-times higher selectivity than their SiO_2 -supported counterparts, while $\gamma\text{-Al}_2\text{O}_3$ -supported ones always had selectivity in the mid-range. Table 7-2 further shows the influence of IL-coating on selectivity performance of the catalysts. IL coating on all supported catalysts—irrespective of single-site or nanoparticles form—increases the selectivity values. For instance, the selectivity for n-butenes over SiO_2 -supported uncoated atomically dispersed

iridium was 42%, while its [EMIM][DEP]-coated counterpart provided an approximately 80% selectivity for *n*-butenes. Similarly, the selectivity of uncoated iridium nanoparticles on SiO₂ (24%) increased to 65% upon coating with [BMIM][Ac].

In addition, individual butene isomers data given in Table A7-3 in Appendix A7 demonstrate that each supported catalyst, independent of the metal nuclearity and the support, have high selectivity for 1-butene formation rather than *trans*-2-butene or *cis*-2-butene formation. We predict that the terminal alkene is isomerized to form nonterminal alkene on our supported catalysts at a lower rate than that of the rate for desorption of the alkene from the catalyst.

7-5. Discussion

Our results given in Table 7-2 indicate that one can change three major design variables in the catalyst structure to alter the catalytic properties: A) the metal nuclearity; B) the electron-donor properties of the support; and C) IL ligands on the iridium species. Thus, we investigated the relative strengths of each of these structural factors in controlling the catalytic performance.

7-5.1. Effect of the Metal Nuclearity and the Support Characteristics on the Performance of Uncoated Supported Catalysts

Our catalytic performance results unravel the metal nuclearity and support effect on the activity of the each supported catalyst in 1,3-butadiene hydrogenation. The results indicate that to maximize the catalytic activity for hydrogenation, iridium is better stabilized in the form of nanoparticles, without the presence of CO/C₂H₄ ligands that inhibit the catalytic activity. In Table 7-2, the conversion of the atomically dispersed iridium species to particles was observed to lead to approximately 5-fold increase in the catalytic activity for 1,3-

butadiene hydrogenation on the supported catalysts. Here we suggest that the dissociation of H_2 on particles is faster on the multiple neighboring unsaturated metal centers in iridium nanoparticles than their atomically dispersed analogous²⁹ because of stronger binding and the interactions between iridium atoms in nanoparticles.²⁻⁴

Since supports act as ligands bound to the metal species,^{8,30} the metal–support interactions play an important role to control the performance and stability of oxide-supported metal catalysts. Our data demonstrate that activity is strongly influenced by the surface electron donor properties of the supports, probed by PZC, as described in Chapter 6. The PZC of metal oxides were measured as pH of 1.7 for SiO_2 , 7.6 for $\gamma-Al_2O_3$ and 9.8 for MgO , consistent with the literature,^{13,31} demonstrating that the electron-donating capabilities of the metal oxides decrease as follows: $MgO > \gamma-Al_2O_3 > SiO_2$. The support oxygen atoms on the metal oxide act as electron–donors and apparently these oxygen atoms have different electron sharing with the iridium species bound to them. Moreover, XANES data of the atomically dispersed supported iridium characterized before in Chapter 6, Section 6-4.2 and of the supported nanoparticles given in Figure A7-20 in Appendix A7 demonstrate that the Ir L_{III} absorption edge energy of each catalyst decreases as PZC of metal oxides increases. These findings lead to the following comparison of the electron densities of the iridium atoms in the complexes and in the nanoparticles: $Ir/MgO > Ir/\gamma-Al_2O_3 \gg Ir/SiO_2$. Consistent with these findings, our activity data indicate that uncoated SiO_2 -supported samples activate H_2 faster than the $\gamma-Al_2O_3$ - and MgO -supported counterparts. We anticipate the support effect such that the electron transfer between support and the active sites leads to the differences in electron occupancies in the valence orbitals of iridium which in turn changes metal’s ability to activate the reactant molecules in catalysis.²⁴ Thus, we conclude that as the iridium species become less electron-rich, the H_2 dissociation rate becomes higher on iridium sites, leading to a higher activity of each catalyst.

The selectivity performance of the supported iridium nanoparticles are in agreement with the general observation that iridium catalysts give yields mostly to butane in hydrogenation of 1,3-butadiene. The highest selectivity for *n*-butene isomers was obtained on MgO-supported uncoated nanoparticles with 39%, which is considered to be less than optimal selectivity. We claim that on supported nanoparticles the interactions between 1,3-butadiene and iridium sites lead to the hydrogenation of two diene bonds, C=C, simultaneously before the release of products, which results in the formation of butane instead of butene isomers. However, when the catalysts are in the form of essentially molecular species, the absence of the neighboring iridium sites and the presence of other ligands such as CO and/or C₂H₄/C₂H₅ ligands in the species change the adsorption properties of the diene molecule and the formation of butane decreases, leading to higher selectivities.³² These results point out that the selectivity depends on the iridium nuclearity.

Data further demonstrate a striking support effect on the catalytic selectivity upon varying metal nuclearity such that as the electron-donating strength of the metal oxide increases with an increase in the PZC and decrease in the Ir L_{III} edge energy, atomically dispersed supported iridium and supported iridium nanoparticles become more selective for partial hydrogenation. The support effect is more pronounced when the metal species are smaller.

7-5.2. Effect of IL Coating Layer on the Performance of Supported Catalysts

Our outcomes for this study demonstrate that catalytic performance of iridium for partial hydrogenation of 1,3-butadiene can be tuned when there is a control over the nuclearity/size of the catalytic species and the surface electron-donating character of the supports bound to them. We aimed to boost the modification of the active sites for fine-tuning of the electronic environment as well as catalytic performance by coating them with ILs with their ligand

effect. Early communicated results show that 1,3-dialkylimidazolium-type IL coatings significantly influenced the electronic structure of iridium carbonyl complexes supported on alumina, $\text{Ir}(\text{CO})_2/\gamma\text{-Al}_2\text{O}_3$, thereby the catalyst performance of related iridium complexes for partial hydrogenation of 1,3-butadiene.²³ Thus, we envision that the ILs offer broad and intriguing prospects for tuning supported catalysts,¹³⁻¹⁵ and our goal in the work reported here was to follow a strategy to unravel the synergistic effects of metal nuclearity and supports with those of ILs.

Our catalytic performance measurements with IL-coated supported catalysts indicate that IL coating decreases the activity. Similar to what a carbonyl ligand does on an electron-donating support,^{10,33} ILs also hinders the activation of other species, such as alkenes and H_2 . We also observed a decrease in the TOF of the IL-coated catalysts as a function of increasing PZC of the metal oxide of the supported catalysts, similar to the trend that was obtained on the uncoated analogous.

The results further demonstrate that upon being coated with seven different 1,3-dialkylimidazolium type ILs the iridium sites led become more selective for partial hydrogenation on each catalyst. Aiming at understanding the influence of the IL structure, we probed the stretching vibrations of the most acidic proton in the imidazolium ring,³⁴ $\nu(\text{C2H})$ which may represent the electron-donating tendency of the ILs, described in Chapter 5 and 6. Figure 7-2 demonstrates the variation in the partial hydrogenation selectivity of the catalysts upon coating with different ILs, as a function of $\nu(\text{C2H})$ of individual ILs. When the interionic interaction energy increases, the influence of the IL on electron density over iridium is more pronounced, thereby the effect of ILs on the selectivity performance increases with a very strong correlation.

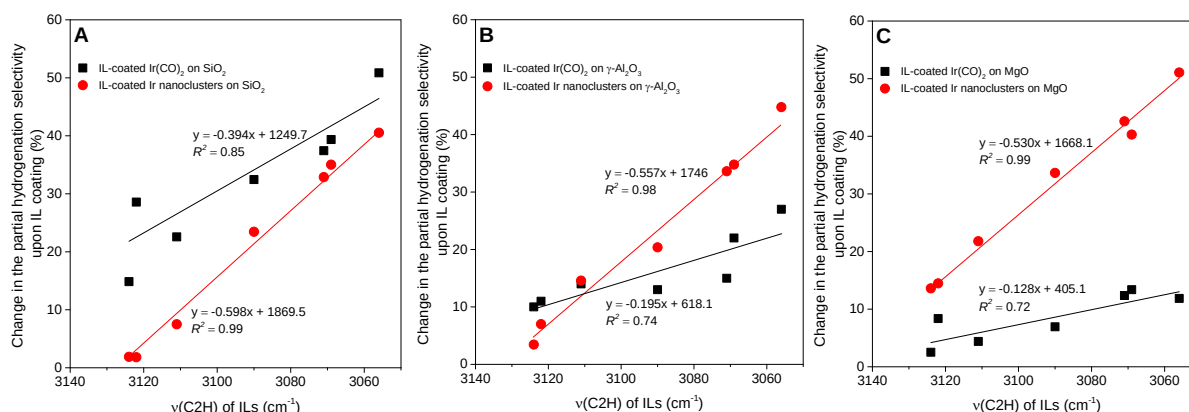


Figure 7-2. Change in partial hydrogenation selectivity in each catalyst upon coating with ILs as a function of interionic interactions in corresponding IL probed by $\nu(\text{C2H})$: black solid symbols represent atomically dispersed iridium complexes and red solid symbols represent iridium nanoparticles supported on A) SiO_2 ; B) $\gamma\text{-Al}_2\text{O}_3$; and C) MgO .

Figure 7-2 further illustrates that the trend of the $\nu(\text{C2H})$ –selectivity difference is independent of the metal nuclearity and the type of the support. However, the change in the selectivity that each IL provides to the active sites depends on the metal nuclearity of the supported catalysts, leading to have different slopes in plots of $\nu(\text{C2H})$ vs difference in partial hydrogenation upon coating the catalysts with ILs. For instance, in Figure 7-2A, the slope of the curve for IL-coated SiO_2 -supported atomically dispersed iridium species was -0.394, while that of its nanoparticle counterpart was -0.598. We aim at understanding the influence of the metal nuclearity and the type of support on the electron donation and selectivity improvement performance of the IL coatings on supported catalysts. Therefore we plot the slope of the each correlation presented in Figure 7-2A, 2B, and 2C as a function of the PZC of the metal oxide, given in Figure 7-3A. Accordingly, the influence of the ILs on supported metal nanoparticles on the selectivity performance of the catalyst is always higher than that of atomically dispersed supported iridium complexes. We suppose that the ILs affect the ability of the metal to coordinate multiple ligands, resulting in a higher selectivity for partial

hydrogenation for the nanoparticles upon coating them with ILs in comparison with that observed on the atomically dispersed iridium species.

Results show a decline in the slopes of the $\nu(\text{C2H})$ –selectivity difference curves as the PZC of the metal oxide increases, leading to the inference that the influence of the ILs becomes less significant when the iridium sites are already electron-rich by the electron transfer from the support, such as for MgO-supported catalysts, and vice versa. We further investigate the highest amount of the change in the selectivity of the supported catalysts upon IL coating as a function of the PZC of each metal oxide, given in Figure 7-3B. Data demonstrate that SiO_2 -supported single-site iridium has the highest change upon IL coating, whereas its nanoparticle form has the highest change on MgO-supported catalyst. Consistent with other findings, the influence of the IL on nanoparticles is more significant in comparison with the support (probed by PZC), because each iridium atom is in contact with another iridium atom rather than the support.

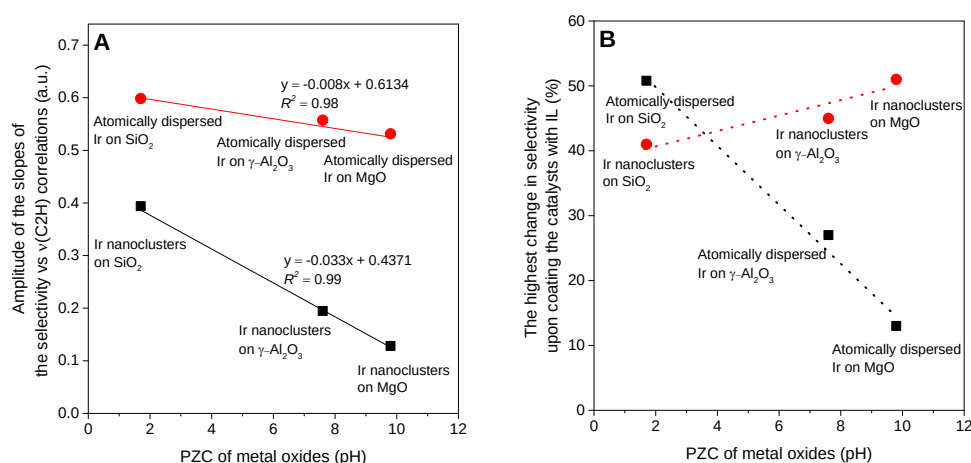


Figure 7-3. A) Variations of the slopes (given in amplitude) values of selectivity lines of IL-coated atomically dispersed supported iridium complexes (black ■) and supported iridium nanoparticles (red ●), given in Figure 7-2A, 2B, and 2C, as a function of PZC of metal oxides. B) The amount of the highest change in selectivity upon coating the atomically dispersed supported iridium species (black ■) and supported iridium nanoparticles (red ●) with ILs, as a function of PZC of metal oxides.

Our results even illustrate exceptional selectivity when we set the design variables to optimum. Accordingly, when the iridium species are in the form of nanoparticles and supported on electron-donating MgO and when the catalyst is coated with [BMIM][Ac], the selectivity for *n*-butenes increases up to 90% with a decrease in the TOF by 10-fold.

Our outcomes in this work let us comment on unraveling the influence of the metal nuclearity and the ligand modification by support type and ILs on the performance of catalyst. We have shown that the ligand effects of supports and ILs are strongly dependent on the size of the active species, where the support effect is more dominant on single-site species and the IL layer strongly controls the performance when the active species are in the form of nanoparticles. The combined effect of the size of the active species, the electron-donating character of the oxide supports and the presence of ILs as ligands with various interionic interaction energies allow us fine-tune the catalytic performance for hydrogenation of dienes in terms of selectivity and activity.

7-6. Conclusions

The size and the structure of the metal species and the ligands bond to them are the key variables influencing the electron density on the metal, and its consecutive performance. We varied the size of the metals by first synthesizing atomically dispersed supported iridium complexes and then converting them into supported iridium nanoparticles with average nanoparticle size of approximately 1.2 nm on each support, confirmed by EXAFS spectroscopy and HAADF-STEM imaging. Each supported catalyst was coated with imidazolium ILs. The performance of uncoated and IL-coated catalysts were tested for partial hydrogenation of 1,3-butadiene. We have shown that both supports and ILs work as electron-donating ligands, however, their influence on the performance changes when the size of the active sites changes from single-site to nanoparticles. The influence of the support's electron-

donor ability is more pronounced when the active sites are site-isolated, and the IL's ligand effect is more significant on small nanoparticles. The routes provided in this study to synthesize custom-made IL-coated supported catalysts with the effects of metal nuclearity, support and IL coatings can be utilized to have the maximum control over the selectivity and activity performance of the catalysts.

7-7. Acknowledgment

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7-8. Supplementary Materials

Plots of residuals and individual shells characterizing EXAFS data and fits for the supported iridium nanoparticles, table summarizing goodness of fit parameters, characterization of the nanoparticles by XRD, XANES and by IR, BET/BJH surface area and pore volume results of the uncoated and IL-coated supported nanoparticles, SEM/EDX spectra of IL-coated samples

and calculated IL loadings with ICP-MS, representative IR spectra of IL-coated supported nanoparticles before and after activation, IR spectra of the samples before and after ethylene exposure.

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Chapter 8

Tailoring the Performance of Supported Small Metal Nanoparticles by Ligand Modification



8-1. Abstract

We synthesized iridium nanoparticles on high surface area SiO_2 , $\gamma\text{-Al}_2\text{O}_3$, and MgO , and coated them with 23 different imidazolium-type ionic liquids (ILs). Scanning transmission electron microscopy (STEM) images and extended X-ray absorption fine structure (EXAFS) data indicate that the iridium nanoparticles are nearly uniform and ± 1.2 nm in size on each support. Catalytic performance of each uncoated and IL-coated sample was measured for 1,3-butadiene hydrogenation at 333 K and atmospheric pressure and at differential conversions to elucidate the structure-performance relationships. Results indicate that the selectivity towards butenes increases with an increase in electron-donor character of the metal-oxide, as a consequence of increased electron density on iridium sites characterized by a linear decrease in Ir L_{III} edge energy of X-ray absorption near edge structure (XANES). Moreover, the structures of the IL coatings were systematically changed and the resulting partial hydrogenation performance was evaluated as a function of IL structure. The structural factors on ILs investigated were change in the size of anion/cation, the methylation on C2 site of the imidazolium ring, and the substitution of alkyl groups on the imidazolium ring with various functional groups. Data showed that the selectivity and activity of IL-coated supported nanoparticles change as electron donating/withdrawing properties of the ILs change. Moreover, there is a strong correlation between butenes selectivity and interionic interaction strength (inversely correlated with $\nu(\text{C2H})$ of the corresponding IL). Accordingly, stronger interionic interaction of the ILs leads to a higher selectivity towards partial hydrogenation and lower activity, as a result of a higher electron density on iridium sites. Based on these findings, we have also developed a model for predicting the butenes selectivity on IL-coated supported iridium particles, based on the IL and support type. Results of this study present the structure-performance relationships in supported metal catalysts coated with imidazolium type ILs and offer a guideline for rational design of IL-coated supported metals.

8-2. Introduction

Ionic liquids (ILs) have attracted attention because of their exceptional physicochemical properties¹ and their wide application areas including catalysis.¹⁻³ When the supported catalysts are coated with ILs, the IL coating layer offers two different functions: filter and ligand effects where the former one stands for controlling the active concentrations of reactive species over the active sites and the latter one is controlling the electronic structure.⁴⁻⁹ Therefore, IL coating on the active sites enhances the performance of the catalysts. For instance, Jess et al.¹⁰⁻¹¹ investigated the effect of ILs on the selective hydrogenation of cyclooctadiene on IL-coated commercial Ni/SiO₂ catalyst. Their results indicate that the maximum yield for the cyclooctene almost doubles upon IL coating. Barrault et al.¹² investigated that Prins cyclization of α -methylstyrene in aqueous solution of formaldehyde proceeded selectively on SiO₂-SO₃H coated with IL with 94% yield, whereas only a 24% of yield was obtained on uncoated catalyst due to lack of selectivity. Jalal et al.¹³ reported that coating a commercial supported nickel catalysts with [BMIM][BF₄] improved the selectivity towards butenes for 1,3-butadiene hydrogenation to over 95% throughout whole conversion range.¹³ Characterization of the IL-coated catalyst provided direct evidence on the electron donation from IL layer to the metal sites. Density functional theory (DFT) calculations confirmed these results and showed that electron donation weakens the adsorption behavior on nickel. Moreover, the filter effect confirmed by Conductor-Like Screening Model For Realistic Solvents (COSMO-RS) calculations, on the other hand, helps to maintain this exceptional selectivity at all conversion levels by controlling active concentrations of 1,3-butadiene/butenes on nickel sites.¹³ In another study of Jalal et al.¹⁴ upon coating the nickel/silica-alumina catalyst with tributyl(methyl) phosphonium methyl sulfate IL, the selectivity for butenes in partial hydrogenation of 1,3-butadiene becomes record high for that catalyst with $99.5 \pm 0.2\%$.

Catalysis studies on IL-coated supported metal nanoparticles indicate the importance of IL coating in enhancing the catalytic performance, especially the selectivity, of the catalysts. In fact, for a rational design of IL-coated catalysts, the understanding of the interactions between IL and the active sites should be well-understood, since that information is valuable for understanding the structural factors of ILs and consequent influence on the active sites.^{5-6,15-20} Sobota, Libuda and Wasserscheid investigated the interaction of [BMIM][NTf₂] with Pd and Pt nanoparticles supported on thin and ordered Al₂O₃/NiAl(110) films under UHV conditions.¹⁸ Time-resolved infrared reflection absorption spectroscopy (TR-IRAS) to compare IL-coated and uncoated supported metal catalysts and investigated that only [NTf₂]⁻ anion interact with Pd sites *via* the (SO₂) groups. Strongly chemisorbed adsorbates, like carbon monoxide can be easily replaced because of strong interactions between IL and the nanoparticles. Ionic liquid showed a ligand-type effect that is specific for the applied ionic liquid–metal combination and selective to particular sites. In the study of Steinrück et al.¹⁷ the interactions between IL and Pd was further investigated. X-ray photoelectron spectroscopy (XPS) measurements revealed chemical state of surface palladium is modified when IL is deposited on Pd/SiO₂. The anion of the IL acts as ligand to the metal and Pd is partially transformed to Pd²⁺ and undergoes complexation with the [N(CN)₂]⁻. Lercher's group also investigated the interactions between IL, silica support and Pt nanoparticles.⁷ They revealed that support-IL interactions are via hydrogen bonds. Electron density on the IL is influenced by the Pt particles and IL prevents platinum particle from oxidation. The ethane hydrogenation reaction results indicate that the interaction of IL-Pt surface is weaker than that of ethane-Pt.

Although there are many studies demonstrating the performance enhancement of the catalysts upon IL-coating, there is a lack of understanding on the structural factors controlling the catalytic performance of IL-coated catalysts in the light of understanding the interactions

between ILs and the active sites. Elucidation of the structure-performance relationship in IL-coated supported catalyst require catalysts with almost uniformly distributed active sites, since conventional catalysts have complex structures and it's difficult to eliminate the influence of the IL. To address this problem, we first synthesized well-defined $\gamma\text{-Al}_2\text{O}_3$ -supported $\text{Ir}(\text{CO})_2$ complexes coated with various ILs to elucidate the ligand effect of ILs.¹⁹ Results illustrated that IL layer strongly controls the electron density of metal sites by donating/accepting electrons to/from iridium site; and there is a strong correlation between the interionic interactions in ILs and the degree of electron donation to the metal. Moreover, when these IL-coated samples were tested as catalysts for partial hydrogenation of 1,3-butadiene, the increased electron density on iridium leads to increase in selectivity for butene isomers, which is tunable as the structure of the IL is tunable. On the other hand, the influence of the IL changes when the metal nuclearity changes from one to several. As discussed in Chapter 7, the effect of the IL on the electron density as well as the performance partial hydrogenation of 1,3-butadiene on the supported iridium nanoparticles (with an average nanoparticle size of 1.2 nm) is more dominant than that on atomically dispersed supported iridium complexes. Therefore, to elucidate the influence of the IL structure on the performance of the catalysts, we worked on IL-coated supported nanoparticles.

Now we extend this study on very small supported metal nanoparticles to understand the direct influence of the IL ligands. We synthesized nearly uniform iridium nanoparticles on SiO_2 , $\gamma\text{-Al}_2\text{O}_3$, and MgO with varying surface properties and coated them with 23 imidazolium-type ILs with different structures. The catalysts have similar sizes to rule out the differences in performance which might be originated from the variations in the sizes of nanoparticles. The ligand effect of the ILs upon coating on iridium nanoparticles supported on metal oxides with varying electron-donor characteristics were investigated based on the differences in electron density of the active sites. To assess the consequences of these ligand

effects on the catalytic performance, the coated and uncoated catalysts were tested for 1,3-butadiene hydrogenation. The reason for focusing on this test reaction is as follows: i) it is a simple reaction requiring relatively mild conditions, ii) it has an importance for petrochemicals and crude oil refining industries, where a high selectivity for partial hydrogenation is desired for increasing the product quality while reducing the hydrogen consumption in treating the unwanted 1,3-butadiene in C_{3-4} feeds.²¹ We, then, elucidated the influence of the changes in IL structure on the performance of the catalysts in terms of selectivity and activity. A simple mathematical model was developed to predict the hydrogenation selectivity of 1,3-butadiene based on the support's and IL's properties. The results illustrate reveal the structure-performance relationships in this relatively new class of heterogeneous catalysts and offer a detailed guideline for the rational design.

8-3. Experimental

8-3.1. Materials & Methods

All sample handling and preparations were done with standard air-exclusion techniques. Uncoated and IL-coated supported iridium nanoparticles were synthesized as described in Chapter 7, Section 7-3.1. All of the samples were stored in the argon-filled glove box after synthesis.

8-3.2. X-Ray Absorption Spectroscopy

8-3.2.1. Extended X-ray Absorption Fine Structure (EXAFS) Measurements and Data Analysis

EXAFS and X-ray absorption near edge structure (XANES) data were collected, analyzed as described in Chapter 7, Section 7-3.2.

8-3.3. High Angle Angular Dark Field Scanning Transmission Electron Microscopy (HAADF-STEM)

HAADF-STEM images were obtained as described in Chapter 7, Section 7-3.3.

8-3.4. CO Pulse Chemisorption Analysis

CO chemisorption analysis was performed as described in Chapter 7, Section 7-3.4.

8-3.5. Brunauer–Emmett–Teller (BET) Pore Volume and Surface Area Analysis

BET analysis of representative uncoated and IL-coated supported nanoparticles was performed as described in Chapter 7, Section 7-3.5.

8-3.6. Point of Zero Charge (PZC) Measurements

PZC of metal oxides were determined as described in Chapter 3, Section 3-3.2.

8-3.7. Scanning Electron Microscopy coupled with Energy-Dispersive X-Ray Spectroscopy (SEM/EDX)

SEM/EDX imaging of the samples were performed as described in Chapter 6, Section 6-3.5.

8-3.8. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for IL loading calculations

ICP-MS measurements were performed as described in Chapter 7, Section 7-3.8.

8-3.9. Catalyst Performance Measurements

Each uncoated and IL-coated supported catalyst was tested for partial hydrogenation of 1,3-butadiene. Catalyst performance measurements were described in Chapter 7, Section 7-3.9.

8-4. Results

8-4.1. Preparation and Characterization of Supported Iridium Nanoparticles

Atomically dispersed iridium complexes supported on SiO_2 , $\gamma\text{-Al}_2\text{O}_3$, and MgO were synthesized as before²² with 1 wt% metal loading. Treatment of the samples in flowing H_2 at 673 K for 1 h leads to the removal of CO ligands and the formation of supported iridium nanoparticles.²² EXAFS data characterizing the supported nanoparticles provided in Table 7-1 in Chapter 7 indicate that the average Ir–Ir coordination number was 6.5 at a bonding distance of 2.63 ± 0.05 Å. Details of the EXAFS data are provided in Chapter 7, Section 7-4.2.

HAADF-STEM images presented in Figure 8-1 and particle size distribution analysis (given in Chapter 7, Figure 7-1) indicate that the supported iridium nanoparticles on SiO_2 have an average diameter of 1.47 ± 0.39 nm. The corresponding average particle diameters are 1.17 ± 0.32 nm and 1.10 ± 0.41 nm on $\gamma\text{-Al}_2\text{O}_3$ and of MgO , respectively. CO pulse chemisorption analysis performed on a representative sample, $\gamma\text{-Al}_2\text{O}_3$ -supported iridium nanoparticles are in agreement with the particle size calculated in EXAFS data with a metal dispersion of 76% (nanoparticle size of approximately 1.2 nm).

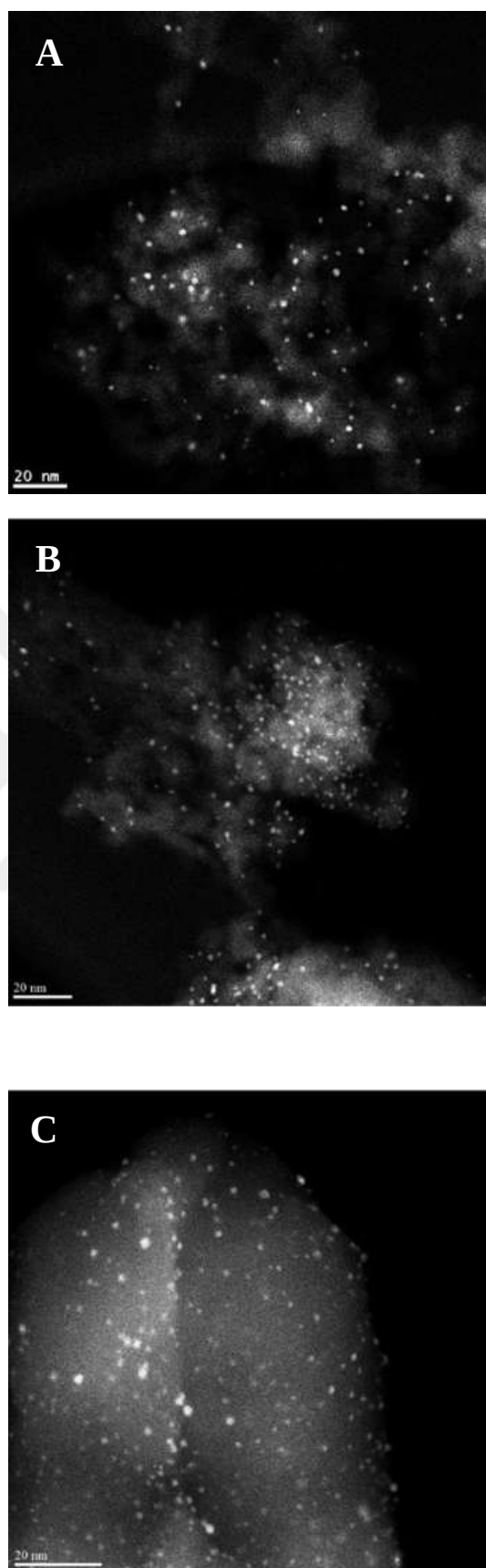


Figure 8-1. STEM images characterizing the Ir nanoparticles supported on A) SiO₂, B) γ-Al₂O₃, and C) MgO.

8-4.2. Electronic Structure of Iridium Nanoparticles Supported on Different Metal Oxides

The XANES data measured at the Ir L_{III} edge indicate that the edge energies were 11216.3, 11216.0, and 11215.6 eV, for iridium nanoparticles supported on SiO₂, γ -Al₂O₃, and MgO respectively. This order is consistent with the PZC values characterizing the electron-donor character of the metal oxides (Figure 8-2).²³⁻²⁴ PZC is based on simple acid-base titration and is a good measure to investigate the electronegativity, valence metal, and surface acidity of the oxide surfaces (described in Chapter 7, Section 7-5.1). Our measurements indicate that the PZC of metal oxides were 1.7 for SiO₂, 7.6 for γ -Al₂O₃, and 9.8 for MgO. Figure 8-2 presents correlation between the Ir L_{III} edge energy of corresponding metal oxide supported iridium nanoparticles with an increase in the PZC of the metal oxide support. The data further show that the white line intensities of the supported nanoparticles given in Figure A7-20 in Appendix A7 are different from that of bulk iridium, indicating that the electronic properties of the nanoparticles are different from those of the bulk iridium.²²

Table 8-1. Edge energy values and selectivity, TOF, and activation energy values measured at steady-state and differential conversions (below 2%) characterizing partial hydrogenation of 1,3-butadiene at an H₂:1,3-butadiene feed molar ratio of 2:1 at 333 K and 1 atm catalyzed by Ir nanoparticles supported on metal oxides with various electron-donor characteristics.

Catalysts	PZC of the support (pH)	Ir L _{III} edge energy (eV)	TOF $\times 10^3$ (mole of 1,3-butadiene converted) $\times$ (Ir site $\times$ s) ⁻¹	Selectivity for partial hydrogenation of 1,3-butadiene at 333 K (%)	Activation energy for partial hydrogenation of 1,3-butadiene E_a (kJ/mol)*
Ir nanoparticles on SiO ₂	1.7	11216.3	53.0	24	46.5
Ir nanoparticles on γ -Al ₂ O ₃	7.6	11216.0	34.2	32	55.3
Ir nanoparticles on MgO	9.8	11215.6	9.7	39	60.1

*Activation energy values were measured at temperatures varying from 40 to 333 K.

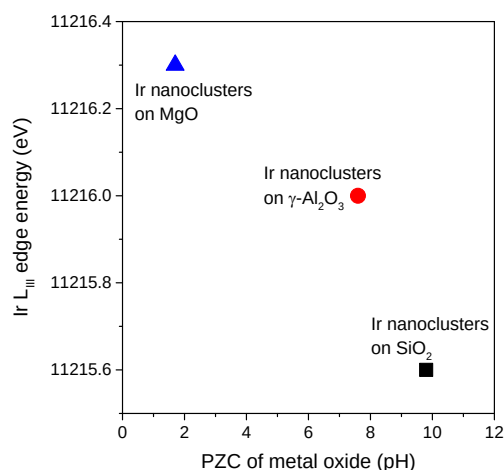


Figure 8-2. The correlation between PZC of metal oxides and Ir L_{III} edge energy of corresponding supported Ir nanoparticles.

8-4.3. Catalytic Performance of Uncoated Supported Ir Nanoparticles

The data indicate differences in the electronic environment of the iridium nanoparticles upon supporting them on metal oxides with varying surface electronic properties. We tested these uncoated catalysts for the partial hydrogenation of 1,3-butadiene to elucidate the impact of these changes in electronic structure of the iridium sites on the catalytic performance. Each uncoated supported nanoparticle catalyst, which was previously passivated at 303 K in flowing 3 vol% O₂ in balance with He, were re-activated before the catalytic performance testing at 373 K in flowing H₂ for 1 h. Such re-activation of the previously passivated catalysts ensures that the physically adsorbed oxygen species were removed from the nanoparticle surface.¹³ Then each catalyst was cooled down to 333 K in flowing helium. And then the flow of reactant stream consisting of H₂:1,3-butadiene in a molar ratio of 2:1 was started. Partial hydrogenation of 1,3-butadiene was conducted for each catalyst at differential conversion conditions (<2%) at 313 to 333 K to determine the activation energy values as well.

Table 8-1 summarizes the TOF, selectivity, and activation energy data characterizing each catalyst and Figure 8-3A shows the changes in TOF and total partial hydrogenation selectivity of the catalysts with changes in electron density on supported iridium, probed by the Ir L_{III} edge energy. The catalytic performance data of the uncoated SiO₂-supported iridium nanoparticles indicate a TOF of 53.0×10^{-3} (mol of 1,3-butadiene converted) $\times$ (Ir site $\times$ s)⁻¹ (Table 8-1) with a selectivity for butenes (sum of 1-butene (15%), *trans*-2-butene (4%), and *cis*-2-butene (5%)) of approximately 24% (Figure 8-3A). On the other hand, the selectivity for butenes increases to 39% with a decrease in TOF to 9.7×10^{-3} (mol of 1,3-butadiene converted) $\times$ (Ir site $\times$ s)⁻¹ when nanoparticles were supported on a good electron-donor support, MgO (Table 8-1, Figure 8-3A). Moreover, the activation energy for hydrogenation of 1,3-butadiene was higher when the iridium nanoparticles were supported on weak electron-donor support, SiO₂, (62 kJ/mol) as compared to strong electron-donor MgO, as expected, given in Figure 8-3B. The difference in catalytic performance was expected as the dissociation of H₂ on SiO₂-supported iridium is easier than the case on MgO, as the active iridium sites have a lower electron density.²⁵

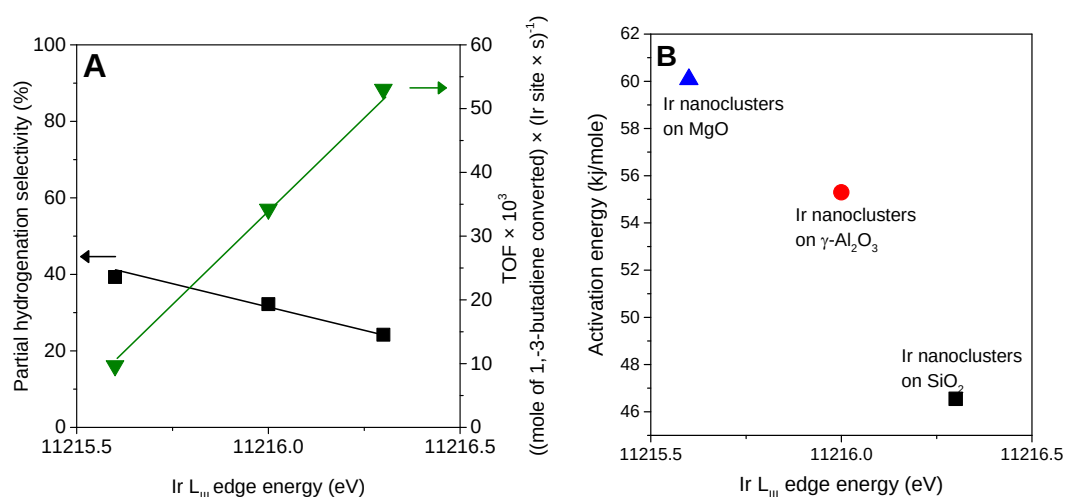


Figure 8-3. A) Changes in TOF and partial hydrogenation selectivity total (*sum* of 1-butene, *cis*-2-butene and *trans*-2-butene) and B) activation energy for partial hydrogenation reaction with respect to Ir L_{III} edge energy values of uncoated supported Ir nanoparticles.

8-4.4. IL coating of the Supported Nanoparticles

Supported iridium nanoparticles were coated with 23 different ILs of imidazolium family. The names and the corresponding abbreviations, and structures of these ILs are given in Table A8-1 in the Appendix A8. The IL loadings in each sample were determined by ICP-MS (Table A7-8 in Appendix A7) as 18.5 and 20.6 wt% for γ -Al₂O₃- and MgO-supported nanoparticles in agreement with the stoichiometric IL loading which was set to 20 wt%. The corresponding IL thicknesses were calculated by dividing the pore volume differences of the uncoated and IL coated samples by the surface area of the uncoated samples (BET/BJH results are given in Section A7-7 in Appendix A7). The data indicate that the thickness of IL layer was 4.9, 0.9, and 2.7 nm in SiO₂-, γ -Al₂O₃-, and MgO-supported nanoparticles, corresponding to an average of only a few layers of IL. The proper dispersion of the IL on the nanoparticles is shown by SEM images and EDX spectra (Figures A7-21 and 22 in Appendix A7).

8-4.5. Catalytic Performance of IL-coated Supported Ir Nanoparticles

Each uncoated and IL-coated supported nanoparticles was tested for catalyst for hydrogenation of 1,3-butadiene. The passivation and re-activation of the catalysts before each performance measurement is described in Chapter 7, Section 7-3.9. Catalytic performance measurements were performed at 333 K with 2:1 molar ratio of H₂:1,3-butadiene flow and collected at differential conversion conditions (<2%). The TOF and selectivity for partial hydrogenation of 1,3-butadiene over IL-coated supported iridium nanoparticles are provided in Table 8-2.

Table 8-2. Selectivity and TOF values measured at steady-state and differential conversions (below 2%) characterizing partial hydrogenation of 1,3-butadiene at an H₂:BD feed molar ratio of 2:1 at 333 K and 1 atm catalyzed by uncoated and IL-coated Ir nanoparticles supported on metal oxides with various electron-donor characteristics. TOF was calculated by using the average nanoparticles sizes estimated from HAADF-STEM.

Catalysts	TOF × 10 ³ (mole of 1,3-butadiene converted) × (Ir site × s) ⁻¹ at 333 K			Selectivity for partial hydrogenation of 1,3-butadiene (%) at 333 K		
	Ir on SiO ₂	Ir on γ-Al ₂ O ₃	Ir on MgO	Ir on SiO ₂	Ir on γ-Al ₂ O ₃	Ir on MgO
Uncoated	53.0	34.2	9.7	24	32	39
[EMIM][BF ₄]-coated	22.3	9.1	4.3	28	36	51
[EMIM][EtSO ₄]-coated	17.3	4.5	2.5	36	55	69
[EMIM][TfO]-coated	24.4	4.8	1.4	30	42	59
[EMIM][MSO ₄]-coated	17.9	8.7	0.6	41	42	66
[EMIM][DEP]-coated	8.4	4.0	1.7	57	66	82
[BMIM][NTf ₂]-coated	22.8	7.9	4.8	26	36	53
[BMIM][BF ₄]-coated	23.6	9.6	2.9	26	39	54
[BMIM][OS]-coated	16.0	6.9	3.7	31	40	60
[BMIM][TOS]-coated	16.0	3.8	1.9	36	55	71
[BMIM][TFA]-coated	12.8	4.6	1.9	48	53	73
[BMIM][HSO ₄]-coated	14.6	4.9	1.6	39	45	77
[BMIM][Ac]-coated	5.1	0.8	0.2	65	77	90
[BDMIM][BF ₄]-coated	21.9	6.8	4.0	29	40	58
[C ₁₀ MIM][BF ₄]-coated	19.5	6.3	2.2	32	43	59
[DMIM][DMP]-coated	6.6	2.4	0.8	59	67	80
[DMIM][MSO ₄]-coated	20.9	9.0	2.6	32	47	61
[HMIM][BF ₄]-coated	21.4	7.3	3.2	30	39	53
[BMIM][DCA]-coated	9.4	0.2	2.8	24	27	35
[CPMIM][NTf ₂]-coated	8.5	2.0	2.4	23	18	34
[DHIM][NTf ₂]-coated	18.0	8.9	4.7	24	27	33
[DMOIM][NTf ₂]-coated	18.0	8.8	4.8	22	29	32
[DEOIM][NTf ₂]-coated	35.6	10.7	2.2	23	29	38
[SUMIM][NTf ₂]-coated	35.9	16.5	14.6	12	15	28

The data indicate that the corresponding TOF of the IL-coated supported iridium nanoparticles were always less than their uncoated counterparts. Moreover, most of the IL-coated catalysts indicate an enhancement in the selectivity. Table 8-2 demonstrates the dependency of the performance of the IL-coated catalysts on the IL's structure. The influence of the IL on the catalyst performance also depends on the support type (Table 8-2).

8-5. Discussion

8-5.1. Uncoated Supported Iridium Nanoparticles

The characteristics of the active sites dispersed on the metal oxide surfaces can be influenced by the size and shape of the particles and their dispersion on the supports as supports act as ligands.²⁶⁻²⁷ Thus, we worked on nanoparticles of more or less the same size to be able to minimize the possibility of having an influence of particle size on the catalytic performance on nanoparticles prepared on different metal oxides. Our STEM images complemented by EXAFS and CO pulse chemisorption findings indicate that the size of the nanoparticles was almost the same on each support with a slight variation of less than 5%. Moreover, having an almost uniformly distribution of the metal nanoparticles on each of the supports offers a proper comparison of the data.

Elucidation of the metal–support interactions is crucial to ultimately control the performance and stability of oxide-supported metal catalysts. Our results indicate that when the support becomes more electron donor with an increase in PZC ($\text{SiO}_2 < \gamma\text{-Al}_2\text{O}_3 < \text{MgO}$), the supported iridium nanoparticles become more electron rich as shown by a decrease in Ir L_{III} edge energy with an increase in the PZC of metal oxide (Figure 8-2). The increasing electron density on iridium sites leads to a higher partial hydrogenation selectivity and a lower activity (TOF) as a result of the change in hydrogen dissociation rate on active sites. A lower electron density on SiO_2 -supported iridium along with the neighboring iridium sites enables the activation of hydrogen and 1,3-butadiene and facilitates the catalysis in a better way than its MgO-supported counterparts.

8-5.2. Dependency of the Catalyst Performance of IL-coated Supported Nanoparticles on IL Structure

Another essential result of the study presented here is that performance of the IL-coated supported iridium catalysts is significantly influenced by the structure of the ILs (Table 8-2). Some IL structures enhance the selective hydrogenation of 1,3-butadiene probably as IL serves as a competing adsorbent and inhibits the readsorption of intermediates on the catalyst. However, some of the ILs causes a lower selectivity towards partial hydrogenation. ILs utilized on supported nanoparticles here have a wide range of structural variations. Thus, analysis of the effects of variations in IL structure taking account of the ligand effect of the support itself on the performance of supported iridium nanoparticles (of similar size on each support) is crucial to elucidate the structure-performance relationship in these IL-coated catalysts. Here, the structural variations on the IL coatings include changes in anion type and anion size, anion functionalization, variations in alkyl chain size and methylation in the cation and functionalization of the cation.

8-5.2.1. Effect of Anion Type on the Catalytic Performance

One of the most important changes in the structure of the imidazolium ILs is the changes in the anion structure. The changes in this ion play a major role in determining the interionic interactions in ILs, and the consequent physical and chemical properties, including the thermal stability limits.²⁸ Here, to investigate the effect of anion structure on the catalytic properties, we first focused on the ILs from the family of [BMIM]⁺ cation. Figure 8-4A demonstrates the changes in the hydrogenation selectivity of iridium nanoparticles supported on SiO₂, γ -Al₂O₃, and MgO coated with eight different ILs having [BMIM]⁺ cation and different anions. Accordingly, the selectivity for butenes over the IL-coated SiO₂-supported nanoparticles increase in the following order of anions: [DCA]⁻ < [NTf₂]⁻ < [BF₄]⁻ < [OS]⁻ <

$[\text{TOS}]^- < [\text{HSO}_4]^- < [\text{TFA}]^- < [\text{Ac}]^-$. Improvement in butenes selectivity upon changes in IL's anion is attributed to site-specific interactions, and solubility differences, as well as possible surface diffusion effects.⁹ Also, the trend in the anion type can be originated from van der Waals interactions and hydrogen bonding in ILs for which the polarity and bond length difference of cation-anion pairs are inversely proportional that may influence the solubilities of the reactants and intermediates in ILs.²⁹⁻³⁰ Lei et al. investigated the H_2 solubilities in $[\text{BMIM}]^+$ type ILs with different anions. They revealed that H_2 solubility increases as the anion of the IL changes as follows: $[\text{NTf}_2]^- < [\text{BF}_4]^- < [\text{MeSO}_4]^-$, indicating that due to hydrogen can be involved in hydrogenation reactions easily in $[\text{BMIM}][\text{BF}_4]$ than $[\text{BMIM}][\text{NTf}_2]$ does. Anthony et al.³¹ also demonstrated that alkenes have lower solubilities in $[\text{NTf}_2]^-$ anion-based ILs than their $[\text{BMIM}]^-$ -type analogous. Therefore, we expected to obtain selectivity in this order because of the influence of the ILs structural interactions which is directly related with the anion type.³²⁻³³ The trend is the same for $\gamma\text{-Al}_2\text{O}_3$ -supported iridium nanoparticles coated with the same set of ILs. The partial hydrogenation selectivity on MgO -supported nanoparticles increase in a similar order with only difference in the order of anions was $[\text{TFA}]^- < [\text{HSO}_4]^-$. Such a trend in the partial hydrogenation selectivity as a function of anion structure is expected because for metal(I) complexes, bulkiness, and acidity of the anion creates a significant effect on the charge symmetry,³⁴ distracting the electron density over the IL. Moreover, when compared the uncoated counterpart of each catalyst, almost all of the IL-coated counterparts have a higher partial hydrogenation selectivity because of the electron donation from ILs to the iridium active sites.³⁵ However, coating the supported nanoparticles with $[\text{BMIM}][\text{DCA}]$ gives an opposite trend. This different behavior might be originated from the presence of a highly electron-withdrawing nitrile group in the anion.³⁶

On the other hand, Table 8-2 demonstrates that the TOF for partial hydrogenation of 1,3-butadiene over IL-coated iridium nanoparticles on all supports increases in the following

order: $[\text{DCA}]^- > [\text{NTf}_2]^- \sim [\text{BF}_4]^- > [\text{OS}]^- > [\text{TOS}]^- > [\text{HSO}_4]^- > [\text{TFA}]^- > [\text{Ac}]^-$. This trend is exactly opposite of the trend in the selectivity, as expected. The only two ILs that are not following this trend on $\gamma\text{-Al}_2\text{O}_3$ - and MgO-supported nanoparticles are $[\text{BMIM}][\text{OS}]$ and $[\text{BMIM}][\text{HSO}_4]$. This different behavior should be related with the exceptionally large size of the anion of these ILs. Based on this observation, we infer that when the ILs have a very large ion, it³⁷ they may sterically hinder the interaction of substrate with the catalyst surface, leading to a decrease in the catalytic activity.

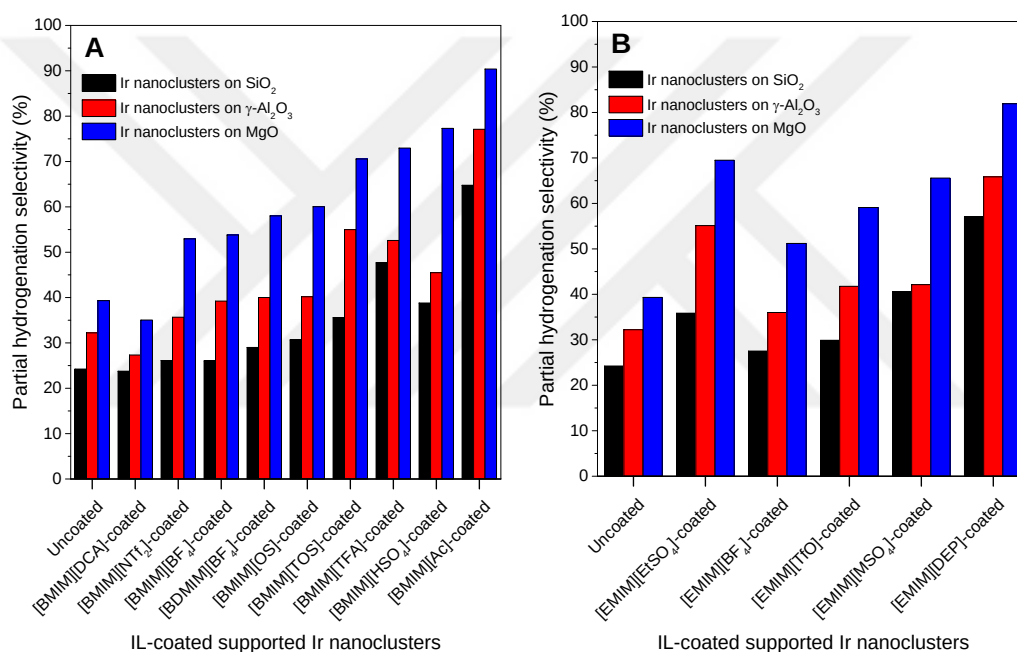


Figure 8-4. Partial hydrogenation selectivity of supported iridium nanoparticles coated with ILs with A) $[\text{BMIM}]^+$ cation and B) $[\text{EMIM}]^+$ cation. Partial hydrogenation of 1,3-butadiene was conducted at an H_2 :1,3-butadiene feed molar ratio of 2:1 at 333 K and 1 atm.

The effect of IL-coatings composed of $[\text{EMIM}]^+$ cation and different anions on the partial hydrogenation selectivity on supported iridium nanoparticles is also presented in Table 8-2 and Figure 8-4B. On SiO_2 - and $\gamma\text{-Al}_2\text{O}_3$ -supported nanoparticles, the selectivity increases in the following order of anions: $[\text{DEP}]^- > [\text{MSO}_4]^- > [\text{EtSO}_4]^- \sim [\text{BF}_4]^- > [\text{TfO}]^-$. There is

not a remarkable change in the order of the anions when the nanoparticles are supported on MgO because structural parameters of [EMIM]⁺ cation and anions do not change significantly compared to their isolated conditions when there is highly electron-donating support is present as illustrated in the previous chapter.³⁰ Therefore, we expected to observed similar results for MgO-supported materials because of the structural stability of the ILs.

8-5.2.2. Effect of Size of Anion on the Catalytic Performance

Another possible structural variation in the anion of the ILs is the size variations. To investigate the consequences of this effect on the catalytic performance, the partial hydrogenation selectivity of [BMIM][HSO₄]- and its octyl-substituted counterpart [BMIM][OS]-coated supported iridium nanoparticles were compared. Figure 8-4A demonstrates that the selectivity of [BMIM][HSO₄]-coated catalyst supported on SiO₂, γ -Al₂O₃, and MgO was 39, 45, and 77%, respectively, while those of [BMIM][OS]-coated catalyst were 31, 40, and 60%, respectively. The reduced selectivity in the supported catalysts with octyl-substituted IL was attributed to a decrease in direct interactions between the IL molecule and the active metal sites because of the steric limitations originated from the presence of a very large anion on this IL. We infer that because the IL was too large, its interaction with the active sites was not as effective as the one that can be possible with the IL with a small anion, which can get closer to the active centers to establish an effective interaction.³⁸

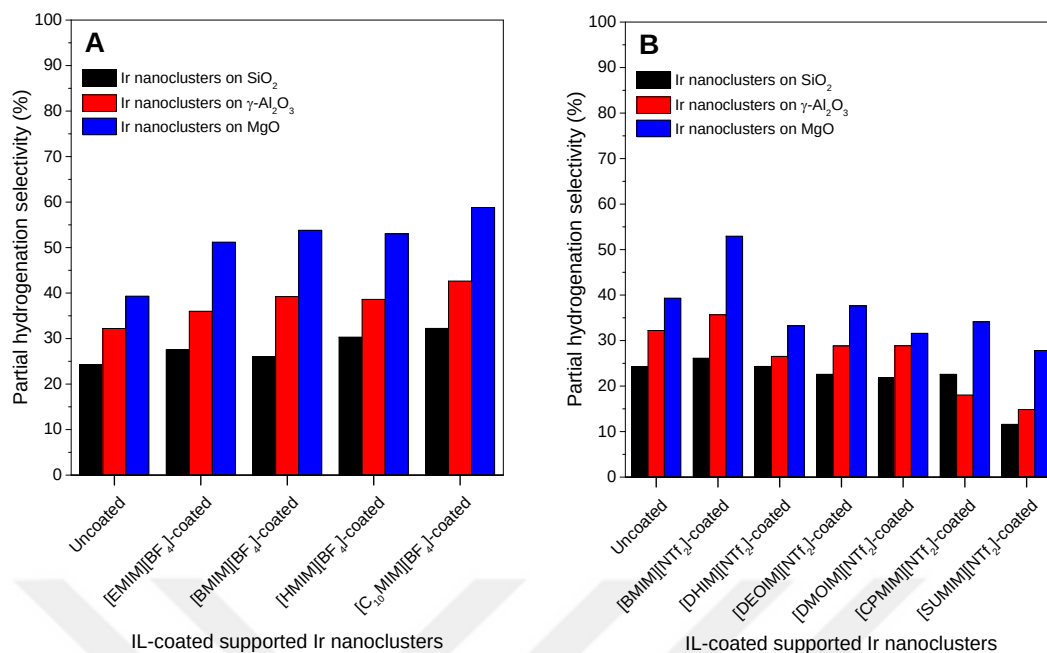


Figure 8-5. Partial hydrogenation selectivity of supported iridium nanoparticles coated with ILs with A) $[\text{BF}_4]^-$ anion and B) $[\text{NTf}_2]^-$ anion. Partial hydrogenation of 1,3-butadiene was conducted at an H_2 :1,3-butadiene feed molar ratio of 2:1 at 333 K and 1 atm.

On the other hand, TOF values of the catalysts have the exactly opposite trend. Accordingly, the [BMIM][OS]-coated supported nanoparticles have a higher TOF than those of [BMIM][HSO₄]-coated ones. The difference in the TOF values of the [BMIM][OS]-coated samples on SiO₂-supported (16.0×10^{-3} mole of 1,3-butadiene converted $\times (\text{Ir site} \times \text{s})^{-1}$) and on γ-Al₂O₃-supported nanoparticles are not significant (6.0×10^{-3} mole of 1,3-butadiene converted $\times (\text{Ir site} \times \text{s})^{-1}$). However, activity of [BMIM][OS]-coated MgO-supported nanoparticles is approximately 3-fold higher than those of [BMIM][HSO₄]-coated counterparts. Here, we claim that the synergistic influence of the electron-donor MgO and the IL was significant, suggesting that the interactions of the active iridium sites with supports and the ILs are dominant factors determining the performance of the catalysts. The enhancement in the activity of catalyst coated with the octyl-substituted [BMIM][OS] is attributed to the strong Coulombic interaction and hydrogen bonding network between the

cation and anion. Alternatively, because the anion is very large, the IL can not get closer to the active sites, thus, it can not influence the electronic environment sufficiently. Thus, the performance of the [BMIM][OS]-coated catalysts remains more similar to that of uncoated catalysts.

8-5.2.3. Effect of Fluorination of Anion on the Catalytic Performance

One of the other possible structural factors on the IL is the electronic structure of the anion. Researchers have shown that fluorination of the anion enhances the physicochemical properties of the ILs, such as stability.^{28,39} To investigate the influence of electronic structure of the anion, we tested the performance of [BMIM][Ac]-coated and [BMIM][TFA]-coated supported iridium nanoparticles. Results given in Table 8-2 and Figure 8-5A indicate that [BMIM][Ac]-coated catalysts give better partial hydrogenation selectivity performance than [BMIM][TFA]-coated ones supported on SiO₂, γ -Al₂O₃, and MgO. We predict that the presence of the fluorine atoms in the anion increases the electrophilicity of the anion; thus the electron density between anion and cation decreases, resulting in a lower degree of electron donation to active sites resulting in a lower selectivity performance of the catalyst.³⁹ As expected, the TOF of the catalysts coated with [BMIM][TFA] was higher than those of catalysts coated with [BMIM][Ac] on all supports. Enhancement of the activity upon fluorination of the IL was more notable on γ -Al₂O₃- (~6-fold) and MgO-supported (~9-fold) than SiO₂-supported (~2-fold) nanoparticles. The synergistic influence of the supports and ILs as ligands led to the inference that when the metal oxide support has less electron donor character, such as SiO₂, the H₂ dissociation rate for 1,3-butadiene hydrogenation is high as compared to MgO. Thus, the influence of the IL on the activity on SiO₂-supported nanoparticles is not significant. On the other hand, IL effect is more dominant in terms of

activity of the catalysts when the support has a strong electron donor characters, opposite to the trend in selectivity.

8-5.2.4. Effect of Alkyl Chain Size Located on the Imidazolium Group on the Catalytic Performance

Another possible and simple structural change in the IL structure is the change in the alkyl chain size of the imidazolium ring. We investigated the effect of alkyl chain on the ILs having $[\text{BF}_4]^-$ anion with ethyl, butyl, hexyl, and decyl groups attached to the imidazolium ring. Figure 8-5A demonstrates the effect on the partial hydrogenation performance of the supported iridium nanoparticles, when they were coated with [EMIM][BF_4], [BMIM][BF_4], [HMIM][BF_4], and [C_{10}MIM][BF_4]. Accordingly, the partial hydrogenation selectivity of [EMIM][BF_4]-coated Ir/ SiO_2 catalyst was 28% while that of [BMIM][BF_4]-, [HMIM][BF_4]- and [C_{10}MIM][BF_4]-coated catalysts were 26, 30, and 36%, respectively. The trend was the same on $\gamma\text{-Al}_2\text{O}_3$ -supported nanoparticles with the corresponding selectivity values of 36, 39, 39, and 43%, respectively. MgO-supported nanoparticles have a partial hydrogenation selectivity of 51, 54, 48, and 59% upon coating with the ILs, respectively. Accordingly, we infer that small changes in the size of the alkyl chain of the imidazolium ring does not alter the performance of the IL-coated nanoparticles significantly. However, when the alkyl chain becomes exceptionally long, such as when it is decyl, there is a slight increase in the selectivity of the corresponding catalysts on all supports. In ILs, Coulombic (electrostatic) interactions are considered to be the major sources of attraction with the influence of van der Waals interactions between alkyl chains and hydrogen bonding between polar groups.⁴⁰ In the study of Aguila et al.,⁴¹ there is a significant difference between the polarizability of [EMIM][BF_4] and [HMIM][BF_4], while the dipole moments were nearly the same, indicating that the charge distribution between anion and cation is high. Moreover, Fernandes et al.⁴⁰

investigated the interactions in terms of dissociation energies and they found a decrease in the interaction energies with an increase in the alkyl chain length. Hence, we interpret that as the interaction energies between anion and cation as well as the increased electrostatic interactions increases the electron density on the IL with higher alkyl chain length, which leads to an enhancement in the selectivity.

Consistent with the information gained from the selectivity performance of the catalysts, TOF values of the IL-coated samples decrease when the size of the alkyl chain of the corresponding ILs increase (Table 8-2). For instance, the TOF of the [EMIM][BF₄]- and [C₁₀MIM][BF₄]-coated Ir/SiO₂ catalysts were 22×10^{-3} and 19.5×10^{-3} mole of 1,3-butadiene converted $\times (\text{Ir site} \times \text{s})^{-1}$. The decrease in the TOF of the same IL-coated catalysts on MgO was more significant, approximately 2-fold (Table 8-2). Zhang et al.,⁴² investigated the effects of alkyl chain length on the oxygen reduction reaction by using Pt on a carbon support, which has a strong electron-donating nature similar to that of MgO. In their study, they observed a decrease in the catalytic activity, when the carbon number in the alkyl changes from four to ten.⁴² Therefore, we expect a similar behavior of the ILs in activity performance for hydrogenation of 1,3-butadiene over MgO-supported iridium nanoparticles.

8-5.2.5. Effect of Methylation of the C2-position of Imidazolium Group on the Catalytic Performans

Methylation of the second carbon (C2H) in the imidazolium ring is also one of the structural parameters that might have a significant effect on the performance of the IL-coated catalysts. We analyzed the performance of the supported nanoparticles upon coating them with [BMIM][BF₄] and its methylated counterpart [BDMIM][BF₄]. Results showed an increase in the partial hydrogenation selectivity accompanied by a decrease in the activity when the C2H of the IL was methyl substituted on all supported iridium nanoparticles. C2H position plays an

important role in controlling the charge symmetry between anion and cation pairs.⁴³⁻⁴⁴ Therefore, it directly influences the electron density on the IL.⁴⁰ Here, we interpret that an increase in the electron density on IL leads to a higher degree of transfer of electrons to iridium sites, which in turn enhances the selectivity performance for hydrogenation of 1,3-butadiene. The results were similar to the ones that Holzapfel et al.⁹ investigated. They studied the influence of IL coating on performance for hydrogenation of 1-octyne on nickel/alumina catalyst. Accordingly, the methylated IL doubles the selectivity and the IL was likely to partially block the specific sites for 1-octene hydrogenation working as a site-specific ligand and the reaction favors the hydrogenation of 1-octyne, giving higher partial hydrogenation selectivity.⁹

8-5.2.6. Effects of Functional Group Substitution on the Cation on the Catalytic Performance

8-5.2.6.1. Effect of Nitrile Group Substitution

Functional group substitution on the imidazolium ring is another structural parameter that can have an effect on the catalytic performance. Substitution of the alkyl groups present on the imidazolium ring with nitrile groups is one of the possibilities in this respect. To investigate the effect of nitrile groups on the performance of the IL-coated catalysts, we analyzed the performance of supported nanoparticles of uncoated catalysts with those of [BMIM][NTf₂]-coated and nitrile-substituted [CPMIM][NTf₂]-coated counterparts. Figure 8-5B demonstrates that on SiO₂-supported nanoparticles the presence of the nitrile group does not alter the partial hydrogenation selectivity of the uncoated nanoparticles. On the other hand, γ -Al₂O₃-supported nanoparticles have selectivity values of 36 and 18% when coated with [BMIM][NTf₂] and [CPMIM][NTf₂], respectively. Moreover, MgO-supported counterparts have the selectivity values of 53 and 34%, respectively. Such a decrease in the partial hydrogenation selectivity is

expected as the nitrile group has a strong electron-withdrawing character. We interpret that nitrile group withdraws electron density from supported iridium nanoparticles; thus, iridium sites become more available for the reactants. Apparently, butene molecules can compete with 1,3-butadiene in the adsorption of the active sites in the presence of nitrile group, therefore complete hydrogenation occurs and the formation of butane increases, resulting in a lower selectivity for butenes. In addition, the TOF values on all IL-coated supported Ir nanoparticles decrease upon nitrile group substitution to the IL, opposite to the general observation that activity would increase with a decrease in selectivity values. There might be mass transfer limitations in the use of nitrile-substituted IL that IL layer may inhibit the reactant molecules to access the active sites. The decrease in the catalytic activity can be originated from the increasing polarity of the IL complex because of the nitrile addition.^{32,45} In the study of Zhao et al.,⁴⁶ nitrile functionalized [CPMIM][NTf₂] was reported to have a greater polarity and charge distribution, causing a change in the interaction energy compared to [BMIM][NTf₂] which is consisted with the activity results obtained over supported nanoparticles in this study. Another possibility is that the additional nitrile group can alter the structure of IL and leads to a change in the hydrogen bonding network entirely inside the IL.^{32,45-46} Hydrogen bonding is observed between the H atoms in the imidazolium ring and hydrogen bond acceptor atoms in the counter anion. The strength of the bond directly depends on the counter-anion and thus, an addition of a functionalized group such as nitrile can change the bond strength and leads to a difference on the catalytic activity.

8-5.2.6.2. Effect of Sulfonyl Group Substitution

Another functional group that can be substituted with the alkyl groups on the imidazolium ring is the sulfonyl group. The selectivity and activity of the supported Ir nanoparticles can differ when a highly electron-withdrawing sulfonyl group is present in the IL structure. To

elucidate the effect of sulfonyl group, the performance of [BMIM][NTf₂]- and sulfonyl-substituted [SUMIM][NTf₂]-coated supported catalysts were investigated. Results in Figure 8-5B and Table 8-2 indicate that the partial hydrogenation selectivity of SiO₂-, γ -Al₂O₃-, and MgO-supported nanoparticles are 26, 36, and 53%, respectively, upon coating them with [BMIM][NTf₂]. On the other hand, the selectivity of the [SUMIM][NTf₂]-coated counterparts decreased to 12, 15, and 28%, respectively. We infer that the strong electron-withdrawing property of the sulfonyl group⁴⁷ lowers the electron density on the active sites, and this influence leads to an increase in the activity of the iridium sites accompanied by decrease in partial hydrogenation selectivity. Consequently, the TOF values of all supported nanoparticles increase upon coating them with [SUMIM][NTf₂] rather than [BMIM][NTf₂] (given in Table 8-2).

8-5.2.6.3. Effect of Hydroxyl Group Substitution

Hydroxyl group addition to the imidazolium ring may also be one of the other possible functional group substitutions. To investigate the variations in the performance of the catalysts upon –OH addition on the alkyl chains of the cation, the catalytic performance of the supported nanoparticles, both uncoated and coated with [BMIM][NTf₂] and hydroxylated [DHIM][NTf₂] were compared, as given in Figure 8-3D. Results show that when the catalysts are coated with [DHIM][NTf₂], the selectivity for partial hydrogenation decreases. The decline in the selectivity performance is attributed to the presence of the highly chemically active character of the [DHIM][NTf₂] with two of the –OH groups.⁴⁸ Moreover, the [DHIM][NTf₂]-coated supported catalysts are always less selective than their non-hydroxylated [BMIM][NTf₂]-coated counterparts. MgO-supported nanoparticles are the ones that are significantly influenced by the decline in the selectivity with a decrease from 53 to 33% selectivity upon hydroxyl group substitution. Hydroxyl substitution in ILs creates new

hydrogen bonds⁴⁵ which makes the IL very reactive⁴⁹ for many reactions IL complex. Based on the knowledge that an increase in the activity decreases the selectivity performance of the catalysts, we expect a lower selectivity for butene formation. Moreover, the influence of the hydroxyl group on electron-donor MgO is more notable because of the increased interactions of the MgO and IL itself. Thus, we infer that the electron density of MgO and the active sites decreases with decreasing conductivity, which leads to a greater difference in selectivity compared to other supports.

On the other hand, when [BMIM][NTf₂]- and [DHIM][NTf₂]-coated catalysts are compared in terms of activity, hydroxyl group substitution to the IL does not alter the TOF of MgO-supported iridium nanoparticles and it increases the TOF of γ -Al₂O₃-supported counterparts as expected from the chemically active –OH group, given in Table 8-2. However, the activity values of SiO₂-supported nanoparticles coated with [BMIM][NTf₂] and [DHIM][NTf₂] are 2.21×10^{-2} and 1.22×10^{-2} mole of 1,3-butadiene converted $\times$ (Ir site $\times$ s)⁻¹, respectively, indicating that the hydroxyl group decreases the activity on relatively electron-poor SiO₂.⁵⁰ Here we infer that upon the hydroxyl group substitution, IL-coated catalysts' catalytic activity dramatically decreased in SiO₂- supported nanoparticles because of an enhancement of the hydrogen bond.³⁰

8-5.2.6.4. Effect of Methoxyl Group Substitution

Another functional group substitution on the cation is the methoxyl group substitution. Figure 8-3D demonstrates the variations in the selectivity for partial hydrogenation on [BMIM][NTf₂]-coated and methoxylated [DMOIM][NTf₂]-coated supported iridium nanoparticles. Data indicate that on all supported catalysts, the presence of methoxylated IL decreases the partial hydrogenation selectivity, when compared to its uncoated and [BMIM][NTf₂]-coated counterparts. Methoxyl substitution does not significantly change the

selectivity for partial hydrogenation on SiO_2 - and $\gamma\text{-Al}_2\text{O}_3$ -supported nanoparticles. However, selectivity on MgO-supported catalyst decreases from 53 to 32% when the methoxyl group is present on the IL as a result of the electron density decrease in the imidazolium ring because of the direct linkage of oxygen to nitrogen atoms of the imidazolium ring.⁵¹

Moreover, methoxyl group substitution on the imidazolium ring does not change the activity on IL-coated $\gamma\text{-Al}_2\text{O}_3$ - and MgO-supported catalysts and decreases the activity on IL-coated SiO_2 -supported nanoparticles by approximately 2-fold. The variations in the interactions between active iridium sites and ligands (ILs and supports with different electronic structures) alter the behavior of electron-donor methoxyl group on each supported catalyst. $\gamma\text{-Al}_2\text{O}_3$ - and MgO-supported catalysts donate electron density to IL and compensate the low electron density of methoxyl substituted imidazolium ring. However, for SiO_2 -supported nanoparticles with already poor electron density, the catalytic activity was decreased when the IL-coating has a methoxyl group attached on the imidazolium ring.⁵¹

8-5.2.6.5. Effect of Ethoxyl Group Substitution

Ethoxyl group might also be included on the imidazolium ring. The partial hydrogenation selectivity results given in Figure 8-3D indicate that catalysts with ethoxylated [DEOIM][NTf₂] coatings have a lower selectivity on all supports compared to those of their [BMIM][NTf₂]-coated counterparts. For instance, [DEOIM][NTf₂]-coated Ir nanoparticles supported on MgO provide a partial selectivity of 38% while this selectivity increases to 53% on the [BMIM][NTf₂]-coated catalyst. The trend is the same on SiO_2 - and $\gamma\text{-Al}_2\text{O}_3$ -supported catalysts. Here, we infer that although ethoxyl is an electron-donating functional group, the oxygen vacancies present in the group has an electron-withdrawing inductive effect,⁵² which lowers the selectivity for desired butenes and increases the complete hydrogenation behavior of the IL-coated supported nanoparticles on SiO_2 - and $\gamma\text{-Al}_2\text{O}_3$ -supported samples. However,

the electron density over MgO-supported nanoparticles is high because of the electron-donor character of MgO. Thus, the electron withdrawing character of the ethoxyl substituted IL does not influence the electron density on iridium sites on SiO₂ as much as on SiO₂- and γ -Al₂O₃. As a result of that, MgO-supported sample provides higher selectivity for butenes. The TOF values of ethoxyl group substituted IL-coated samples are higher on SiO₂- and γ -Al₂O₃-supported nanoparticles. However, on MgO-supported samples, the presence of ethoxyl group decreases the activity of the catalyst by half, consistent with the increase in the partial hydrogenation selectivity of the IL-coated nanoparticles.

8-5.2.6.6. Comparison of the Effect of Different Functional Groups

The effect of each functional group that can be present on the performance of supported nanoparticles was also elucidated by comparing the hydroxyl-, methoxyl-, and ethoxyl-substituted IL-coated samples. These functional groups have varying electron-donating ability, therefore the elucidation of the influence of the ILs on each supported catalyst is important to understand the interactions between ILs and active sites. Partial hydrogenation performance of the SiO₂-supported nanoparticles decreases in the following order upon coating with the ILs: [DEOIM][NTf₂] < [DMOIM][NTf₂] ~ [DHIM][NTf₂]. γ -Al₂O₃-supported nanoparticles have almost the same selectivity values for partial hydrogenation upon coating. On the other hand, when the catalysts were supported on MgO, the trend of the selectivity changes as follows: [DEOIM][NTf₂] > [DMOIM][NTf₂] ~ [DHIM][NTf₂]. The inverse trend upon supporting the samples on MgO is attributed to the highly electron-donating surface characteristics of this support. Accordingly, when iridium was supported on MgO, the electron-donating ability of the ethoxyl group has a synergistic effect with that of MgO, therefore there is more electron density on active sites supported on MgO when the IL coating is ethoxyl-substituted [DEOIM][NTf₂]. The activity values of the IL-coated supported

nanoparticles compliment the results gained from selectivity values. Table 8-2 indicates that the TOF of SiO₂-supported and γ -Al₂O₃-supported catalysts increases in the following order upon coating them with the corresponding ILs: [DEOIM][NTf₂] > [DMOIM][NTf₂] ~ [DHIM][NTf₂]. On the other hand, MgO-supported catalyst has two-times less activity when coated with [DEOIM][NTf₂] as compared to its [DMOIM][NTf₂]- and [DHIM][NTf₂]-coated counterparts.

8-5.3. Dependency of the Effects of ILs on the Support Type

Interactions between the active sites and IL coatings depend heavily on the nature of the supports as the ILs and support both act as ligands to alter the catalytic properties of the active sites. In our previous study, we presented the insights on the direct interactions between the IL coating layers and atomically dispersed supported iridium complexes.³⁵ Thus, investigation of the influence of ILs on active sites that are supported on the metal oxides with different electron-donor properties is essential. Figure 8-6 illustrates the changes in selectivity for partial hydrogenation of 1,3-butadiene over SiO₂-, γ -Al₂O₃-, and MgO-supported iridium nanoparticles upon coating the uncoated catalysts with different imidazolium type ILs. Data showed that among 23 ILs, 16 of them provides an improvement in the partial hydrogenation selectivity when coating the corresponding supported metal catalyst. For instance, the uncoated iridium nanoparticles have a partial hydrogenation selectivity of 24, 32, and 39% when they were supported on SiO₂, γ -Al₂O₃ and MgO, respectively. These selectivity values increase to 41, 53, and 73%, respectively, upon coating these catalysts with [BMIM][TFA], as given in Figure 8-4A. Figure 8-6 indicates that the change in selectivity was 17, 21, and 34%, respectively. The difference in the quantities of the selectivity changes was attributed to the influence of the metal oxide surfaces. We understand that as the PZC of the metal oxide is high as in the case for MgO, the influence of the ILs on the enhancement of selectivity

performance of the supported nanoparticles is more significant. On the other hand, when the nanoparticles are supported on a less electron-donor metal oxide, such as SiO_2 , the influence of the support on the selectivity performance was more significant rather than that of the ILs. These results are different from those obtained for atomically dispersed supported iridium complexes discussed in Chapter 7. For single-site $\text{Ir}(\text{CO})_2$ complexes, the influence of ILs is significant when the catalyst is supported on less electron donating SiO_2 and vice versa. The reason behind the difference between single-site iridium and nanoparticles is that in single-site iridium the synergistic effect of the presence of the carbonyl ligands and electron donating MgO support already enhances the selectivity and the influence of the IL becomes less significant.

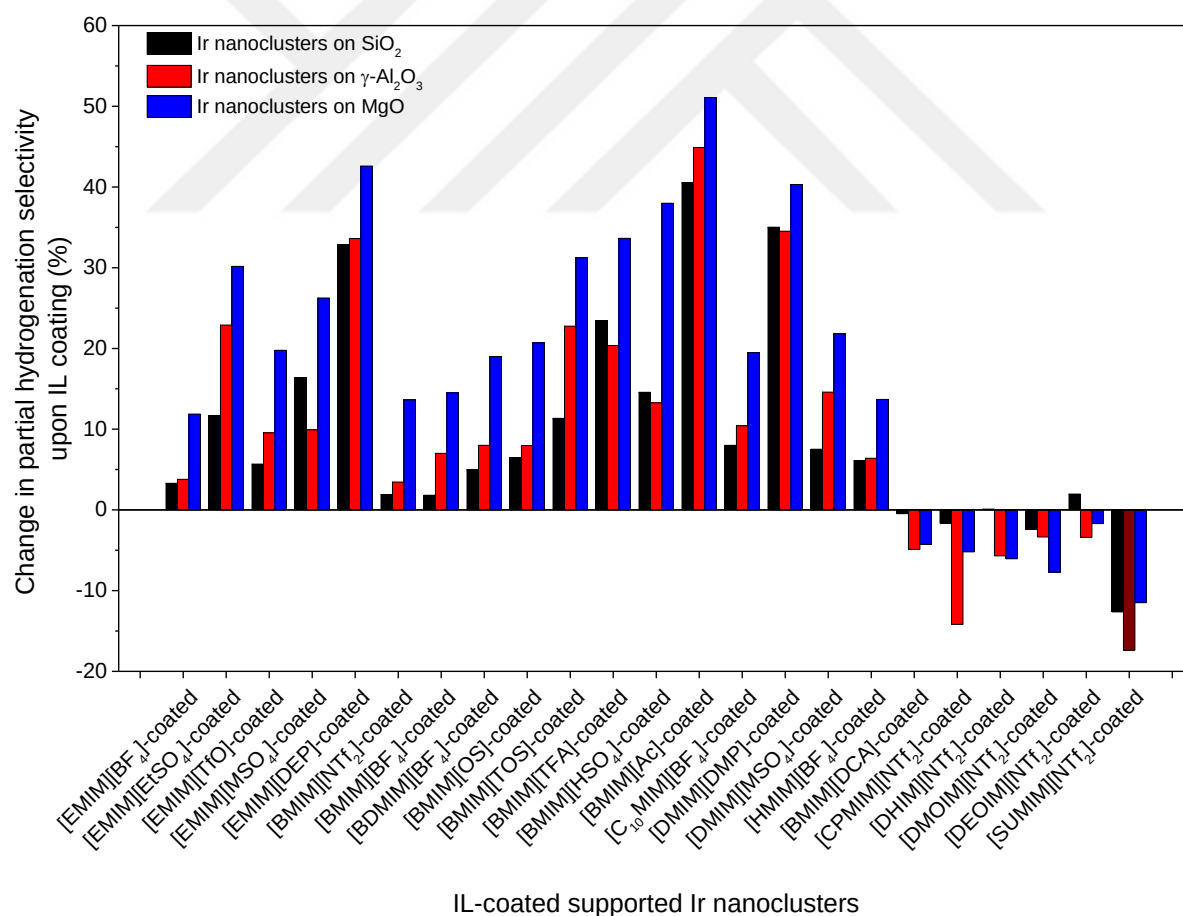


Figure 8-6. Change in partial hydrogenation selectivity of SiO_2 -, $\gamma\text{-Al}_2\text{O}_3$ -, and MgO -supported Ir nanoparticles coated with 23 structurally different imidazolium ILs. Partial

hydrogenation of 1,3-butadiene was conducted at an H_2 :1,3-butadiene feed molar ratio of 2:1 at 333 K and 1 atm.

We further consider the influence of the support effect on the TOFs of the IL-coated catalysts. Table 8-2 indicates that the decrease in the TOF of the supported catalysts upon IL-coating is different when the catalysts were supported on different metal oxides. This finding confirms the idea that we should consider the combined effects of supports and ILs on the performance of the supported catalysts.

8-5.4. Correlations between the Interionic Interaction Energy in ILs (probed by $\nu(\text{C2H})$) and the Catalytic Performance

The synergistic effect of the supports and ILs were further demonstrated in detail by combining the surface nature of the support with that of an important structural parameter on the ILs: interionic interaction energy. The structural parameter that is specific to imidazolium-type ILs is the bonding strength of the second carbon, C2, to hydrogen in imidazolium moiety. C2H is the most acidic proton in the imidazolium ring and the IR stretching vibration of C2H, $\nu(\text{C2H})$, is a good measure to understand the interionic interactions between anion and the cation of the ILs.^{19,40,53-55} In our previous study as presented in Chapter 5,³⁵ we showed that the hydrogenation selectivity over IL-coated atomically dispersed $\gamma\text{-Al}_2\text{O}_3$ -supported iridium complexes are highly dependent on the interionic interactions in the ILs. Accordingly, as the interionic interaction energy of ILs increases (probed by a decrease in $\nu(\text{C2H})$), there is a higher degree of electron donation from IL-coatings to the active sites, resulting in a higher selectivity for the desired butene isomers production. To elucidate the influence of the interionic interaction energies of the ILs on the selectivity and activity performance of iridium nanoparticles supported on different metal oxides, we measured the C2H vibration of 16 different 1,3-dialkylimidazolium ILs (ILs which do not include any

functionalized groups) and plotted the partial hydrogenation (sum of all butenes) selectivity on supported catalysts as a function of $\nu(\text{C2H})$, as given in Figure 8-7A. Data showed a strong correlation. Accordingly, as the interionic interaction energy increases (with a decrease in $\nu(\text{C2H})$ position), there is a higher amount of electron donation from ILs to the active sites. Such increase in electron density on the active sites leads to significant changes in the adsorption properties of the reactant 1,3-butadiene and the butene intermediates on the active sites. As a result of these changes the catalysts become more selective for partial hydrogenation.

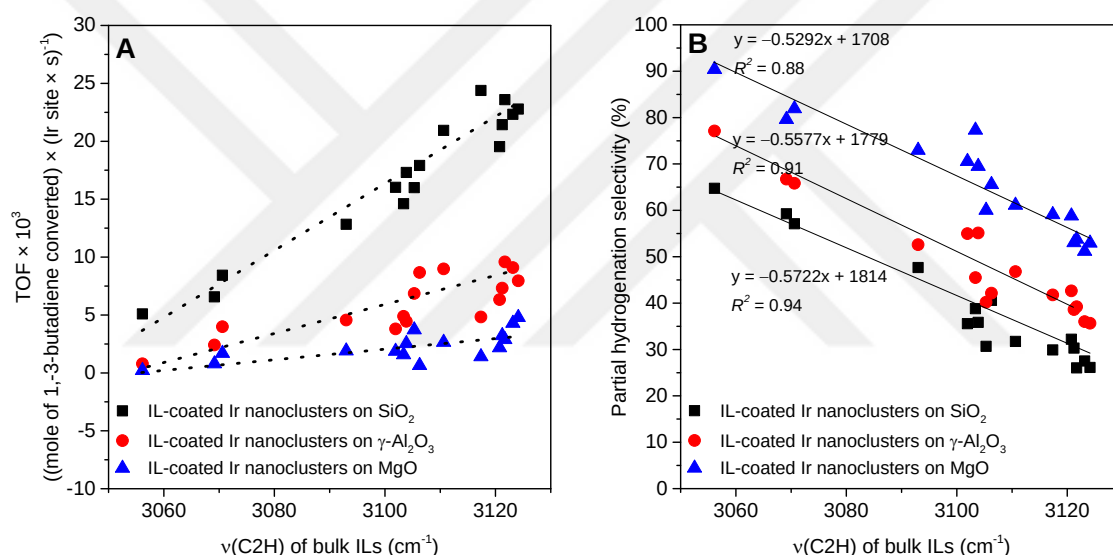


Figure 8-7. Change in A) TOF and B) total partial hydrogenation selectivity (sum of 1-butene, *cis*-2-butene and *trans*-2-butene with change in $\nu(\text{C2H})$ of bulk ILs.

The trend is exactly opposite for the activity of IL-coated supported catalysts. Figure 8-7B demonstrates that a stronger interionic interaction in the ILs results in a lower TOF. A decline in activity is expected when there is an increase in partial hydrogenation selectivity. The reverse correlation between TOF for hydrogenation and $\nu(\text{C2H})$ of the bulk IL indicates that the electron donation from IL to active sites is definite and tunable. Here, we also note that the slopes of TOF– $\nu(\text{C2H})$ curves given in Figure 8-7B are different for nanoparticles

supported on different metal oxides. The steepness of the curve belong to the IL-coated SiO₂-supported nanoparticles is higher compared to others, revealing that the activity of the catalysts are dependent mostly on the IL structure rather than the nature of the support when the metal oxide has a relatively weaker electron-donor character. However, on MgO-supported nanoparticles, the slope of the curve was lower, indicating that when the surface of the support has a highly electron-donating character, as probed by a higher PZC value, the TOF of the catalysts become more dependent on the support rather than the IL's structure. Here, we conclude that strong interactions between active sites and supports as well as between the supported active sites and ILs directly control the catalytic performance.

8-5.5. Derivation of a Model to Predict the Partial Hydrogenation Selectivity for 1,3-Butadiene Hydrogenation over IL-coated Supported Iridium Nanoparticles

Here, we aimed to derive a model to predict the selectivity for partial hydrogenation of 1,3-butadiene over IL-coated supported iridium nanoparticles supported on metal oxides with a given surface acidity of the metal oxide (as measured by PZC) and the $\nu(\text{C}_2\text{H})$ of the 1,3-dialkylimidazolium imidazolium ILs (those lacking any functionalized groups). Thus, in Figure 8-8, we plotted the slope values of the curves (solid black symbols) and intercept values of the curves (solid hollow symbols) ($\nu(\text{C}_2\text{H})$) vs selectivity given in Figure 8-7B) as a function of PZC of the metal oxides. Figure 8-8 illustrate a parabolic decrease in magnitude of slope values and a parabolic increase in the magnitude of intercept values as electron-donating ability of the supports changes in the following order: $\text{MgO} > \gamma\text{-Al}_2\text{O}_3 > \text{SiO}_2$. Results indicate that when the oxide support becomes more electron-donor, the effect of IL structure (probed by interionic interaction energy) on the partial hydrogenation performance is less prominent.

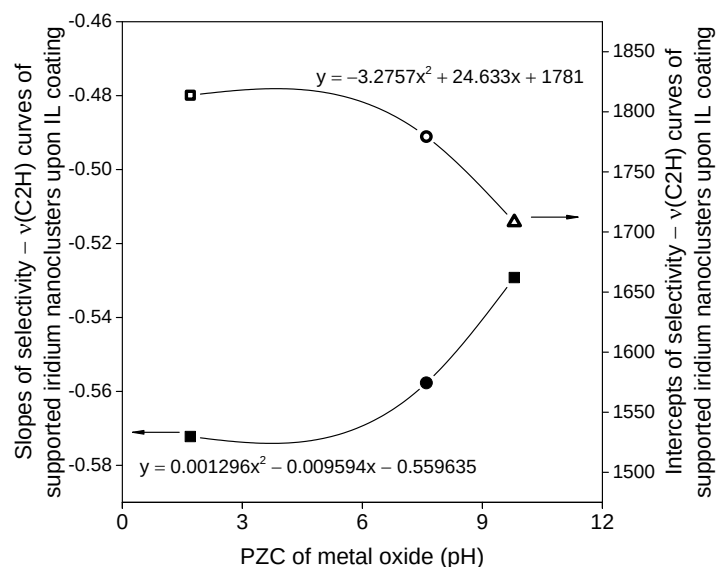


Figure 8-8. Variations in the slope and intercept values of selectivity curves (Figure 8-7B) of catalysts as a function of PZC of metal oxides. Data demonstrate the slope values of the curves in Figure 8-7B of SiO₂-supported (black square, ■), γ-Al₂O₃-supported (black circle, ●), and MgO-supported (black triangle, ▲) Ir nanoparticles and also the intercept values of the curves in Figure 8-7B of SiO₂-supported (hollow square, □), γ-Al₂O₃-supported (hollow circle, ○), and MgO-supported (hollow triangle, △) Ir nanoparticles.

Here we propose a mathematical expression for predicting the selectivity for 1,3-butadiene hydrogenation on IL-coated supported iridium nanoparticles as a function of the interionic interaction energy of the ILs and PZC of metal oxides. The model selectivity expression was estimated based on the fitting of the slope and intercept equations given in Figure 8-8 into second order polynomial ($R^2 = 1$) and obtaining an equation in the form of $y = mx + n$, where y represents the estimated selectivity, m , and n are the slopes and intercept values, respectively, as a function of PZC (in pH), and x is the $v(\text{C2H})$ of the bulk ILs.

$$\text{Model selectivity } (v(\text{C2H}), \text{PZC}) = [(0.001296 \times (\text{PZC})^2 - 0.009594 \times (\text{PZC}) - 0.559635) \times v(\text{C2H})] + [-3.2757 \times (\text{PZC})^2 + 24.633 \times (\text{PZC}) + 1781]$$

Figure 8-9 represents the predicted selectivity values by model expression as a function of the experimentally obtained counterparts. Apparently the model estimates the selectivity for partial hydrogenation of 1,3-butadiene within $\pm 3.9\%$ average relative error and

with a maximum relative error of 15% for catalysts on SiO₂- and MgO-supported catalysts coated with [BMIM][OS], which has an extraordinarily large anion.

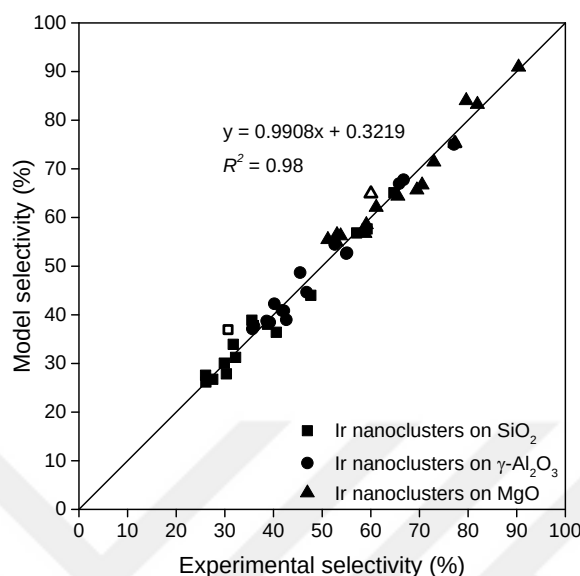


Figure 8-9. Comparison of experimental selectivity values with those of obtained by model. The black hollow square, $\square$, and the black hollow triangle, Δ , represent the selectivity value of [BMIM][OS]-coated Ir nanoparticles on SiO₂ and MgO, respectively, and R^2 was calculated excluding these data points. The solid line indicates the 45° line.

8-6. Conclusions

Iridium nanoparticles with uniform size were prepared on SiO₂, γ -Al₂O₃, and MgO, and coated them with imidazolium ILs having various structures and electron donating/withdrawing properties. Each catalyst was tested for 1,3-butadiene hydrogenation under identical conditions of H₂:1,3-butadiene molar ratio of 2:1 at 333 K and 1 atm under differential conversion conditions. The important results are: A) that both the support and the IL act as ligands determining the electronic properties of the metal, and B) that the electronic properties control the catalytic selectivity and activity (TOF) for partial hydrogenation. Results demonstrate the performance of the IL-coated catalysts depends on the changes in the IL structure in regards of the size of anion/cation, methylation on C2 site, and substitution of

functional groups on the imidazolium ring. Moreover, the interionic interaction energy of the ILs is one of the most essential structural parameter of the ILs, presenting strong correlations between the $\nu(\text{C2H})$ of each IL and selectivity and activity performance of corresponding IL-coated supported catalyst. A simple mathematical expression was developed to predict the butenes selectivity as a function of the $\nu(\text{C2H})$ of the ILs and the electron-donor strength of the support quantified by the point of zero charge of the metal oxides. Results illustrate the structure-performance relationships in these supported metal catalysts with IL-coatings and provide a detailed guideline for the rational design.

8-7. Acknowledgment

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8-8. Supplementary Materials

Names, abbreviations and structures of the ILs.

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Appendix A2

Supplementary Materials for Thermal Stability Limits of Imidazolium Ionic Liquids Immobilized on Metal-Oxides*

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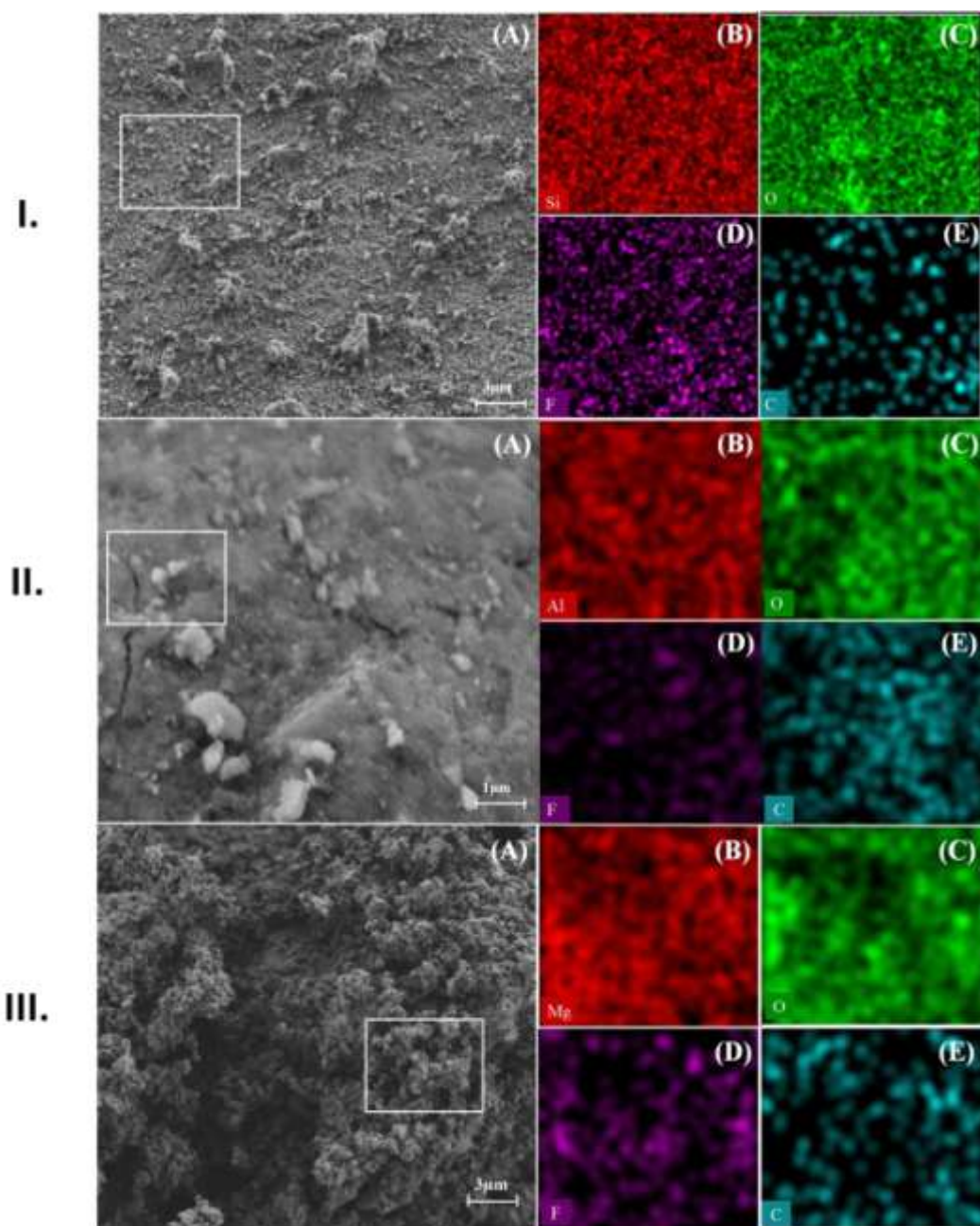
A2-1. Scanning Electron Microscopy Coupled with Energy-Dispersive X-ray Spectroscopy (SEM/EDX) Analysis

Figure A2-1. A representative SEM image characterizing the IL [BMIM][BF₄] on SiO₂ (IA), γ -Al₂O₃ (IIA) and MgO (IIIA). EDX map showing the distribution on individual atoms (IB): silicon; (IIB): aluminum; (IIIB): magnesium; (IC, IIC, IIIC): oxygen; (ID, IID, IIID): fluorine; (IE, IIE, IIIE): carbon.

A2-2. Thermogravimetric Analysis (TGA)

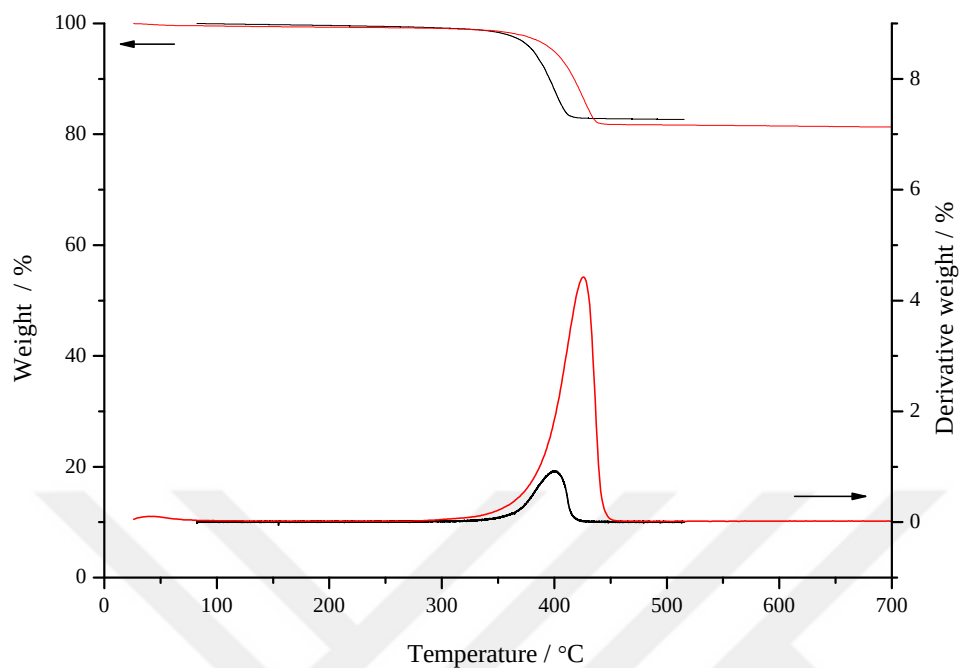


Figure A2-2. Effect of heating rate on the measured T'_{onset} and T_{onset} values for a representative metal-oxide supported IL, [BMIM][NTf₂] on SiO₂. Heating rates: 10 K/min (red lines); 2 K/min (black lines).

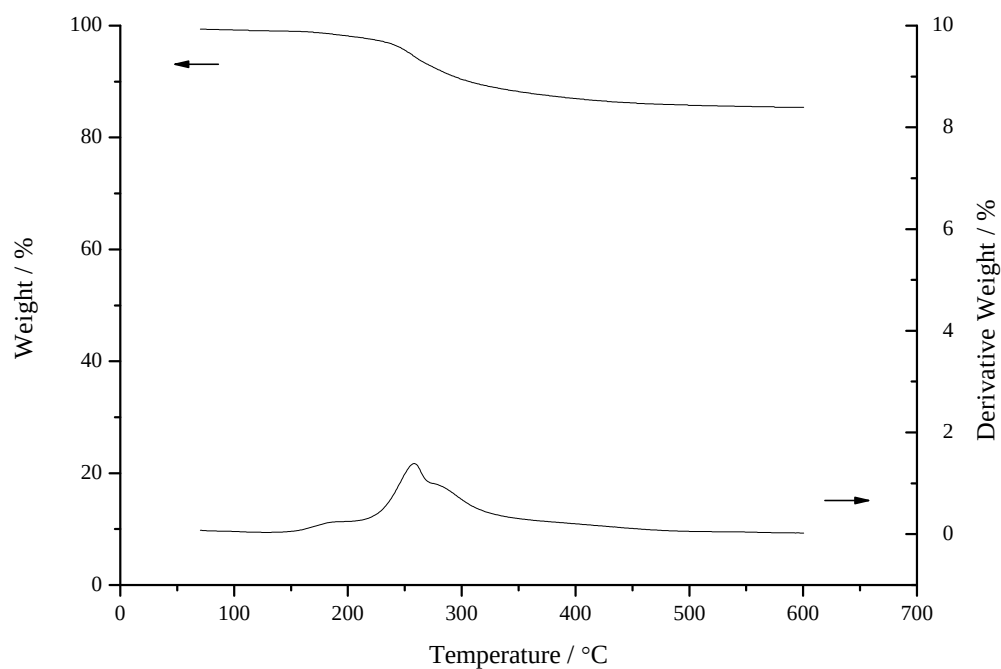


Figure A2-3. TG/DTG curve of [DMIM][DMP] on SiO₂.

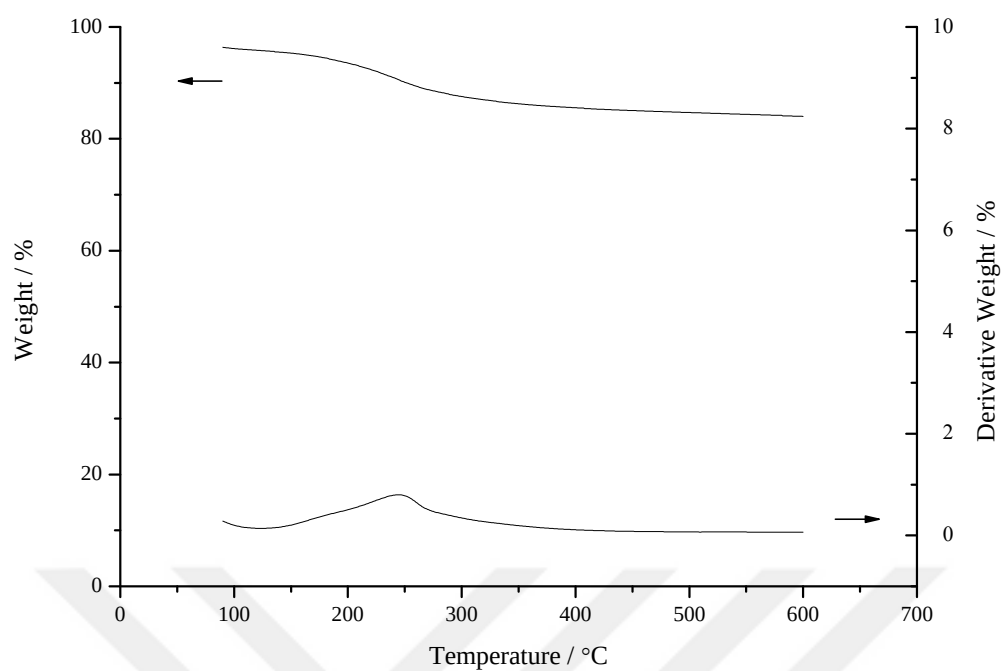


Figure A2-4. TG/DTG curve of [DMIM][DMP] on γ - Al_2O_3 .

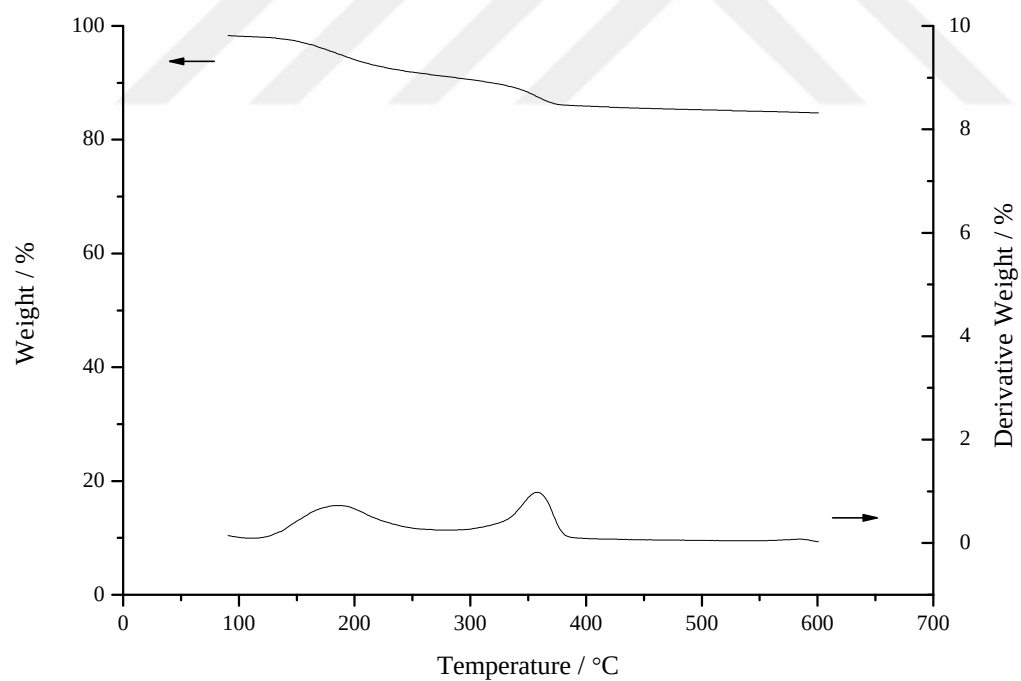


Figure A2-5. TG/DTG curve of [DMIM][DMP] on MgO.

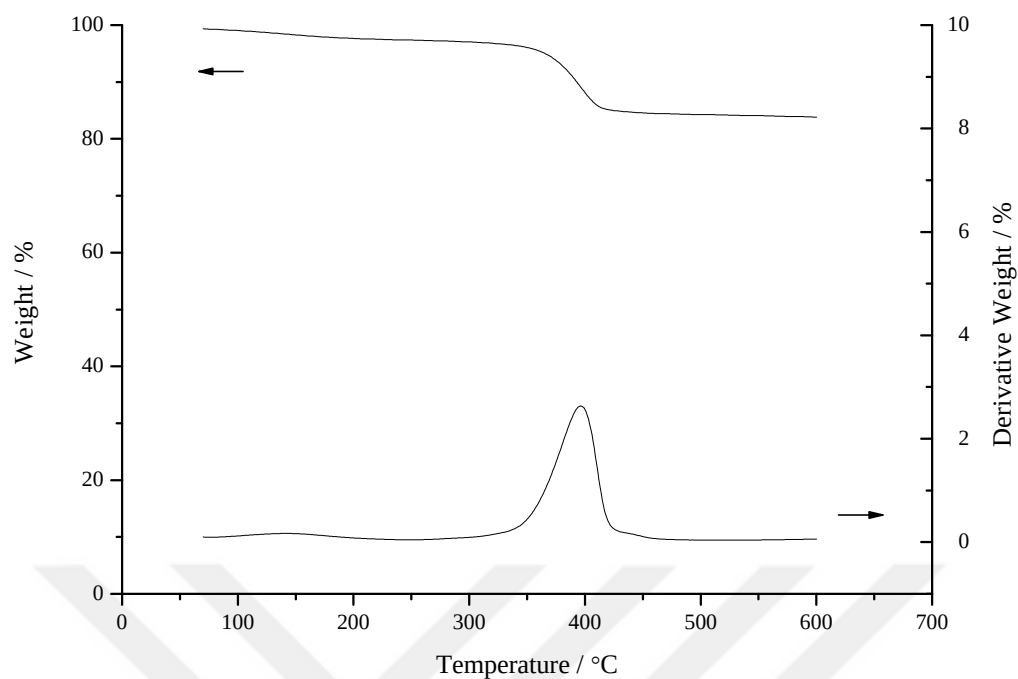


Figure A2-6. TG/DTG curve of [DMIM][MSO₄] on SiO₂.

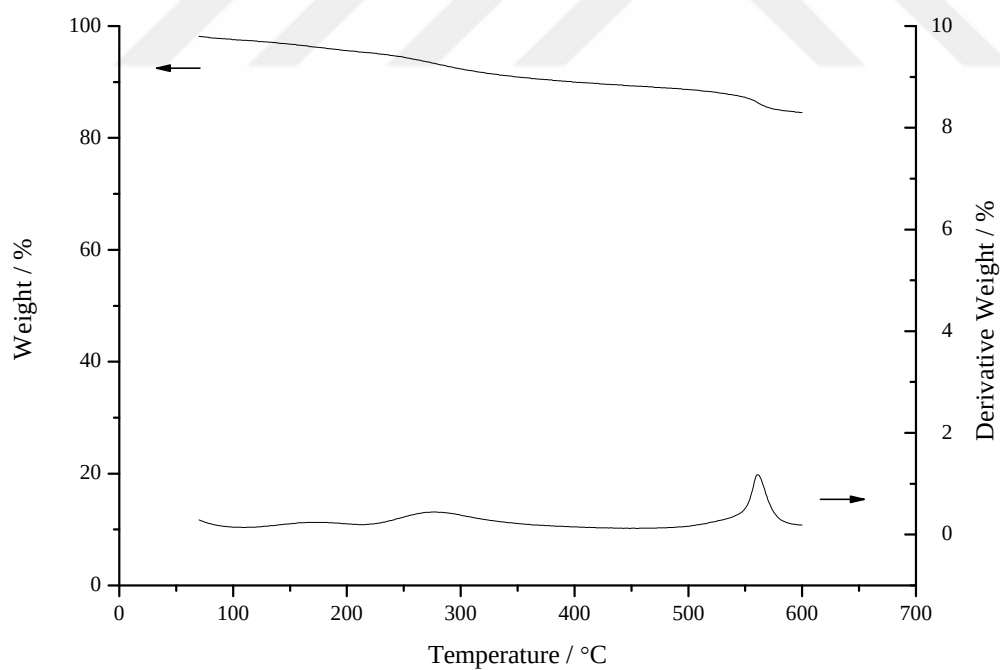


Figure A2-7. TG/DTG curve of [DMIM][MSO₄] on γ -Al₂O₃.

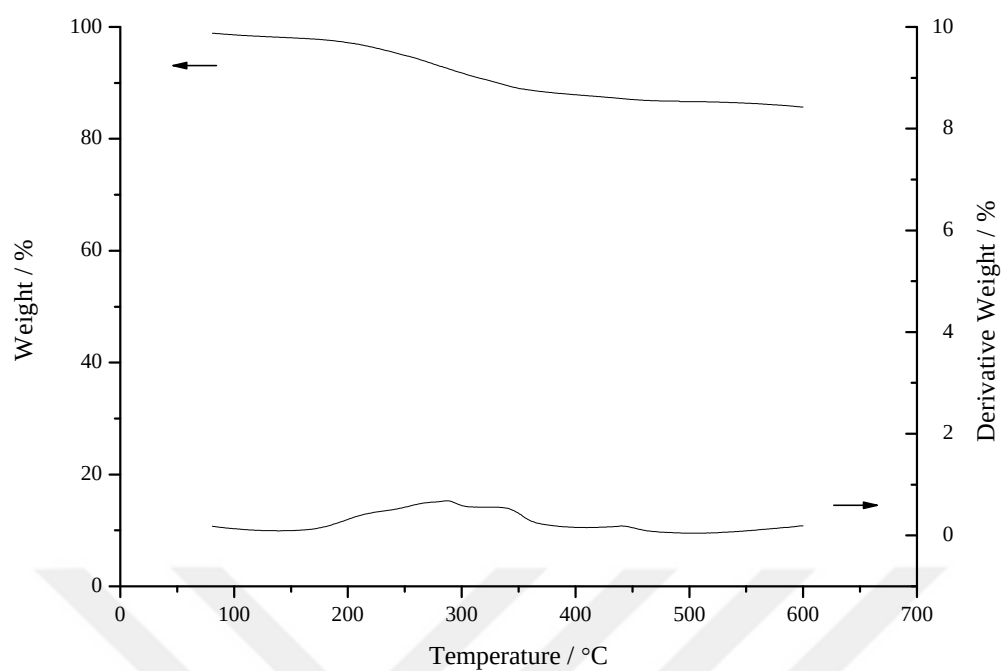


Figure A2-8. TG/DTG curve of [DMIM][MSO₄] on MgO.

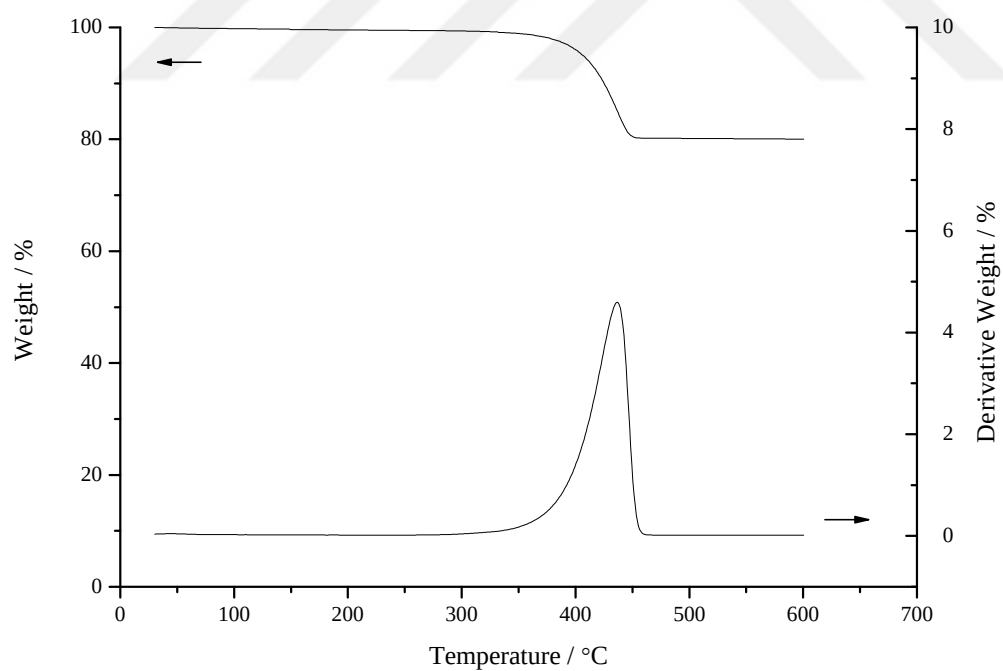


Figure A2-9. TG/DTG curve of [DMPIM][NTf₂] on SiO₂.

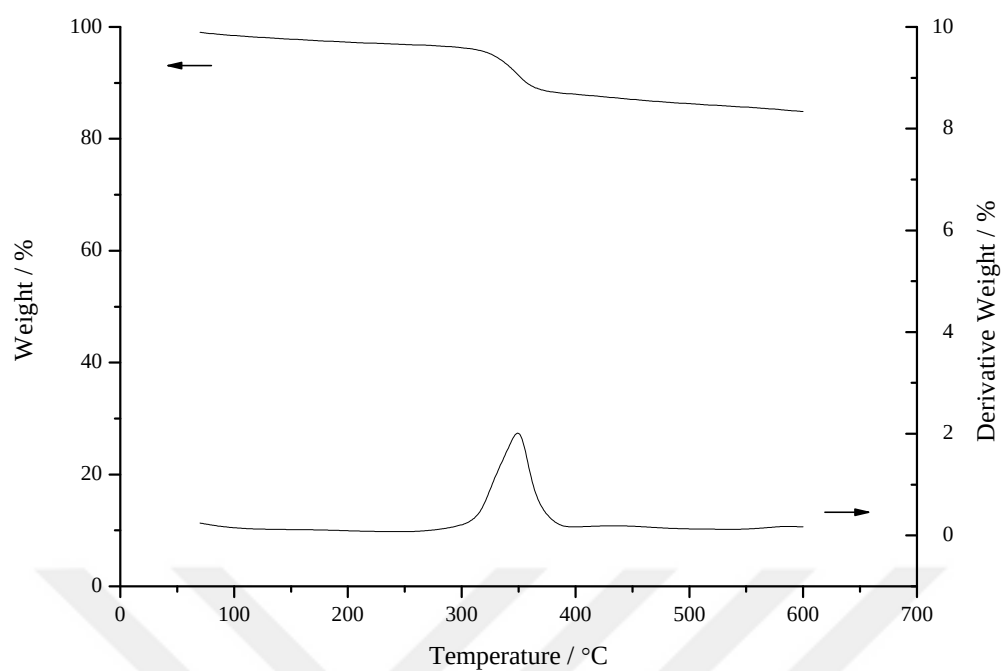


Figure A2-10. TG/DTG curve of [DMPIM][NTf₂] on γ -Al₂O₃.

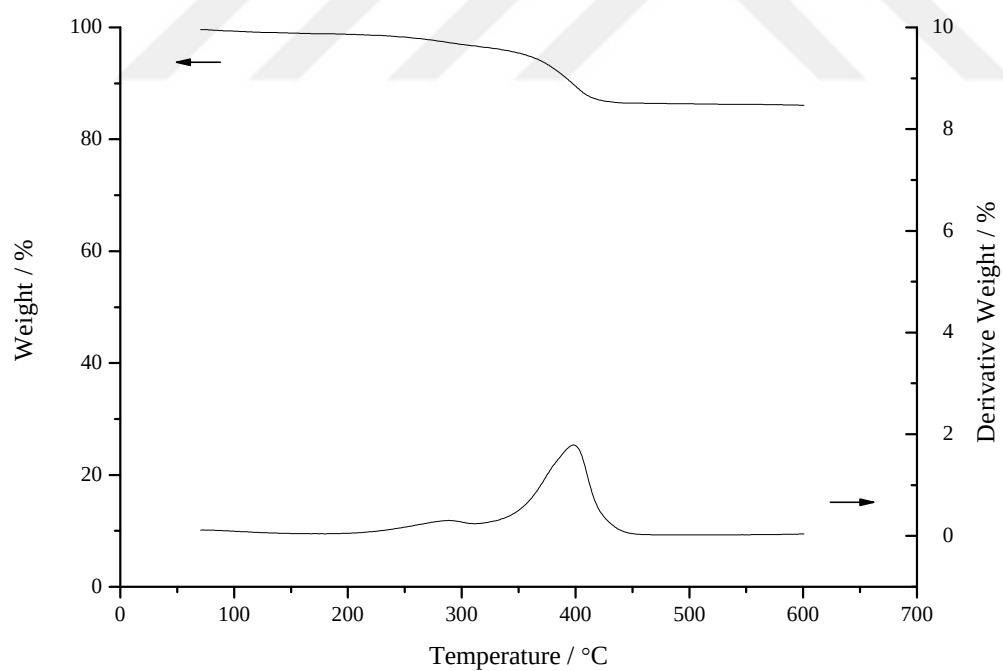


Figure A2-11. TG/DTG curve of [DMPIM][NTf₂] on MgO.

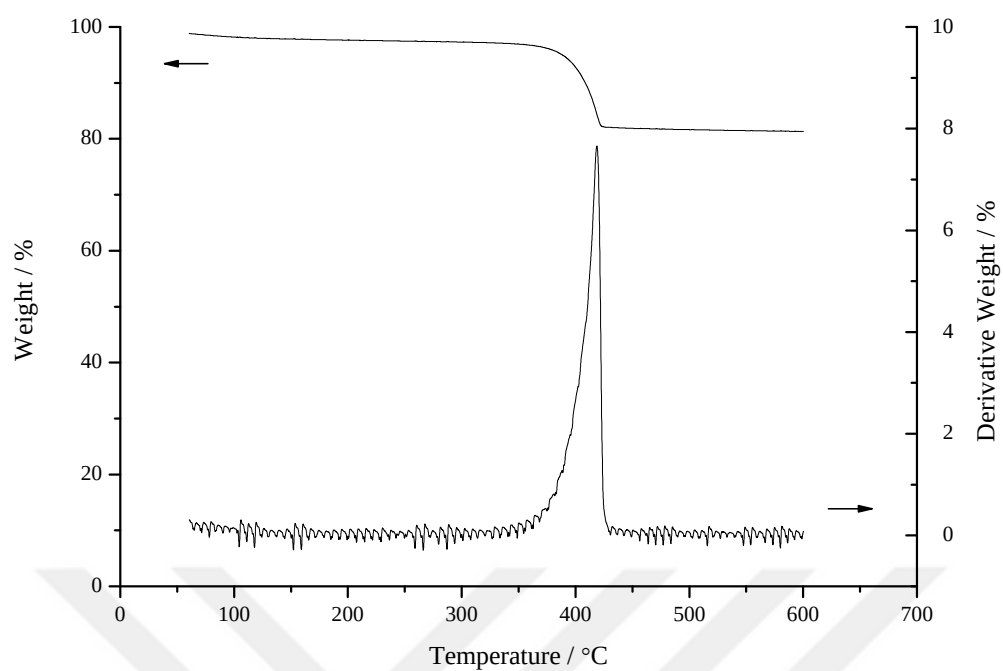


Figure A2-12. TG/DTG curve of [DMPIM][Me] on SiO₂.

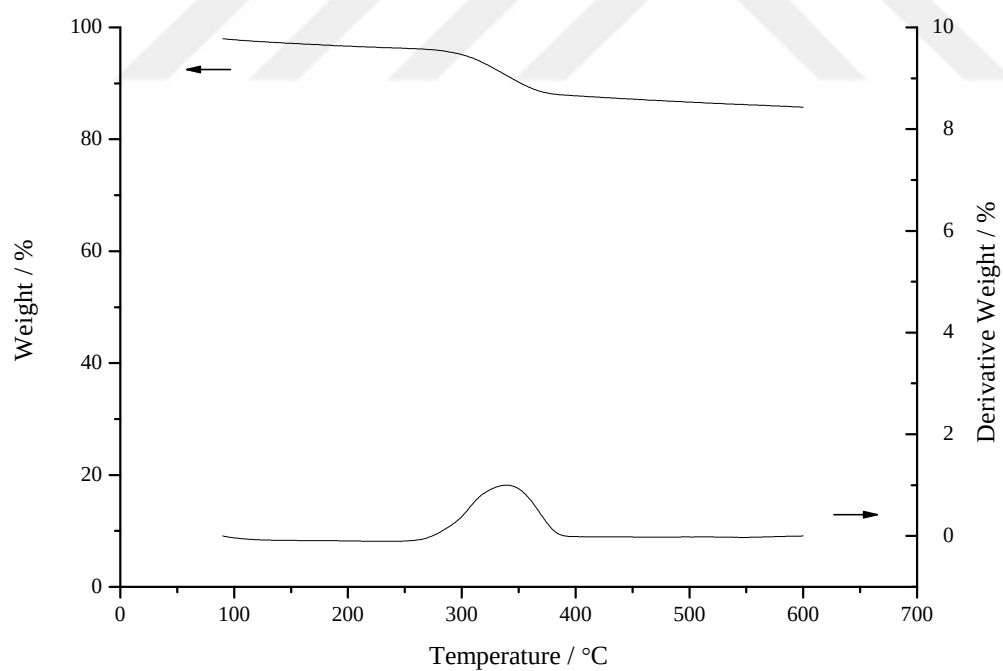


Figure A2-13. TG/DTG curve of [DMPIM][Me] on γ -Al₂O₃.

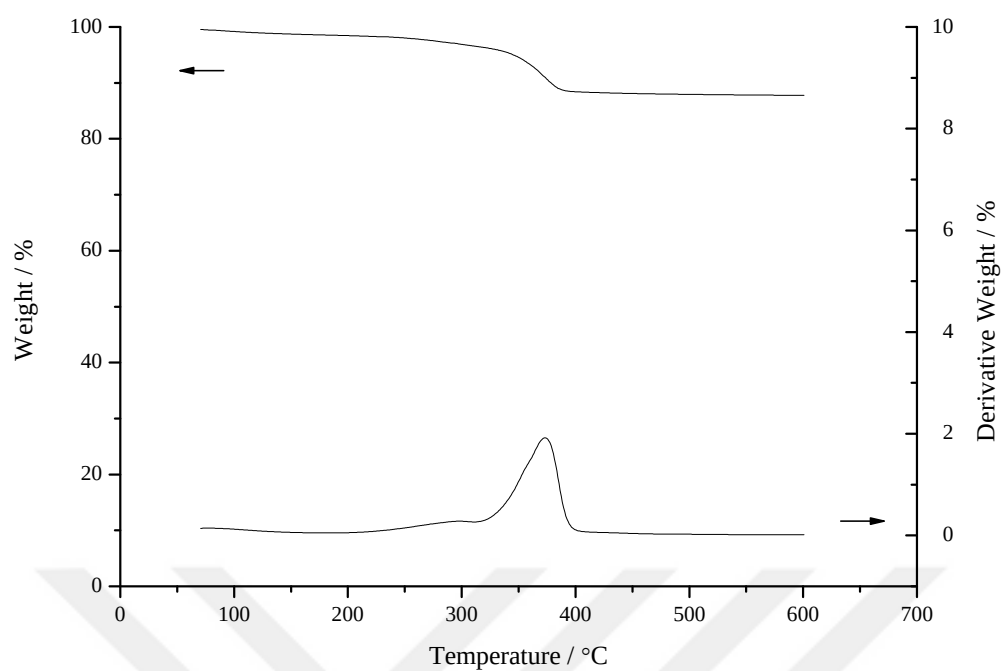


Figure A2-14. TG/DTG curve of [DMPIM][Me] on MgO.

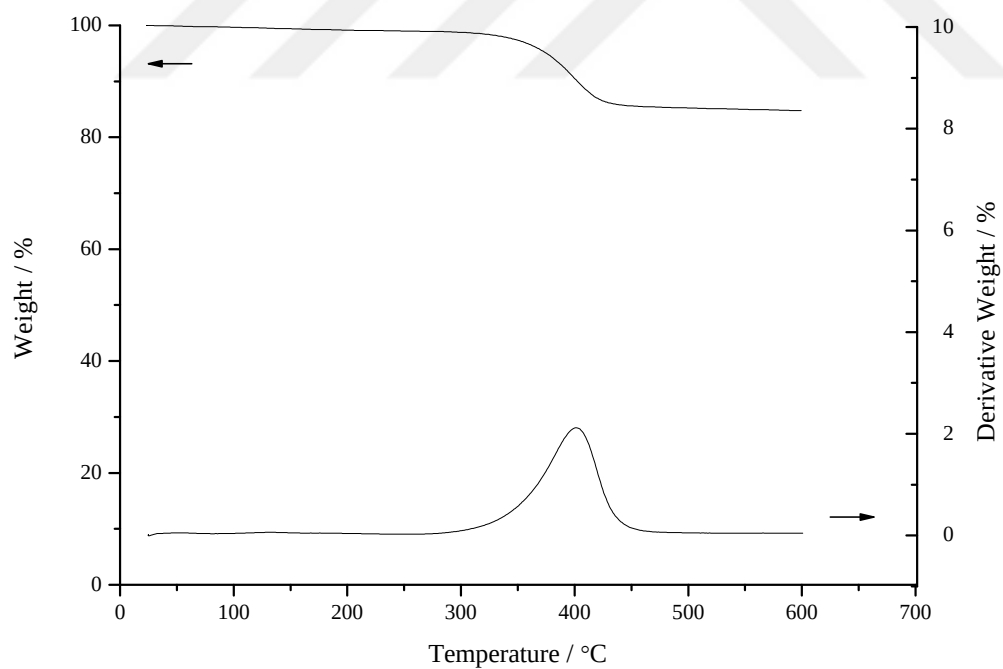


Figure A2-15. TG/DTG curve of [EMIM][BF₄] on SiO₂.

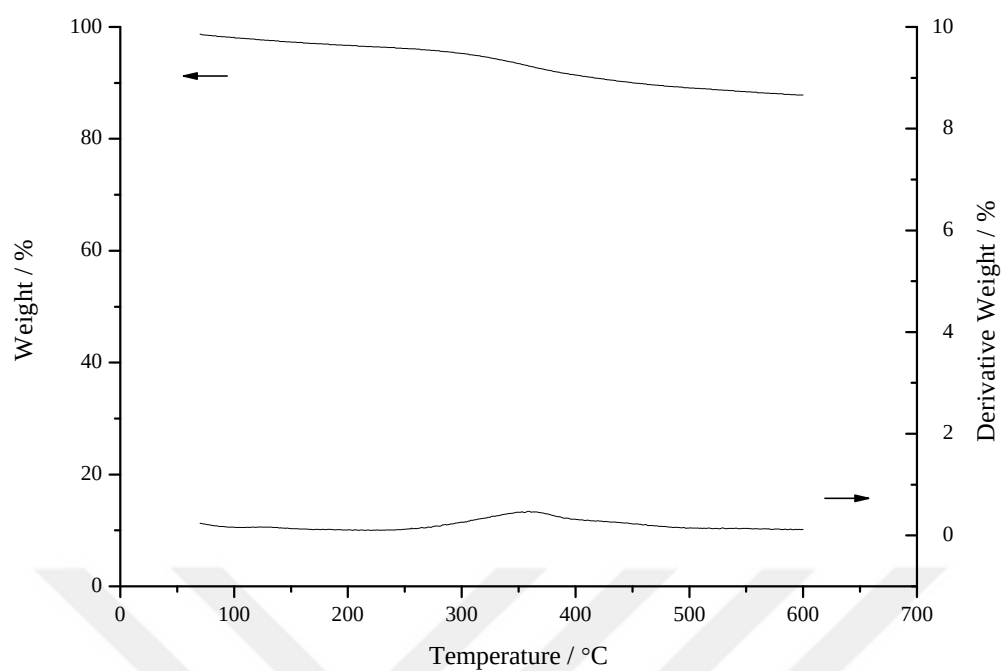


Figure A2-16. TG/DTG curve of [EMIM][BF₄] on γ -Al₂O₃.

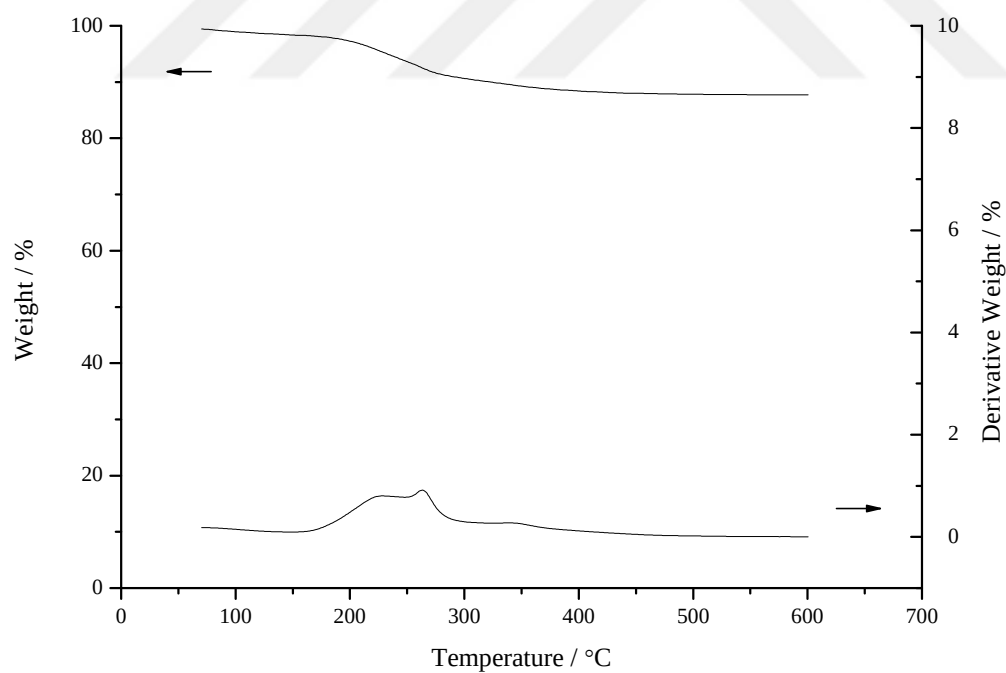


Figure A2-17. TG/DTG curve of [EMIM][BF₄] on MgO.

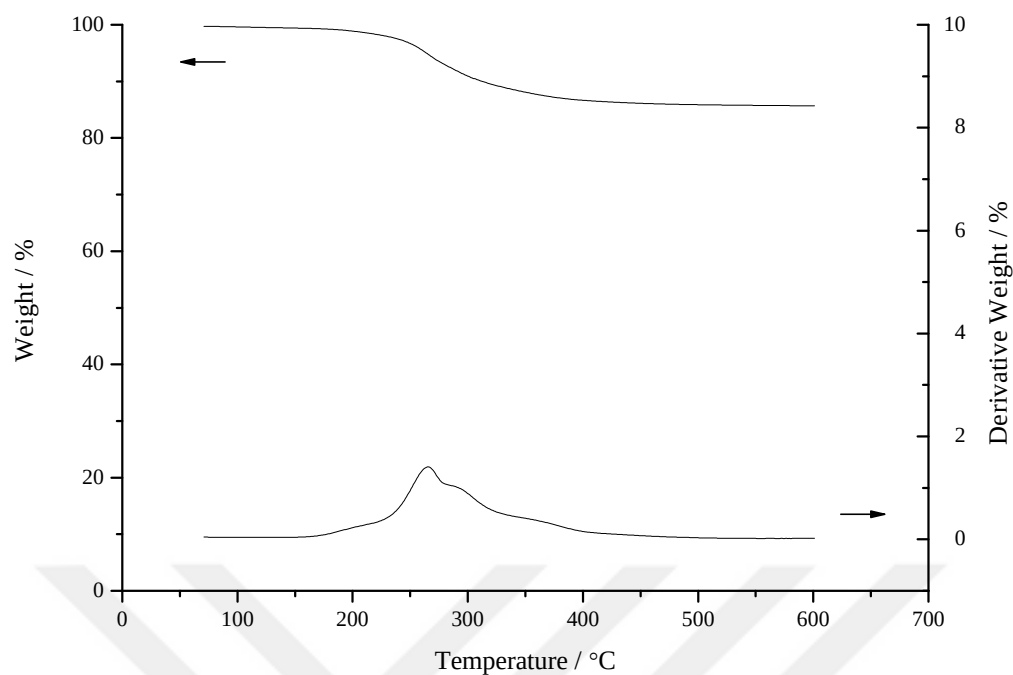


Figure A2-18. TG/DTG curve of [EMIM][DEP] on SiO₂.

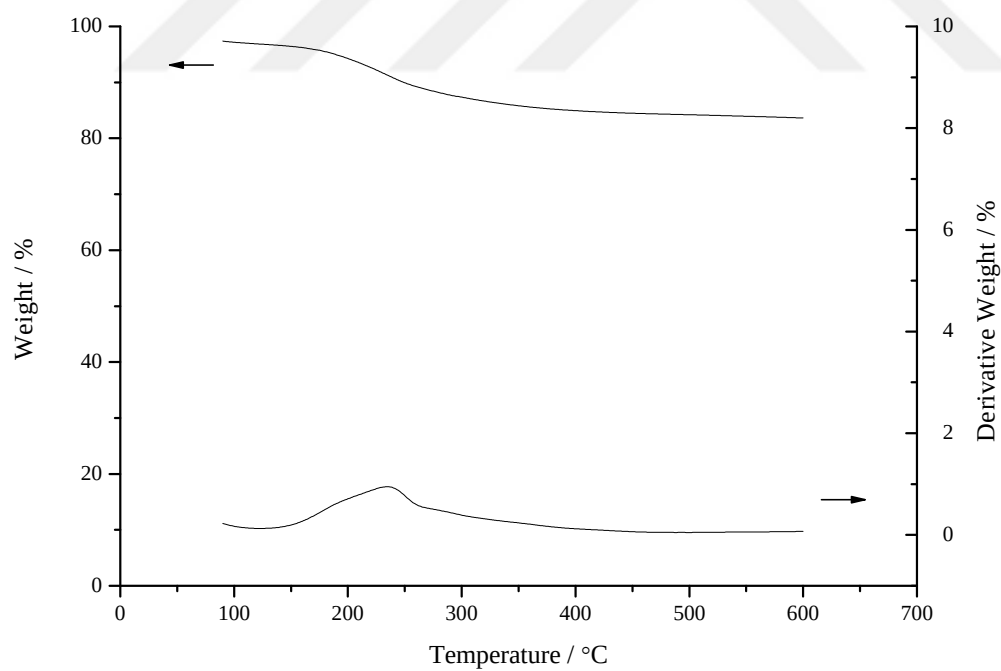


Figure A2-19. TG/DTG curve of [EMIM][DEP] on γ-Al₂O₃.

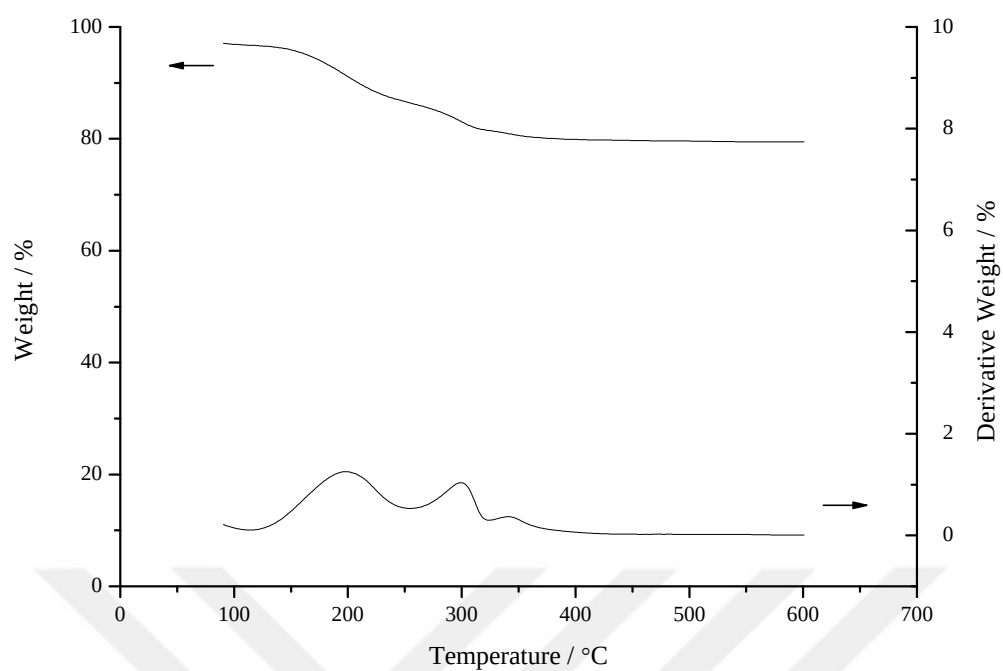


Figure A2-20. TG/DTG curve of [EMIM][DEP] on MgO.

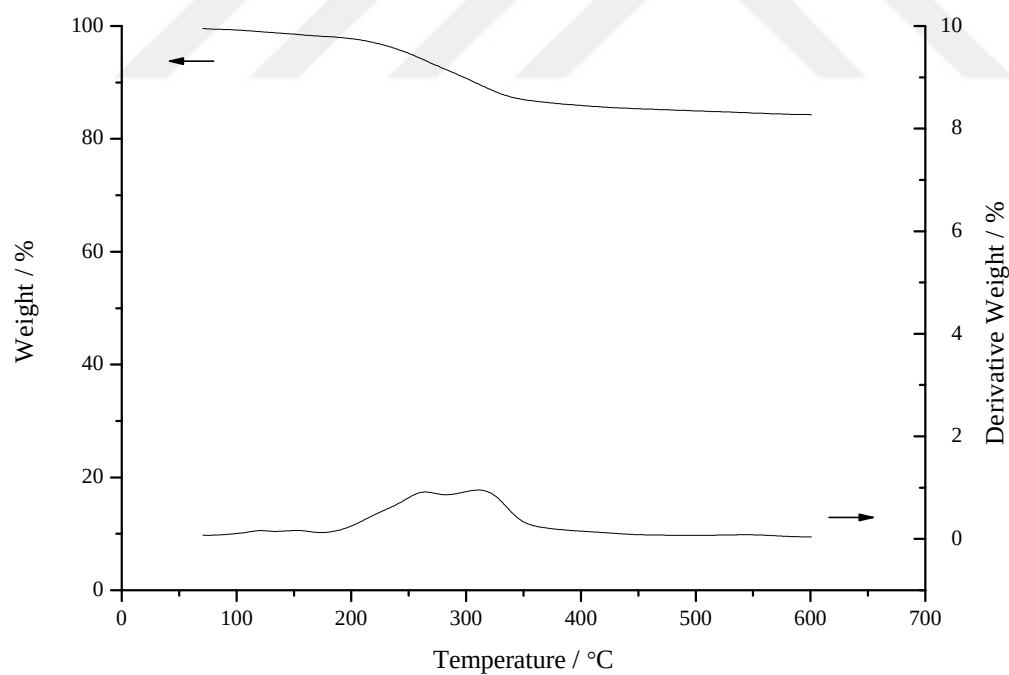


Figure A2-21. TG/DTG curve of [EMIM][LAC] on SiO₂.

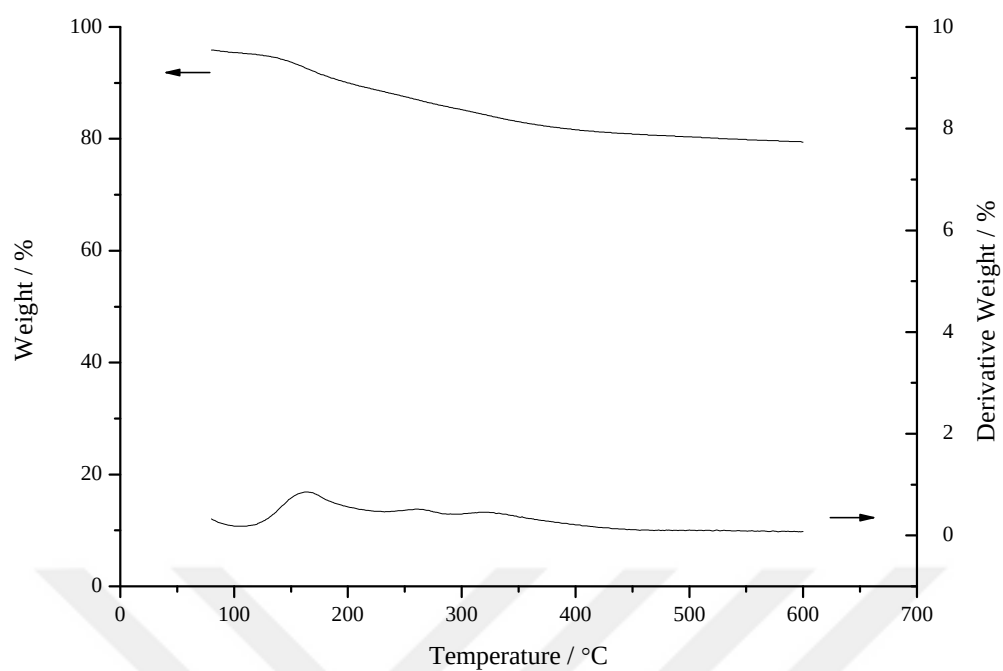


Figure A2-22. TG/DTG curve of [EMIM][LAC] on γ - Al_2O_3 .

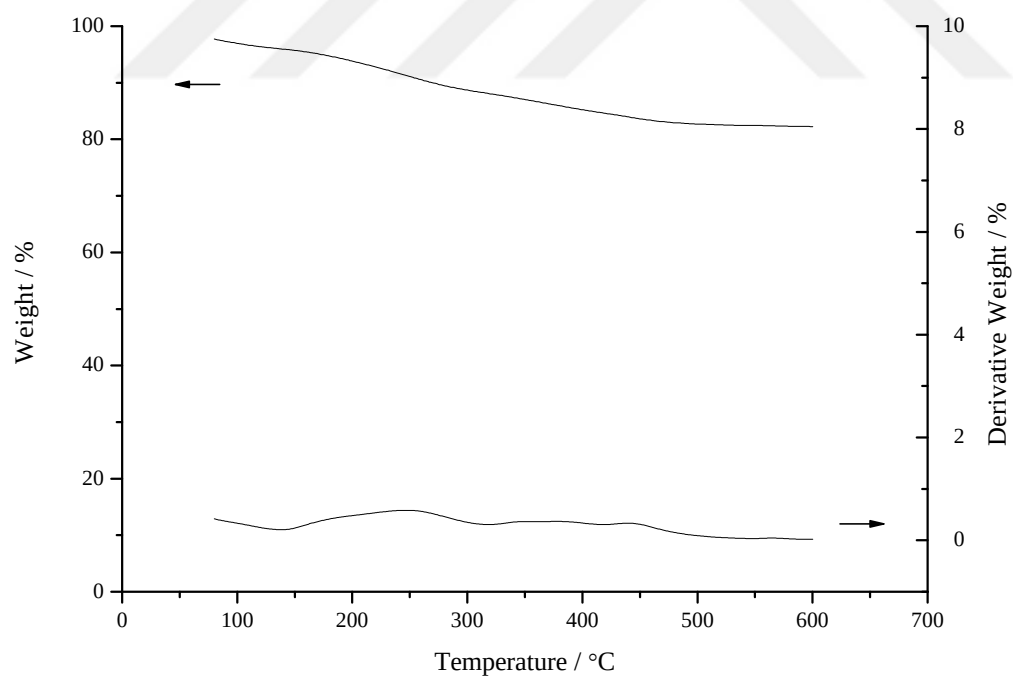


Figure A2-23. TG/DTG curve of [EMIM][LAC] on MgO .

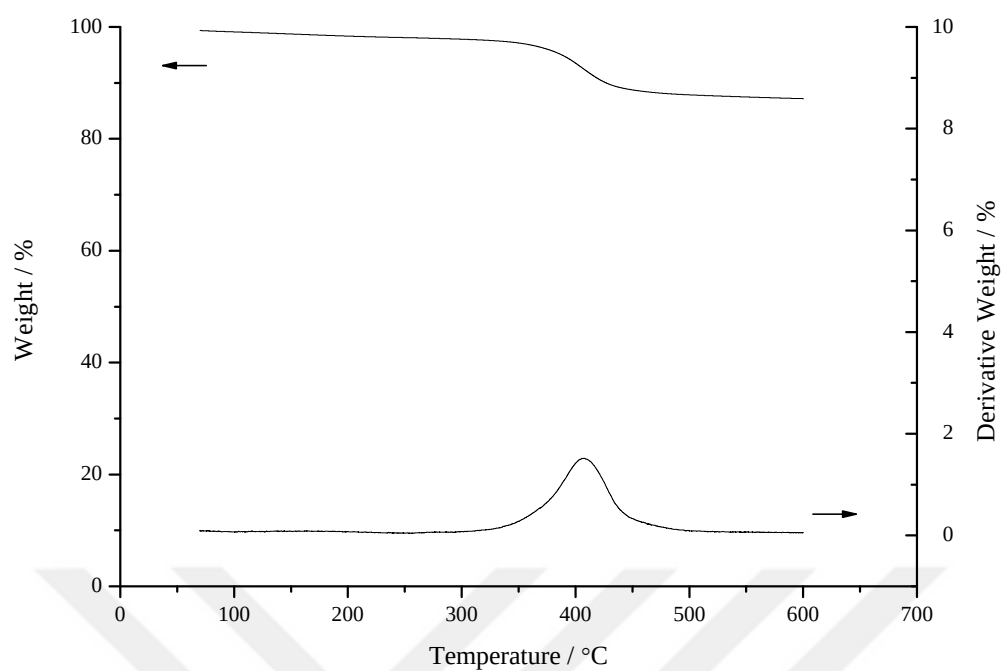


Figure A2-24. TG/DTG curve of [EMIM][EtSO₄] on SiO₂.

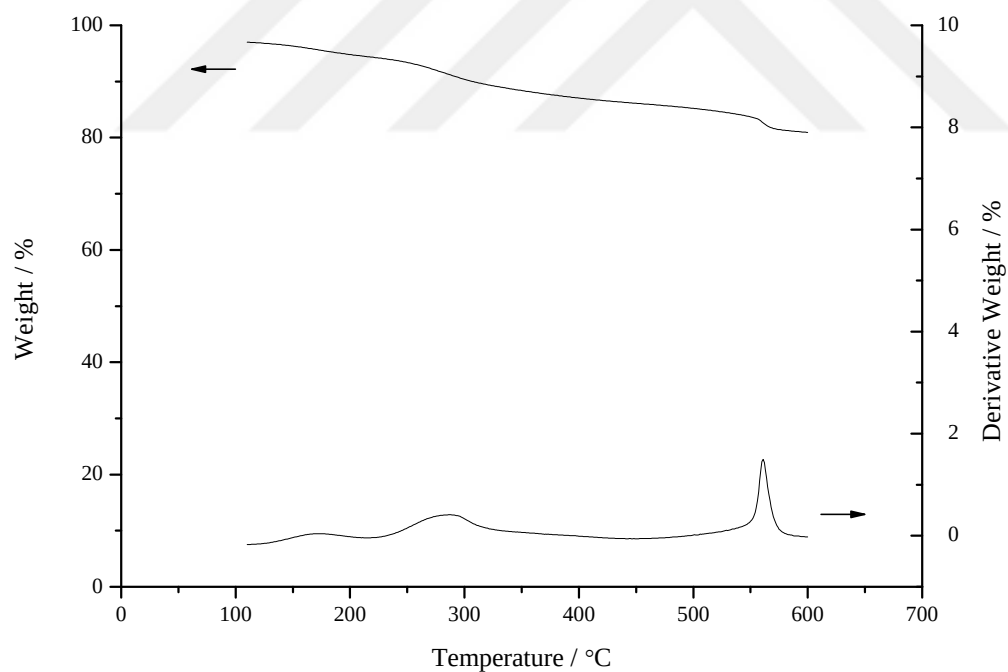


Figure A2-25. TG/DTG curve of [EMIM][EtSO₄] on γ -Al₂O₃.

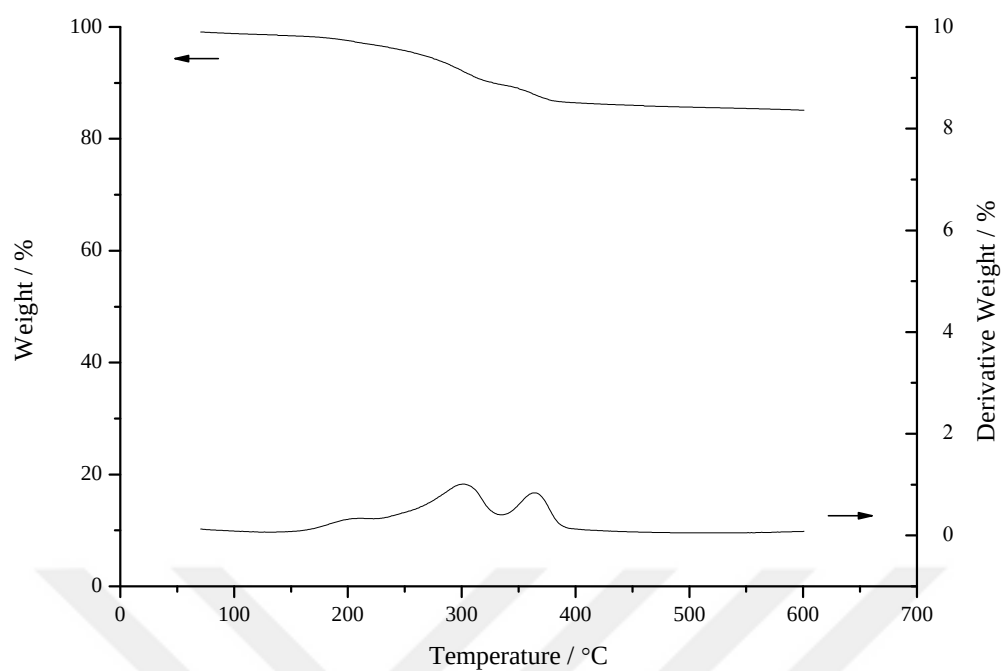


Figure A2-26. TG/DTG curve of [EMIM][EtSO₄] on MgO.

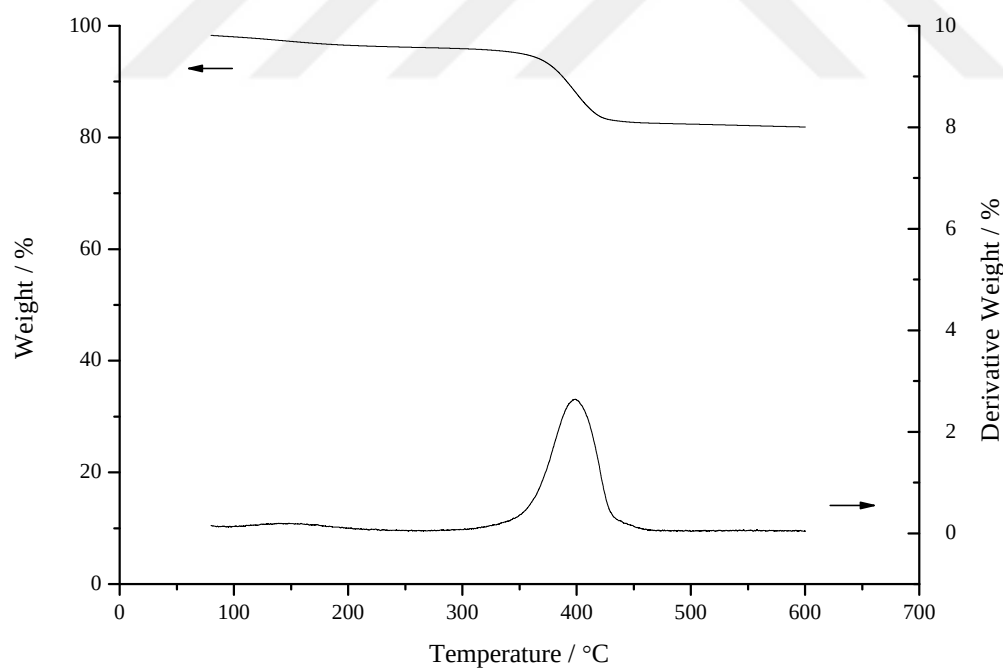


Figure A2-27. TG/DTG curve of [EMIM][MSO₄] on SiO₂.

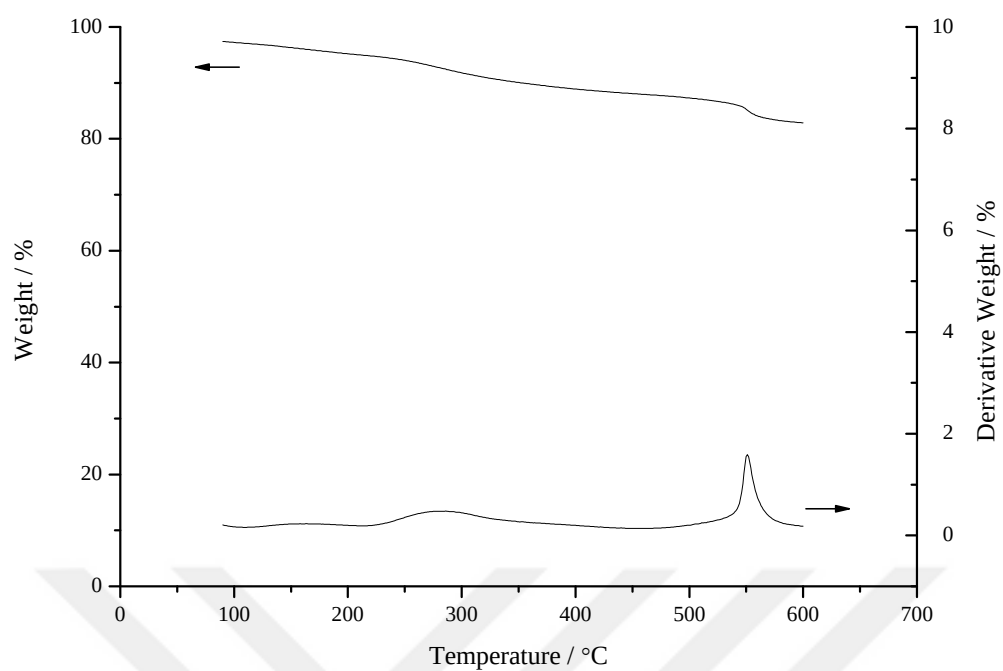


Figure A2-28. TG/DTG curve of [EMIM][MSO₄] on γ -Al₂O₃.

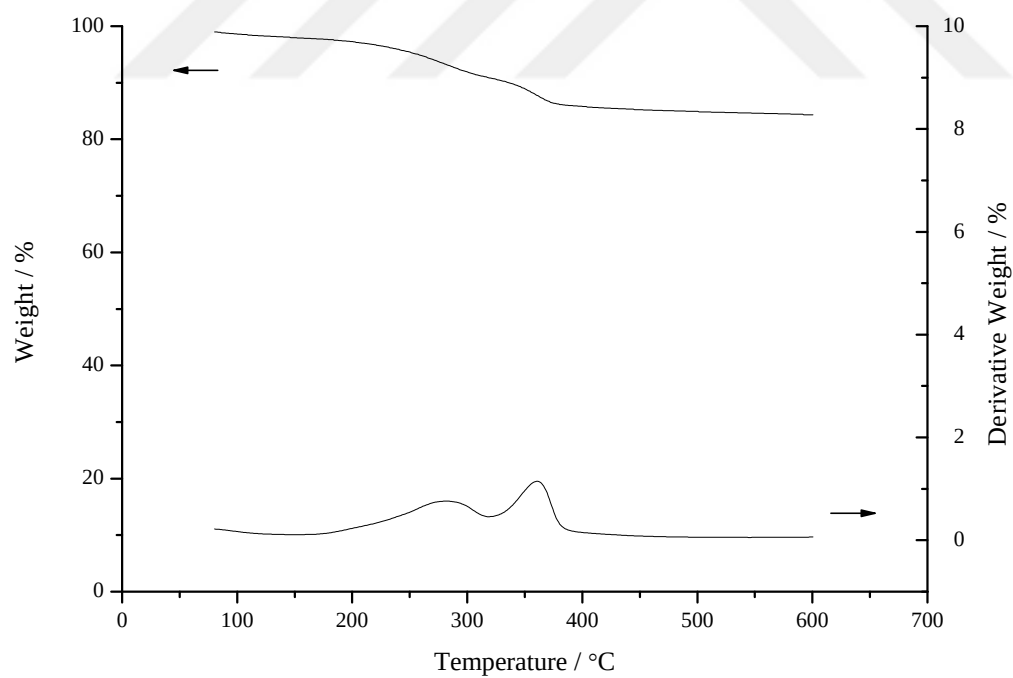


Figure A2-29. TG/DTG curve of [EMIM][MSO₄] on MgO.

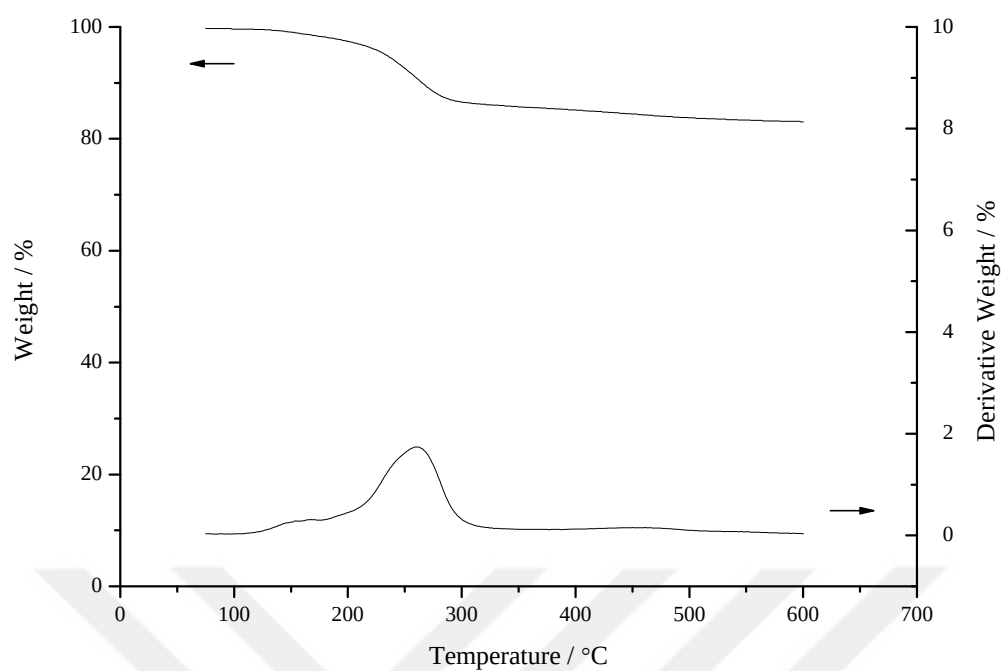


Figure A2-30. TG/DTG curve of [EMIM][DCA] on SiO₂

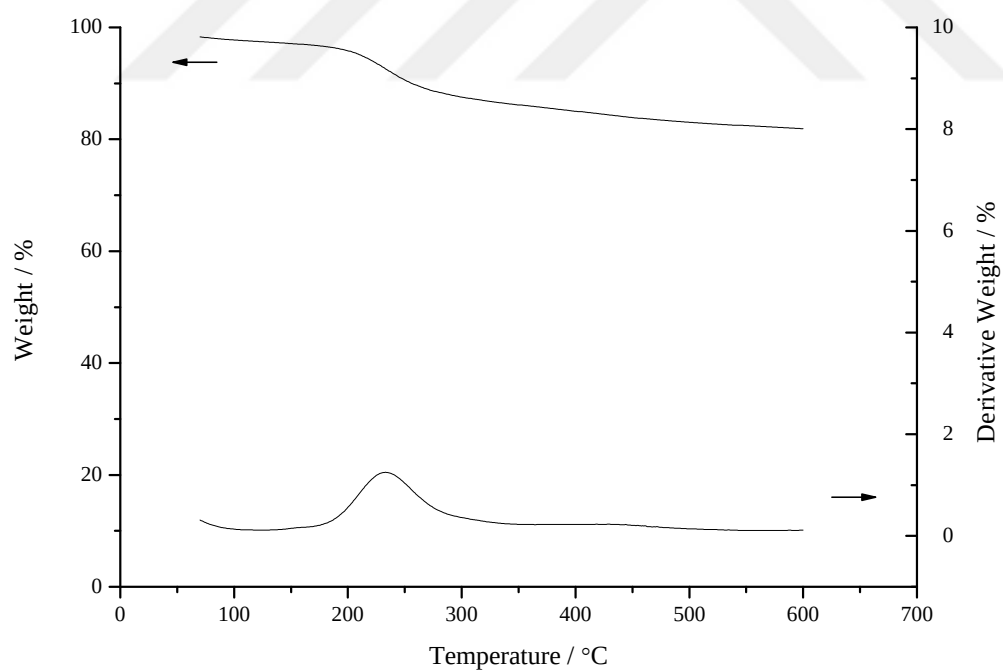


Figure A2-31. TG/DTG curve of [EMIM][DCA] on γ -Al₂O₃.

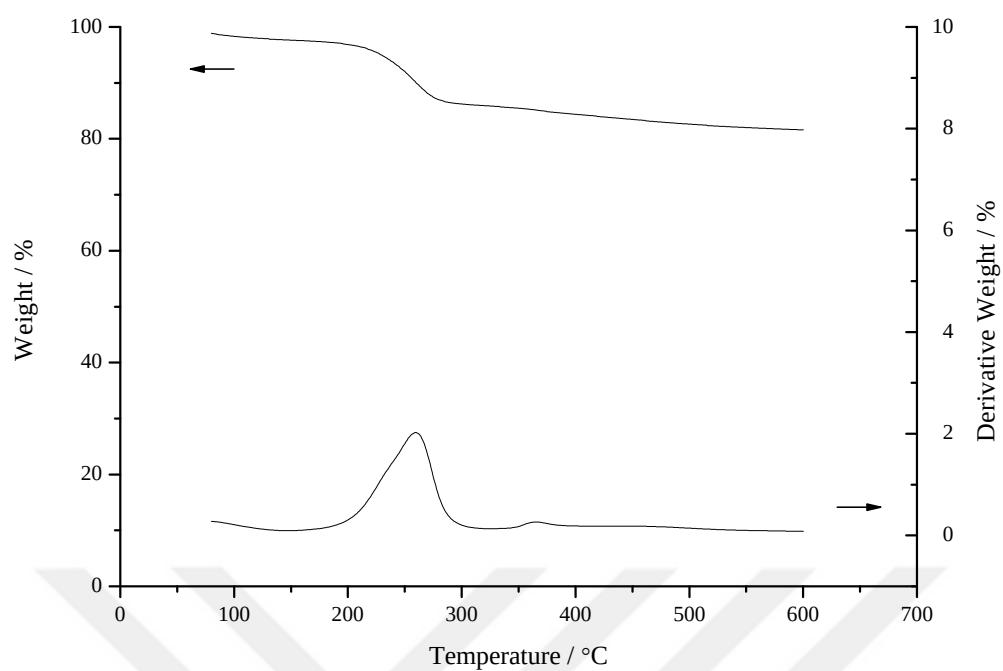


Figure A2-32. TG/DTG curve of [EMIM][DCA] on MgO.

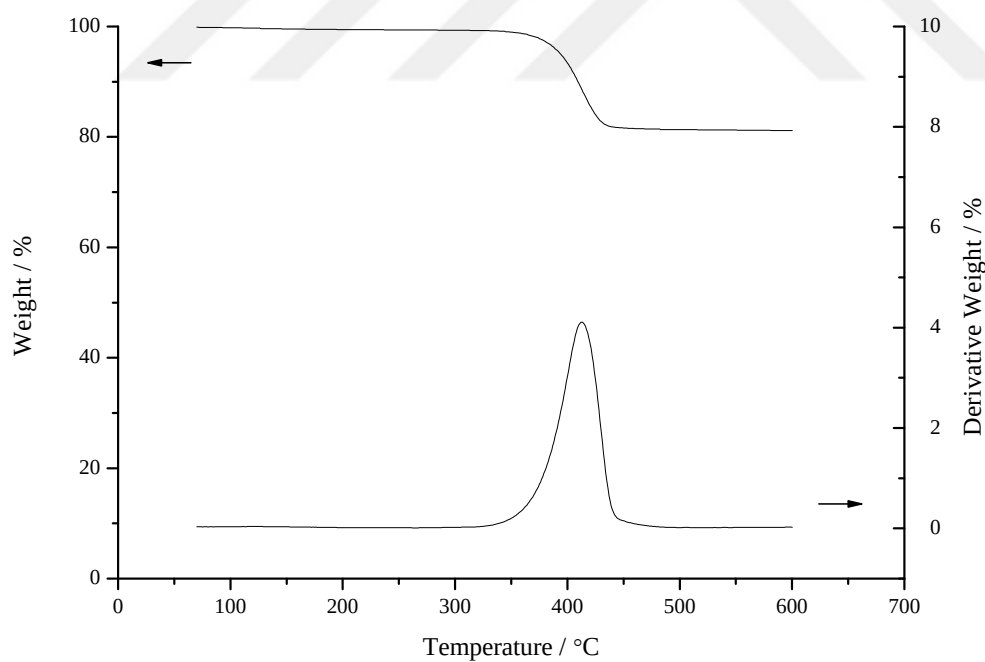


Figure A2-33. TG/DTG curve of [EMIM][TfO] on SiO₂.

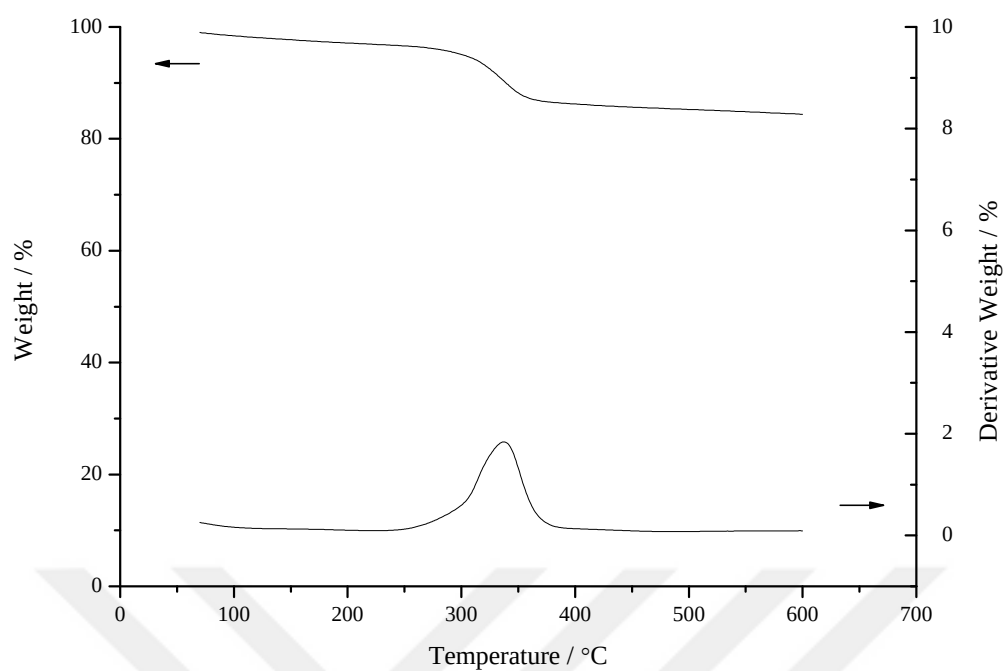


Figure A2-34. TG/DTG curve of [EMIM][TfO] on γ -Al₂O₃.

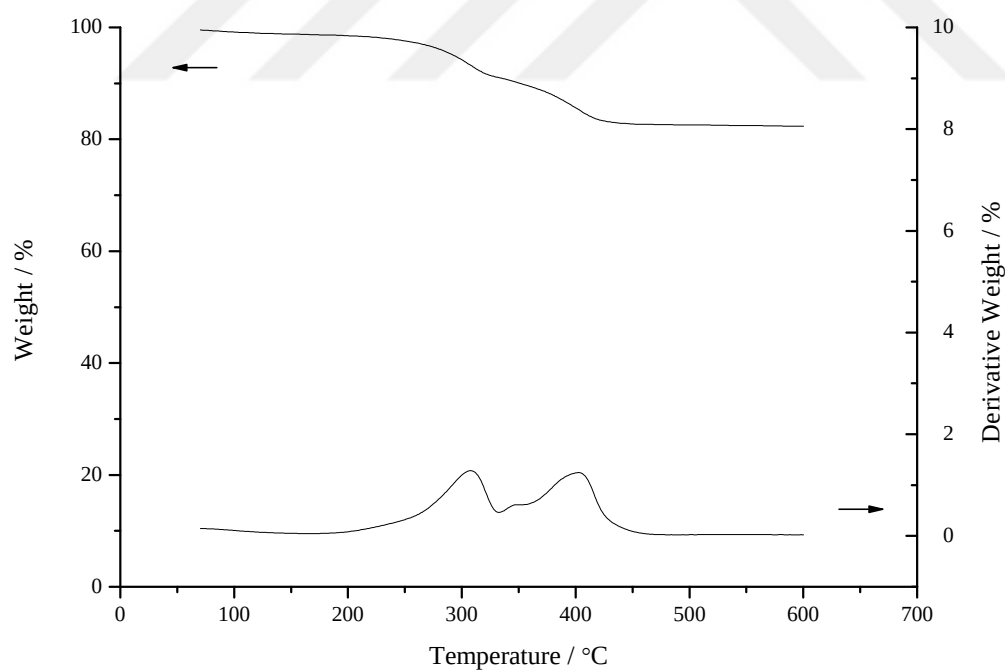


Figure A2-35. TG/DTG curve of [EMIM][TfO] on MgO.

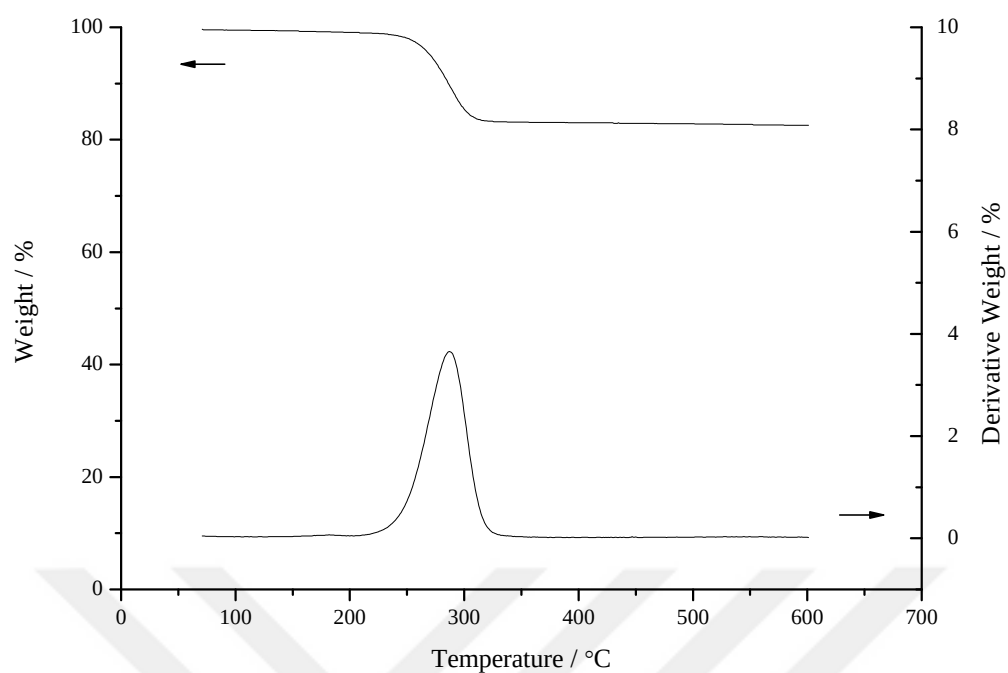


Figure A2-36. TG/DTG curve of [EMIM][SCN] on SiO₂.

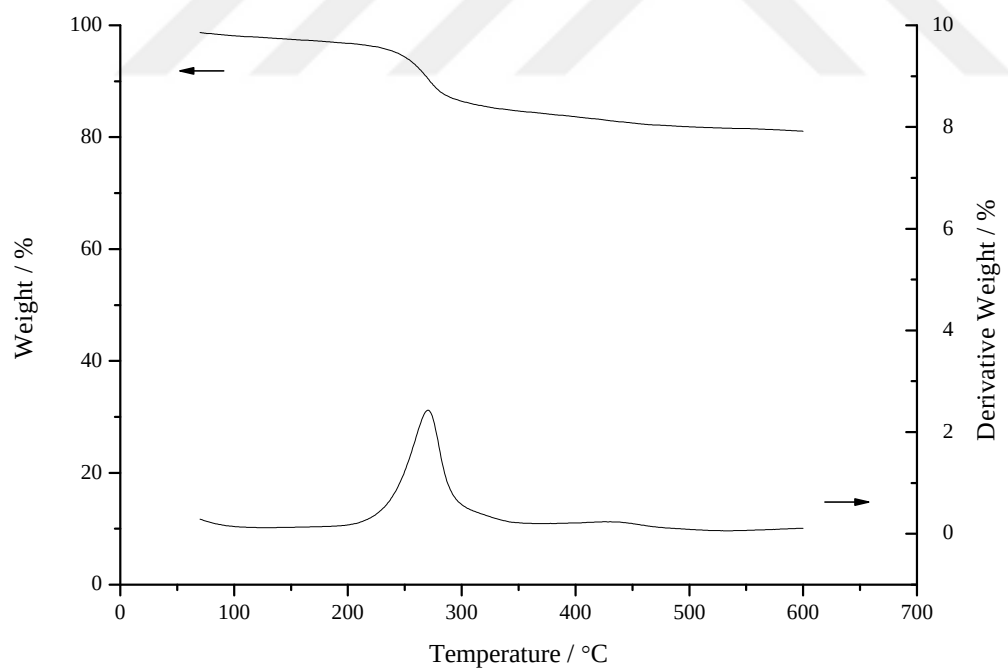


Figure A2-37. TG/DTG curve of [EMIM][SCN] on γ -Al₂O₃.

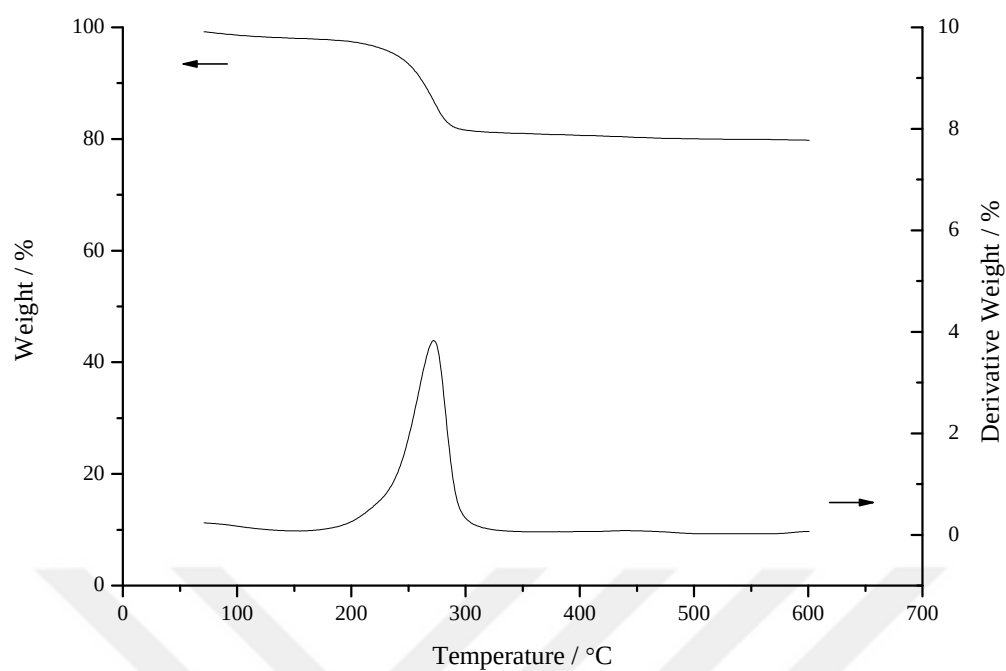


Figure A2-38. TG/DTG curve of [EMIM][SCN] on MgO.

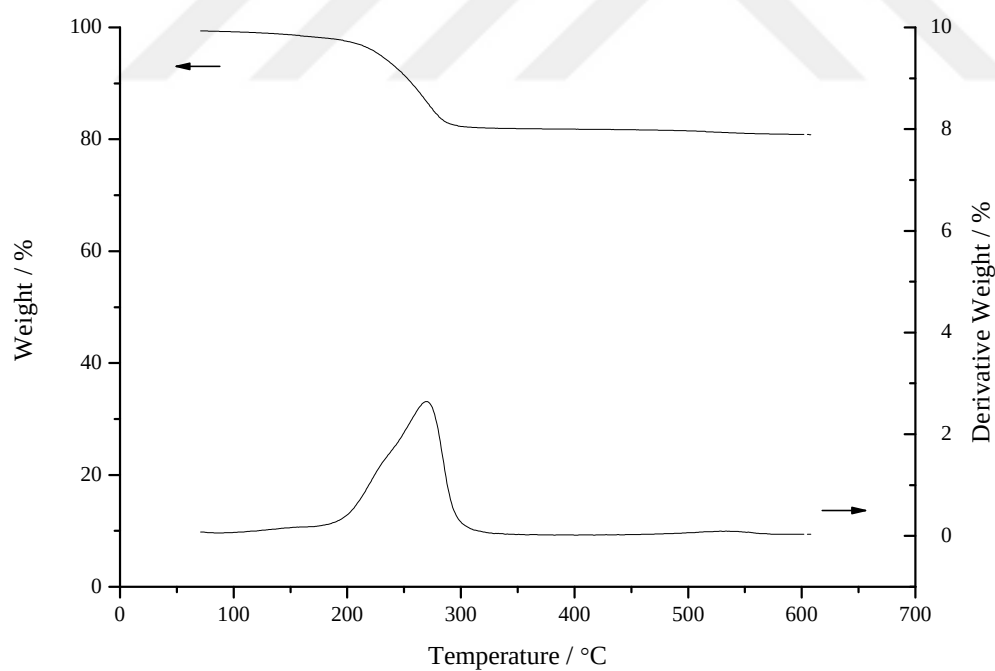


Figure A2-39. TG/DTG curve of [BMIM][Ac] on SiO₂.

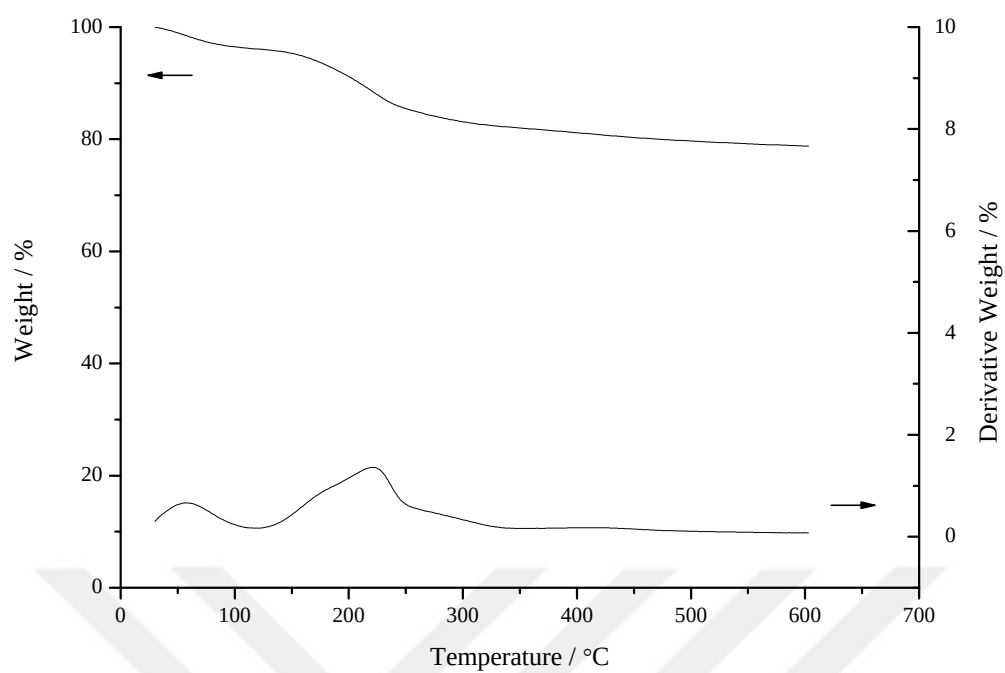


Figure A2-40. TG/DTG curve of [BMIM][Ac] on γ -Al₂O₃.

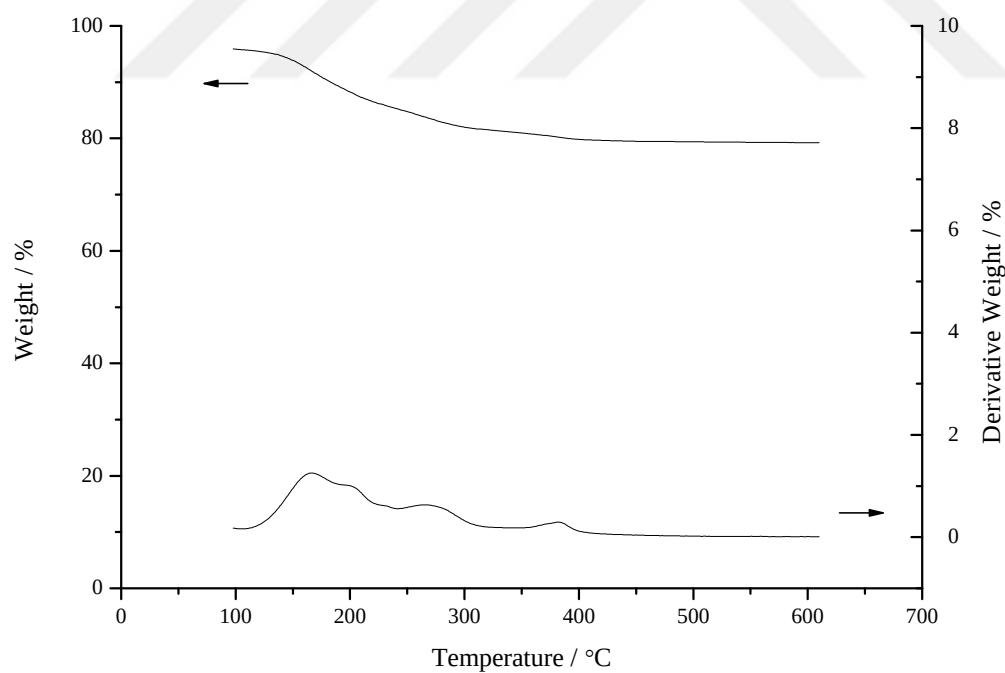


Figure A2-41. TG/DTG curve of [BMIM][Ac] on MgO.

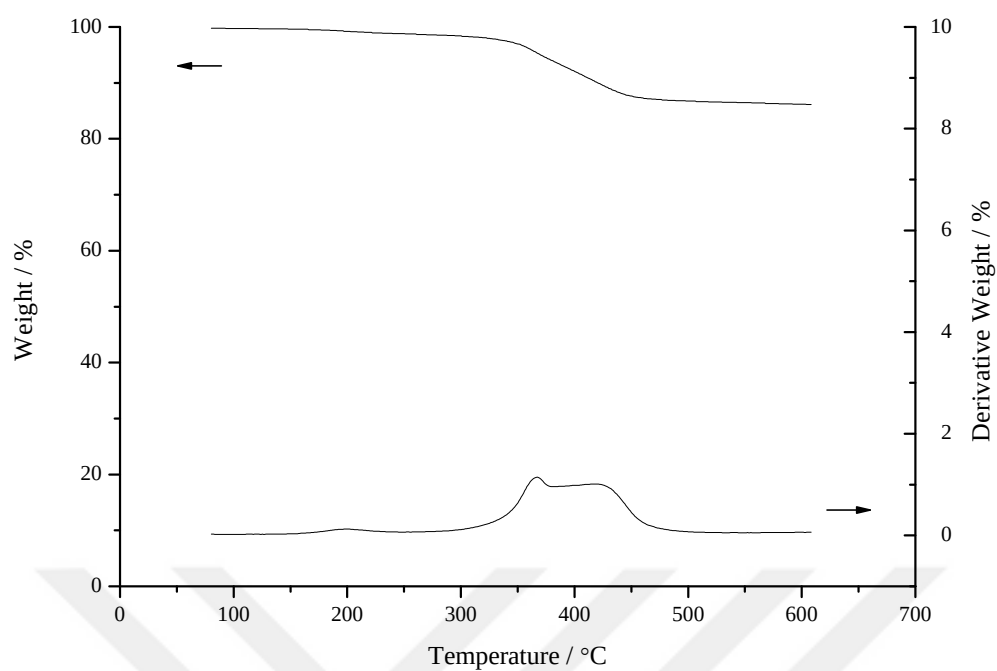


Figure A2-42. TG/DTG curve of [BMIM][SbF₆] on SiO₂.

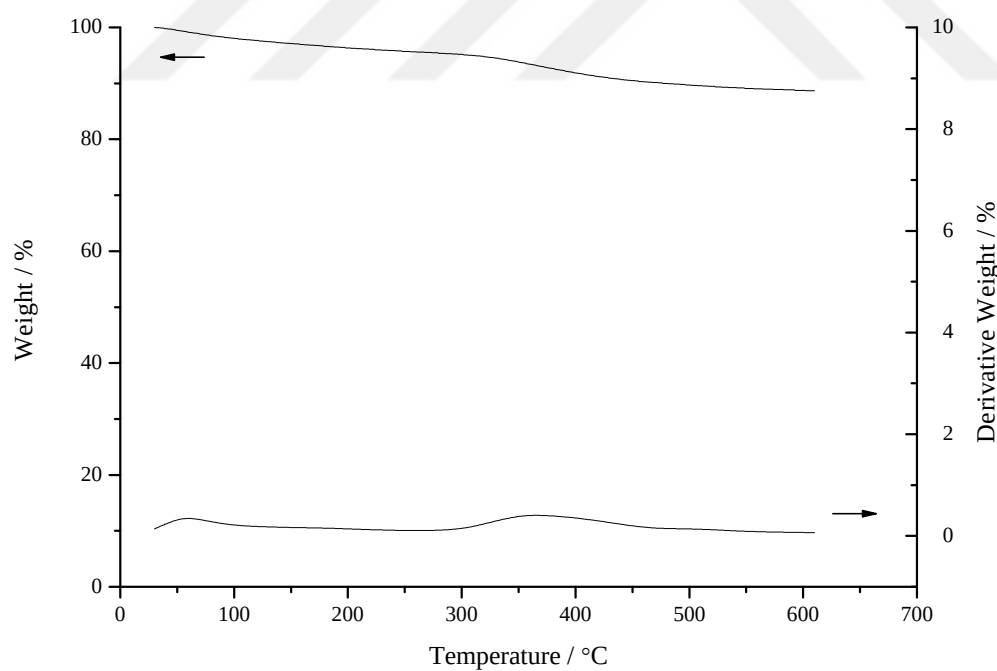


Figure A2-43. TG/DTG curve of [BMIM][SbF₆] on γ -Al₂O₃.

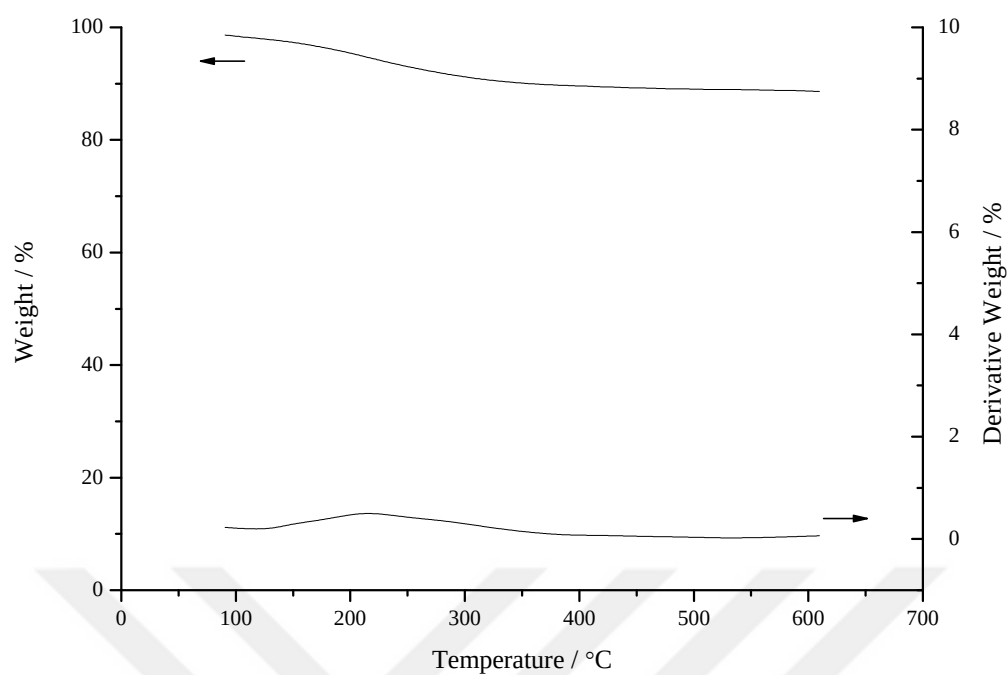


Figure A2-44. TG/DTG curve of [BMIM][SbF₆] on MgO.

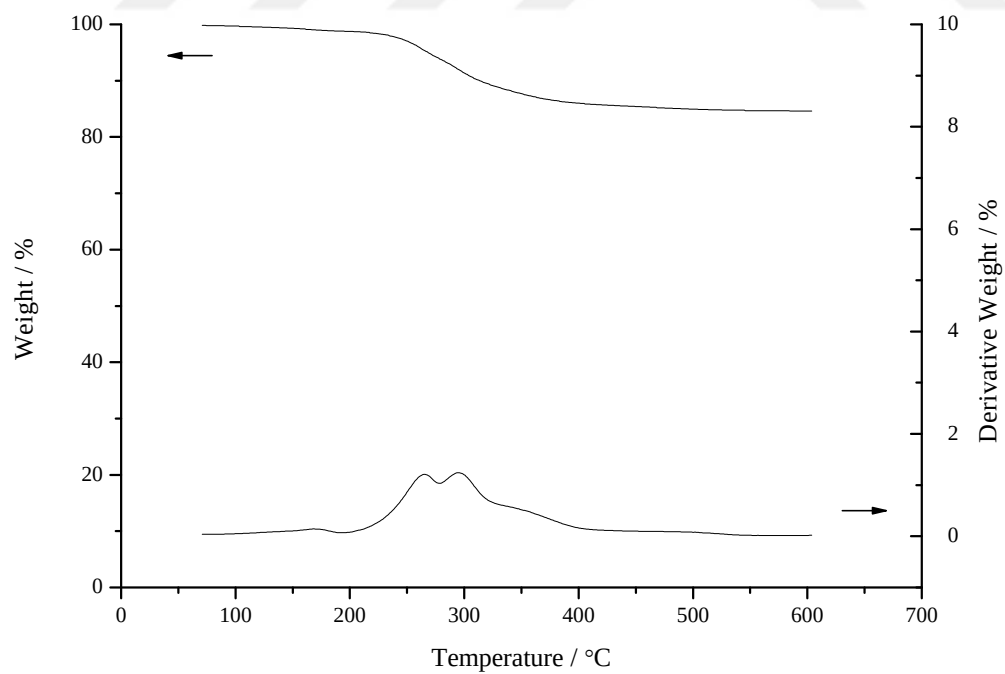


Figure A2-45 TG/DTG curve of [BMIM][DBP] on SiO₂.

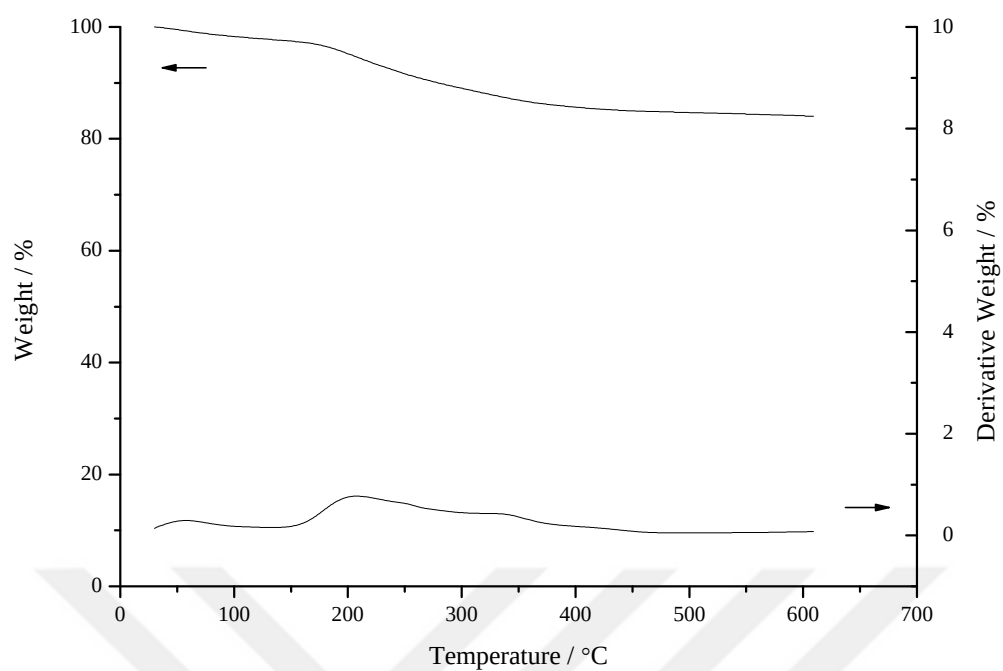


Figure A2-46. TG/DTG curve of [BMIM][DBP] on γ -Al₂O₃.

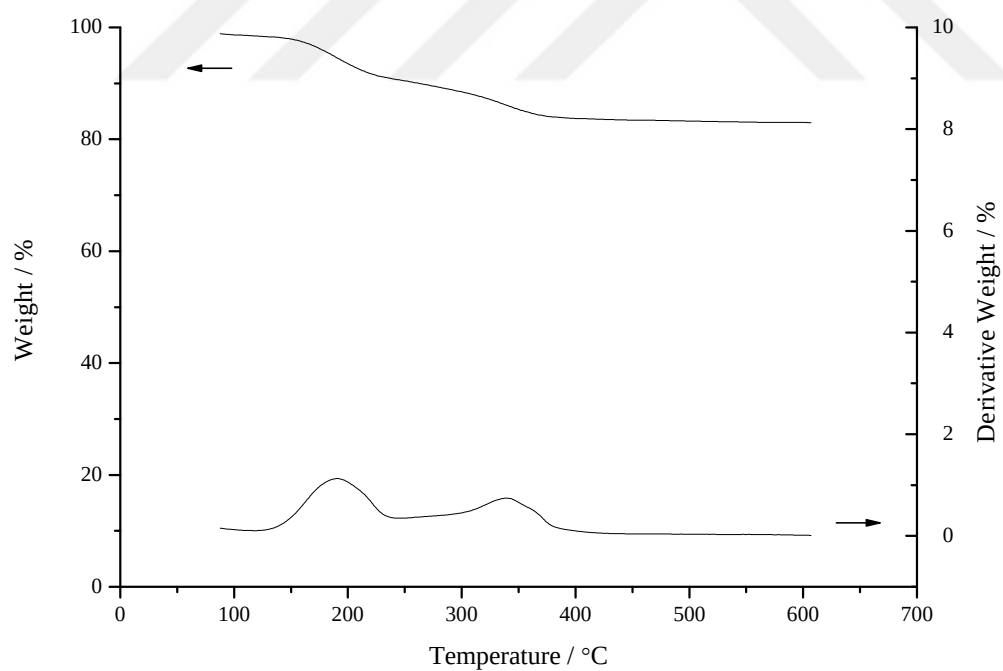


Figure A2-47. TG/DTG curve of [BMIM][DBP] on MgO.

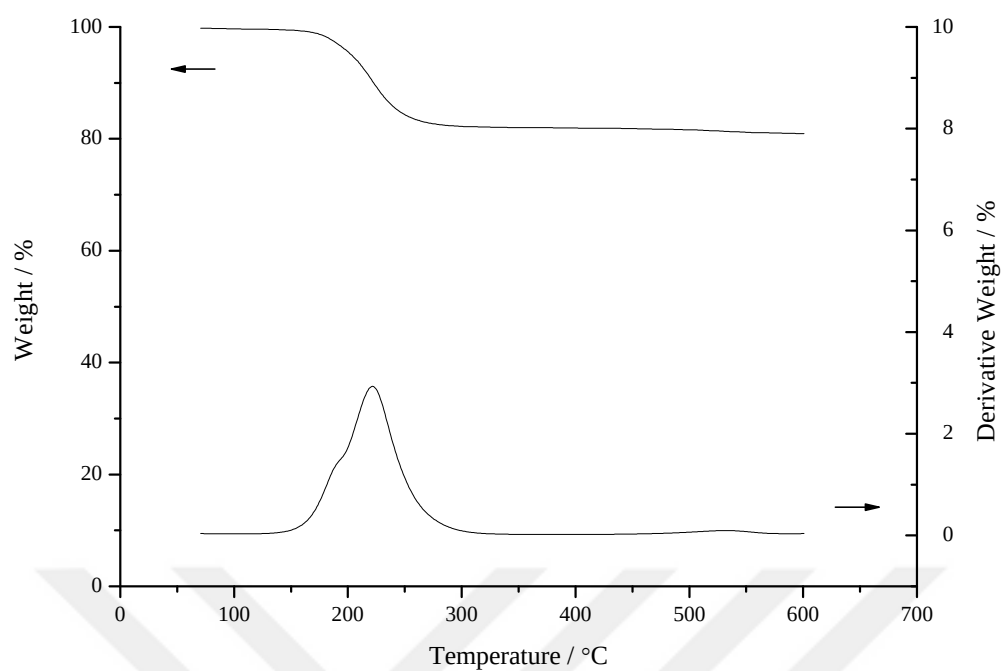


Figure A2-48. TG/DTG curve of [BMIM][TFA] on SiO₂.

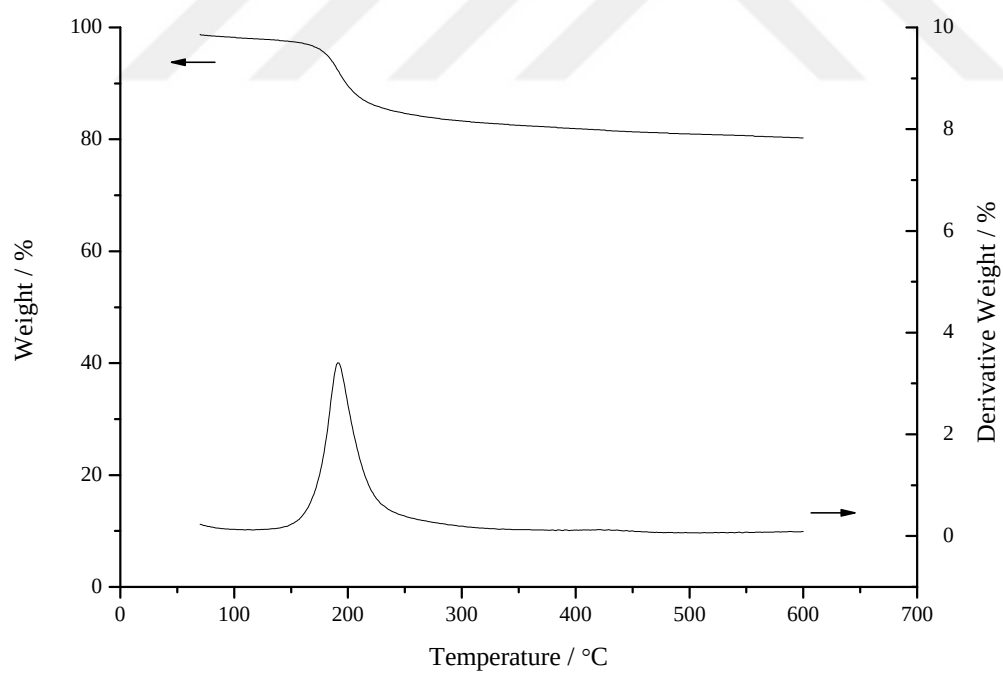


Figure A2-49. TG/DTG curve of [BMIM][TFA] on γ -Al₂O₃.

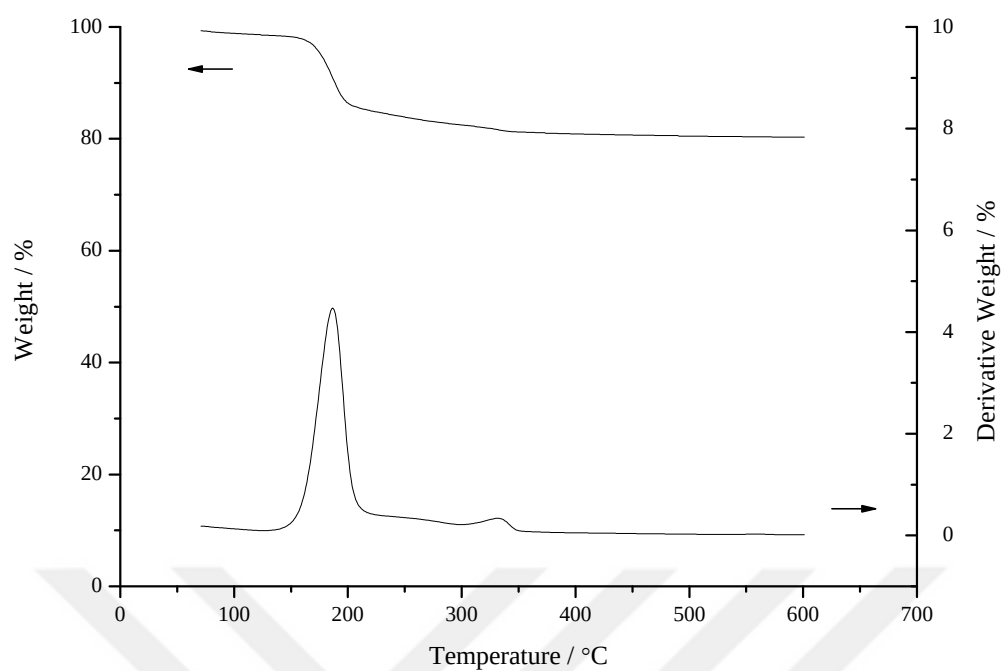


Figure A2-50. TG/DTG curve of [BMIM][TFA] on MgO.

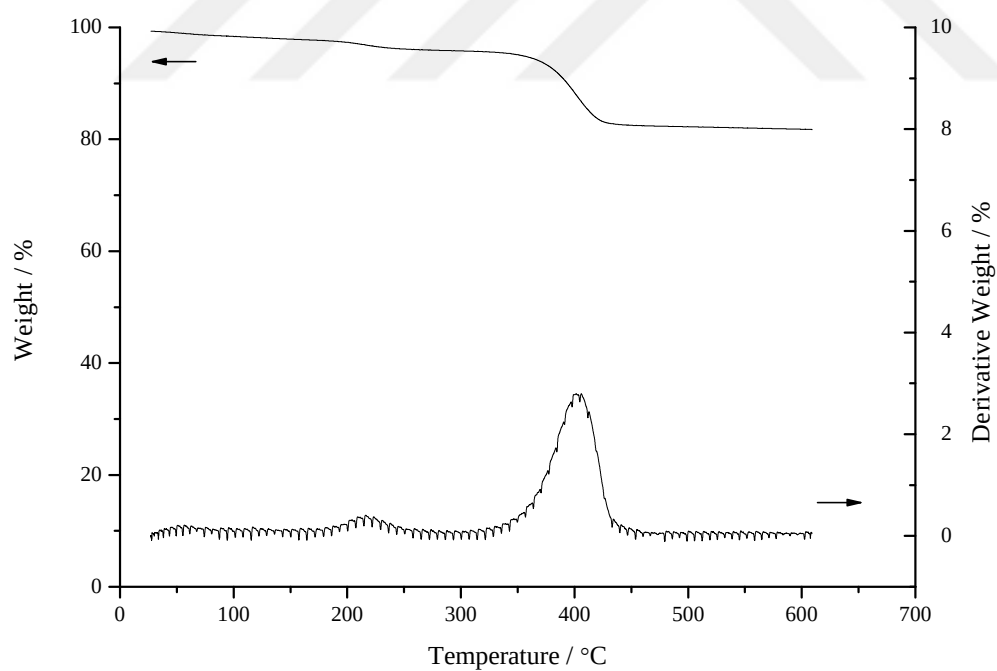


Figure A2-51. TG/DTG curve of [BMIM][HSO₄] on SiO₂.

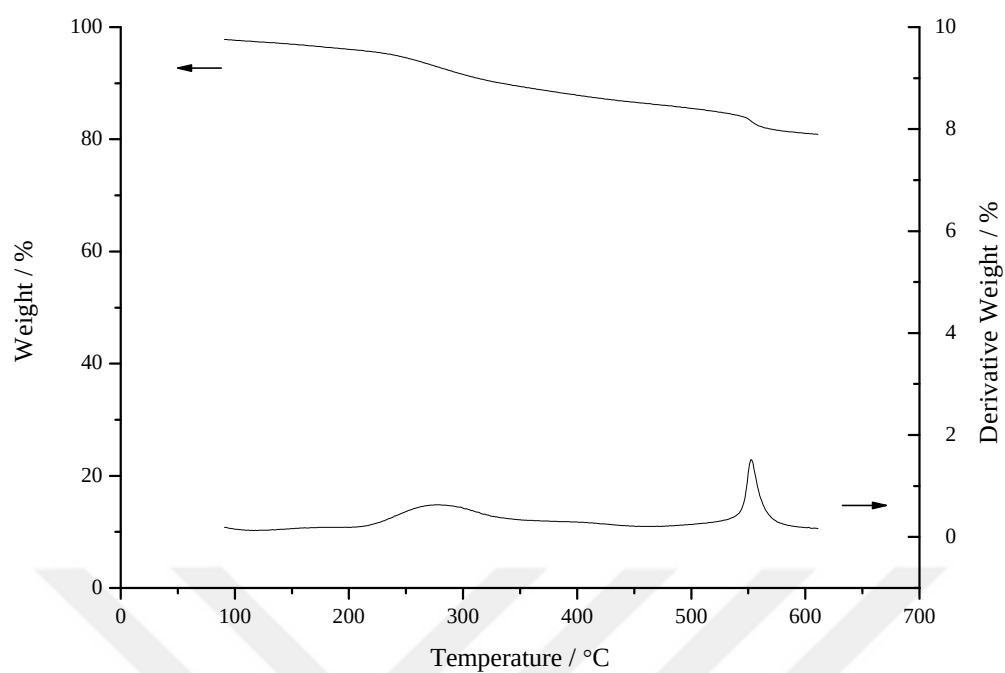


Figure A2-52. TG/DTG curve of [BMIM][HSO₄] on γ -Al₂O₃.

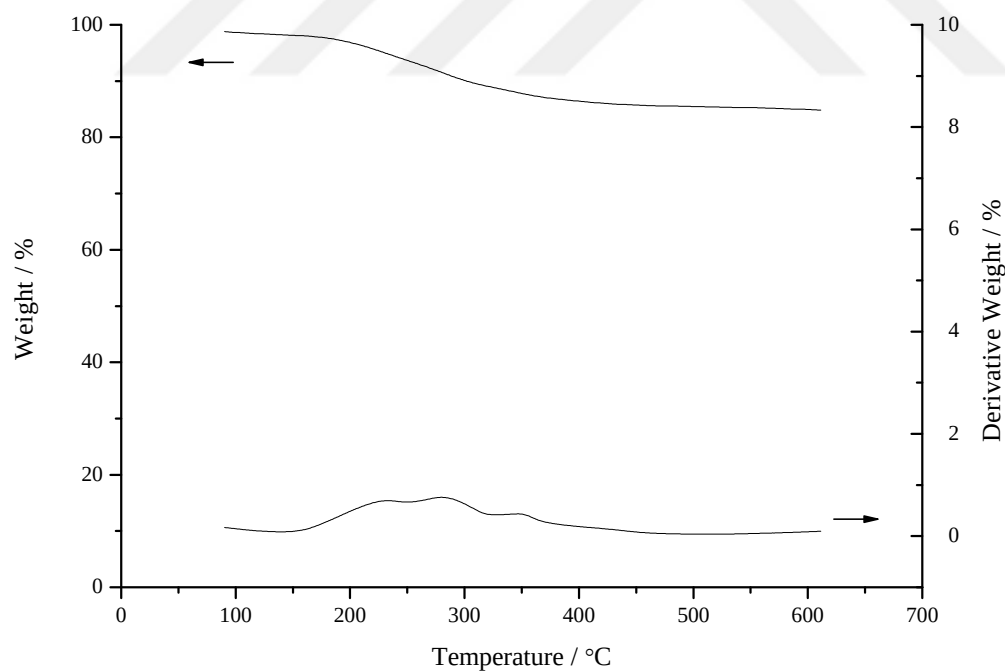


Figure A2-53. TG/DTG curve of [BMIM][HSO₄] on MgO.

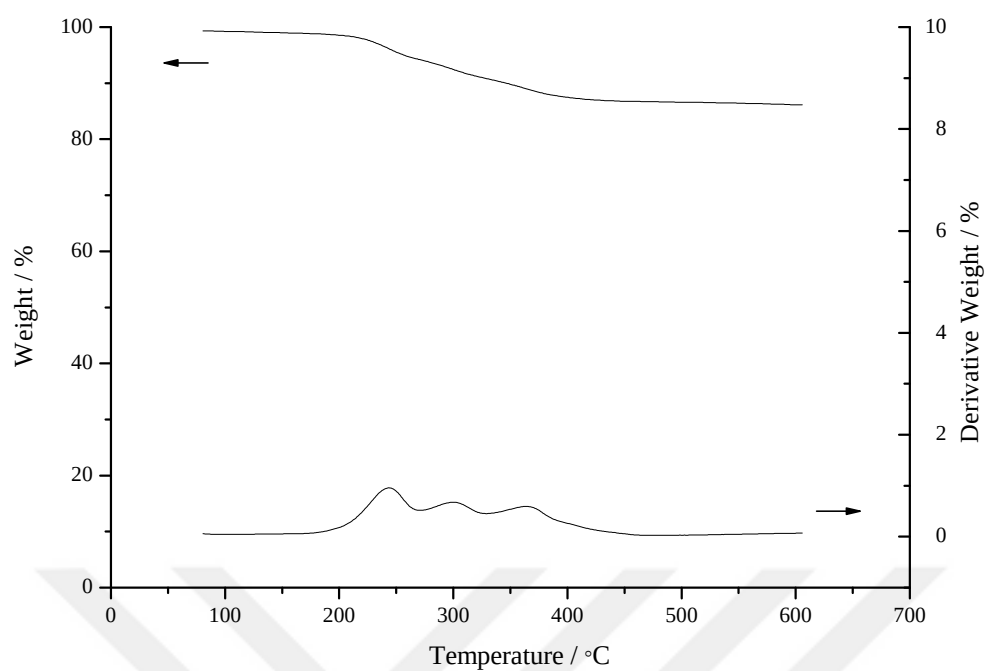


Figure A2-54. TG/DTG curve of [BMIM][BF₄] on SiO₂.

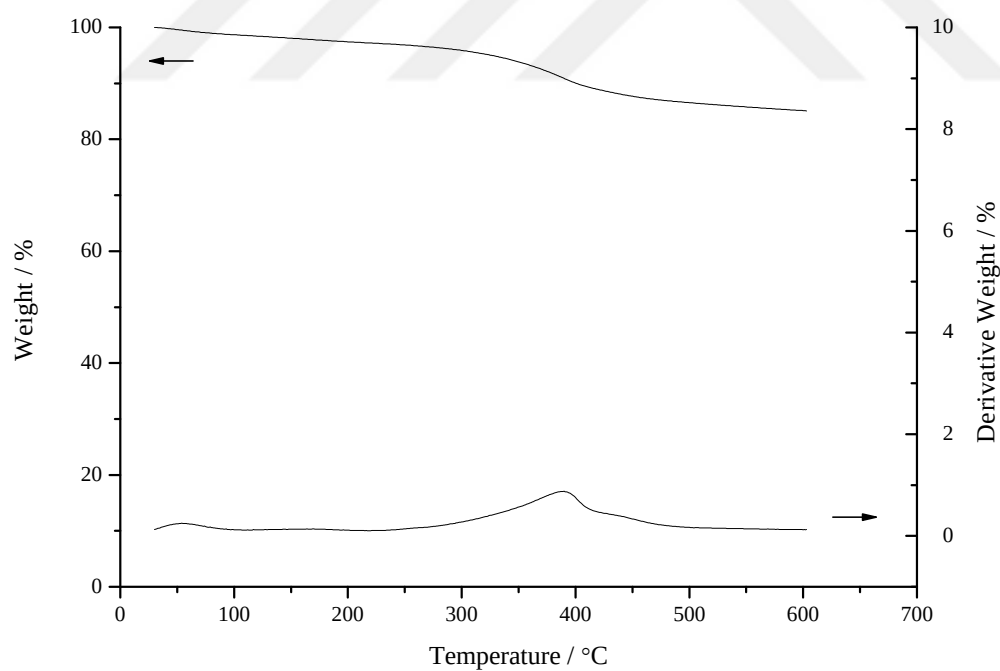


Figure A2-55. TG/DTG curve of [BMIM][BF₄] on γ -Al₂O₃.

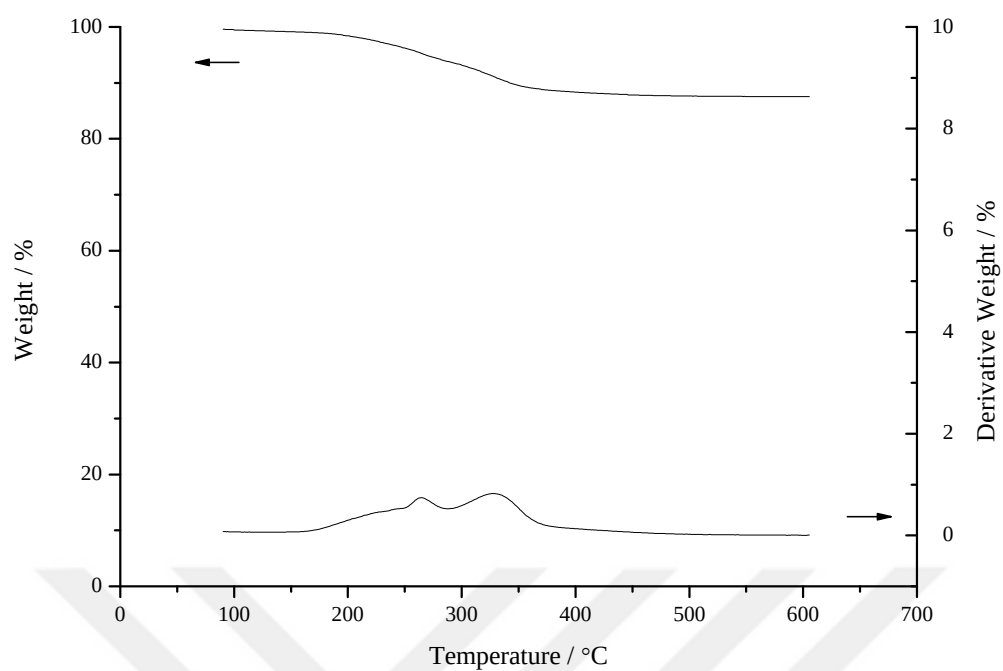


Figure A2-56. TG/DTG curve of [BMIM][BF₄] on MgO.

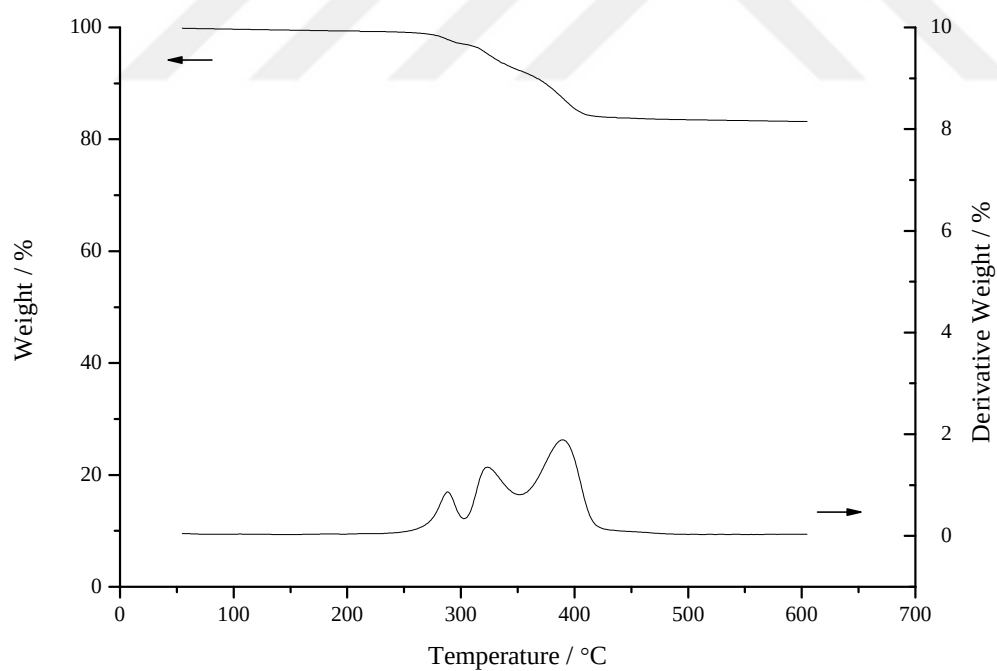


Figure A2-57. TG/DTG curve of [BMIM][OS] on SiO₂.

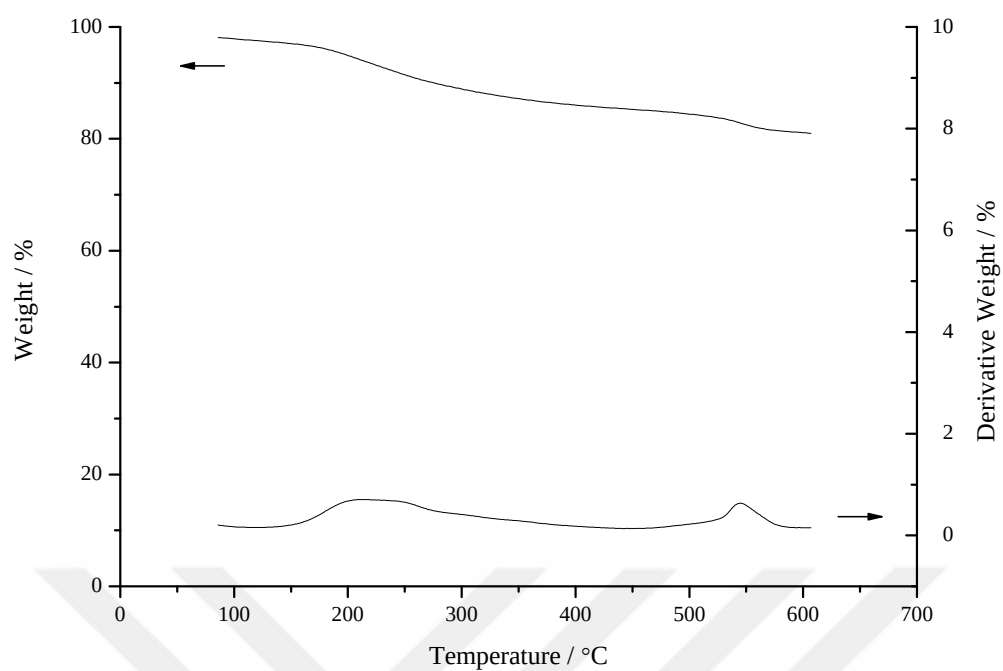


Figure A2-58. TG/DTG curve of [BMIM][OS] on γ -Al₂O₃.

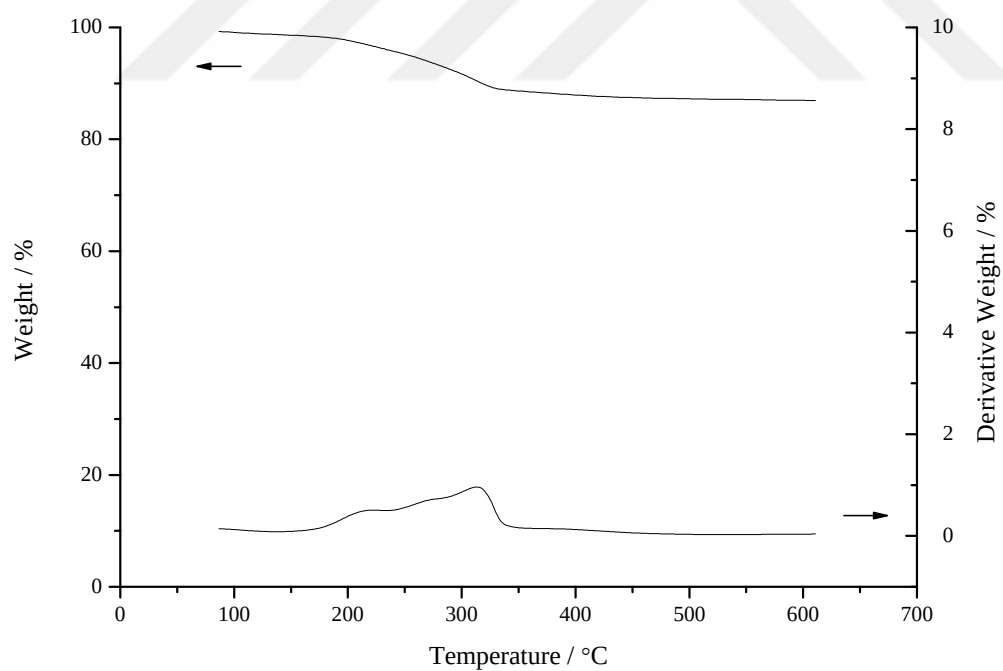


Figure A2-59. TG/DTG curve of [BMIM][OS] on MgO.

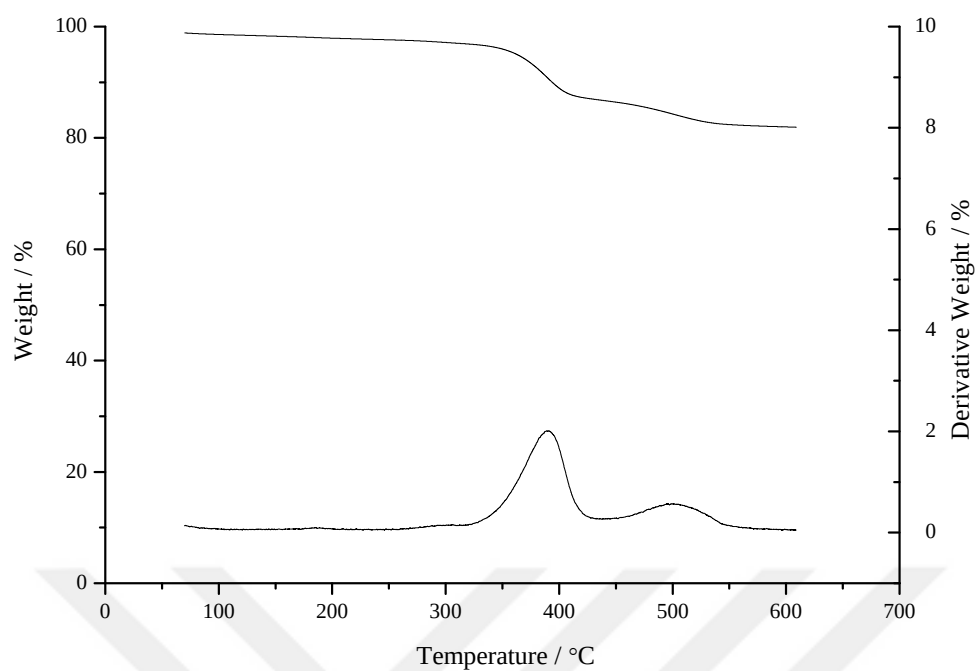


Figure A2-60. TG/DTG curve of [BMIM][TOS] on SiO₂.

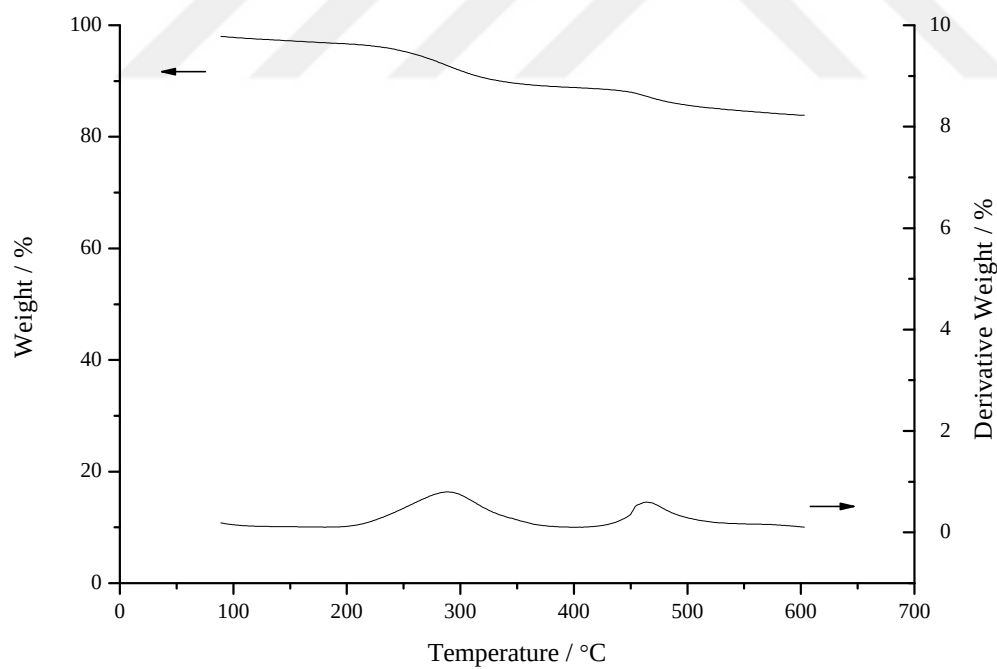


Figure A2-61. TG/DTG curve of [BMIM][TOS] on γ -Al₂O₃.

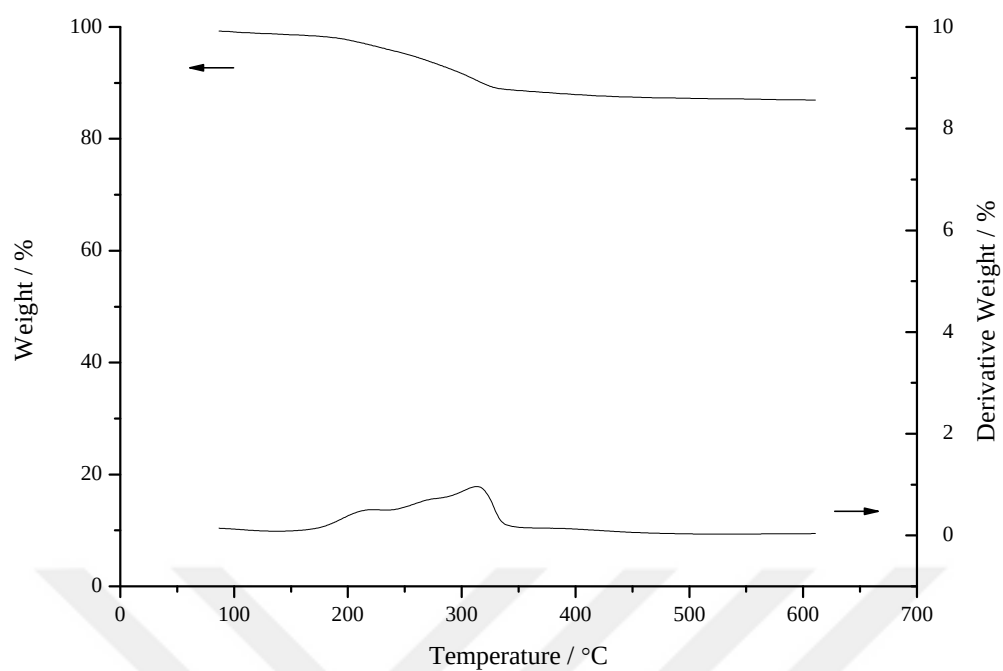


Figure A2-62. TG/DTG curve of [BMIM][TOS] on MgO.

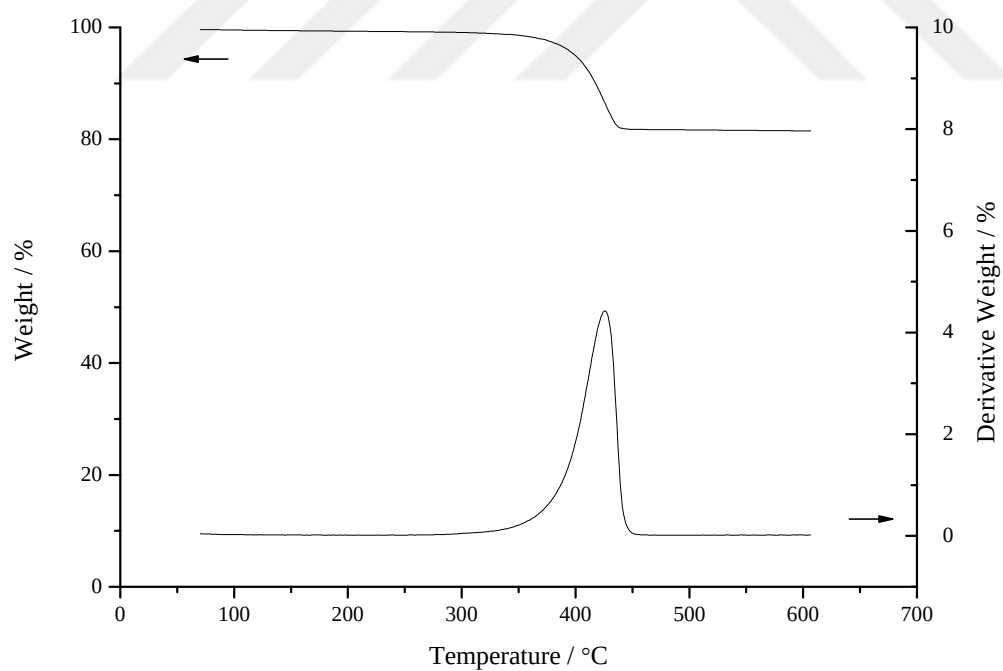


Figure A2-63. TG/DTG curve of [BMIM][NTf₂] on SiO₂.

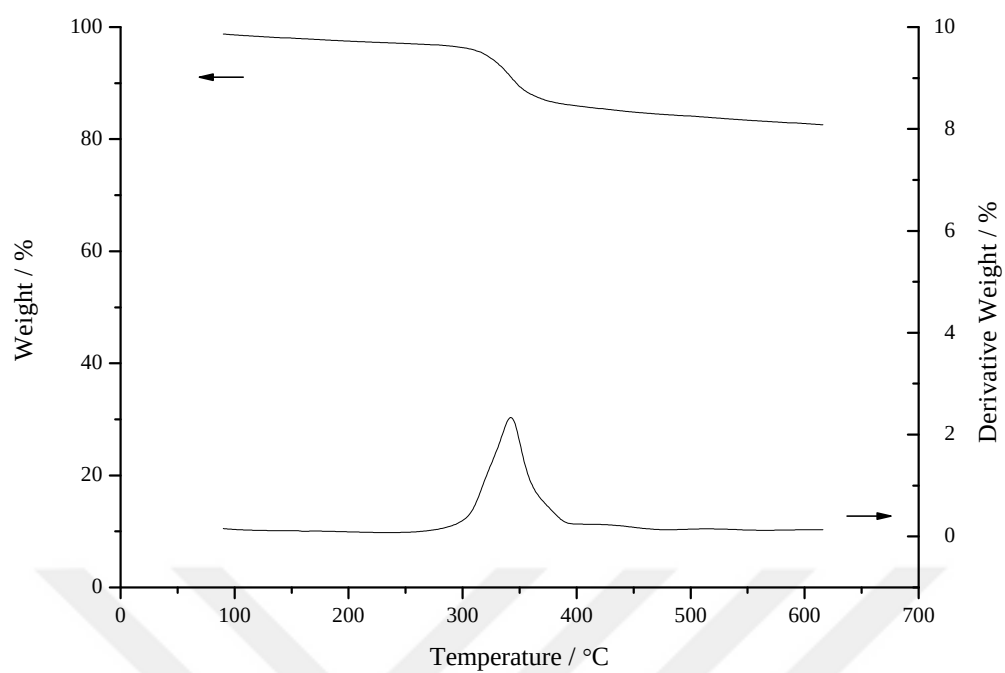


Figure A2-64. TG/DTG curve of [BMIM][NTf₂] on γ -Al₂O₃.

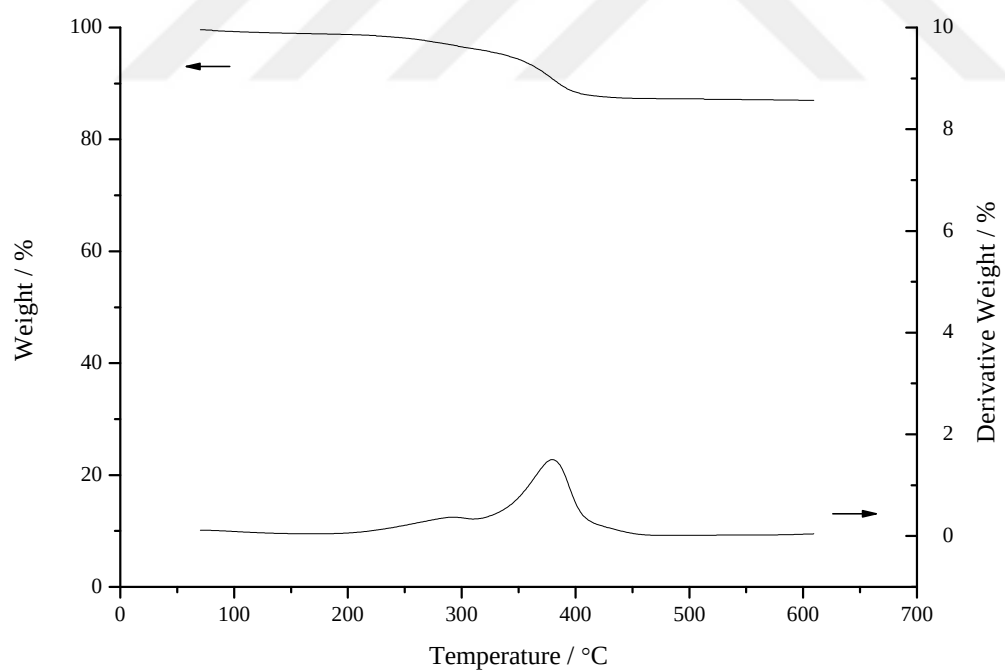


Figure A2-65. TG/DTG curve of [BMIM][NTf₂] on MgO.

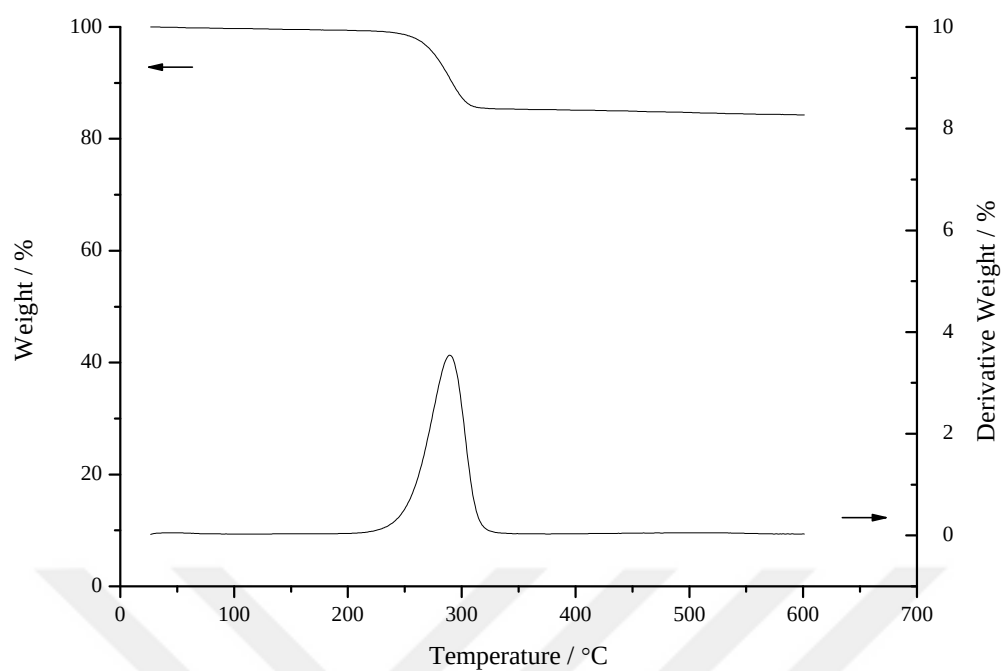


Figure A2-66. TG/DTG curve of [BMIM][SCN] on SiO₂.

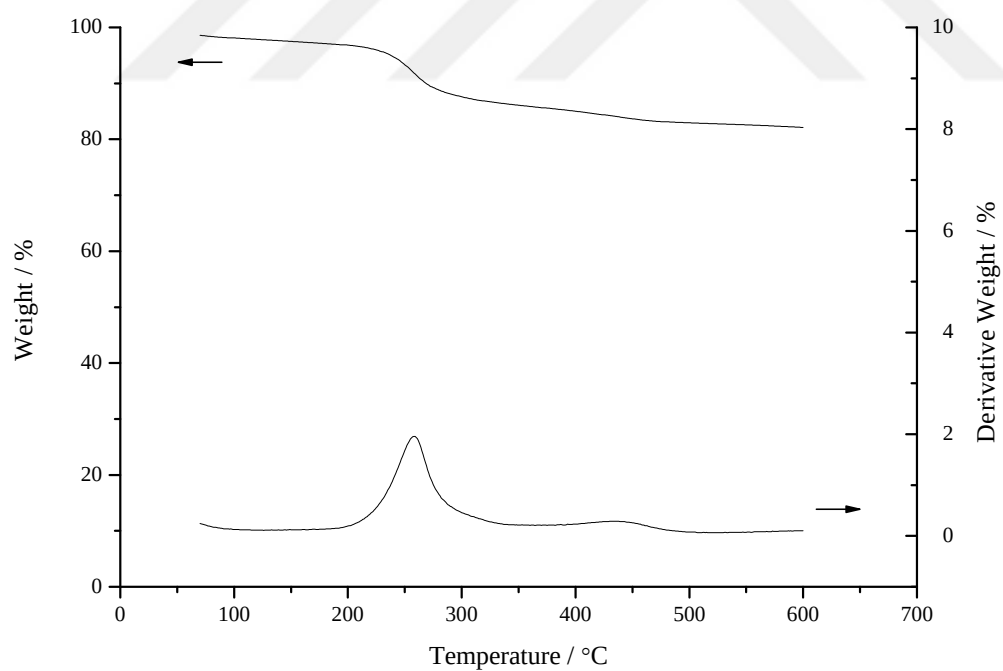


Figure A2-67. TG/DTG curve of [BMIM][SCN] on γ -Al₂O₃.

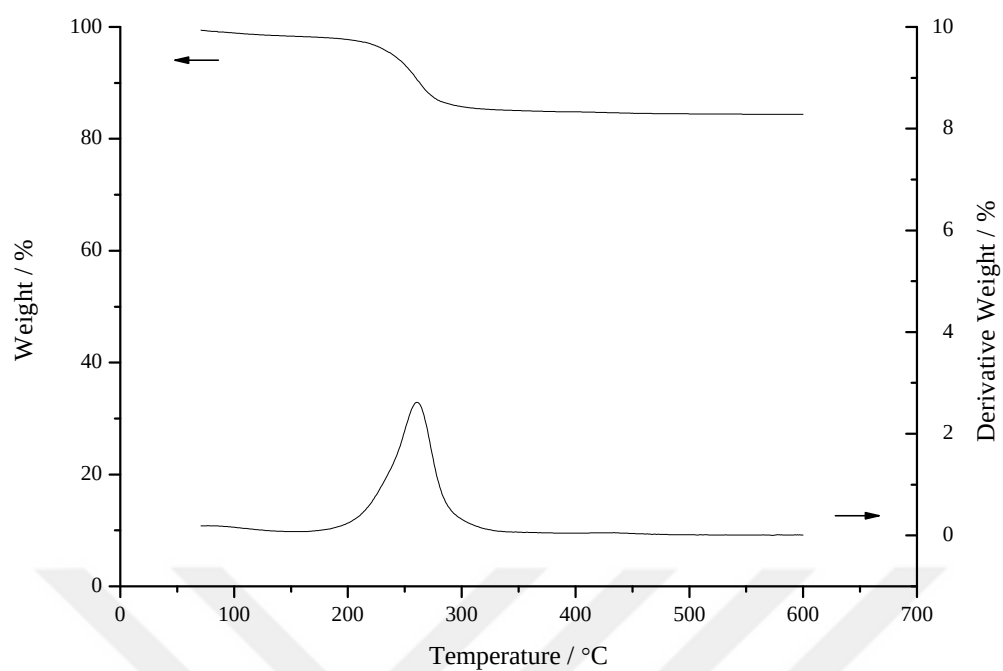


Figure A2-68. TG/DTG curve of [BMIM][SCN] on MgO.

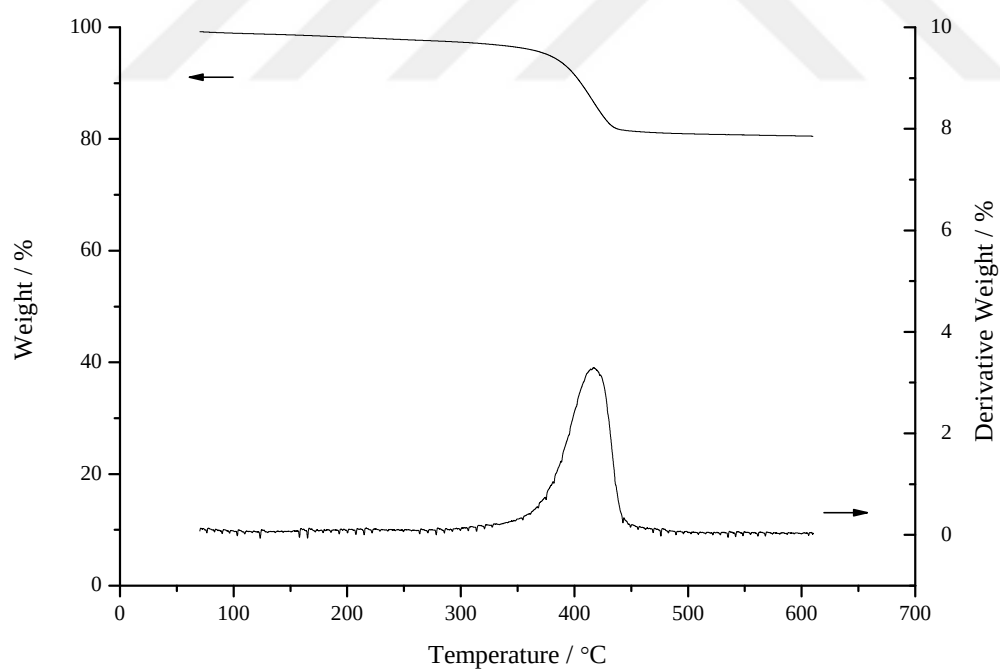


Figure A2-69. TG/DTG curve of [BMIM][TfO] on SiO₂.

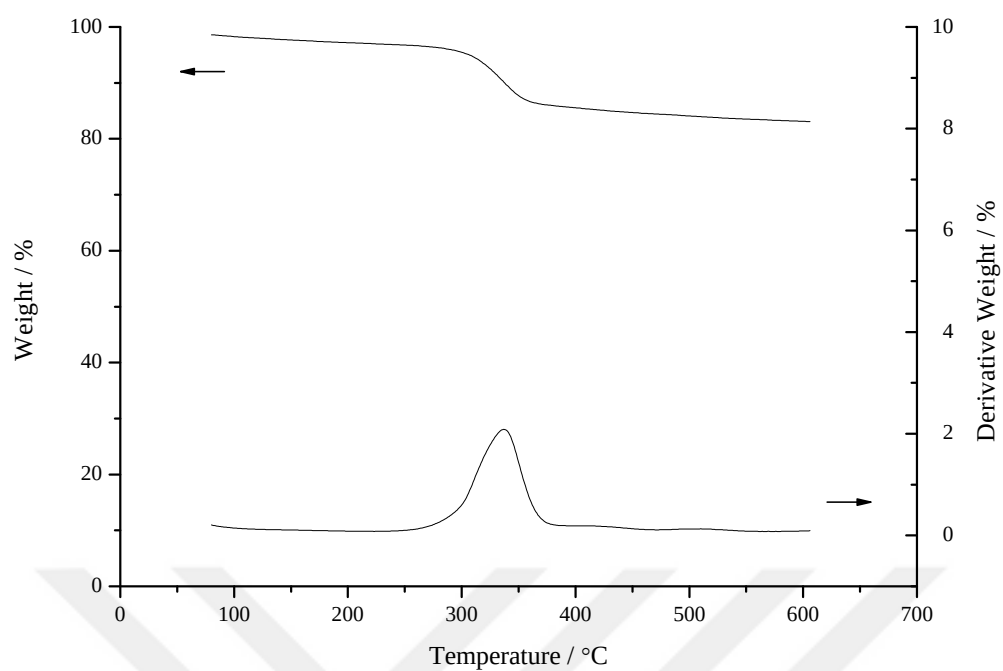


Figure A2-70. TG/DTG curve of [BMIM][TfO] on $\gamma\text{-Al}_2\text{O}_3$.

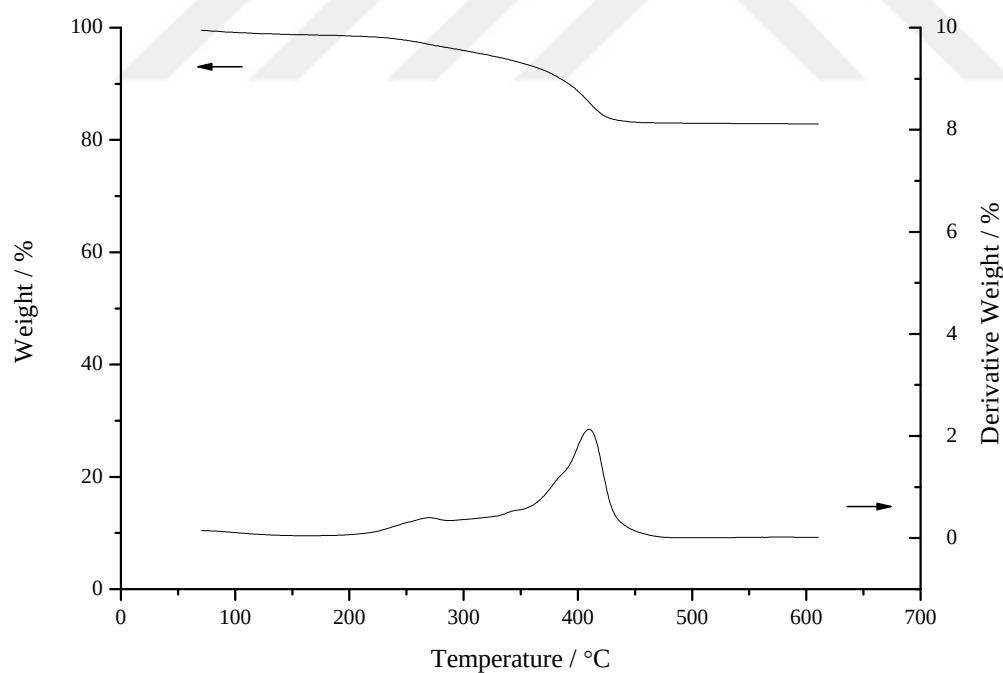


Figure A2-71. TG/DTG curve of [BMIM][TfO] on MgO.

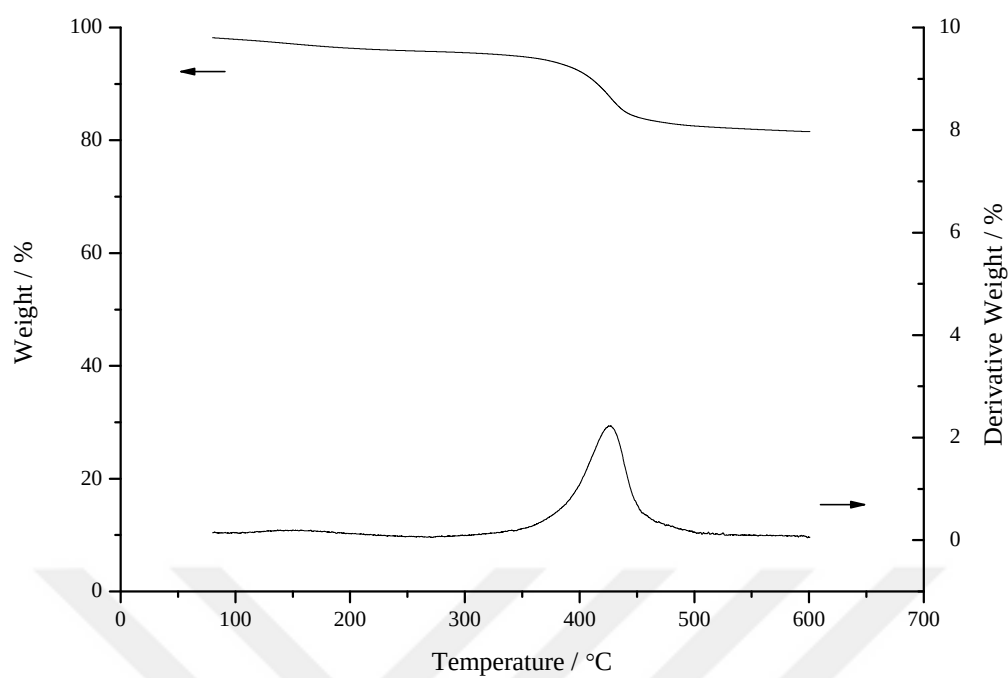


Figure A2-72. TG/DTG curve of [BDMIM][BF₄] on SiO₂.

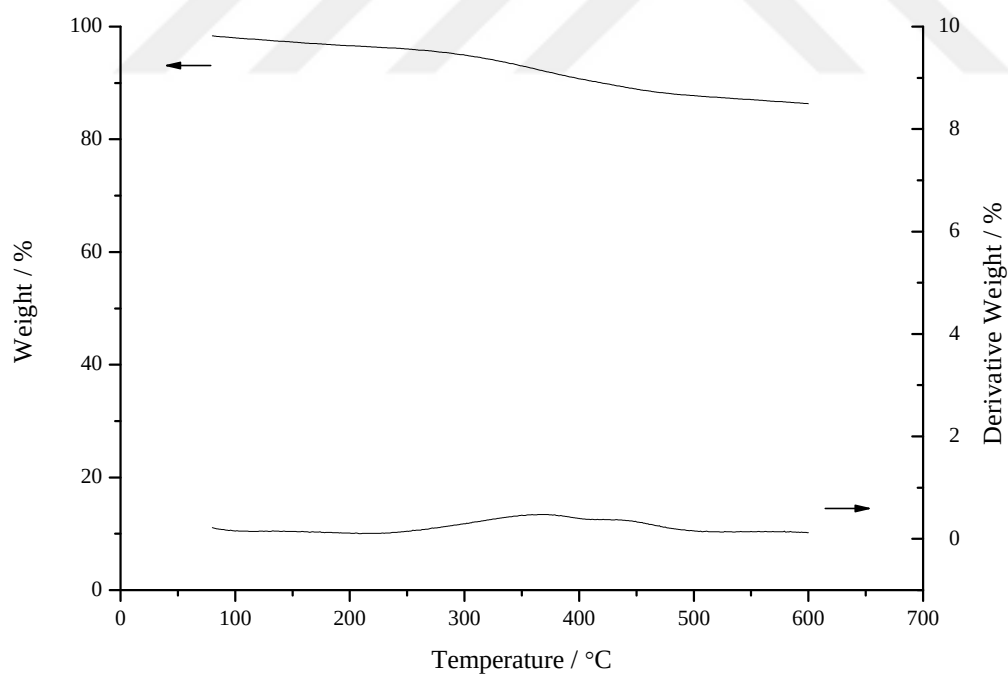


Figure A2-73. TG/DTG curve of [BDMIM][BF₄] on γ -Al₂O₃.

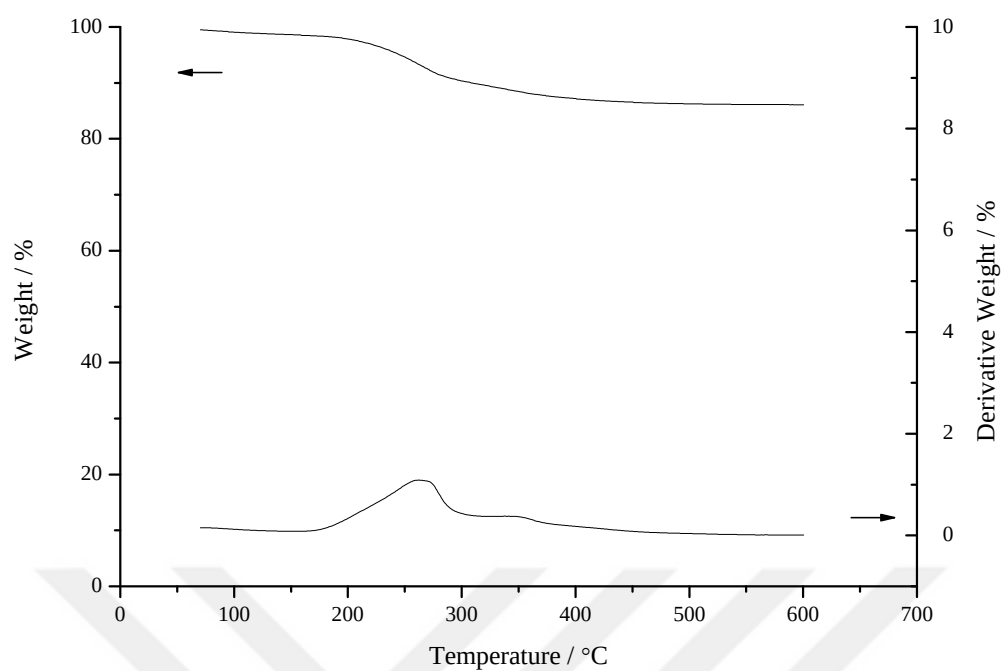


Figure A2-74. TG/DTG curve of [BDMIM][BF₄] on MgO.

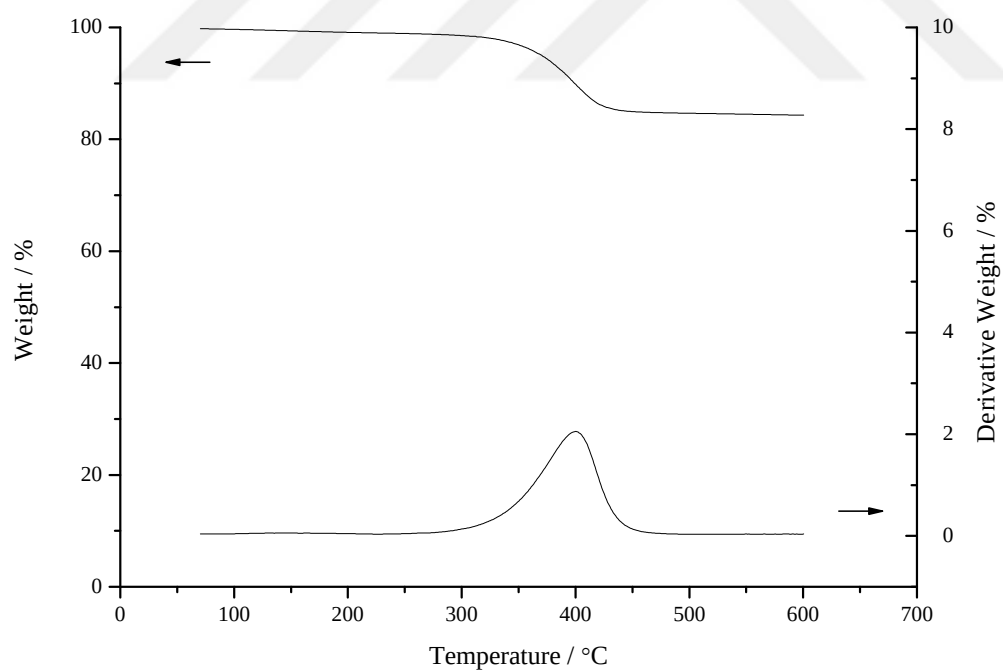


Figure A2-75. TG/DTG curve of [HMIM][BF₄] on SiO₂.

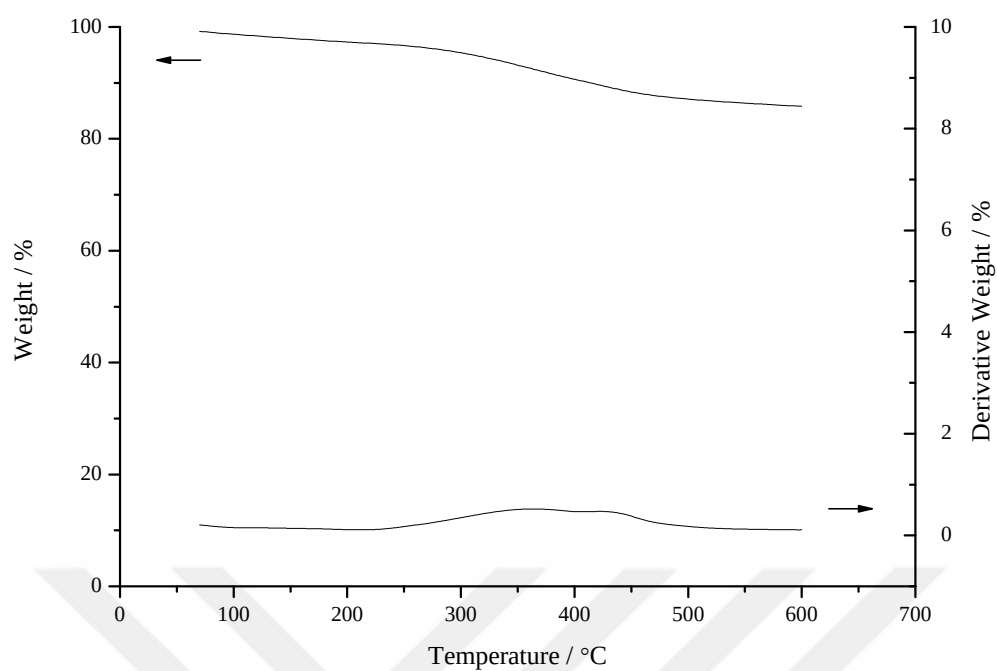


Figure A2-76. TG/DTG curve of [HMIM][BF₄] on γ -Al₂O₃.

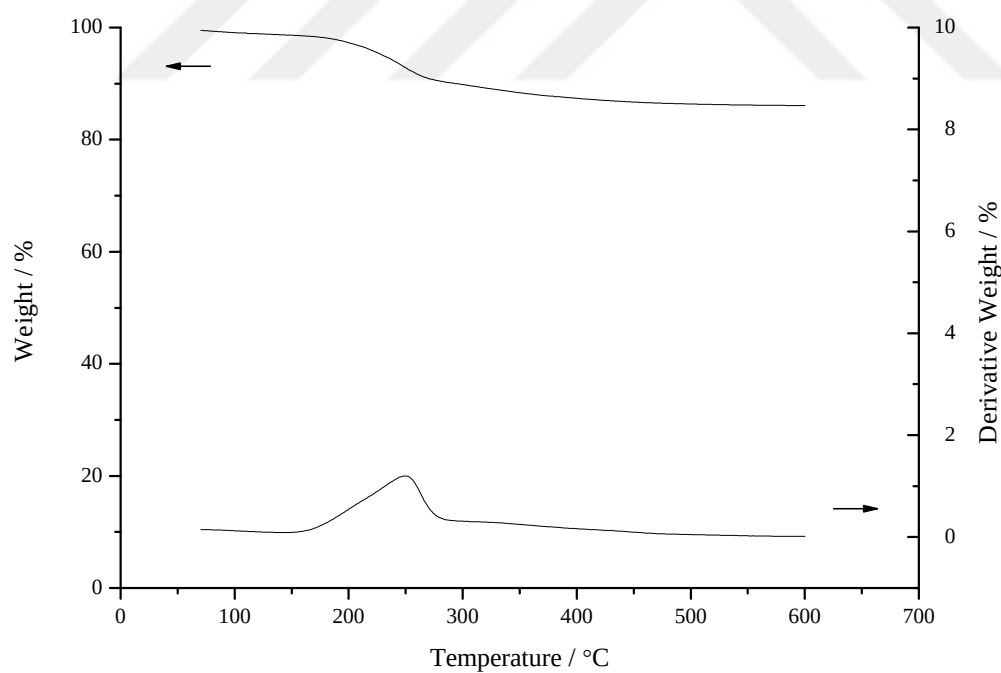


Figure A2-77. TG/DTG curve of [HMIM][BF₄] on MgO.

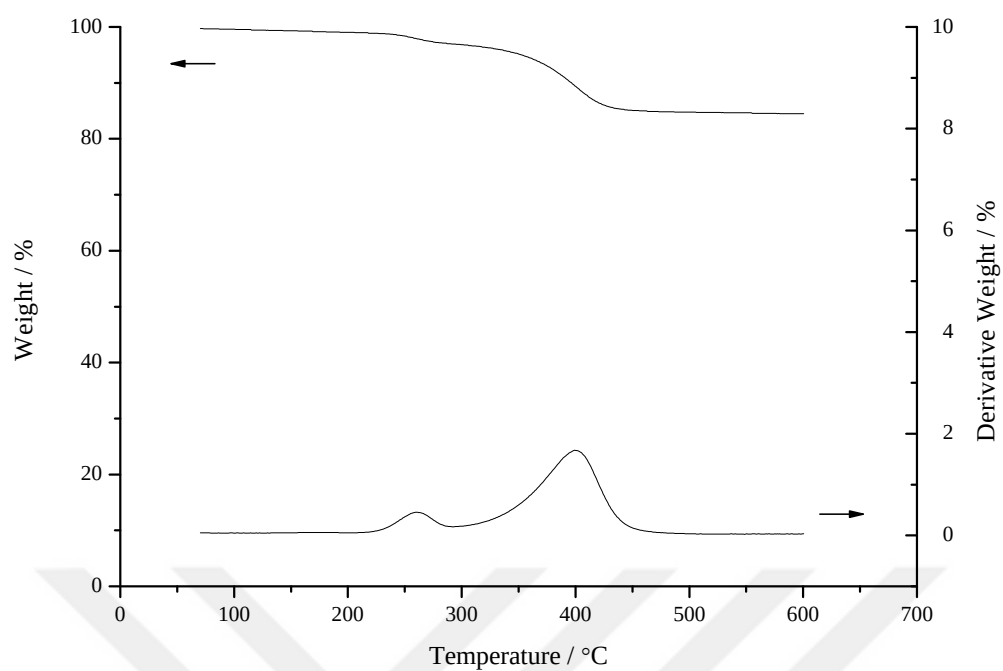


Figure A2-78. TG/DTG curve of $[C_{10}MIM][BF_4]$ on SiO_2 .

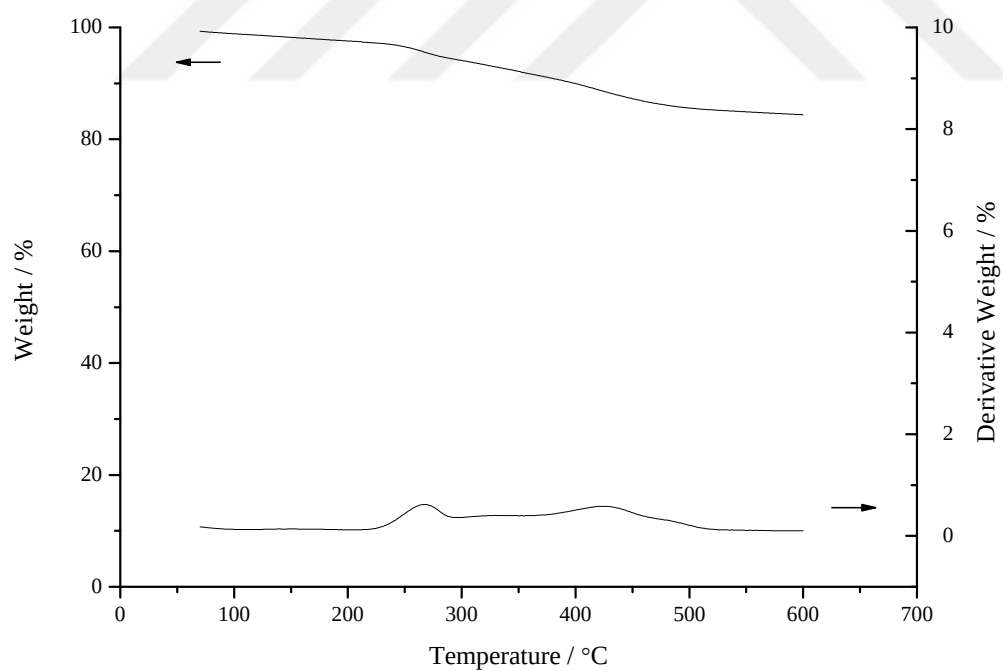


Figure A2-79. TG/DTG curve of $[C_{10}MIM][BF_4]$ on $\gamma-Al_2O_3$.

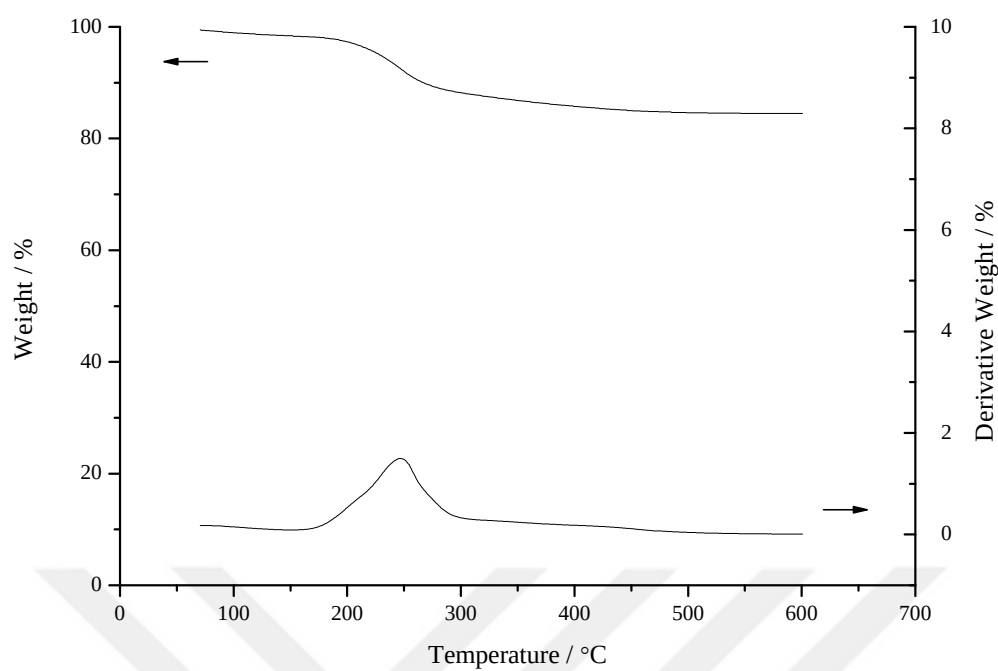


Figure A2-80. TG/DTG curve of $[C_{10}MIM][BF_4] MgO$.

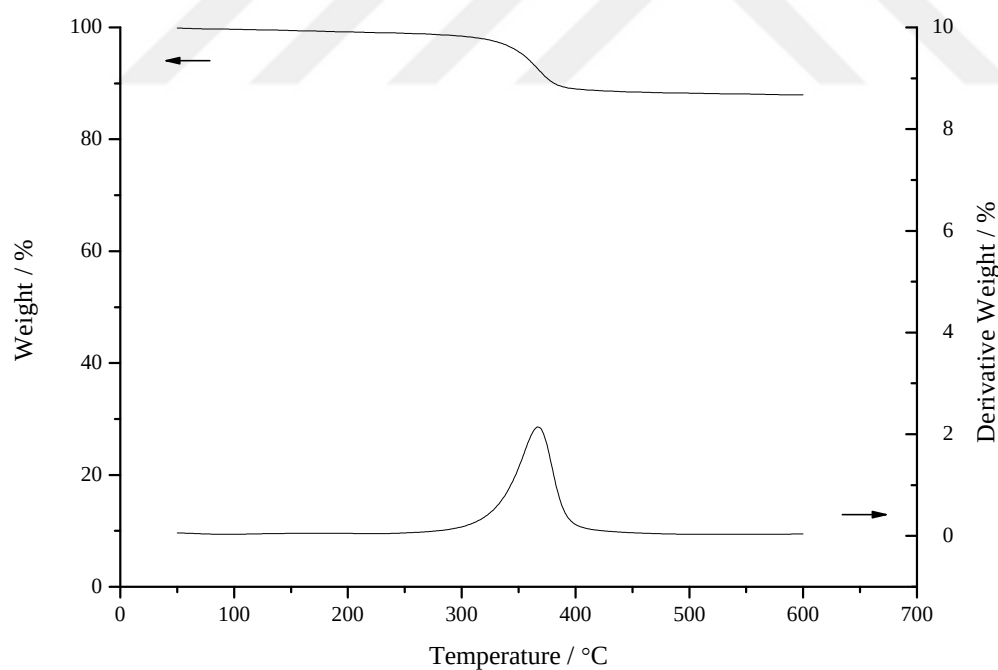


Figure A2-81. TG/DTG curve of $[BzMIM][BF_4]$ on SiO_2 .

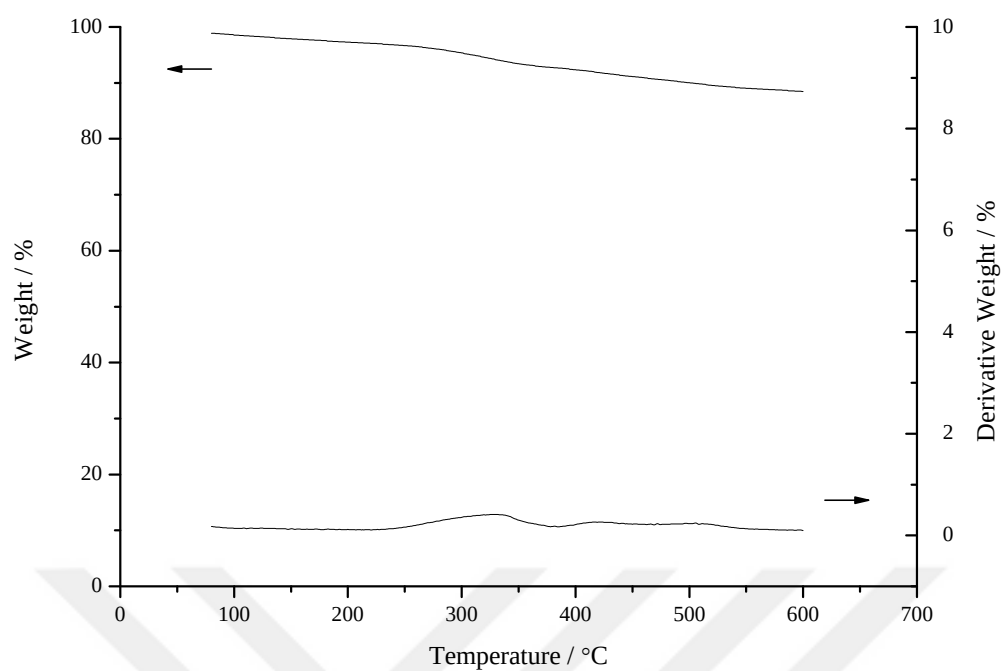


Figure A2-82. TG/DTG curve of [BzMIM][BF₄] on γ -Al₂O₃.

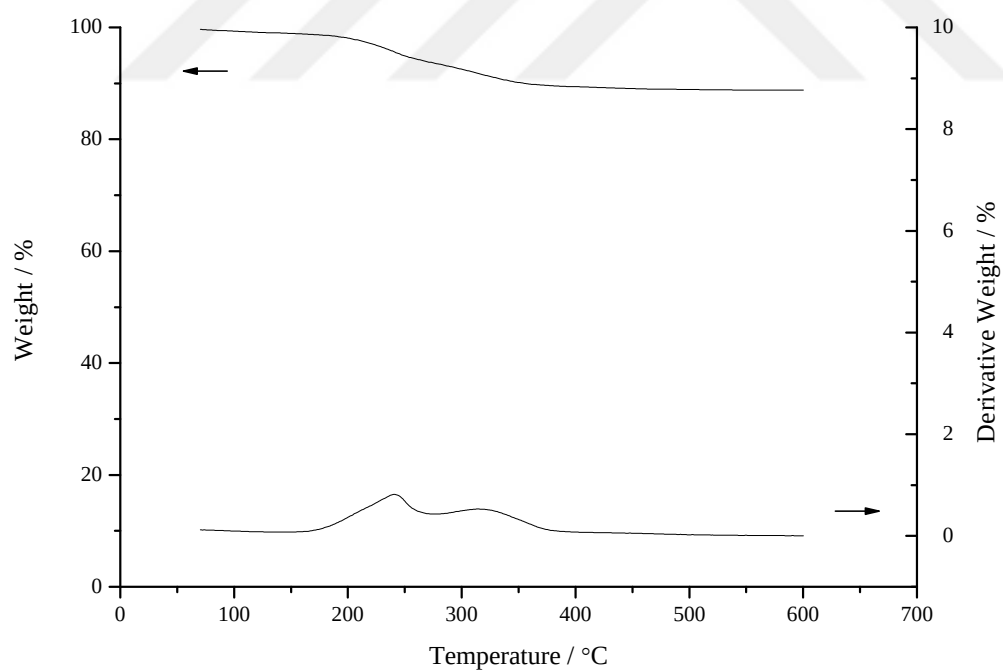


Figure A2-83. TG/DTG curve of [BzMIM][BF₄] on MgO.

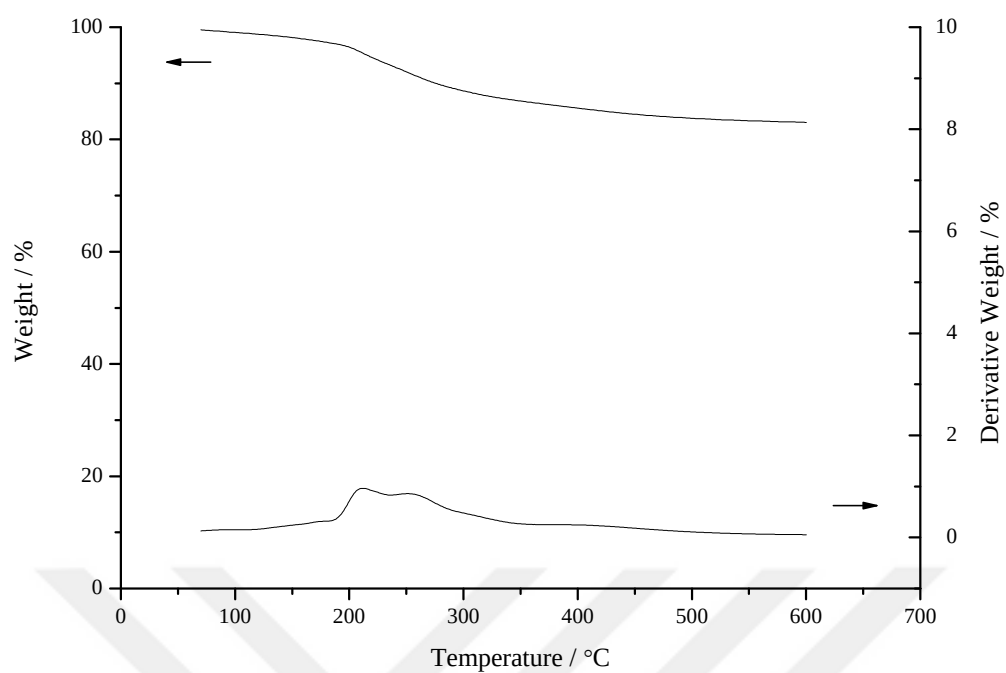


Figure A2-84. TG/DTG curve of [HEMIM][DCA] on SiO₂.

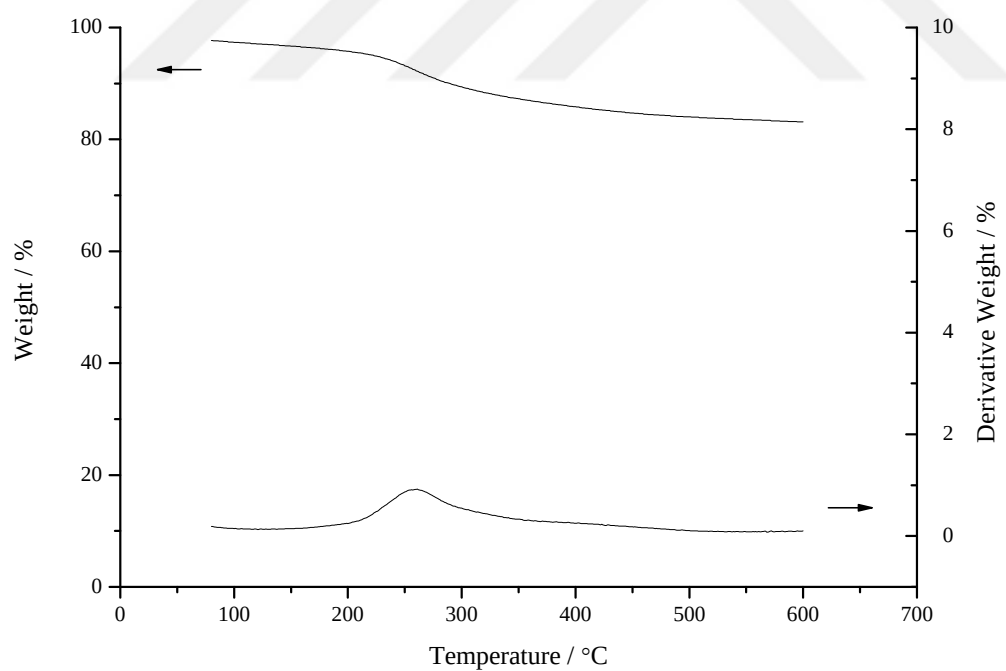


Figure A2-85. TG/DTG curve of [HEMIM][DCA] on γ -Al₂O₃.

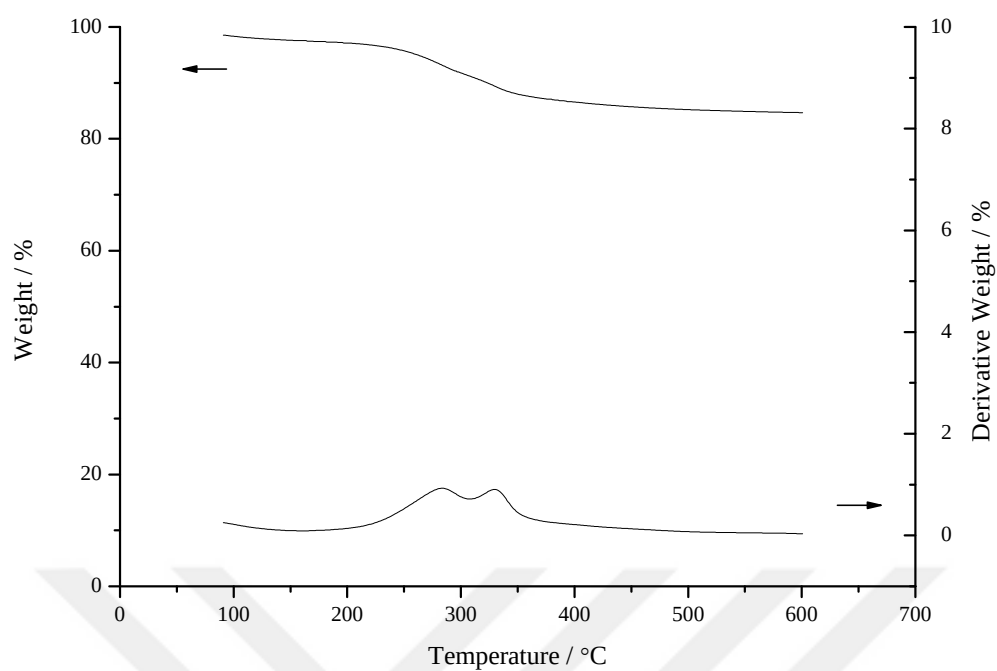


Figure A2-86. TG/DTG curve of [HEMIM][DCA] on MgO.

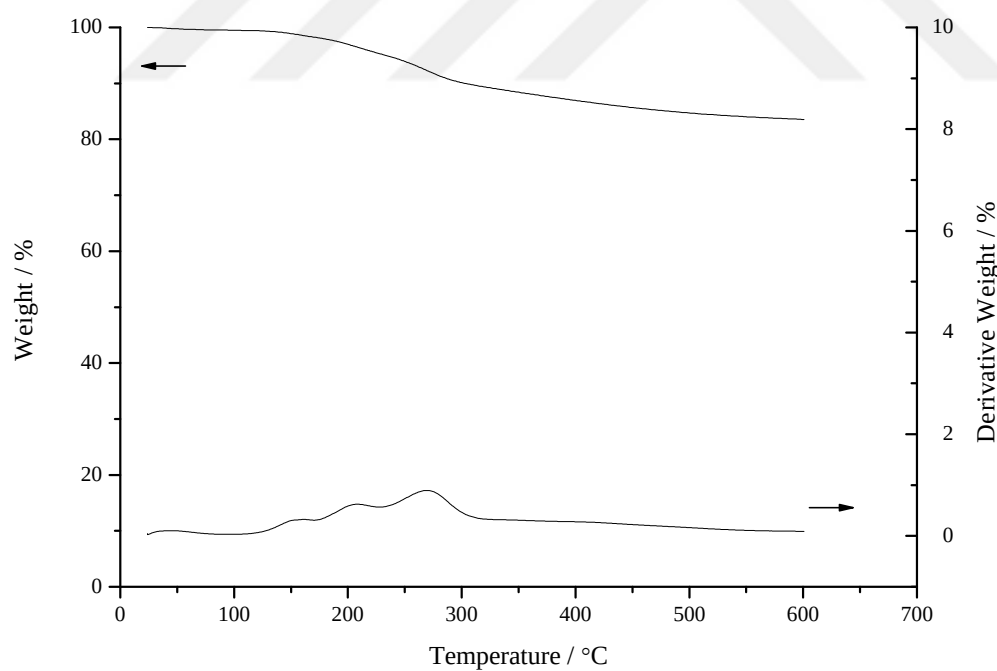


Figure A2-87. TG/DTG curve of [CPMIM][DCA] on SiO₂.

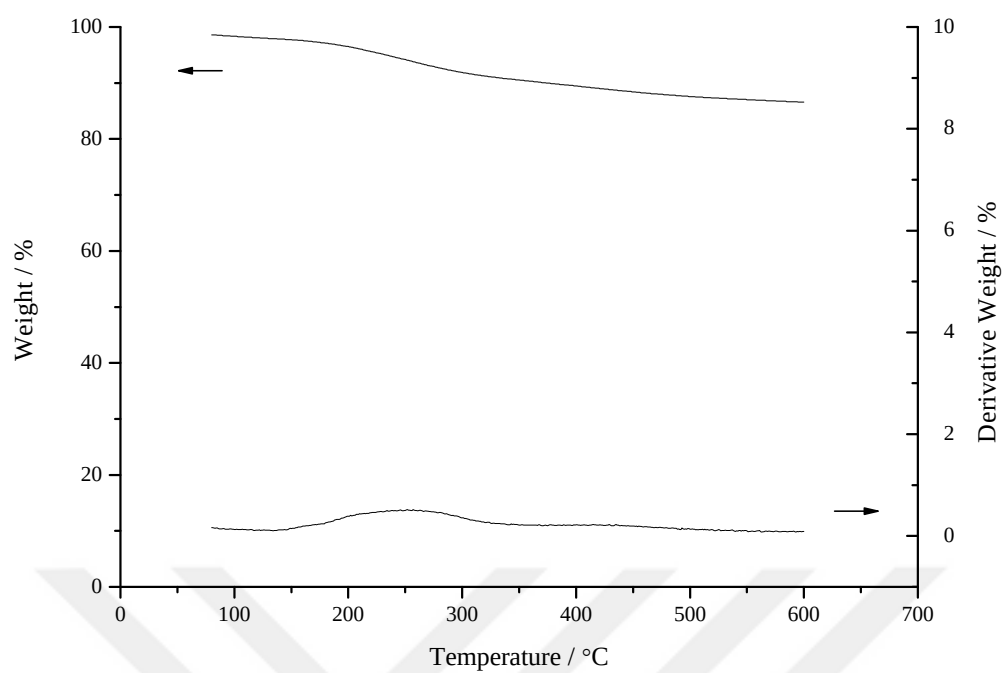


Figure A2-88. TG/DTG curve of [CPMIM][DCA] on γ -Al₂O₃.

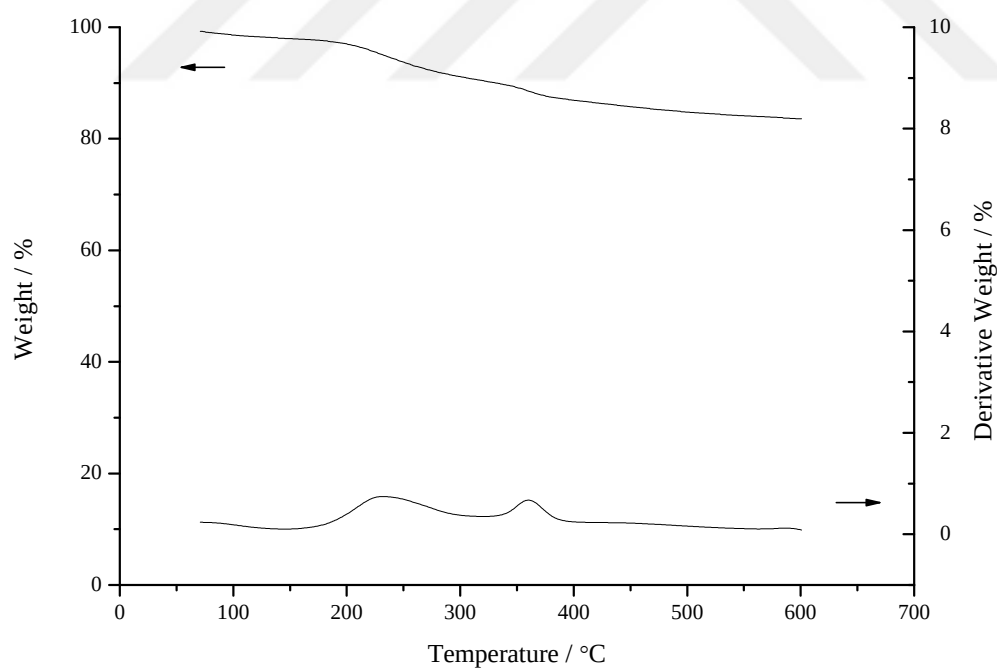


Figure A2-89. TG/DTG curve of [CPMIM][DCA] on MgO.

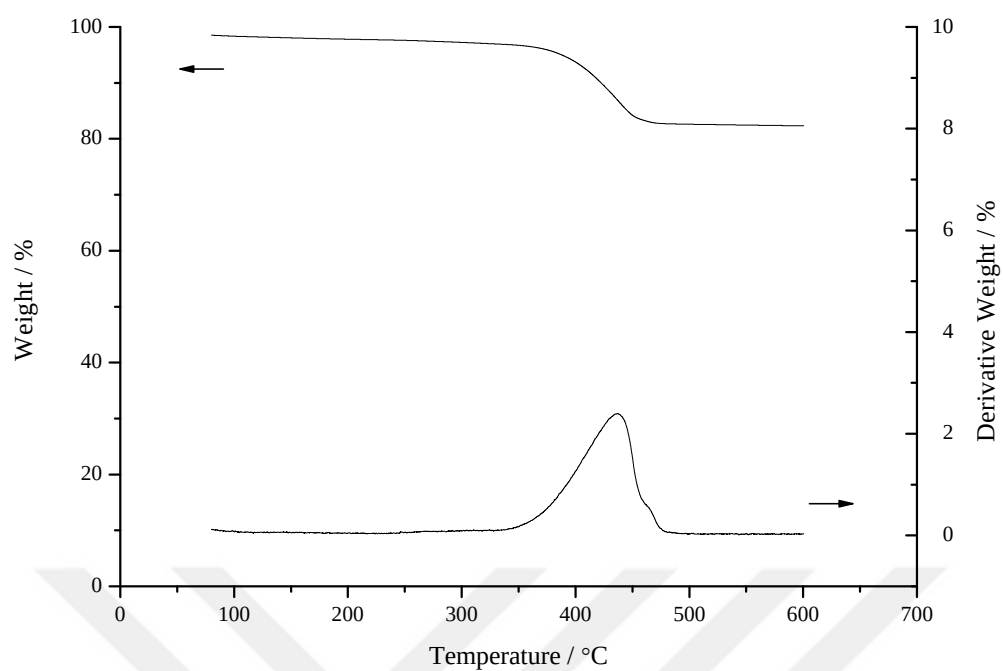


Figure A2-90. TG/DTG curve of [CPMIM][NTf₂] on SiO₂.

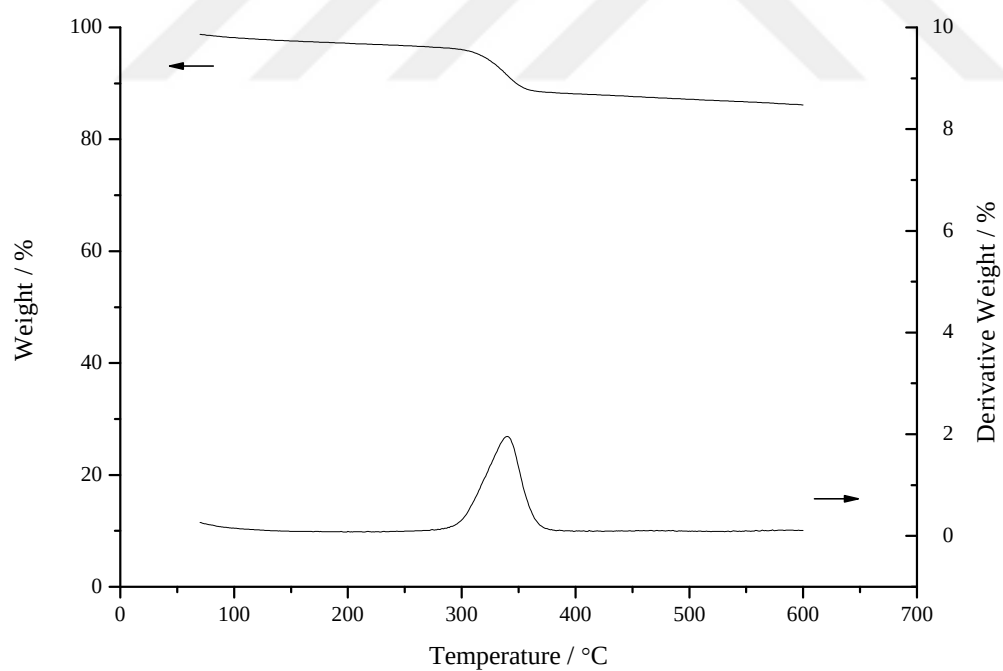


Figure A2-91. TG/DTG curve of [CPMIM][NTf₂] on γ -Al₂O₃.

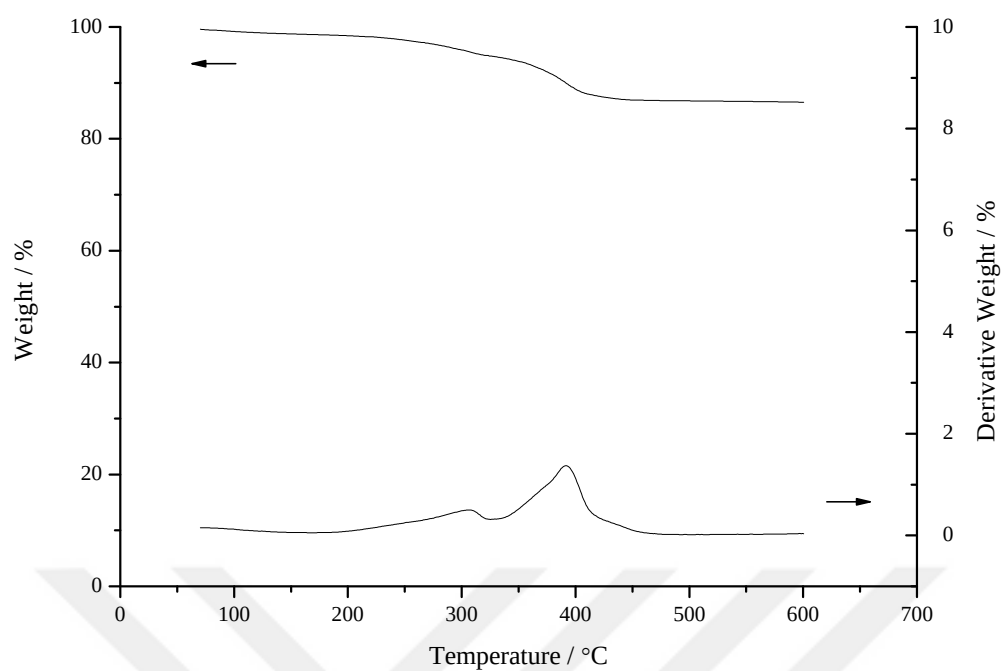


Figure A2-92. TG/DTG curve of [CPMIM][NTf₂] on MgO.

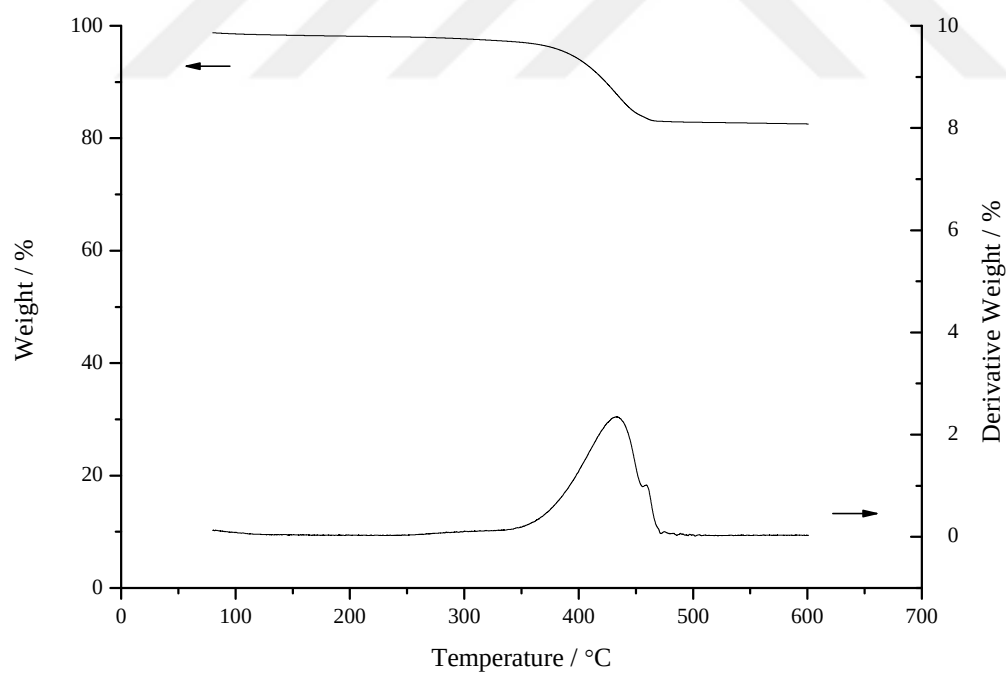


Figure A2-93. TG/DTG curve of [CPCPIM][NTf₂] on SiO₂.

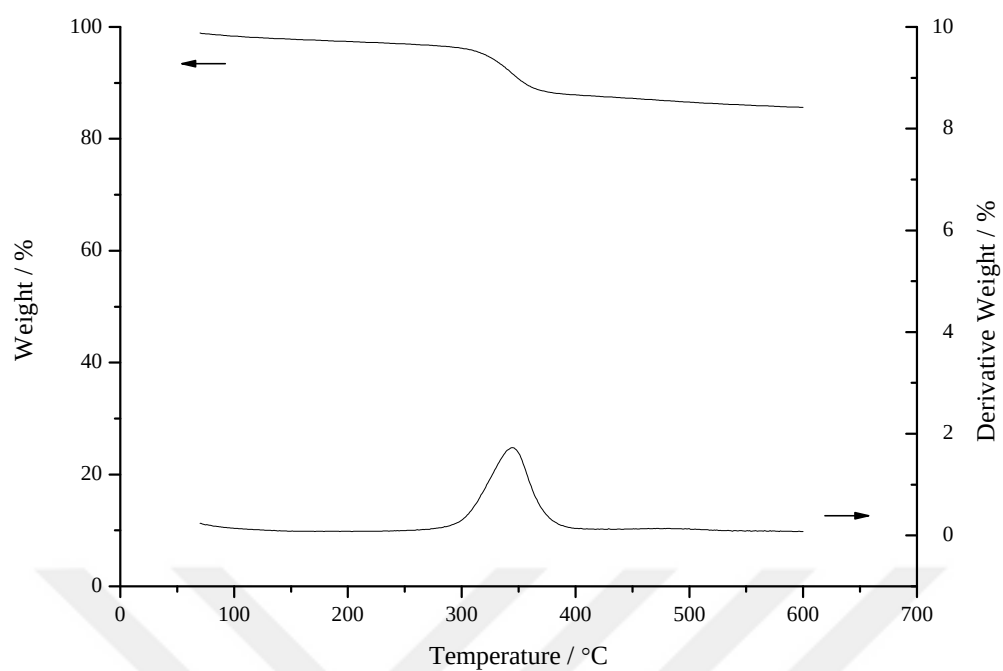


Figure A2-94. TG/DTG curve of [CPCPIM][NTf₂] on γ -Al₂O₃.

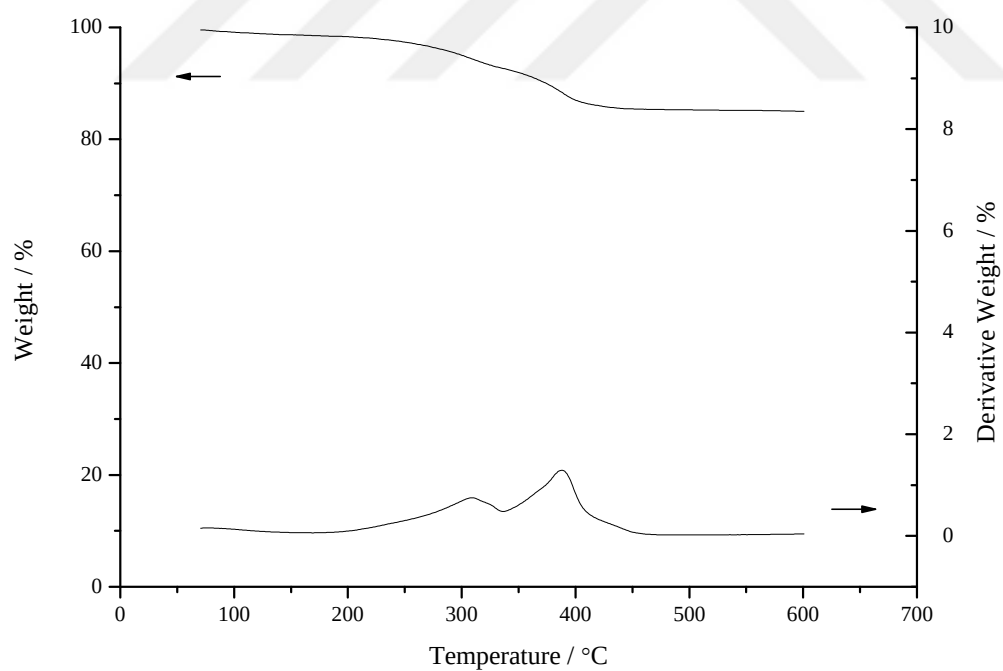


Figure A2-95. TG/DTG curve of [CPCPIM][NTf₂] on MgO.

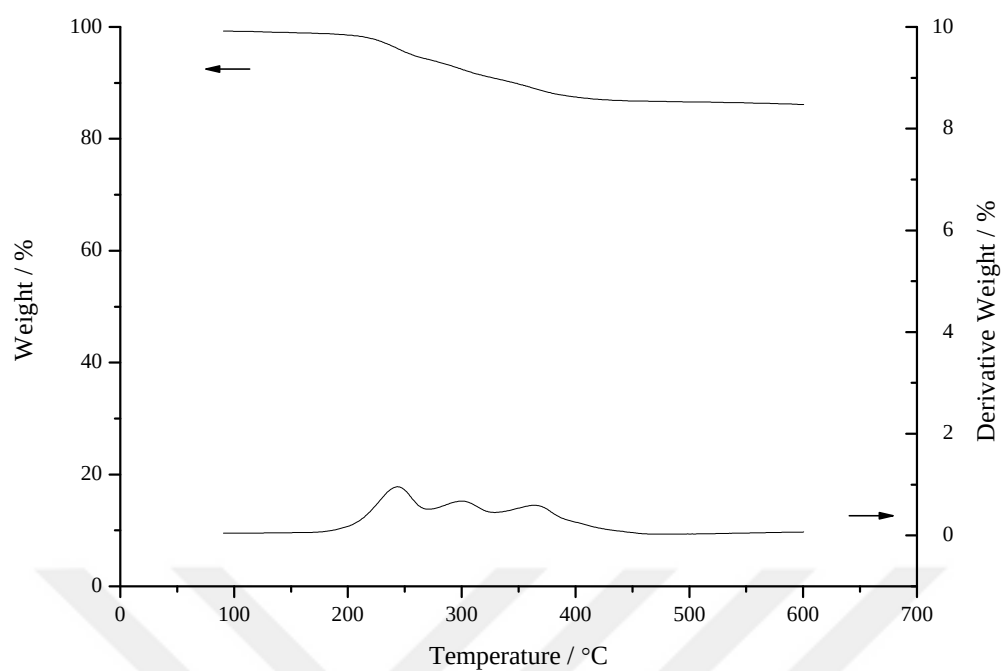


Figure A2-96. TG/DTG curve of [DHIM][NTf₂] on SiO₂.

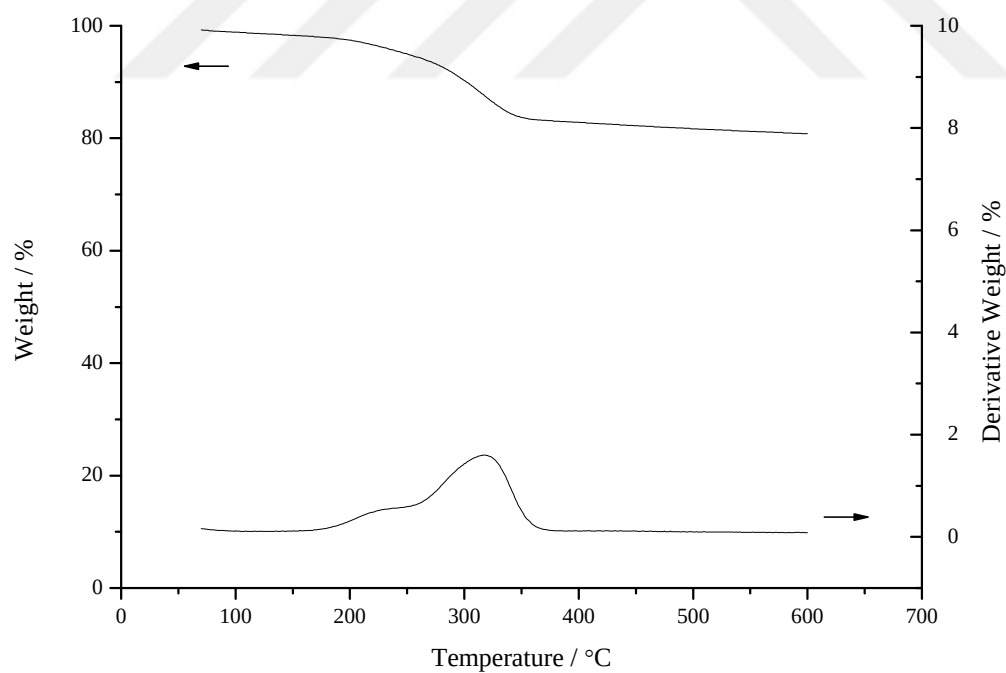


Figure A2-97. TG/DTG curve of [DHIM][NTf₂] on γ-Al₂O₃.

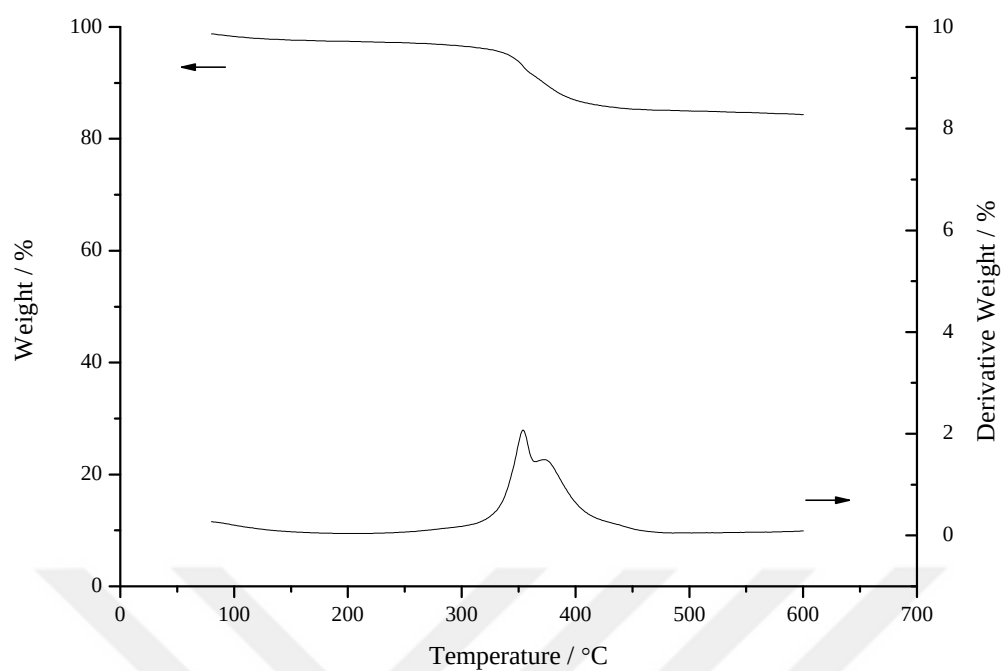


Figure A2-98. TG/DTG curve of [DHIM][NTf₂] on MgO.

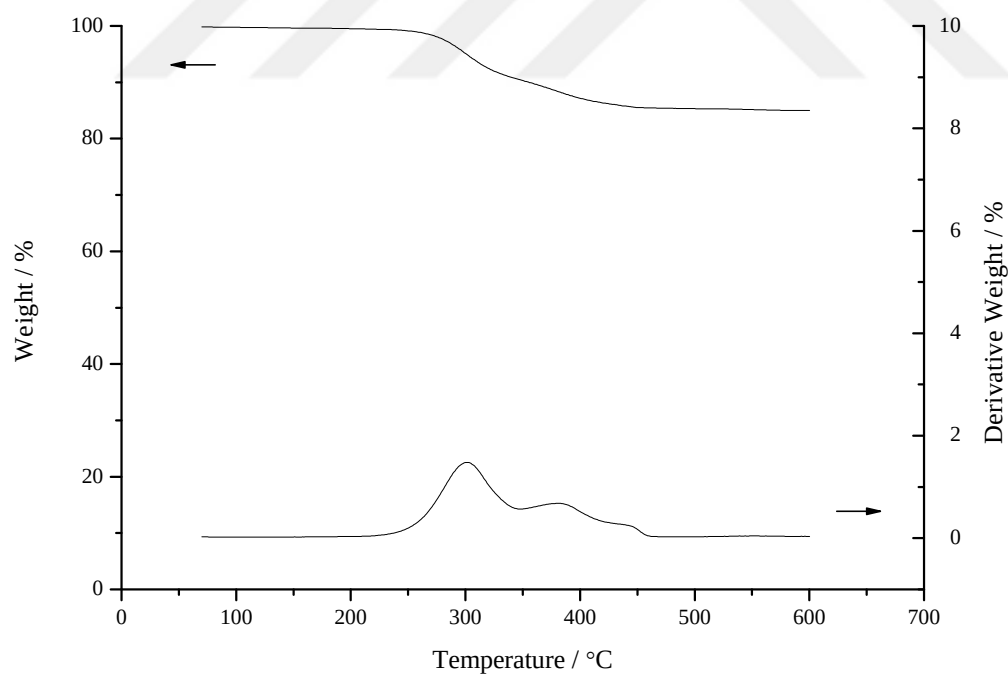


Figure A2-99. TG/DTG curve of [DMOIM][NTf₂] on SiO₂.

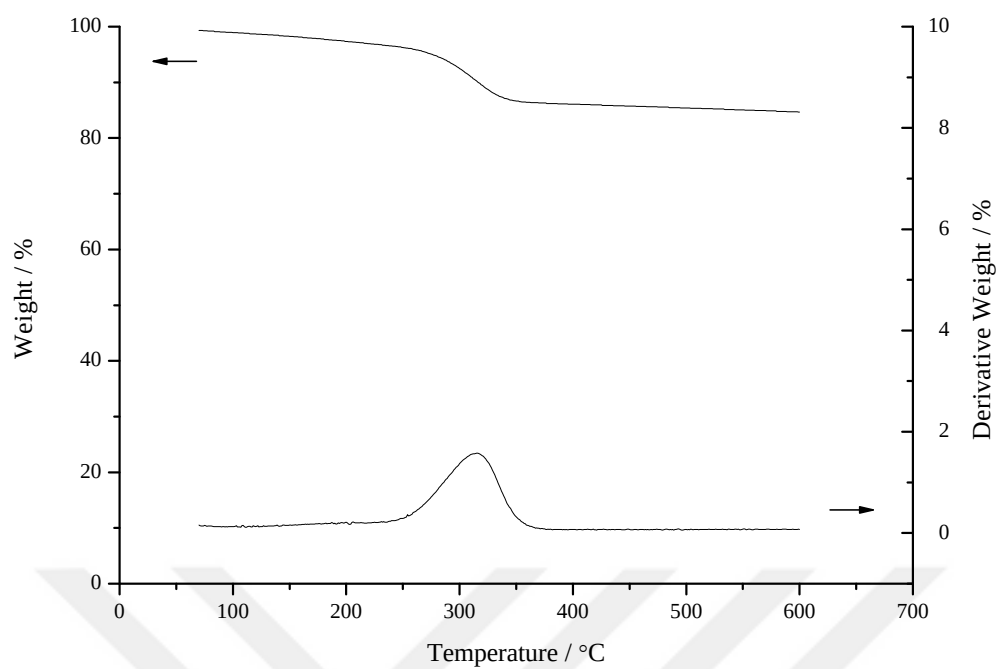


Figure A2-100. TG/DTG curve of [DMOIM][NTf₂] on γ -Al₂O₃.

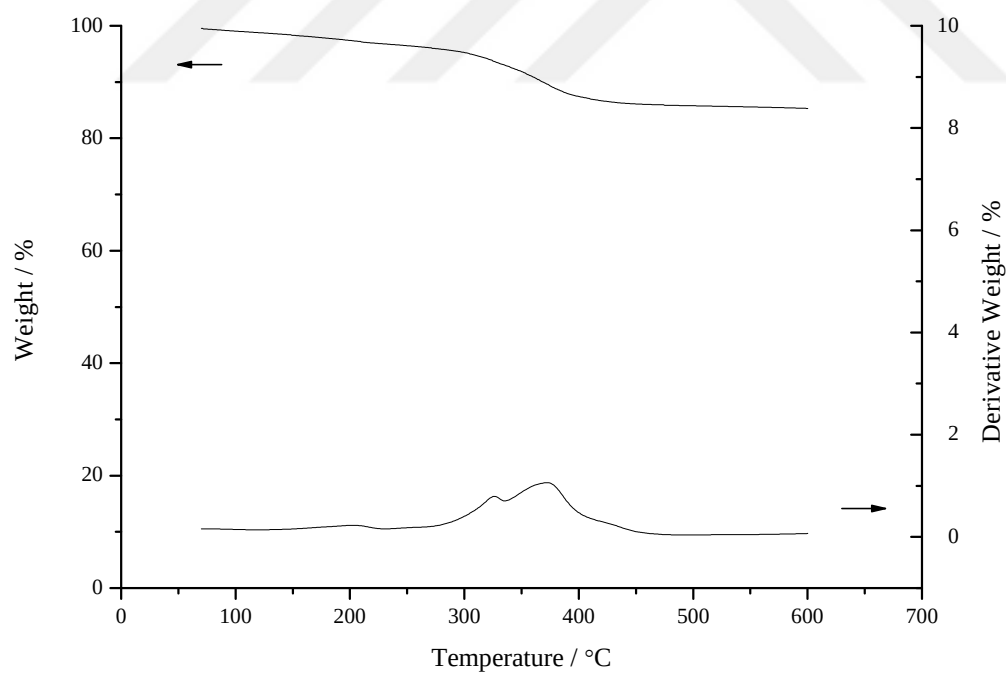


Figure A2-101. TG/DTG curve of [DMOIM][NTf₂] on MgO.

A2-3. Fourier Transform IR (FTIR) Spectroscopy

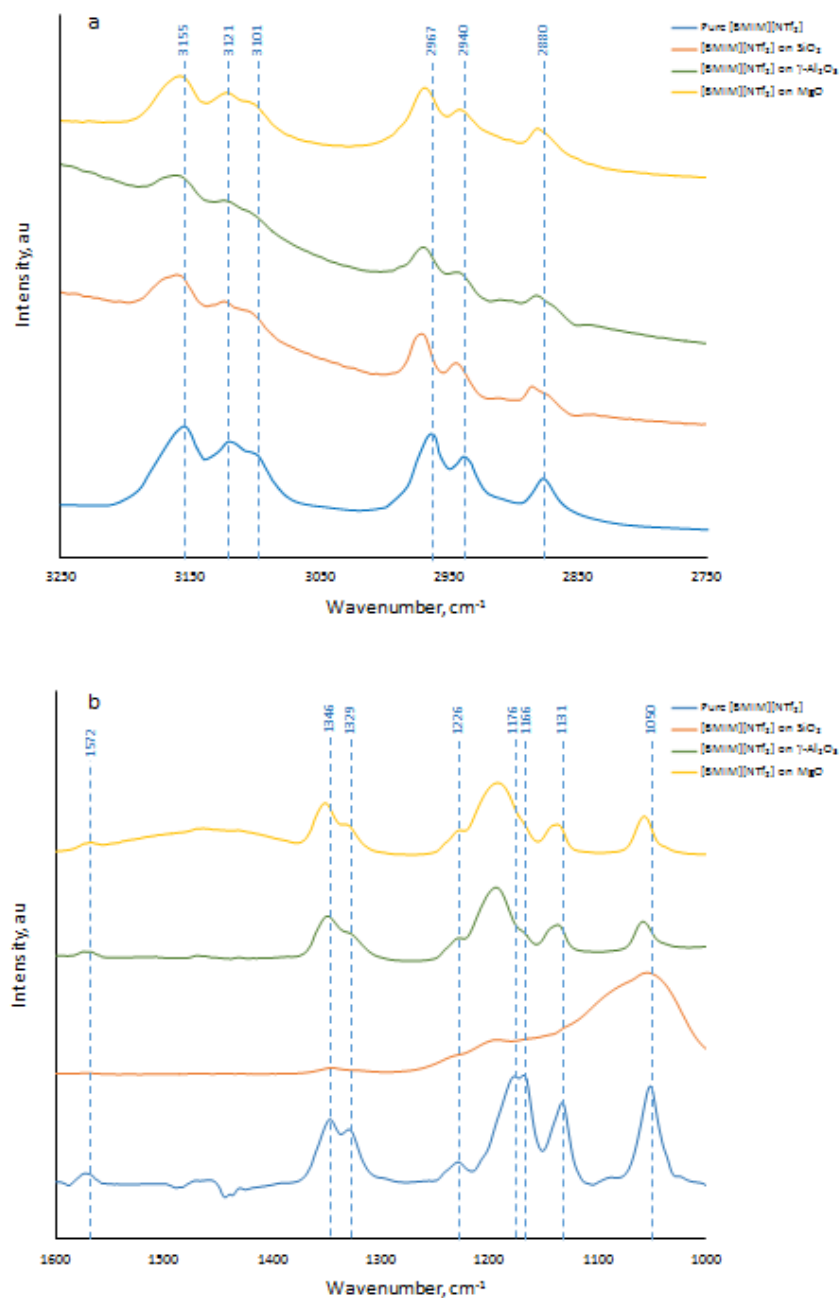


Figure A2-102. FTIR spectra of bulk and supported [BMIM][NTf₂] in the region of a) 2750-3250 cm^{-1} b) 1000-1600 cm^{-1} .

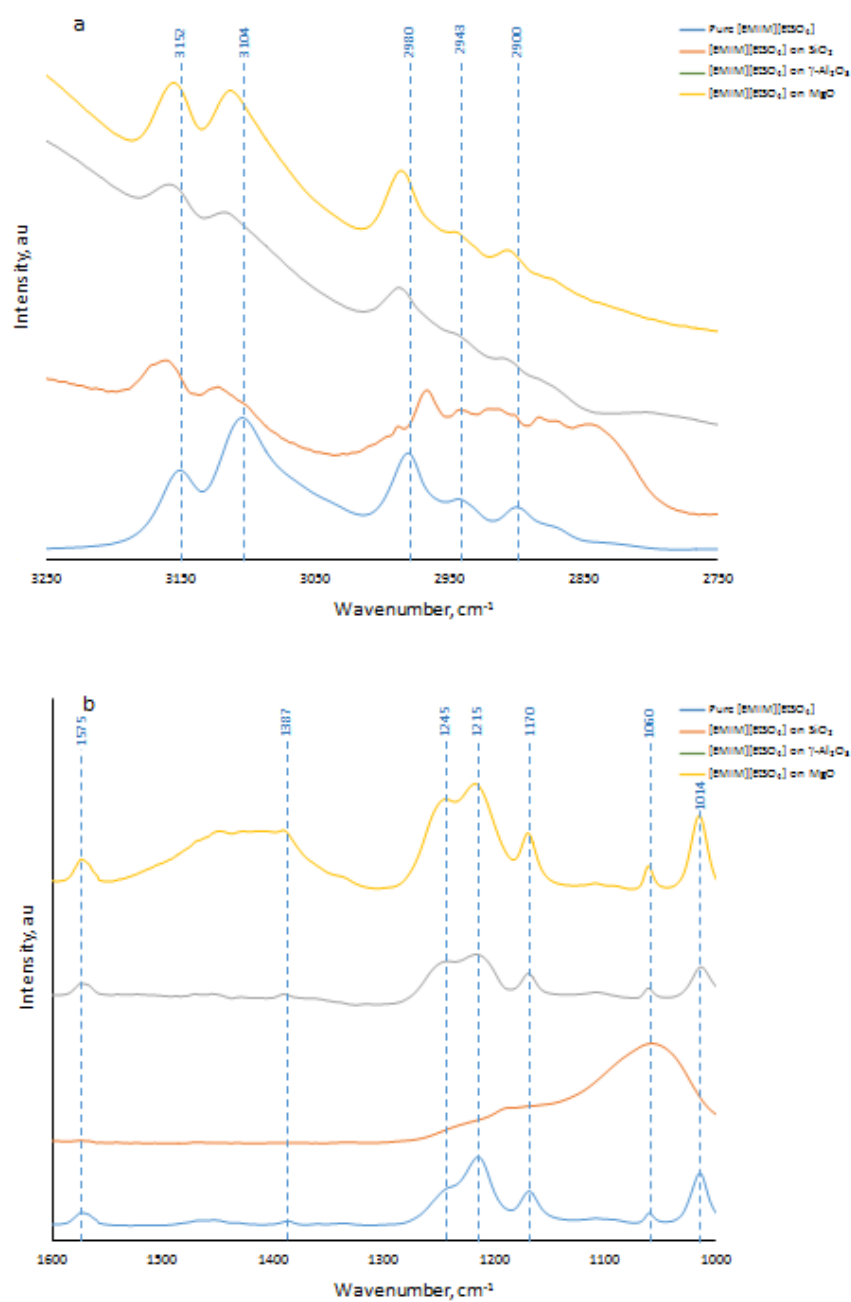


Figure A2-103. FTIR spectra of bulk and supported [EMIM][EtSO₄] in the region of a) 2750-3250 cm^{-1} b) 1000-1600 cm^{-1} .

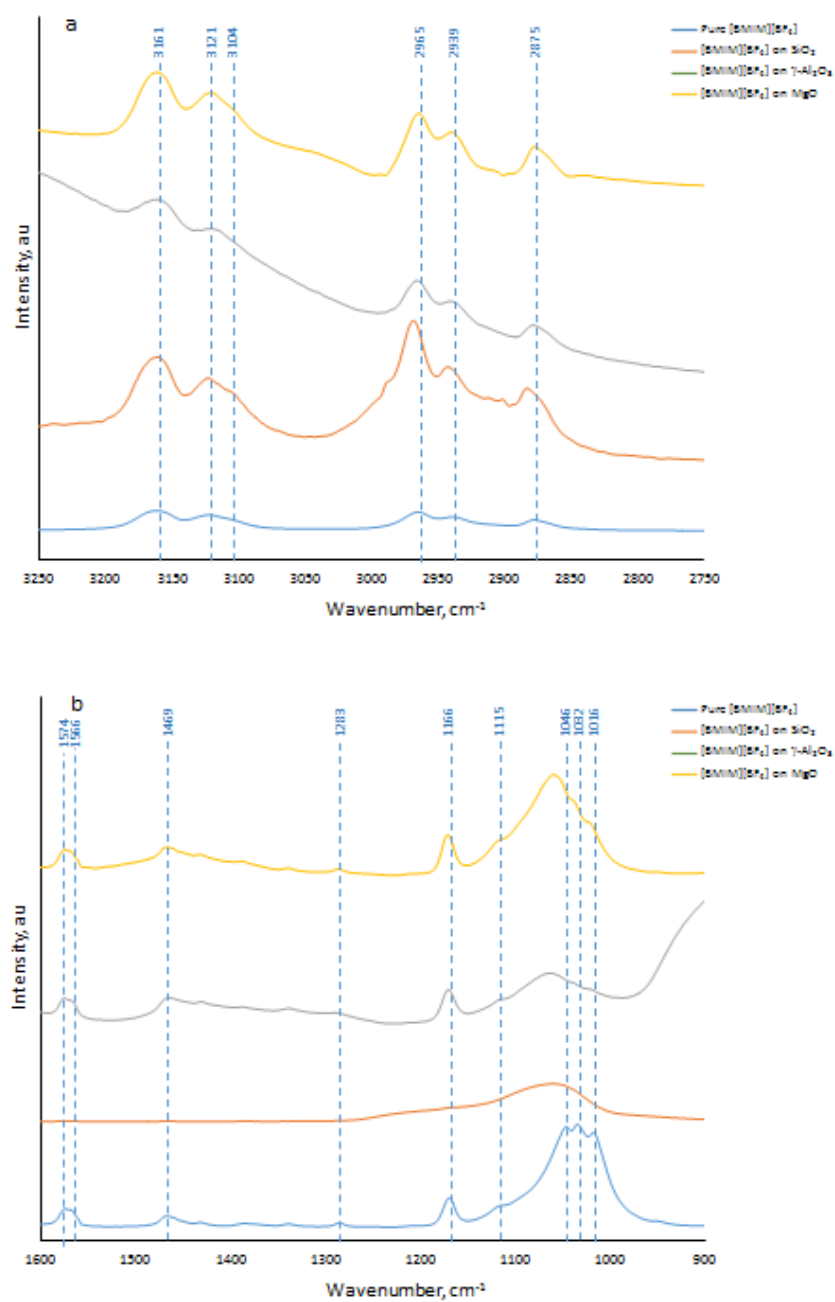


Figure A2-104. FTIR spectra of bulk and supported [BMIM][BF₄] in the region of a) 2750-3250 cm⁻¹ b) 900-1600 cm⁻¹.

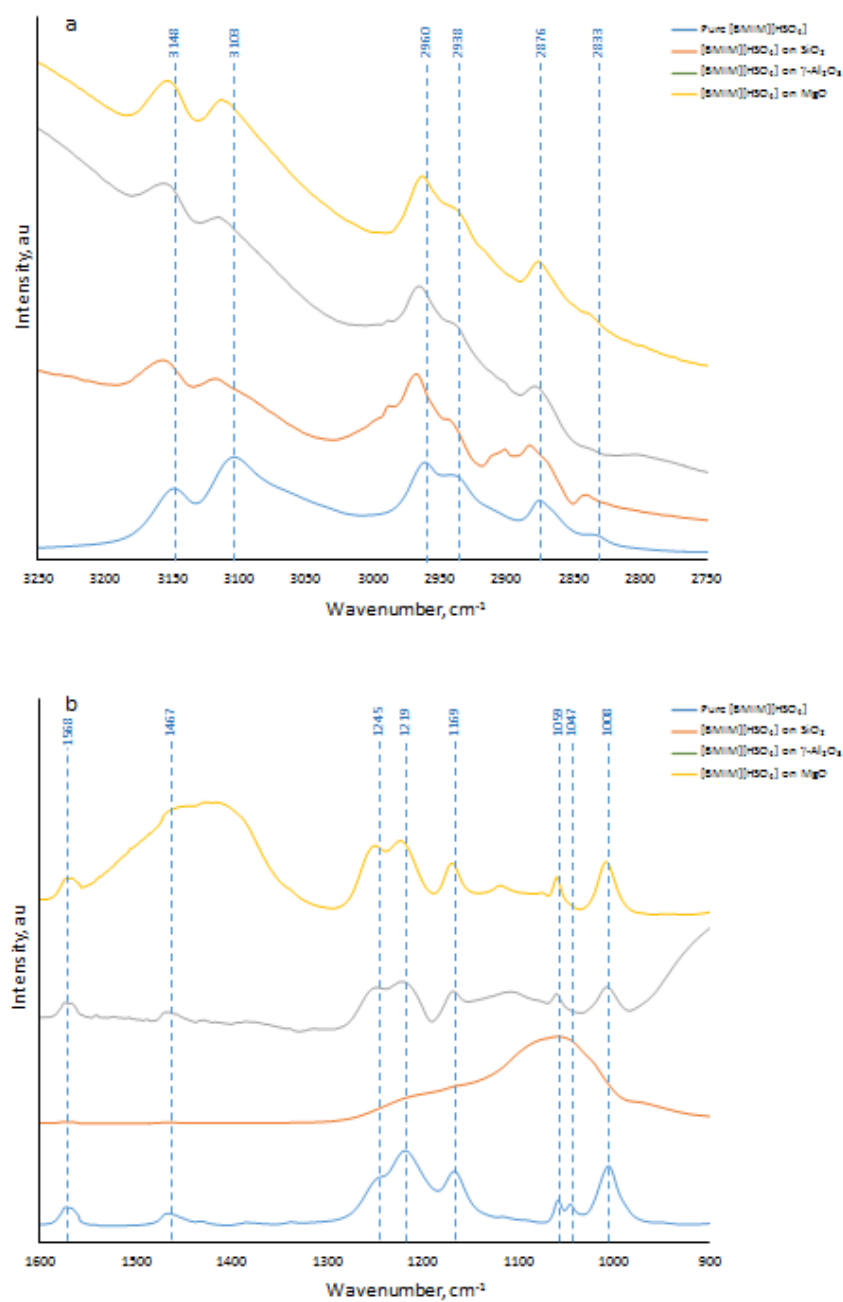


Figure A2-105. FTIR spectra of bulk and supported [BMIM][HSO₄] in the region of a) 2750-3250 cm^{-1} b) 900-1600 cm^{-1} .

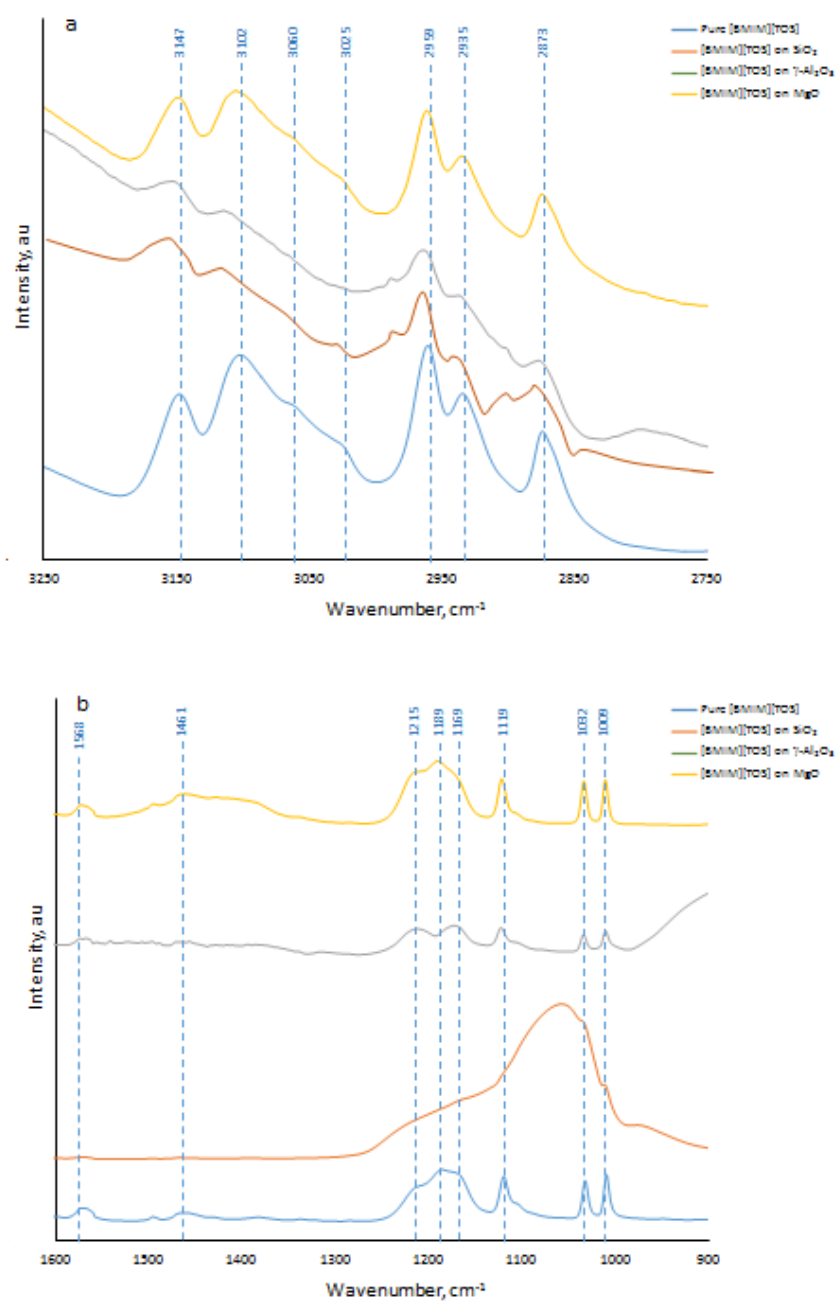


Figure A2-106. FTIR spectra of bulk and supported [BMIM][TOS] in the region of a) 2750-3250 cm^{-1} b) 900-1600 cm^{-1} .

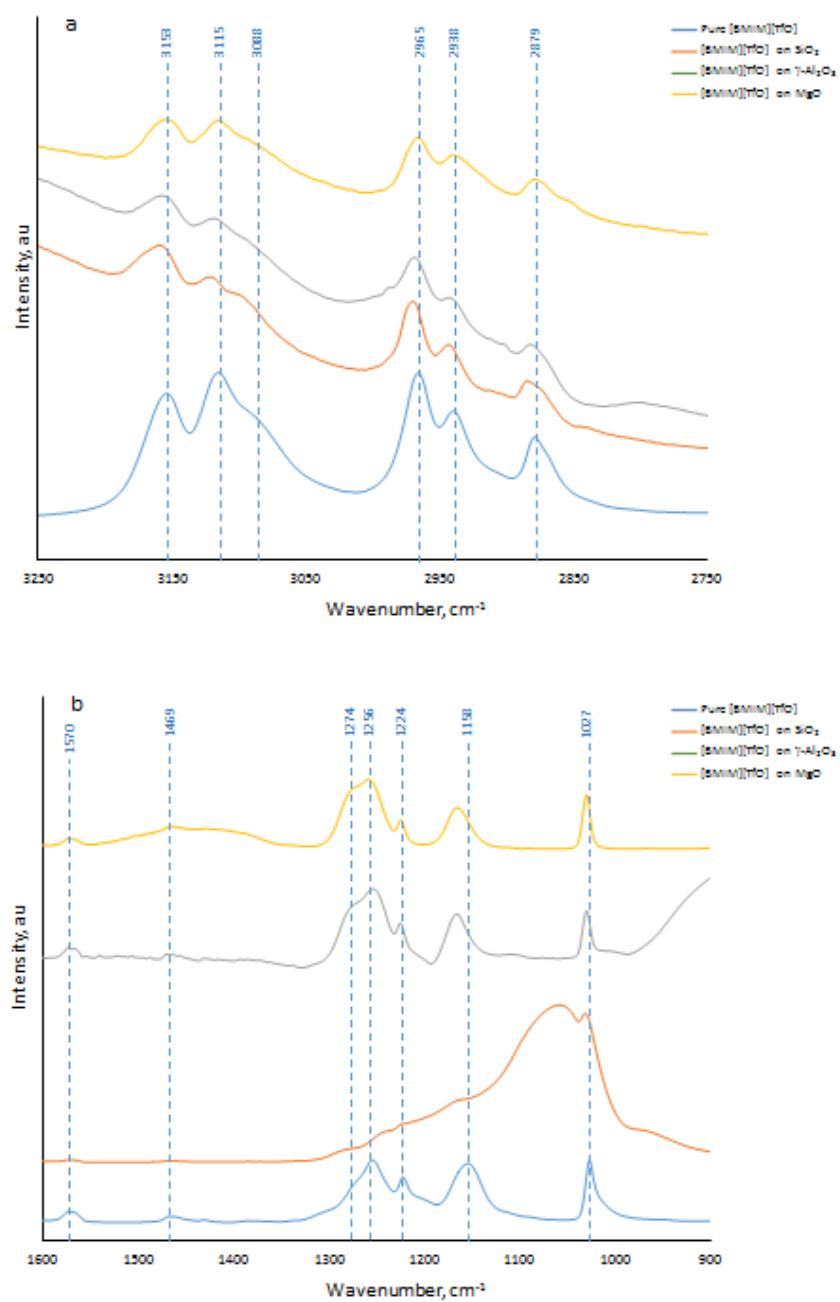


Figure A2-107. FTIR spectra of bulk and supported [BMIM][TfO] in the region of a) 2750-3250 cm^{-1} b) 900-1600 cm^{-1} .

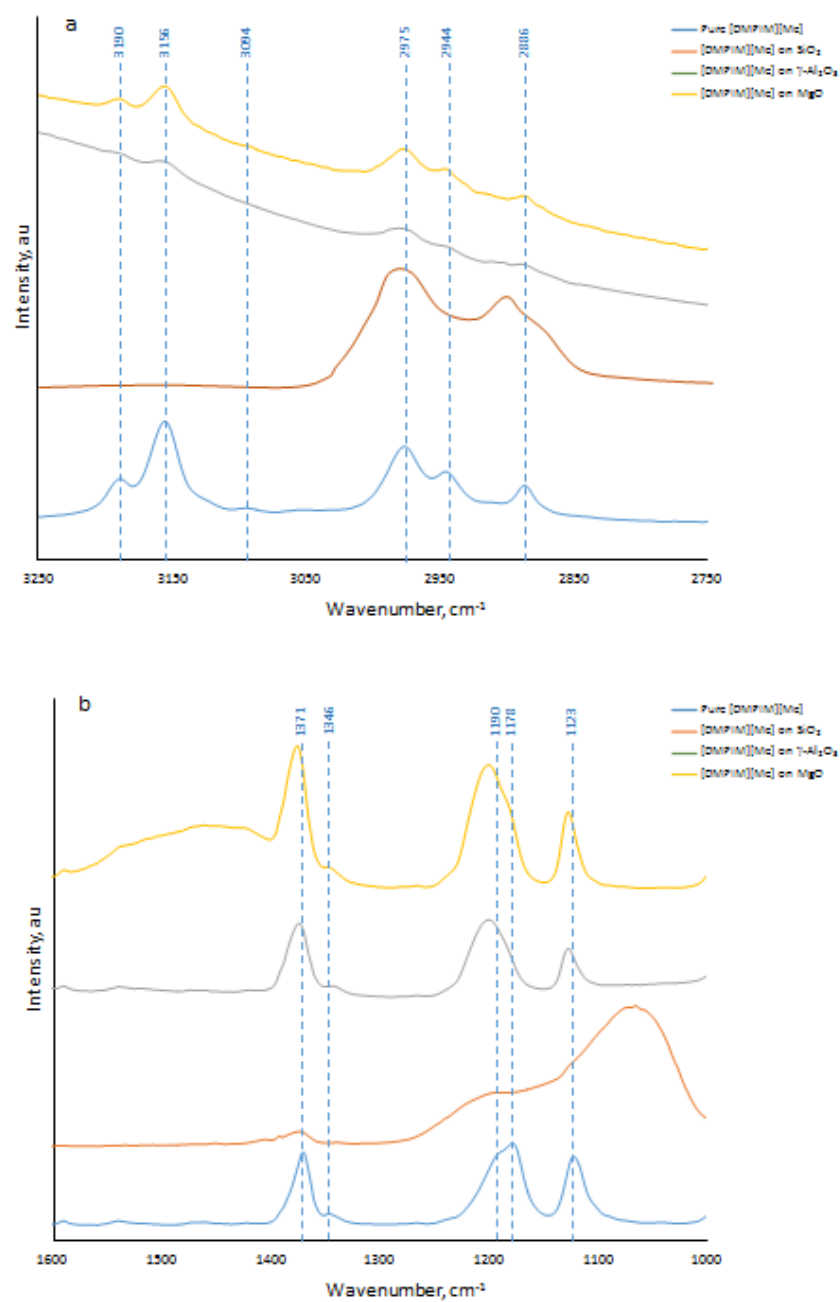


Figure A2-108. FTIR spectra of bulk and supported [DMPIM][Me] in the region of a) 2750-3250 cm^{-1} b) 1000-1600 cm^{-1} .

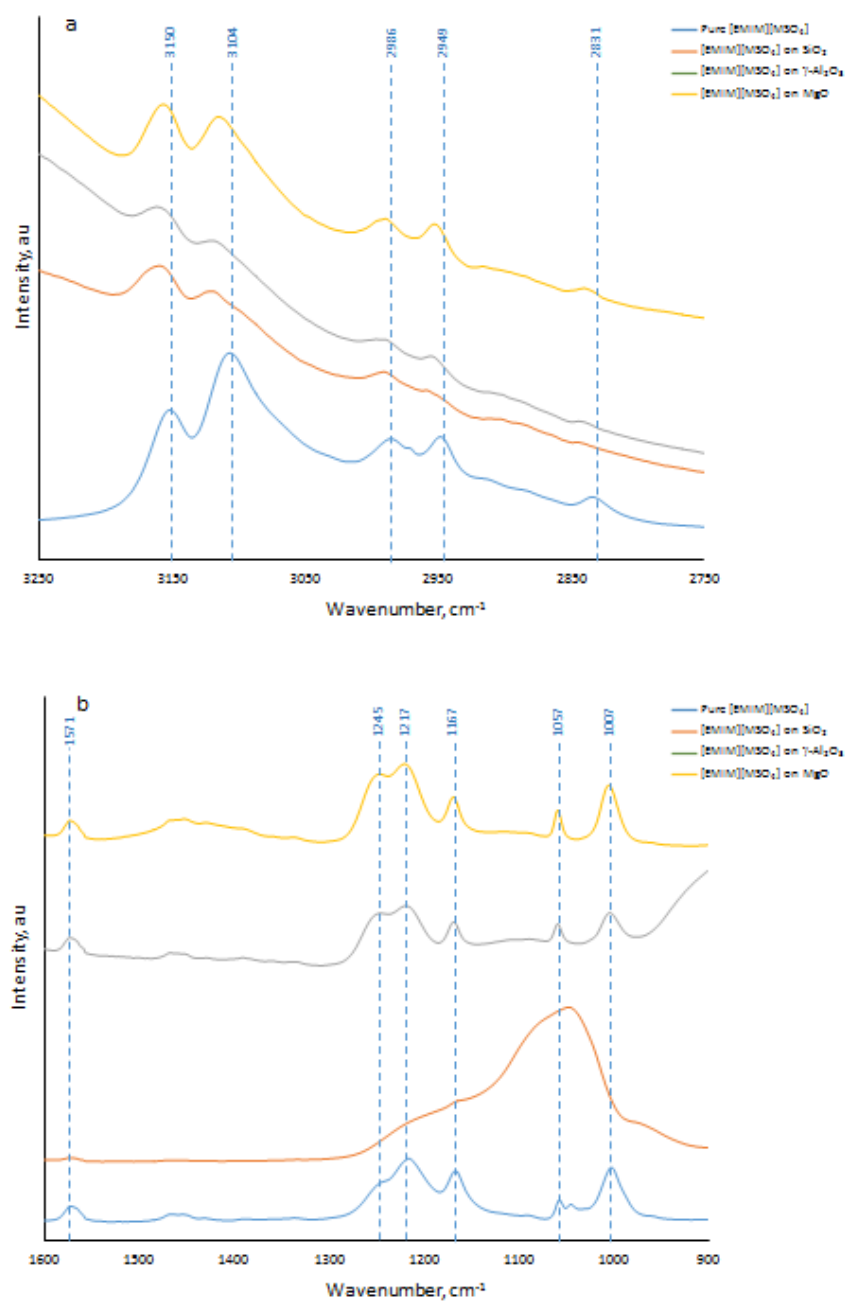


Figure A2-109. FTIR spectra of bulk and supported [EMIM][MSO₄] in the region of a) 2750-3250 cm^{-1} b) 900-1600 cm^{-1} .

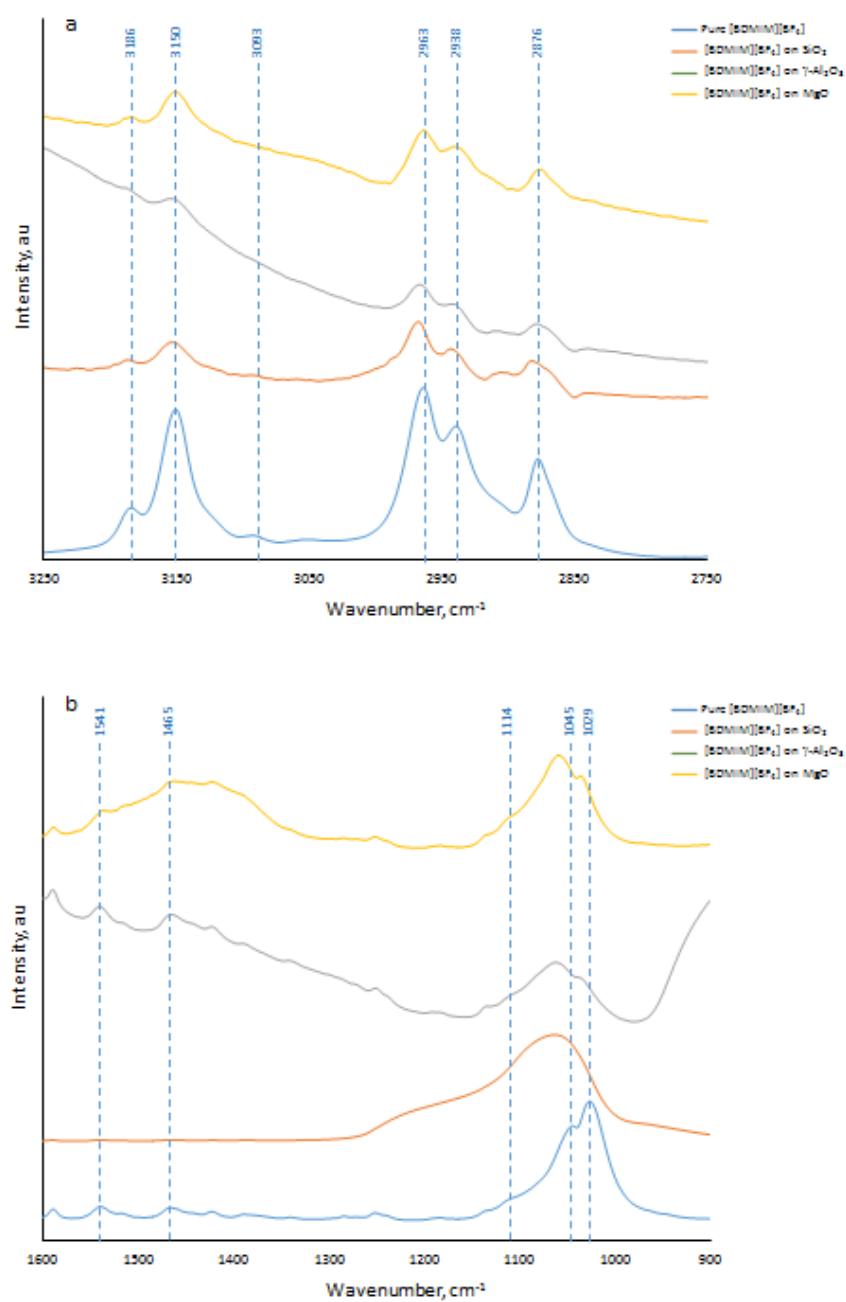


Figure A2-110. FTIR spectra of bulk and supported [BDMIM][BF₄] in the region of a) 2750-3250 cm^{-1} b) 900-1600 cm^{-1} .

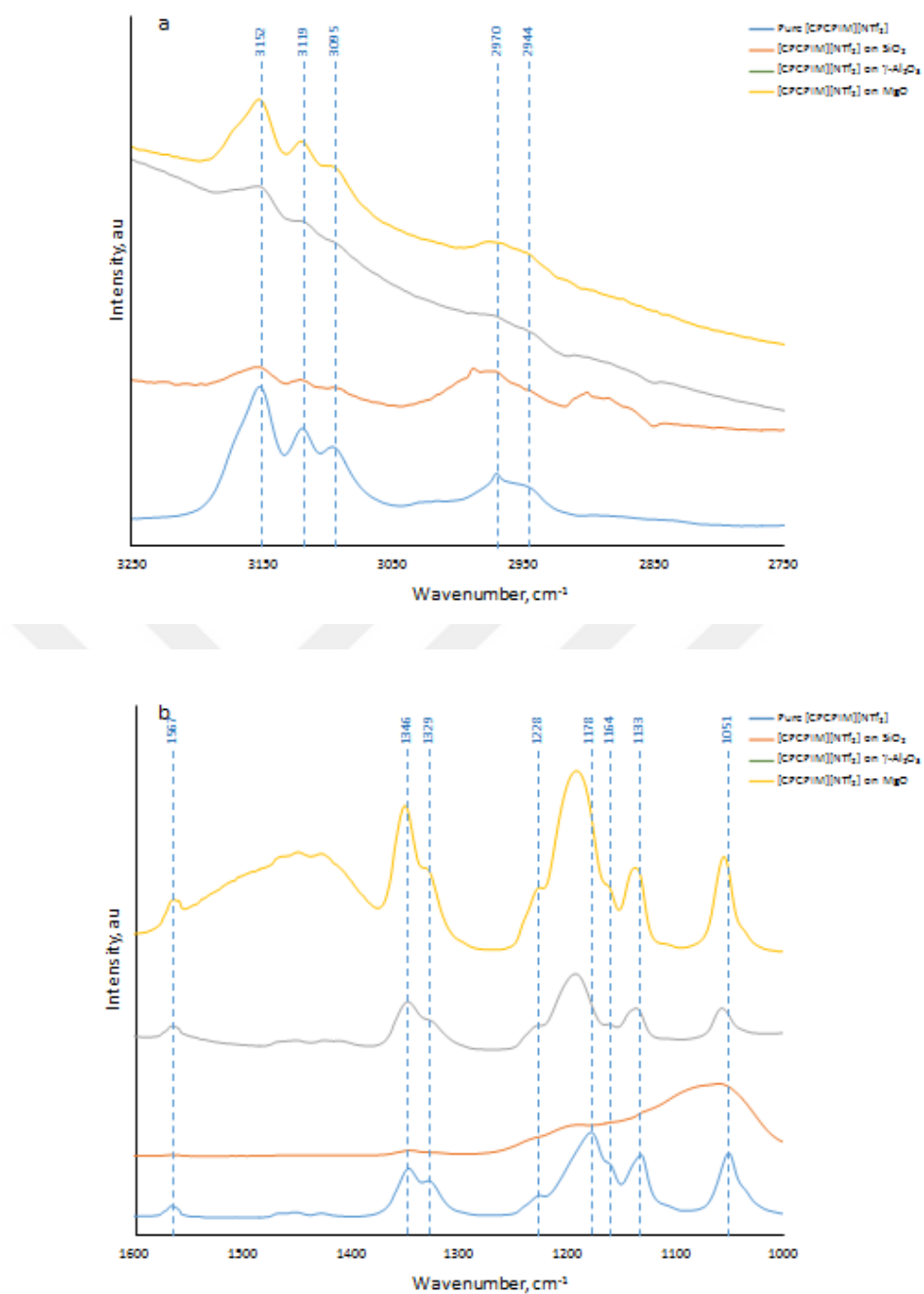


Figure A2-111. FTIR spectra of bulk and supported [CPCPIM][NTf₂] in the region of a) 2750-3250 cm^{-1} b) 1000-1600 cm^{-1} .

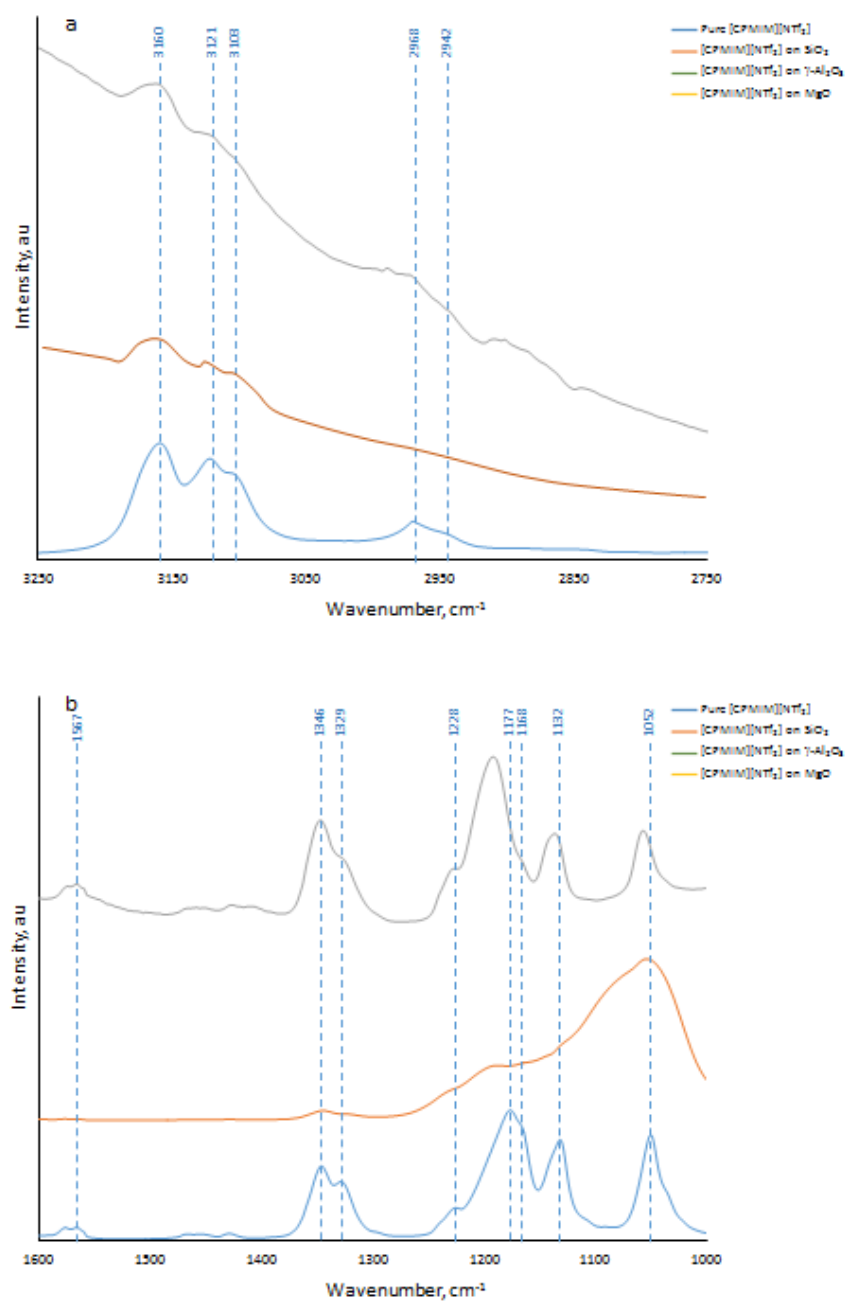


Figure A2-112. FTIR spectra of bulk and supported [CPMIM][NTf₂] in the region of a) 2750-3250 cm^{-1} b) 1000-1600 cm^{-1} .

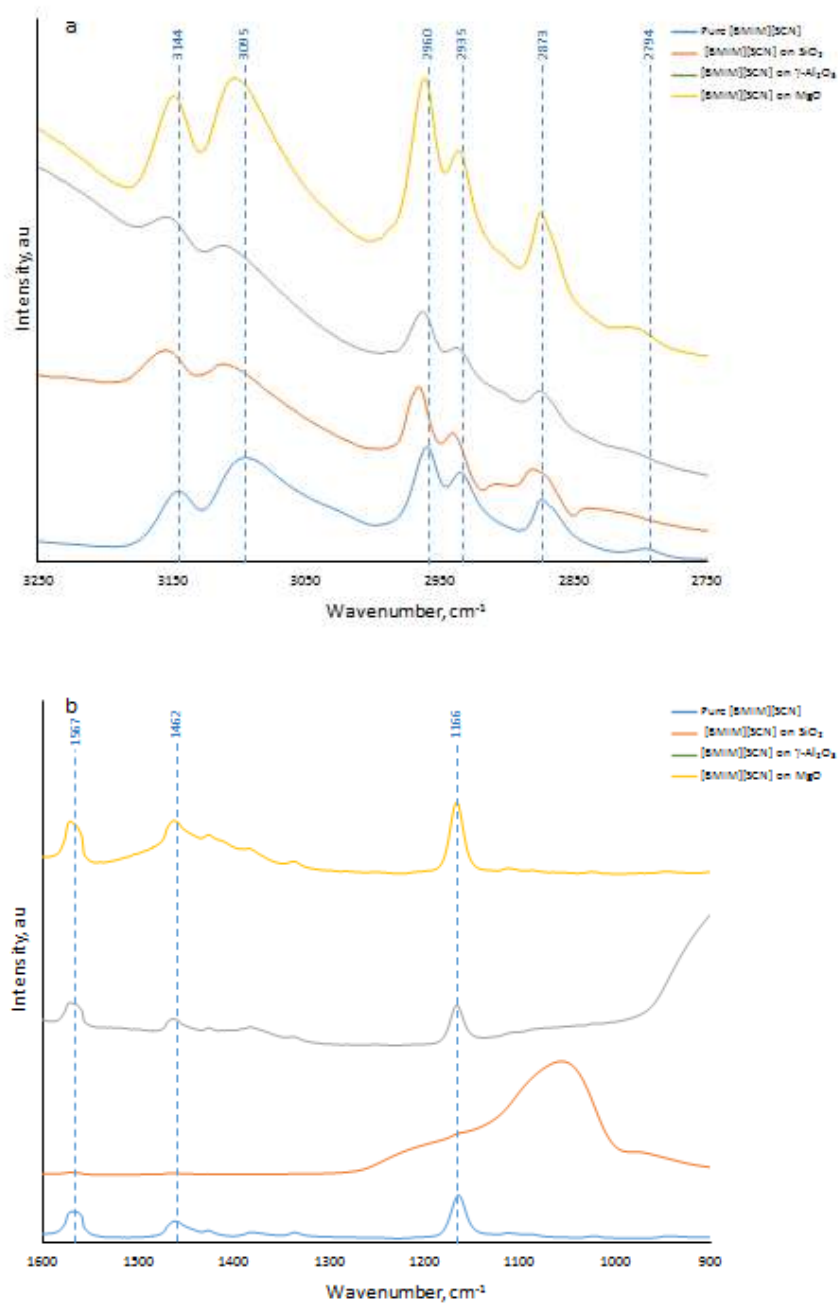


Figure A2-113. FTIR spectra of bulk and supported [BMIM][SCN] in the region of a) 2750-3250 cm^{-1} b) 900-1600 cm^{-1} .

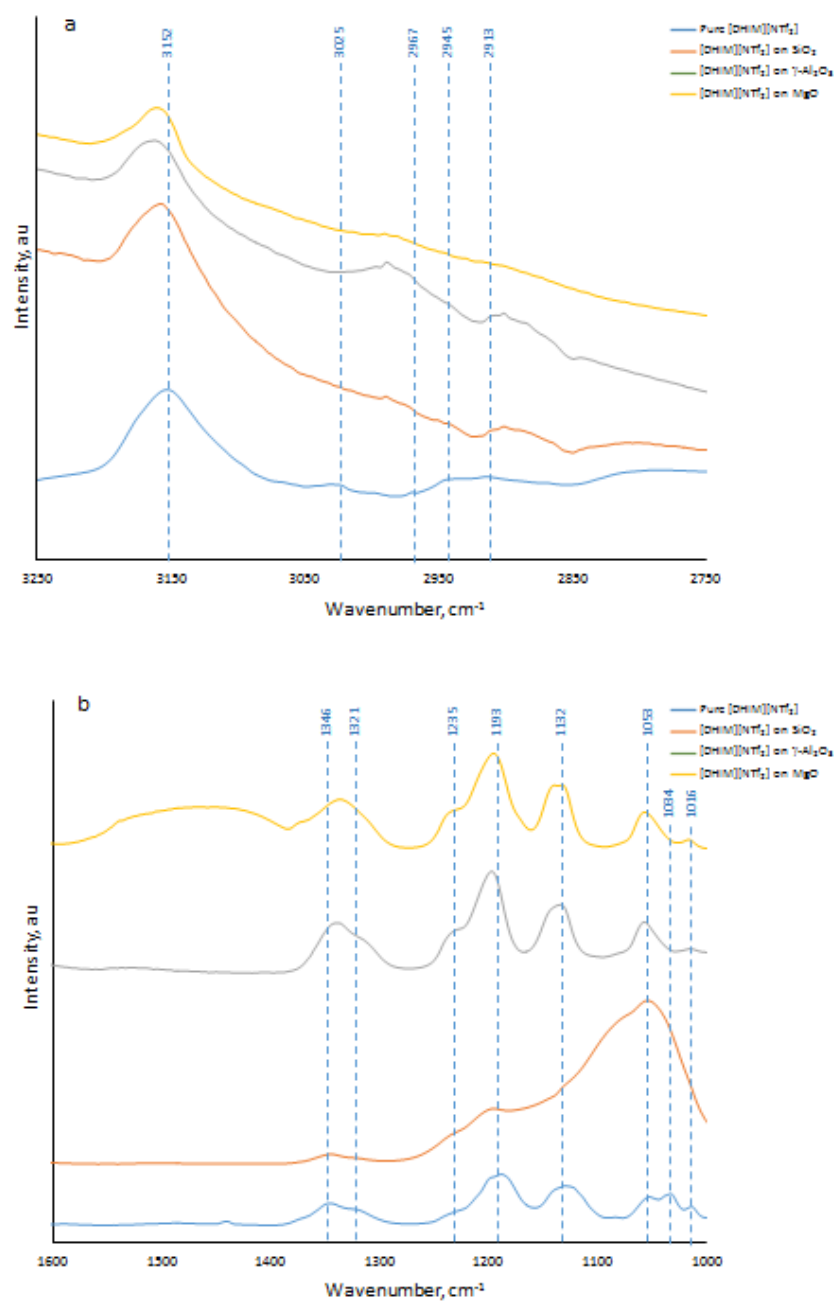


Figure A2-114. FTIR spectra of bulk and supported [DHIM][NTf₂] in the region of a) 2750-3250 cm^{-1} b) 1000-1600 cm^{-1} .

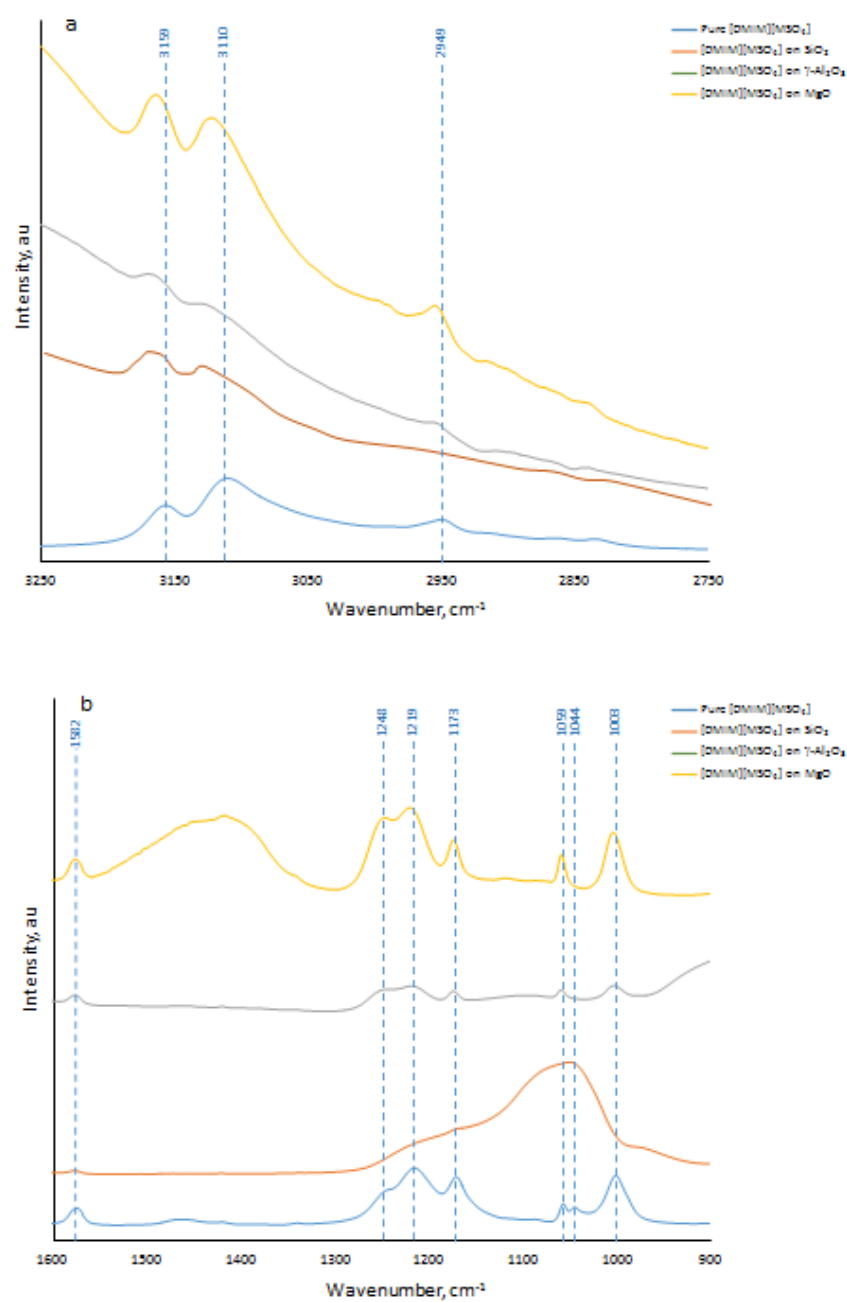


Figure A2-115. FTIR spectra of bulk and supported [DMIM][MSO₄] in the region of a) 2750-3250 cm^{-1} b) 900-1600 cm^{-1} .

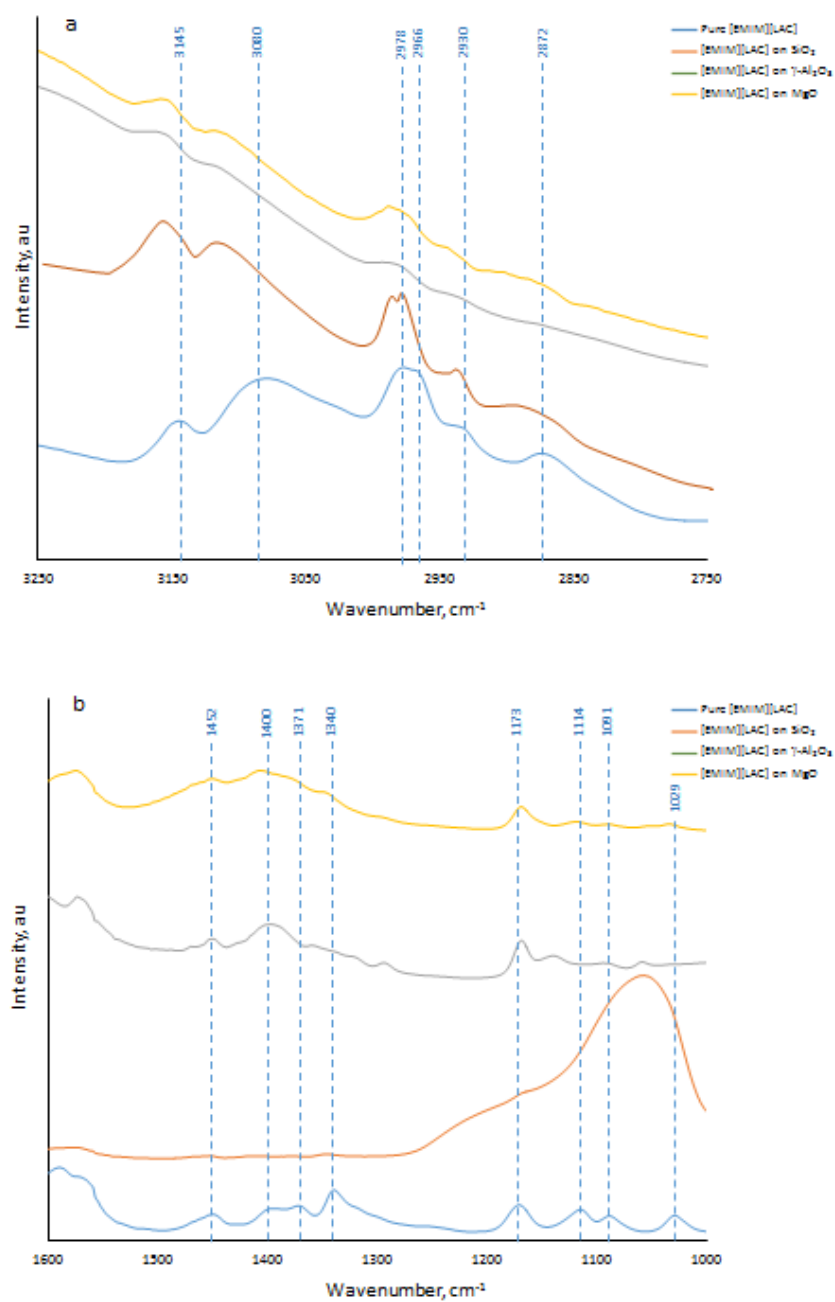


Figure A2-116. FTIR spectra of bulk and supported [EMIM][LAC] in the region of a) 2750-3250 cm^{-1} b) 1000-1600 cm^{-1} .

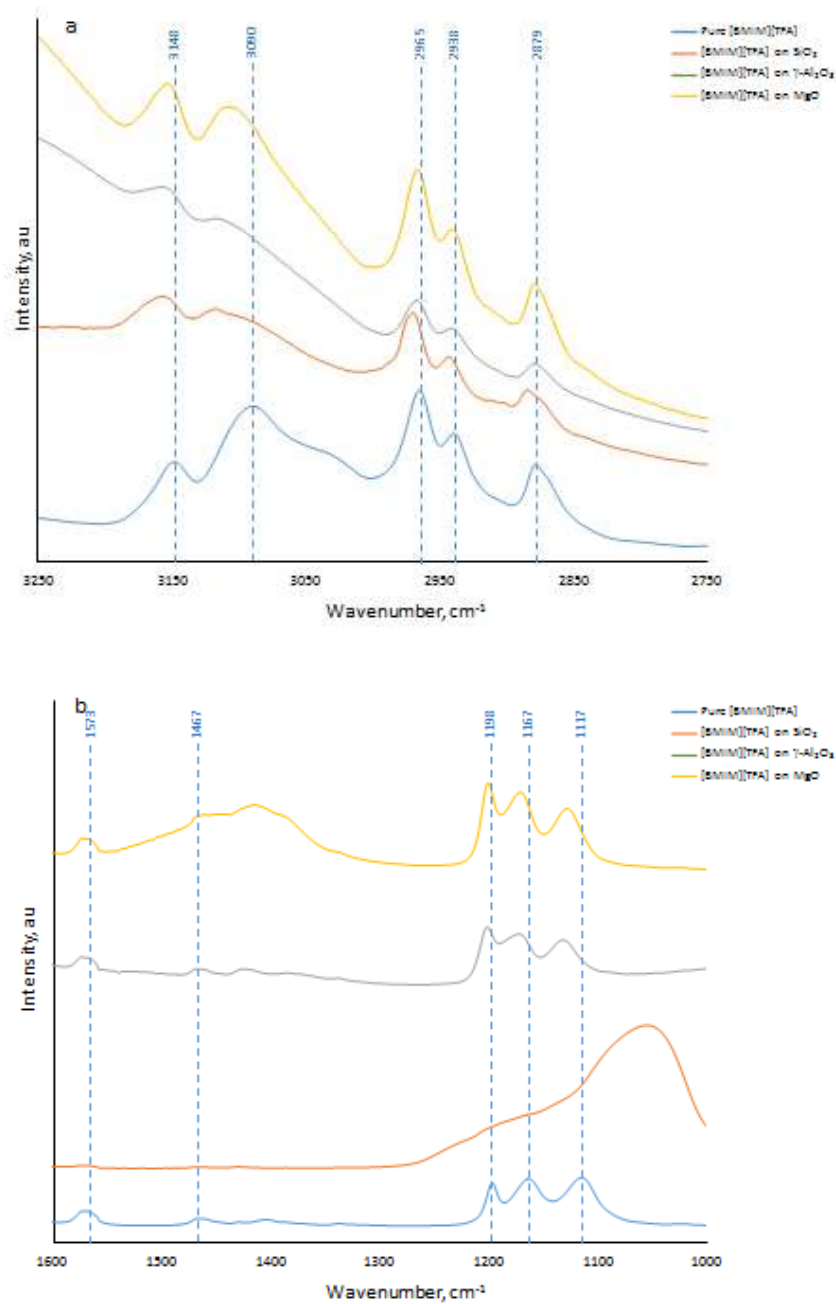


Figure A2-117. FTIR spectra of bulk and supported [BMIM][TFA] in the region of a) 2750-3250 cm^{-1} b) 1000-1600 cm^{-1} .

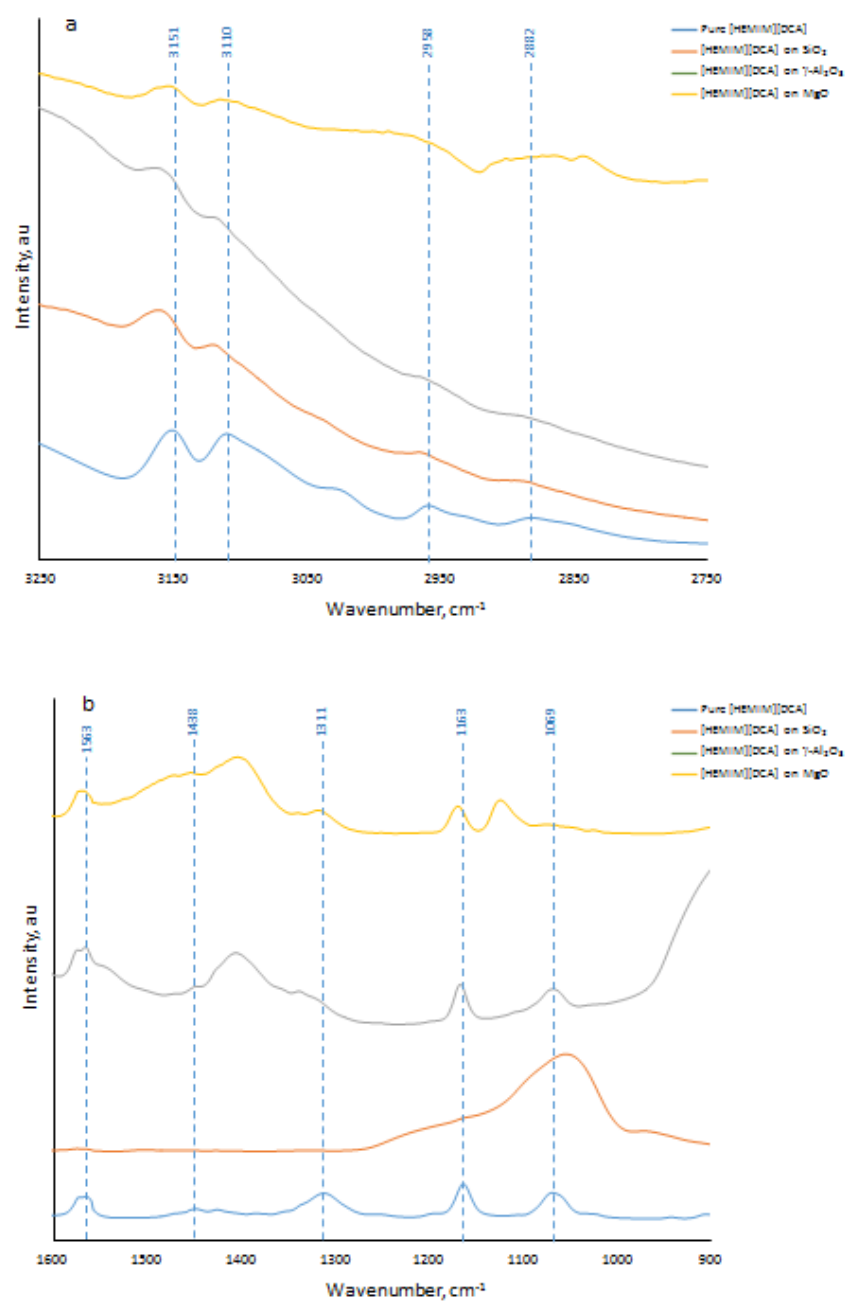


Figure A2-118. FTIR spectra of bulk and supported [HEMIM][DCA] in the region of a) 2750-3250 cm^{-1} b) 900-1600 cm^{-1} .

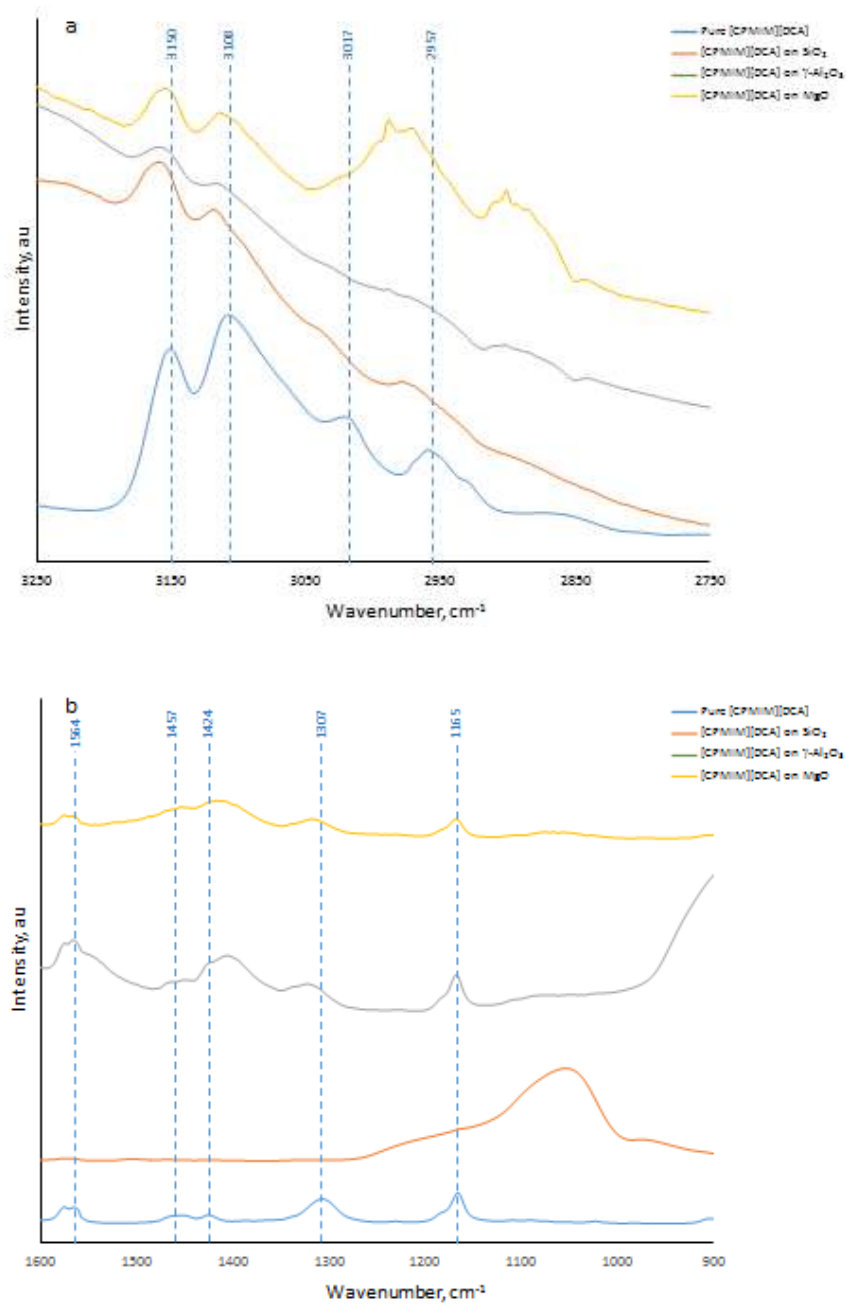


Figure A2-119. FTIR spectra of bulk and supported [CPMIM][DCA] in the region of a) 2750-3250 cm^{-1} b) 900-1600 cm^{-1} .

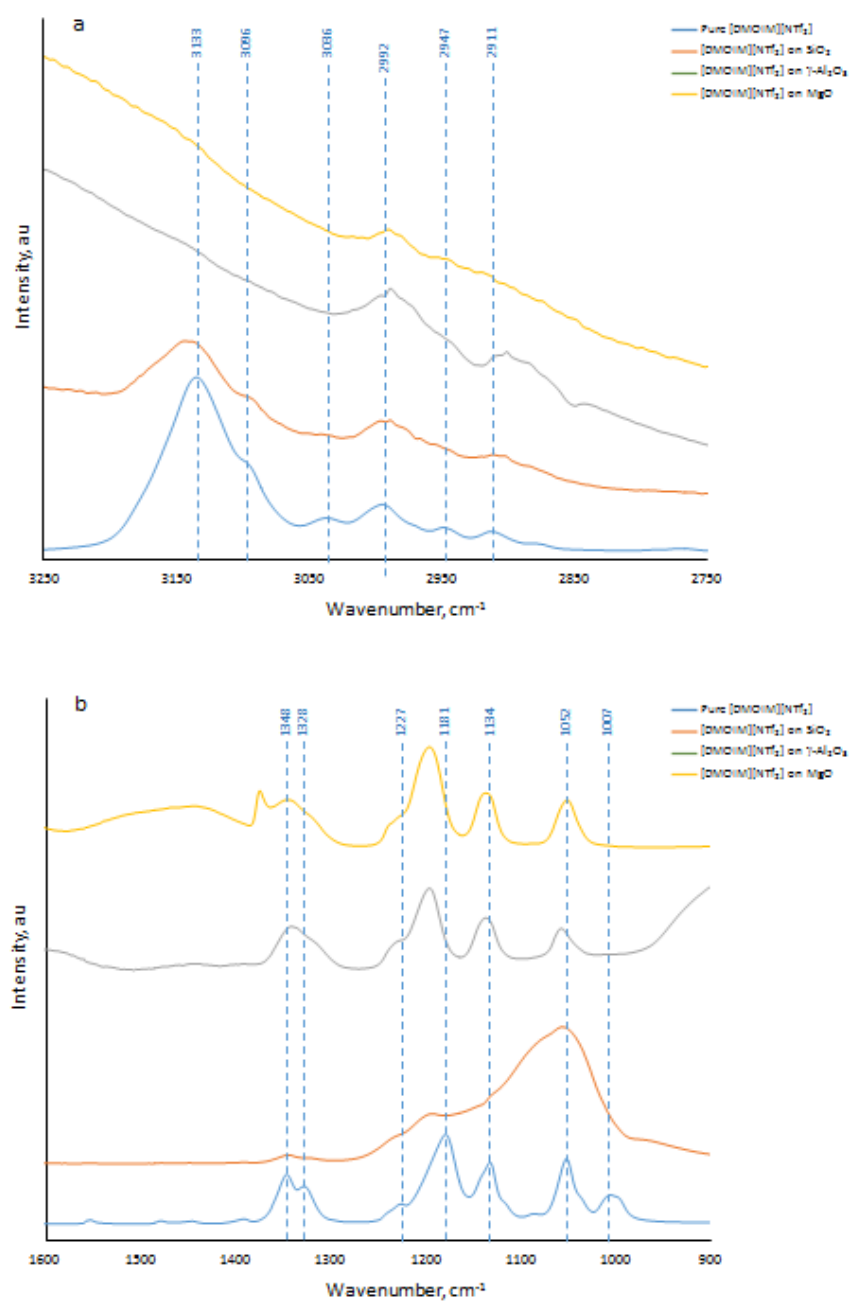


Figure A2-120. FTIR spectra of bulk and supported [DMOIM][NTf₂] in the region of a) 2750-3250 cm^{-1} b) 1000-1600 cm^{-1} .

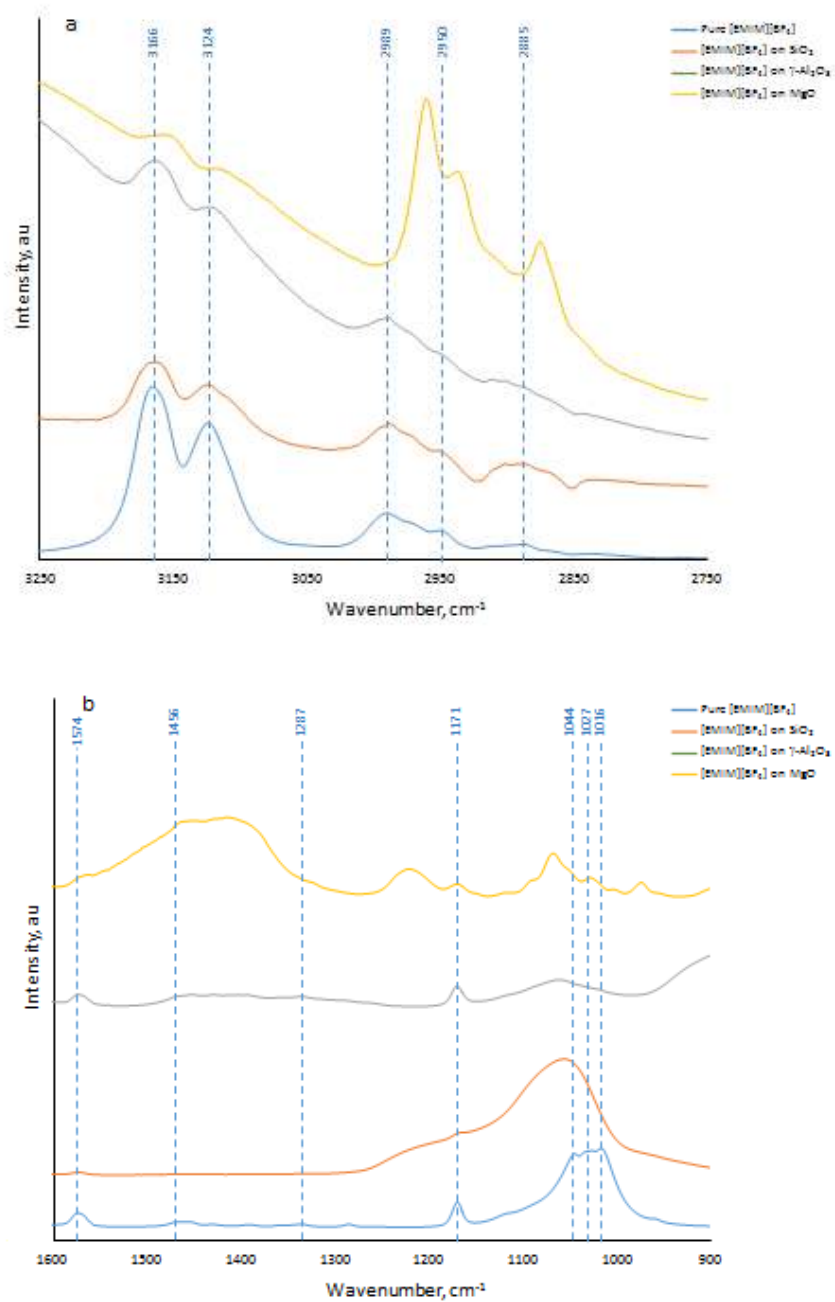


Figure A2-121. FTIR spectra of bulk and supported [EMIM][BF₄] in the region of a) 2750-3250 cm^{-1} b) 900-1600 cm^{-1} .

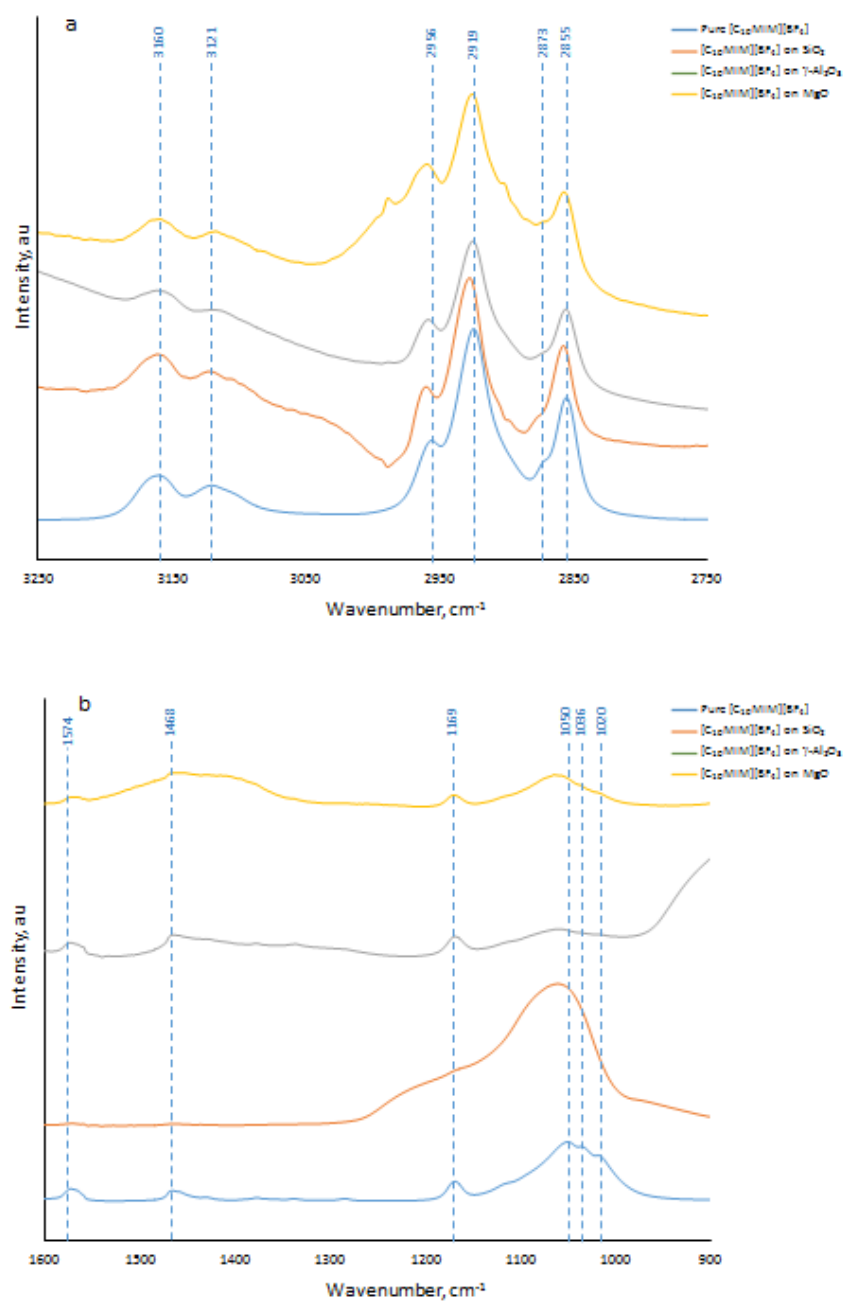


Figure A2-122. FTIR spectra of bulk and supported $[\text{C}_{10}\text{MIM}][\text{BF}_4]$ in the region of a) 2750-3250 cm^{-1} b) 900-1600 cm^{-1} .

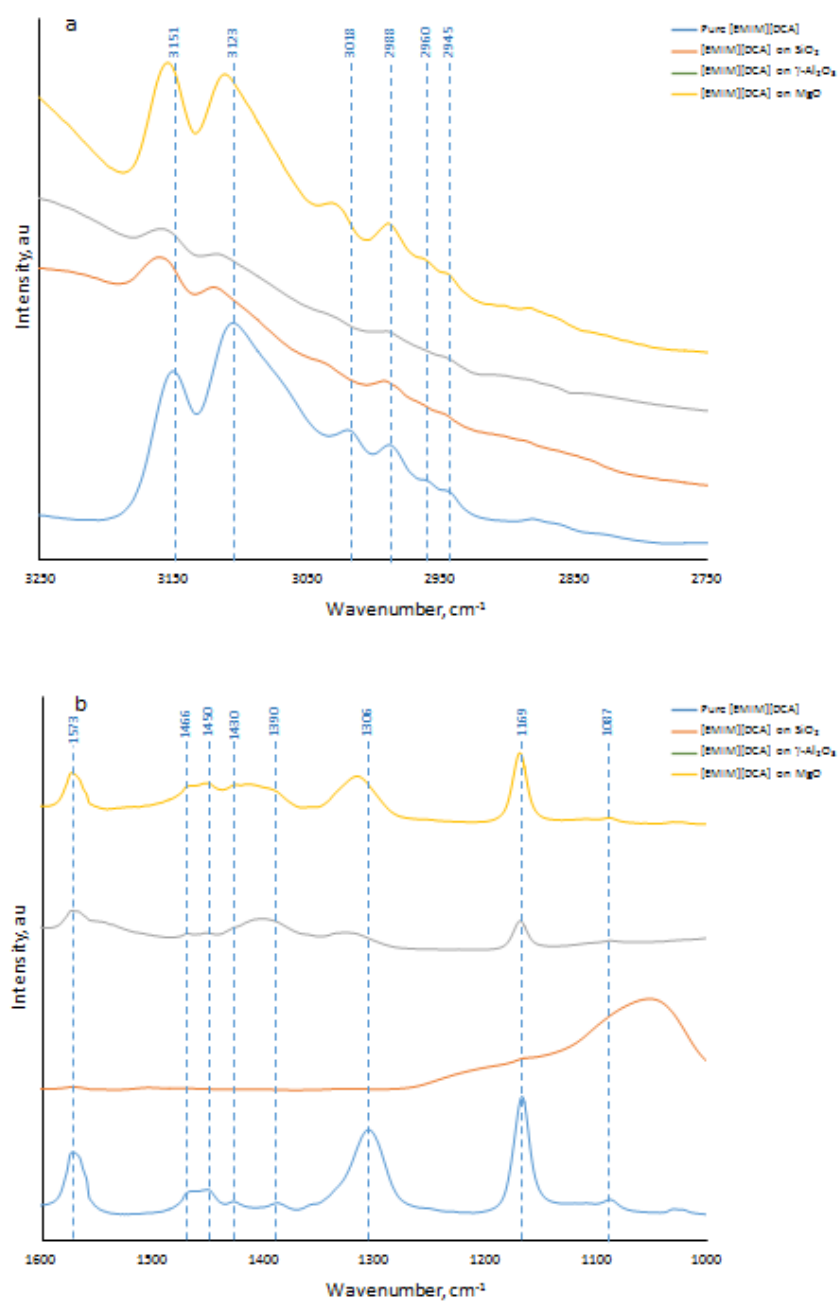


Figure A2-123. FTIR spectra of bulk and supported [EMIM][DCA] in the region of a) 2750-3250 cm^{-1} b) 1000-1600 cm^{-1} .

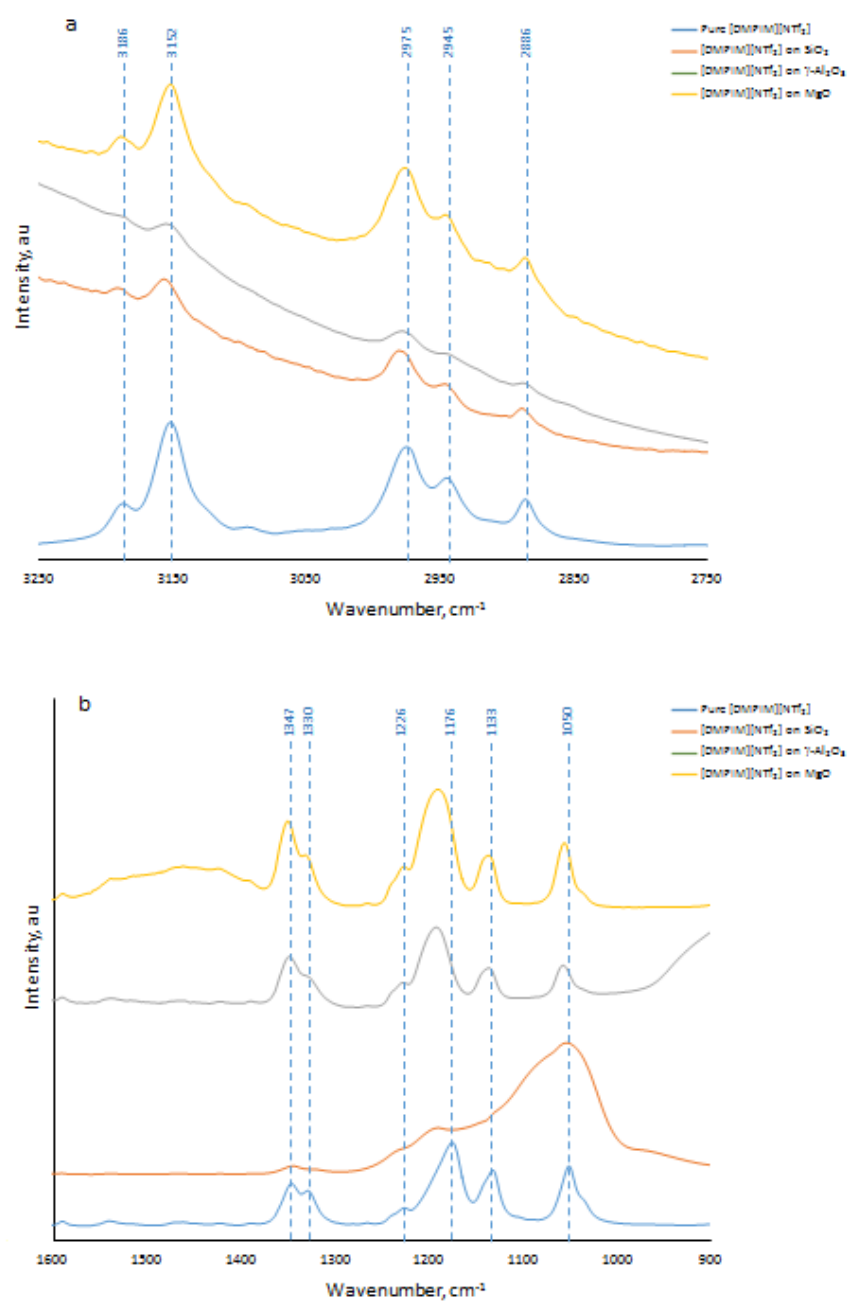


Figure A2-124. FTIR spectra of bulk and supported [DMPIM][NTf₂] in the region of a) 2750-3250 cm⁻¹ b) 900-1600 cm⁻¹.

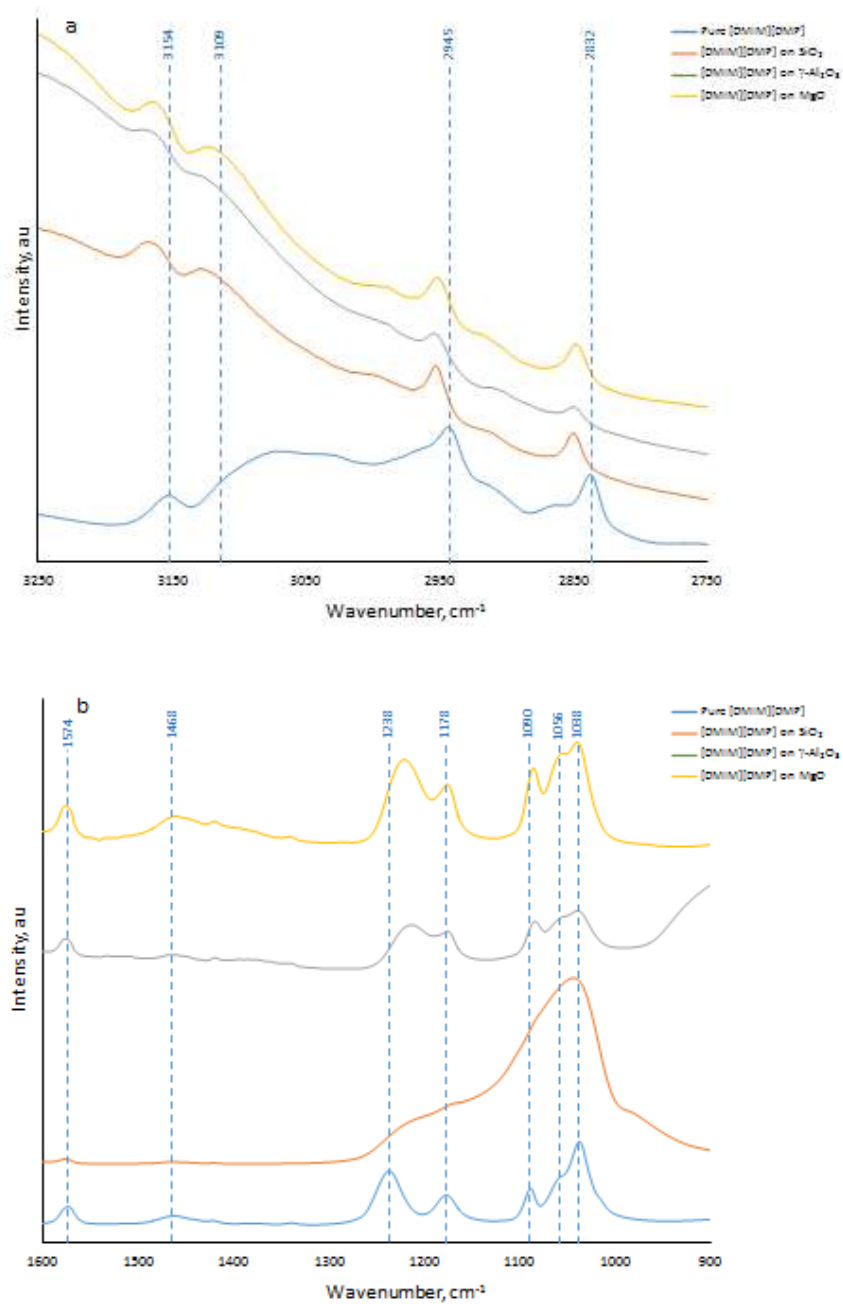


Figure A2-125. FTIR spectra of bulk and supported [DMIM][DMP] in the region of a) 2750-3250 cm^{-1} b) 900-1600 cm^{-1} .

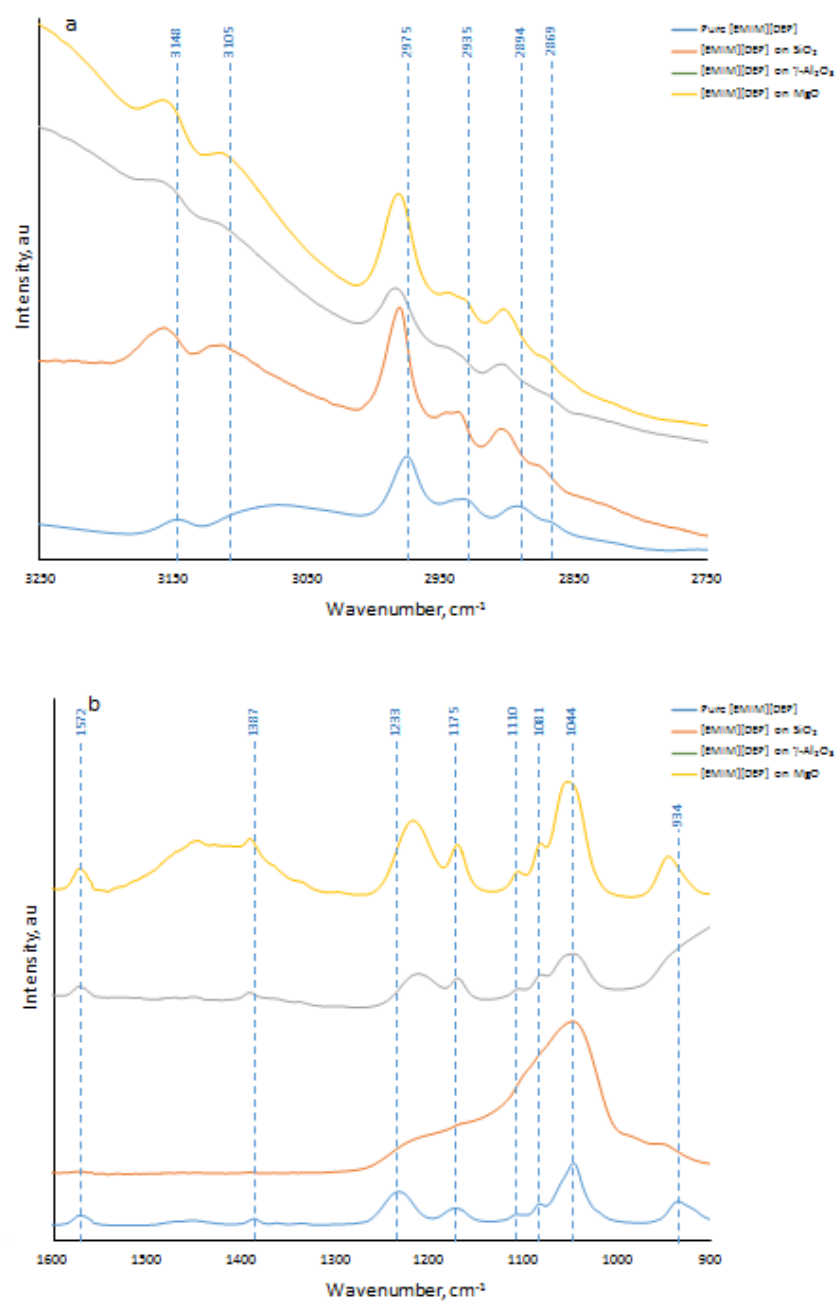


Figure A2-126. FTIR spectra of bulk and supported [EMIM][DEP] in the region of a) 2750-3250 cm^{-1} b) 900-1600 cm^{-1} .

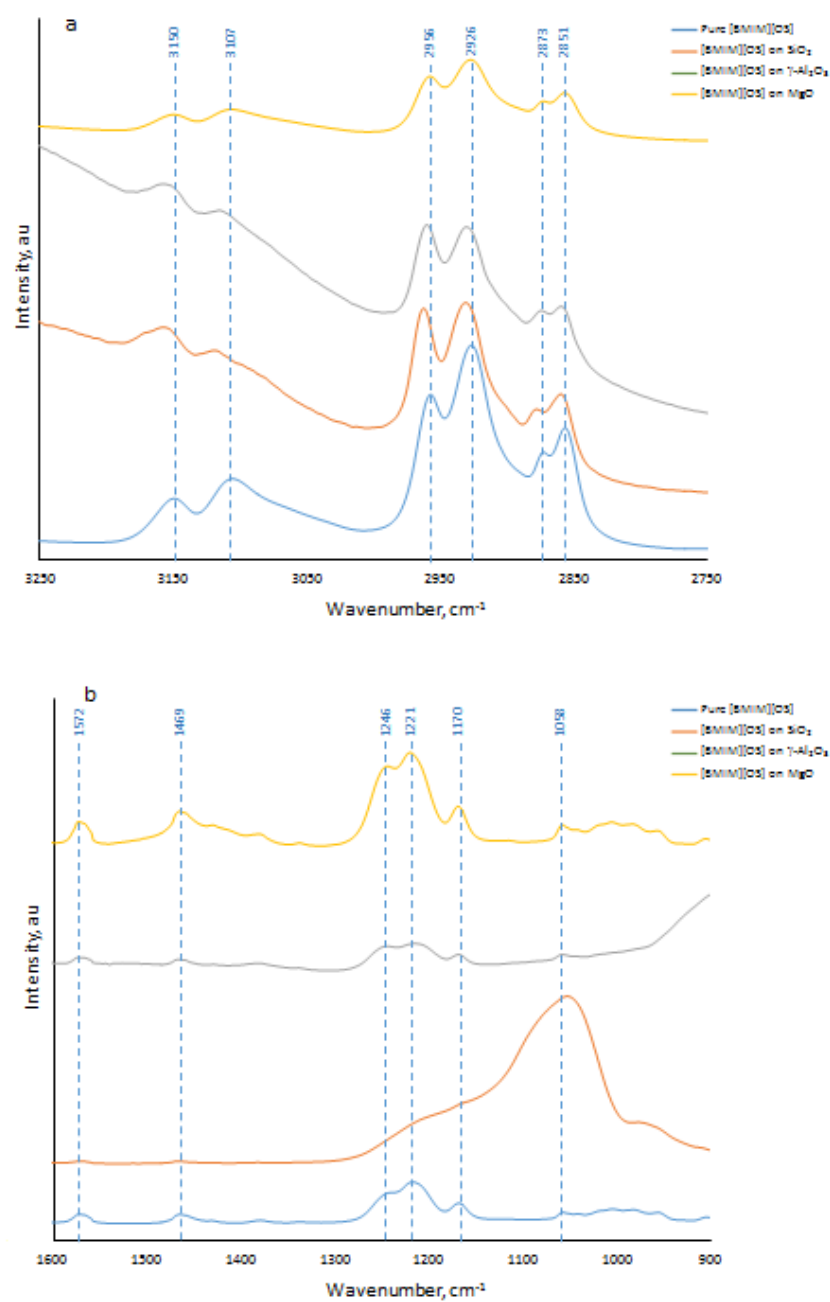


Figure A2-127. FTIR spectra of bulk and supported [BMIM][OS] in the region of a) 2750-3250 cm^{-1} b) 1000-1600 cm^{-1} .

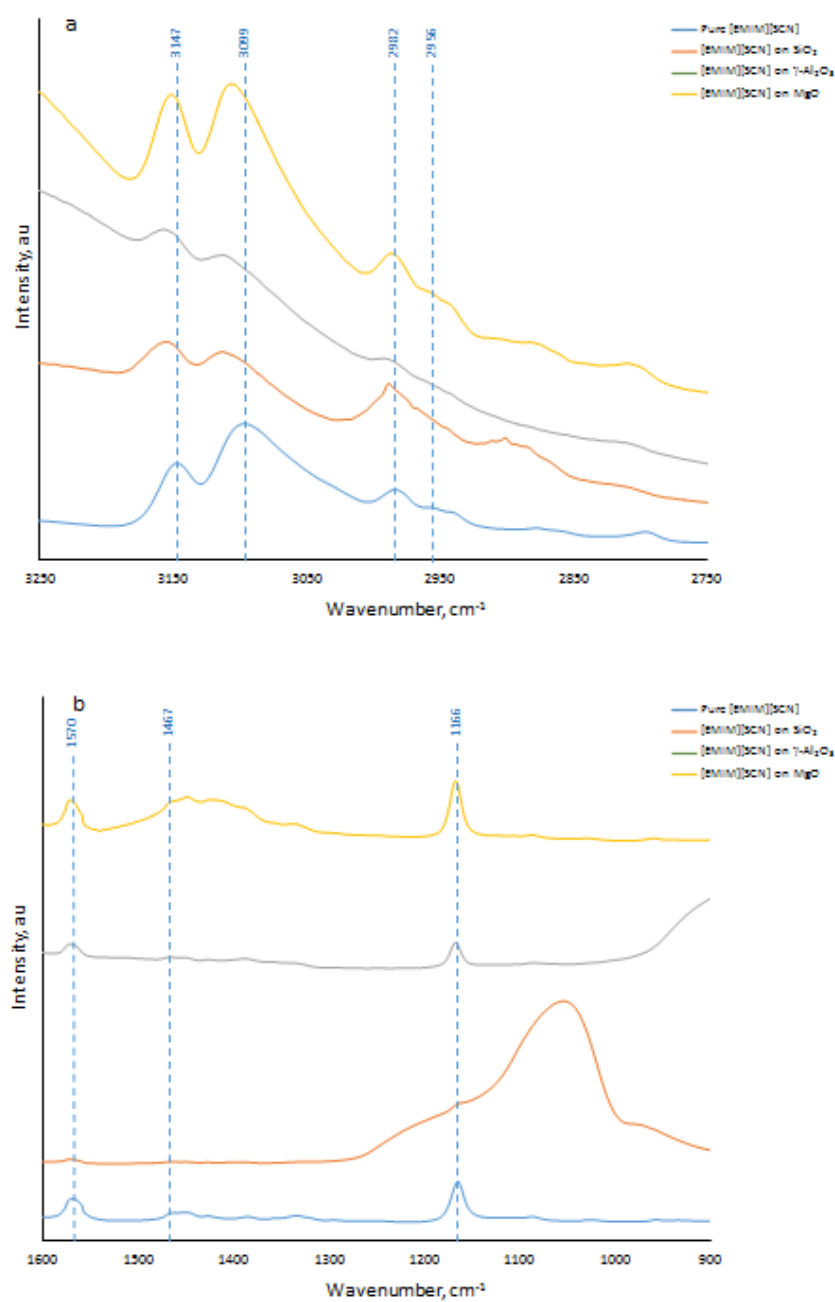


Figure A2-128. FTIR spectra of bulk and supported [EMIM][SCN] in the region of a) 2750-3250 cm^{-1} b) 900-1600 cm^{-1} .

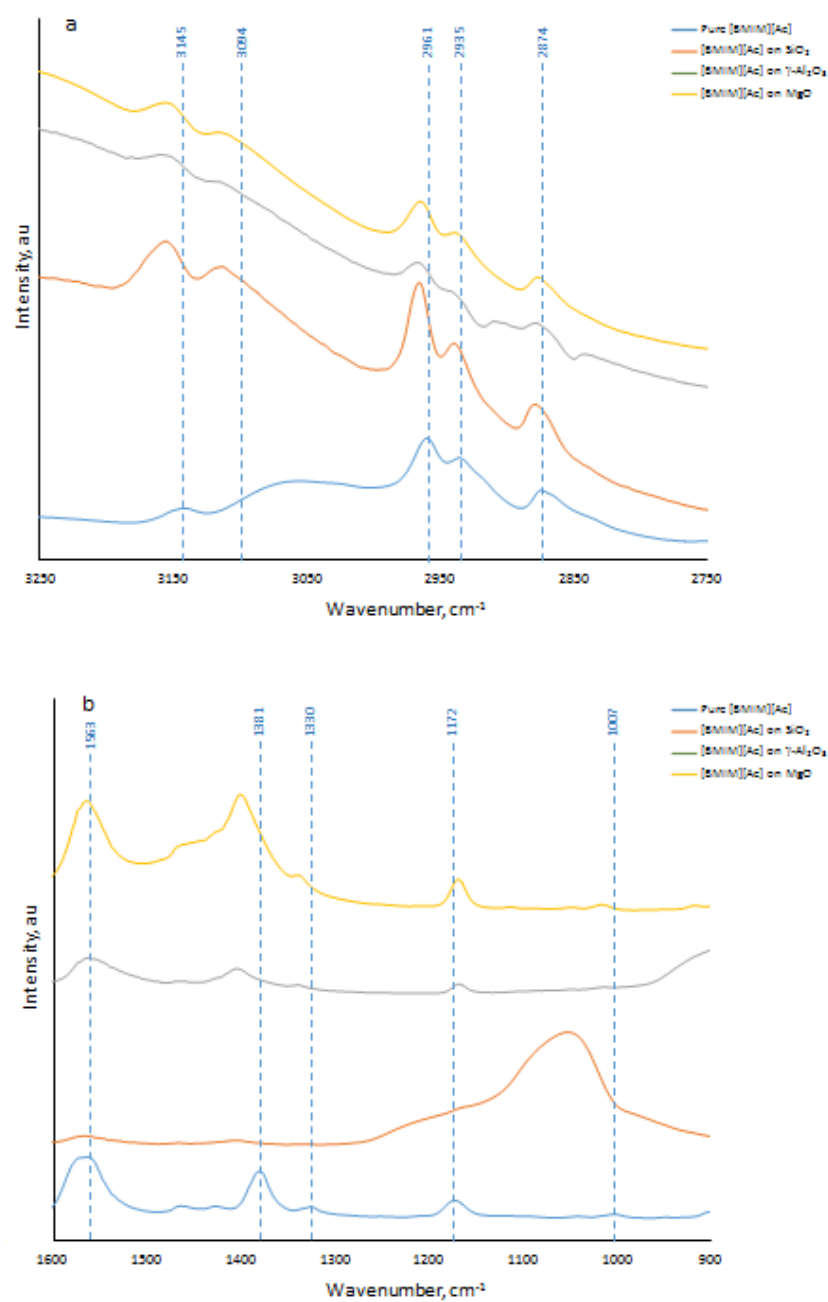


Figure A2-129. FTIR spectra of bulk and supported [BMIM][Ac] in the region of a) 2750-3250 cm^{-1} b) 900-1600 cm^{-1} .

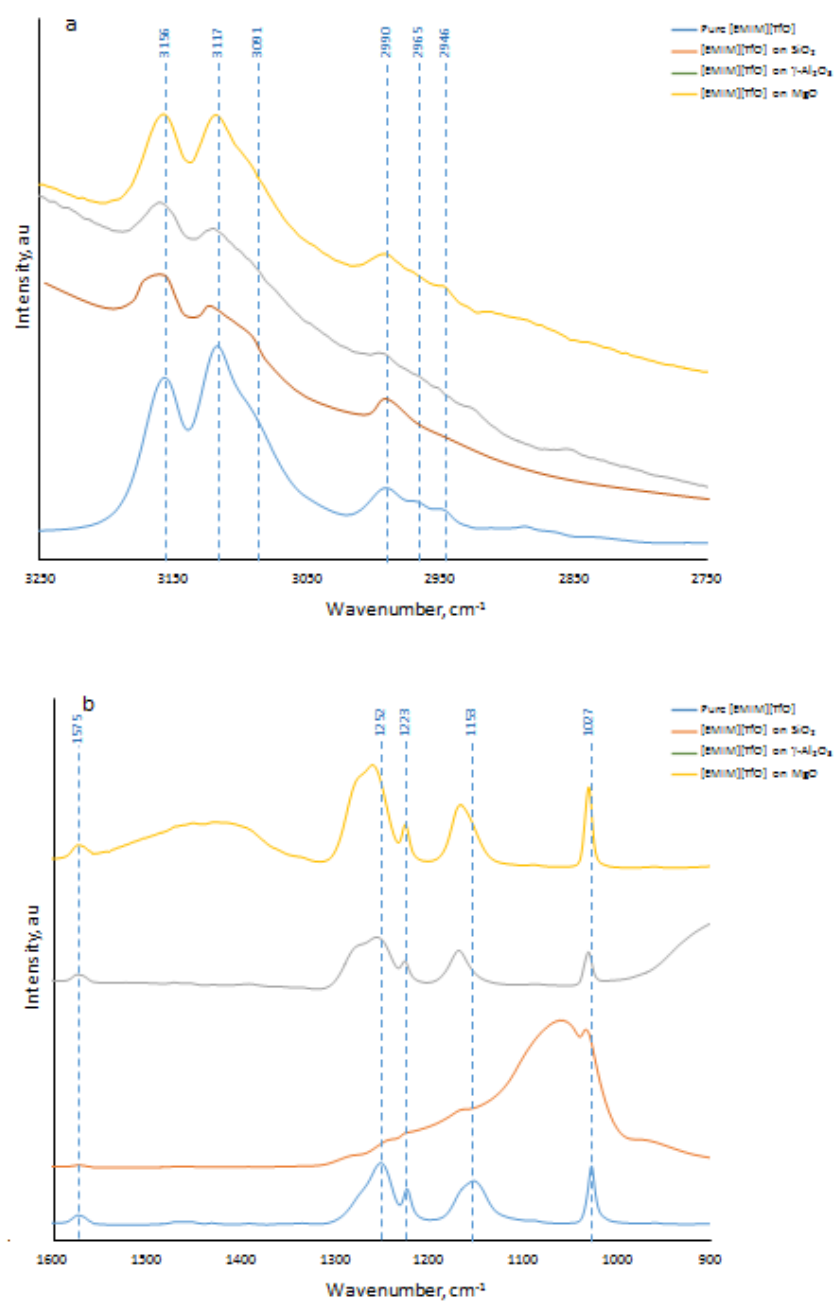


Figure A2-130. FTIR spectra of bulk and supported [EMIM][TfO] in the region of a) 2750-3250 cm^{-1} b) 900-1600 cm^{-1} .

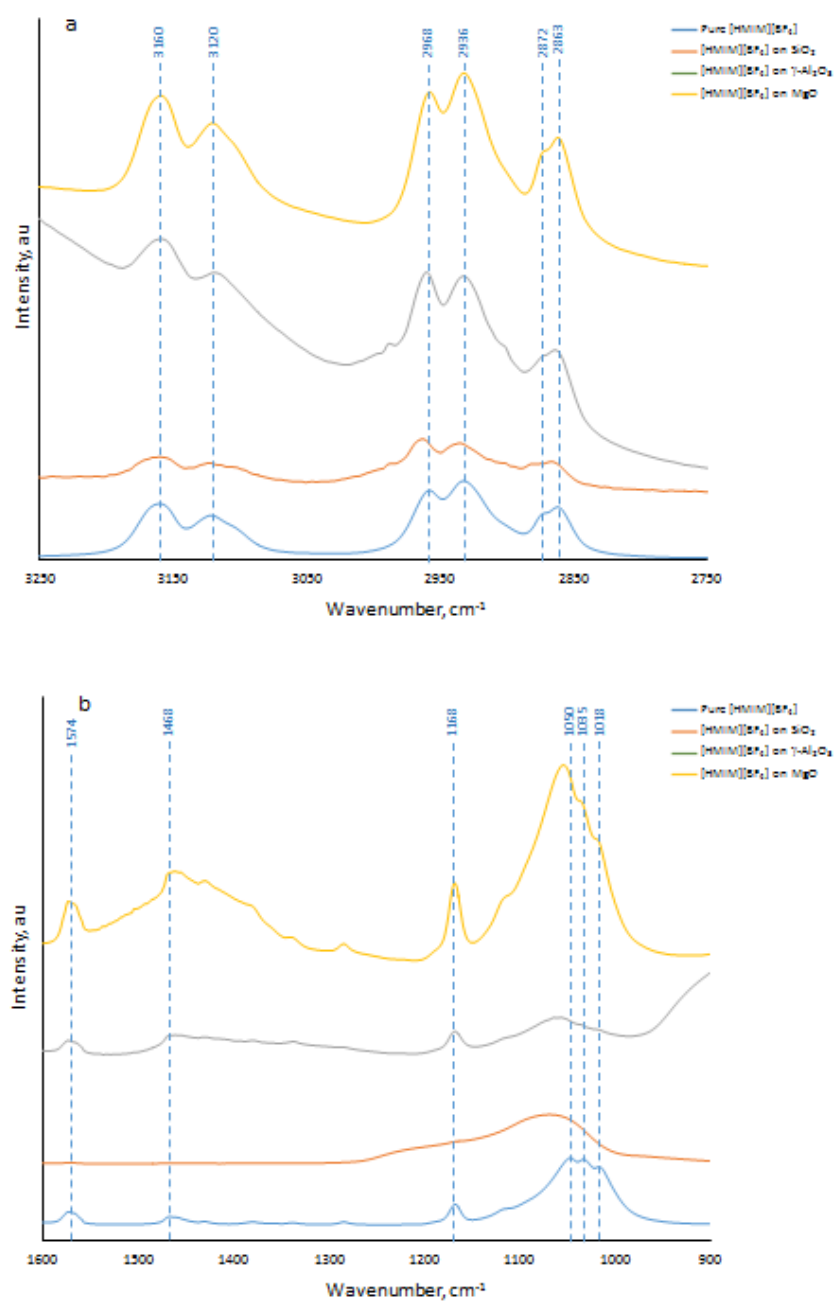


Figure A2-131. FTIR spectra of bulk and supported [HMIM][BF₄] in the region of a) 2750-3250 cm^{-1} b) 900-1600 cm^{-1} .

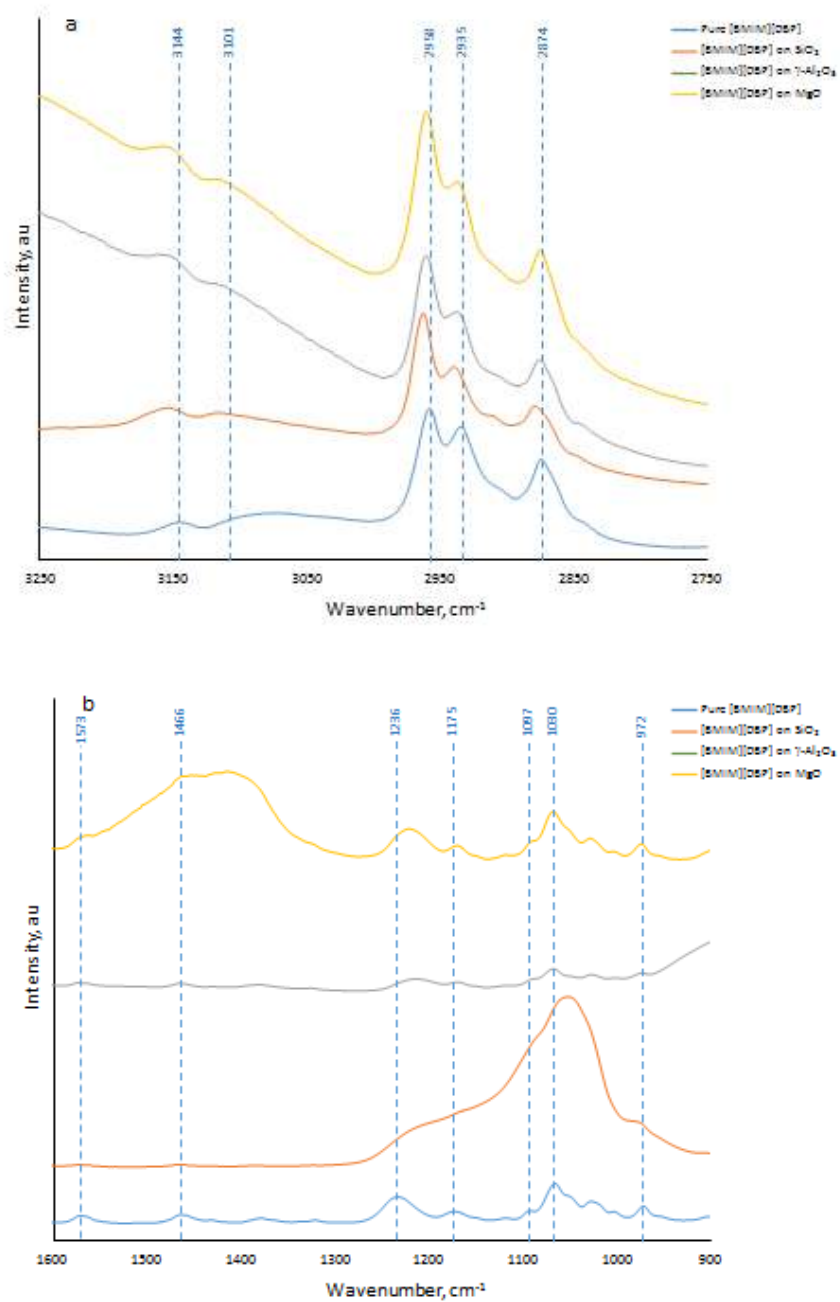


Figure A2-132. FTIR spectra of bulk and supported [BMIM][DBP] in the region of a) 2750-3250 cm^{-1} b) 1000-1600 cm^{-1} .

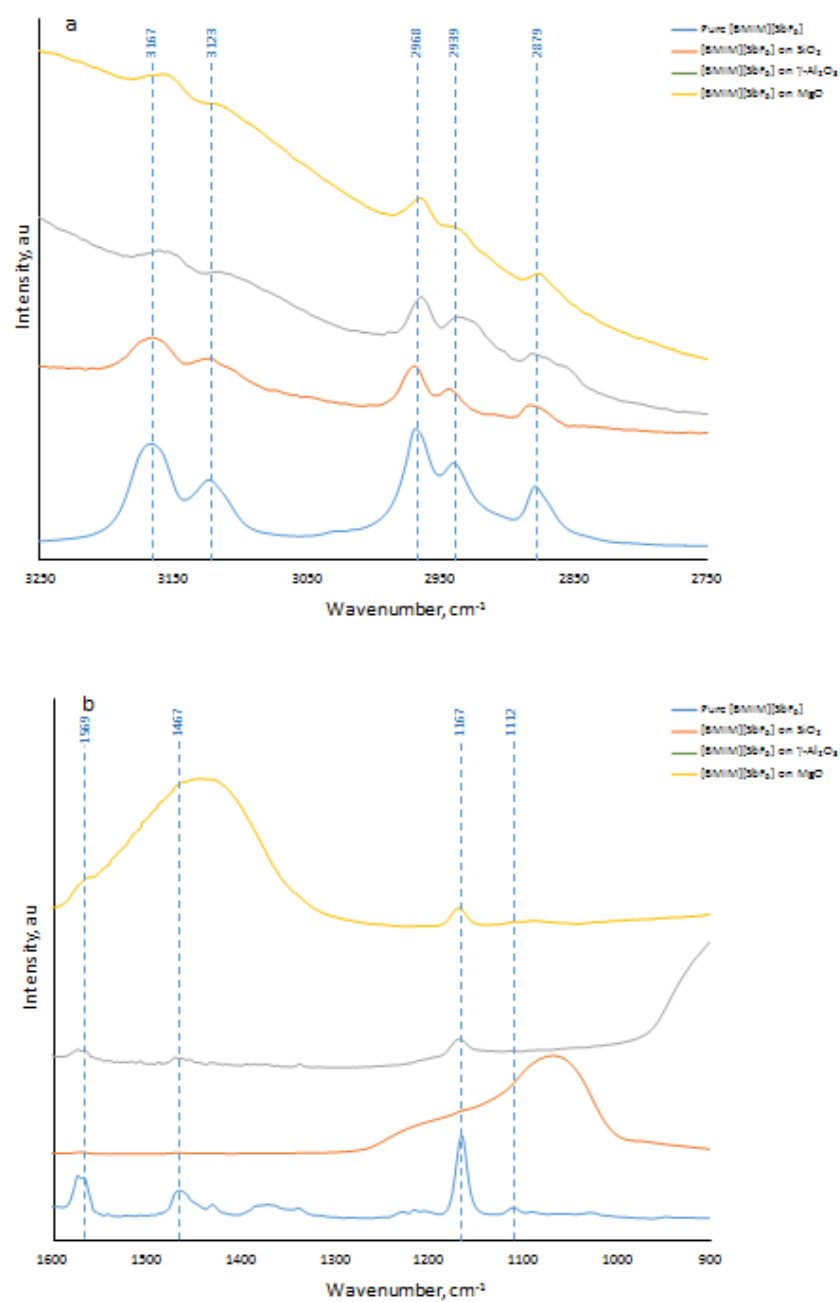


Figure A2-133. FTIR spectra of bulk and supported [BMIM][SbF₆] in the region of a) 2750-3250 cm^{-1} b) 900-1600 cm^{-1} .

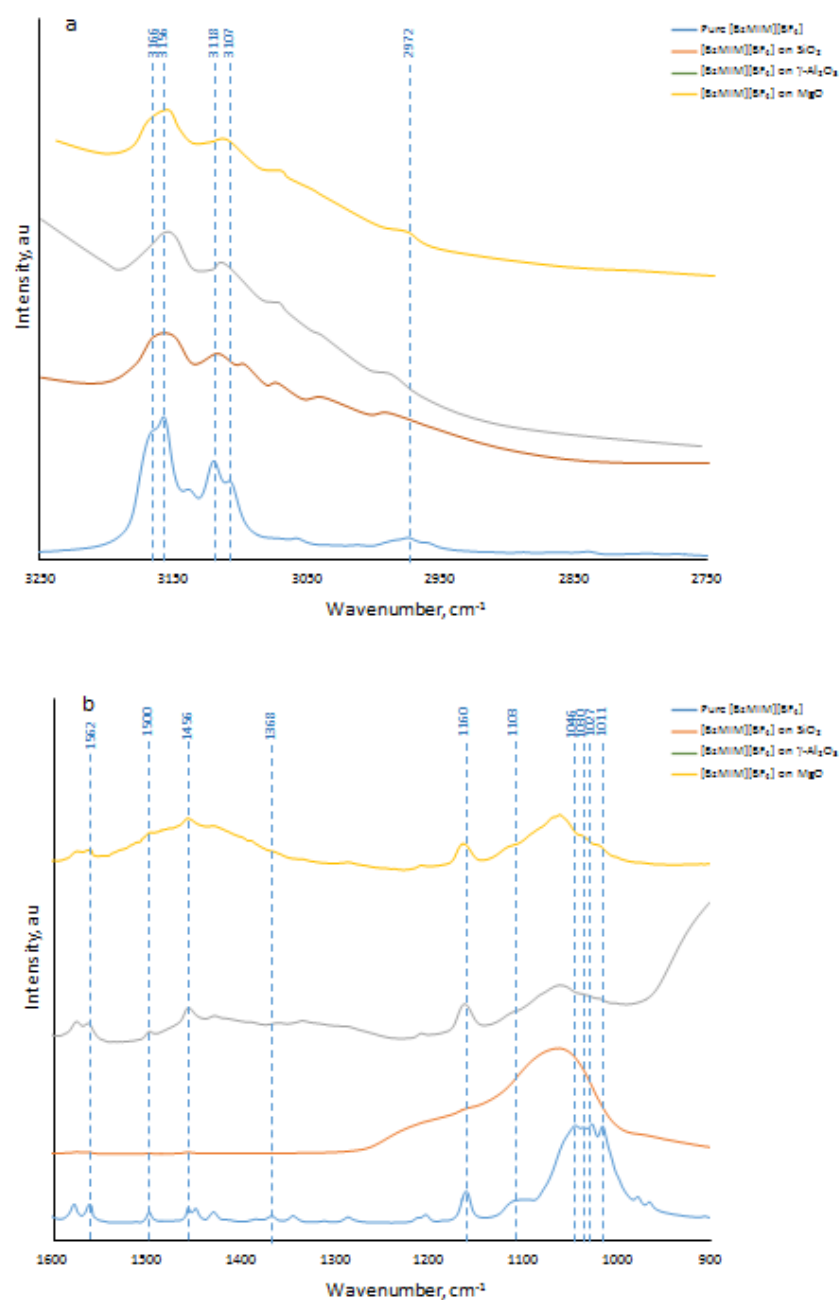


Figure A2-134. FTIR spectra of bulk and supported [BzMIM][BF₄] in the region of a) 2750-3250 cm^{-1} b) 900-1600 cm^{-1} .

Table A2-1. ILs with. FTIR Finger-prints $\nu(\text{C2H})$.

ILs	$\nu(\text{C2H}) / \text{cm}^{-1}$
[DMIM][DMP]	3069.155
[DMIM][MSO ₄]	3110.617
[EMIM][LAC]	3078.797
[EMIM][BF ₄]	3123.152
[EMIM][DEP]	3070.601
[EMIM][EtSO ₄]	3103.867
[EMIM][MSO ₄]	3106.278
[EMIM][SCN]	3095.671
[EMIM][TfO]	3117.366
[BMIM] [OS]	3105.313
[BMIM][Ac]	3056.138
[BMIM][BF ₄]	3121.706
[BMIM][DBP]	3076.869
[BMIM][HSO ₄]	3103.385
[BMIM][NTf ₂]	3124.116
[BMIM][SbF ₆]	3122.670
[BMIM][SCN]	3094.707
[BMIM][TfO]	3114.956
[BMIM][TOS]	3101.939
[HMIM][BF ₄]	3121.223
[C ₁₀ MIM][BF ₄]	3120.741
[BzMIM][BF ₄]	3123.634
[CPCPIM][NTf ₂]	3118.813
[CPMIM][NTf ₂]	3121.223

Table A2-2. Individual percent error values of each supported-ILs with indicated maximum, minimum and average values.

Metal-oxides	ILs	Model T'_{onset} / °C	T'_{onset} / °C	Relative Error / %
SiO ₂	[DMIM][MSO ₄]	328.8	342	3.9
	[DMIM][DMP]	226.3	224	1.0
	[EMIM][TfO]	345.5	352	1.8
	[EMIM][MSO ₄]	318.1	335	5.0
	[EMIM][EtSO ₄]	312.1	321	2.8
	[EMIM][DEP]	229.9	200	14.9
	[EMIM][BF ₄]	359.8	345	4.3
	[EMIM][LAC]	201.0	250	19.6
	[EMIM][SCN]	255.0	292	12.6
	[BMIM][SCN]	251.0	289	13.3
	[BMIM][TOS]	307.4	303	1.4
	[BMIM][TfO]	339.5	340	0.1
	[BMIM][SbF ₆]	358.6	337	6.4
	[BMIM][NTf ₂]	362.2	357	1.5
	[BMIM][HSO ₄]	310.9	318	2.2
	[BMIM][DBP]	245.4	222	10.5
	[BMIM][BF ₄]	356.2	331	7.5
	[BMIM][Ac]	194.1	191	1.6
	[CPMIM][NTf ₂]	355.0	355	0.0
	[CPCPIM][NTf ₂]	349.1	352	0.8
γ-Al ₂ O ₃	[DMIM][MSO ₄]	246.8	228	8.2
	[DMIM][DMP]	153.0	135	13.1
	[EMIM][TfO]	262.1	256	2.4
	[EMIM][MSO ₄]	237.0	229	3.5
	[EMIM][EtSO ₄]	231.5	226	2.4
	[EMIM][DEP]	156.3	151	3.5
	[EMIM][BF ₄]	275.1	272	1.2
	[EMIM][LAC]	174.8	157	11.3
	[EMIM][SCN]	213.0	210	1.4
	[BMIM][SCN]	210.8	211	0.1
	[BMIM][TOS]	227.2	218	4.2
	[BMIM][TfO]	256.6	273	6.0
	[BMIM][SbF ₆]	274.1	269	1.9
	[BMIM][NTf ₂]	277.3	296	6.3
	[BMIM][HSO ₄]	230.4	220	4.7
	[BMIM][DBP]	170.5	162	5.2
	[BMIM][BF ₄]	271.9	262	3.8

	[BMIM][Ac]	123.6	139	11.1
	[CPMIM][NTf ₂]	270.8	292	7.3
	[CPCPIM][NTf ₂]	265.3	286	7.2
MgO	[DMIM][MSO ₄]	189.1	171	10.6
	[DMIM][DMP]	136.0	131	3.9
	[EMIM][TfO]	197.7	203	2.6
	[EMIM][MSO ₄]	183.5	175	4.9
	[EMIM][EtSO ₄]	180.5	167	8.1
	[EMIM][DEP]	137.9	132	4.5
	[EMIM][BF ₄]	205.1	182	12.7
	[EMIM][LAC]	148.4	146	1.6
	[EMIM][SCN]	170.0	183	7.1
	[BMIM][SCN]	168.7	190	11.2
	[BMIM][TOS]	178.0	176	1.1
	[BMIM][TfO]	194.6	204	4.6
	[BMIM][SbF ₆]	204.5	209	2.1
	[BMIM][NTf ₂]	206.4	203	1.7
	[BMIM][HSO ₄]	179.8	164	9.7
	[BMIM][DBP]	145.9	143	2.0
	[BMIM][BF ₄]	203.3	168	21.0
	[BMIM][Ac]	119.4	122	2.1
	[CPMIM][NTf ₂]	202.7	200	1.3
	[CPCPIM][NTf ₂]	199.6	196	1.8
Average Relative Error / % :				5.42
Maximum Relative Error / % :				21.0
Minimum Relative Error / % :				0.1

Appendix A3

Supplementary Materials for Interactions of [BMIM][BF₄] with Metal Oxides and Their Consequences on Stability Limits

*This chapter has been published in *Journal of Physical Chemistry Letters C* **2016**, 120, 20089 by authors M. Babucci, V. Balci, A. Akçay and A. Uzun. The original manuscript has been rearranged to conform to the format requirements of the dissertation.

A3-1. Karl Fisher Titration Analysis

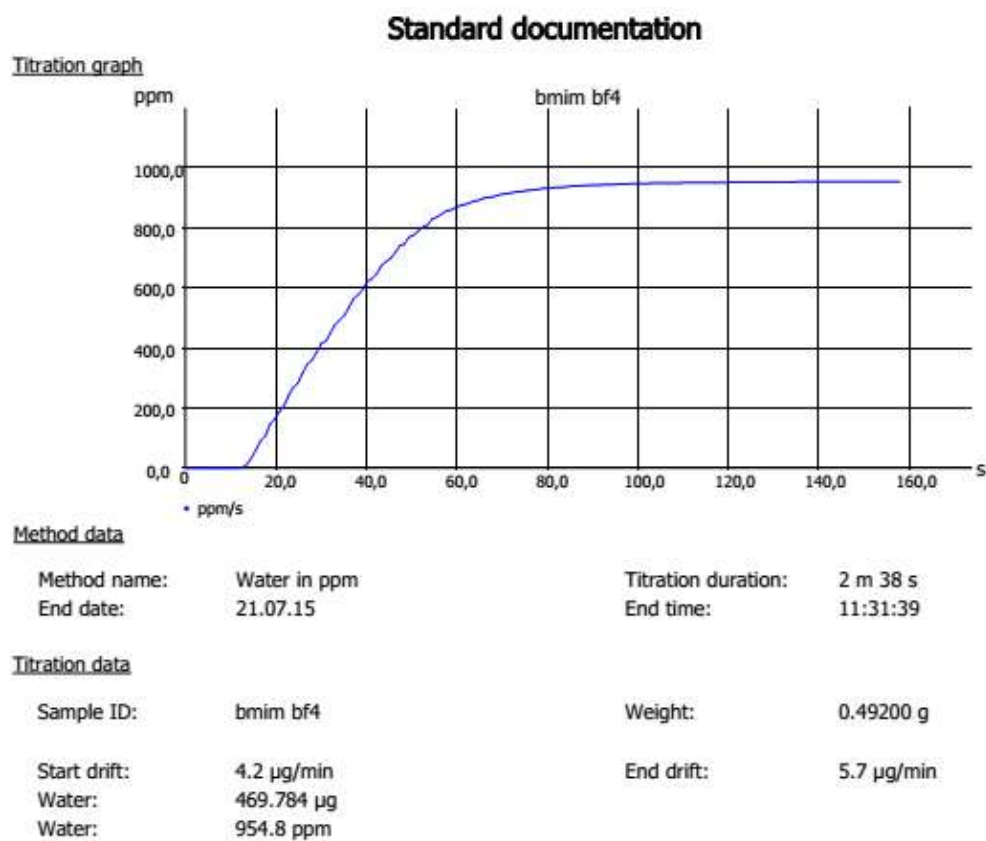


Figure A3-1. Water content report of [BMIM][BF₄] obtained from Karl Fisher titration method.

A3-2. Density Functional Theory (DFT) Calculations**Table A3-1.** Cartesian coordinates of the most stable conformer (conf-1) structure of [BMIM][BF₄] obtained from DFT (Structure of Conf-1 is given in manuscript Figure 1).

C	0.20741800	1.23931300	0.56819600
C	-0.69639000	2.88088700	-0.60554400
C	-1.70461800	2.20183600	0.01350100
N	-1.11897900	1.18245200	0.74374800
H	0.91540400	0.53471500	0.99229400
H	-0.71799500	3.73577300	-1.26354700
H	-2.77294700	2.35031800	-0.00499700
H	-1.21737400	-0.07046400	2.39903500
C	-1.81851800	0.12320700	1.50725000
C	-2.01835700	-1.16881800	0.70606400
H	-2.77268500	0.55533900	1.82596800
C	-2.91889800	-1.03168200	-0.52801400
H	-2.45765700	-1.89510200	1.40455500
H	-1.03721300	-1.56028100	0.41577900
C	-3.13338300	-2.37404100	-1.23816500
H	-2.46844400	-0.32412200	-1.23718500
H	-3.89330600	-0.61031600	-0.23367900
H	-3.77149600	-2.25635400	-2.12167700
H	-2.17718300	-2.79745300	-1.56606800
H	-3.61356000	-3.10262300	-0.57277500
N	0.48878100	2.26134700	-0.24791000
C	1.83811300	2.63508400	-0.69525200
H	2.49686600	1.77788600	-0.54252000
H	1.79716900	2.87563400	-1.75953700
H	2.18747100	3.50316500	-0.12948800
F	2.75598200	-2.55176000	-0.17272900
B	2.10500300	-1.34973900	-0.00203300
F	2.98075000	-0.24123600	-0.18770300
F	1.01496700	-1.20439000	-0.90440000
F	1.56575800	-1.23691700	1.32760200

Table A3-2. Cartesian coordinates of conf-2 structure of [BMIM][BF₄] obtained from DFT.

C	-0.00294600	0.86800500	0.21892900
C	0.44154200	2.94757900	-0.39036100
C	1.22485300	2.11190700	-1.13257100
N	0.93317700	0.81961400	-0.73569600
H	-0.45836700	0.00494100	0.69519600
H	0.35446300	4.02300800	-0.38996400
H	1.94612200	2.32242500	-1.90681800
H	0.57833200	-0.93678000	-1.78407900
C	1.44286100	-0.43394700	-1.34274600
C	2.14764800	-1.34574500	-0.33491200
H	2.12504300	-0.12486600	-2.14034000
C	3.41173400	-0.74908100	0.29777300
H	2.40415900	-2.26495900	-0.87882400
H	1.43074300	-1.64923700	0.43876400
C	4.09868800	-1.71886000	1.26695200
H	3.15862300	0.17749700	0.83256700
H	4.11722500	-0.46379300	-0.49706400
H	4.99704600	-1.27033000	1.70649700
H	3.42756500	-1.99915900	2.08799800
H	4.40117600	-2.64151400	0.75632300
N	-0.31967100	2.14855000	0.44470600
C	-1.34657400	2.59442600	1.39524200
H	-0.88872300	2.82654200	2.36070100
H	-1.83069400	3.48513900	0.99067200
H	-2.08516000	1.79679100	1.49308600
F	-2.91265300	0.02649700	0.34821400
B	-2.38981600	-1.23759200	-0.05056800
F	-1.70819400	-1.06449000	-1.28754300
F	-1.39617900	-1.60193400	0.92686900
F	-3.37518000	-2.19569400	-0.13696000

**Figure A3-2.** Structure of conf-2 in DFT with $\Delta E=0.54$ kJ/mol and $\Delta E_B=-338.32$ kJ/mol.

Table A3-3. Cartesian coordinates of conf-3 structure of [BMIM][BF₄] obtained from DFT.

C	-0.03194500	0.65075300	0.27733500
C	0.37843500	2.65988700	-0.54553100
C	1.19830600	1.76967200	-1.17556500
N	0.92597500	0.51952600	-0.64724700
H	-0.51042700	-0.14941100	0.82778300
H	0.26240100	3.72549100	-0.66899200
H	1.93572000	1.91359700	-1.94977500
H	0.65912800	-1.45715600	-1.20236200
C	1.50373200	-0.77604900	-1.07020800
C	2.52141300	-1.33681400	-0.07162500
H	1.96561100	-0.59938600	-2.04619900
C	3.78285400	-0.48343800	0.11437900
H	2.80005000	-2.33447200	-0.43734600
H	2.02556700	-1.49769600	0.89538200
C	4.78536000	-1.11556800	1.08751200
H	3.50546000	0.51550400	0.47937900
H	4.26630200	-0.33375100	-0.86264300
H	5.67647400	-0.48790100	1.20190200
H	4.34153400	-1.25004800	2.08174200
H	5.11361600	-2.10091700	0.73424500
N	-0.37936800	1.93857800	0.35986200
C	-1.48703000	2.44869900	1.17685100
H	-1.92532400	1.61067500	1.71863500
H	-1.11183800	3.20664100	1.86919300
H	-2.24870400	2.86969900	0.51762800
F	-1.53289300	-1.75469000	-0.62540200
B	-2.63520300	-1.08713100	-0.01165300
F	-3.79190900	-1.83067300	-0.09755700
F	-2.26821900	-0.85793900	1.36264500
F	-2.77504100	0.18721400	-0.62274200

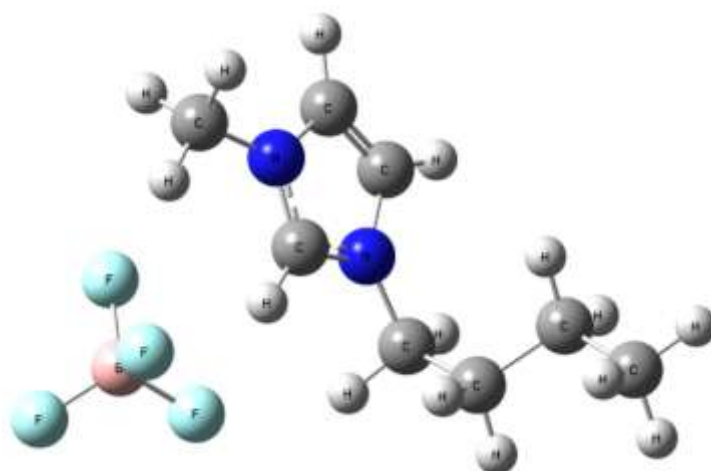
**Figure A3-3.** Structure of conf-3 in DFT with $\Delta E=0.87$ kJ/mol and $\Delta E_B=-337.98$ kJ/mol.

Table A3-4. Cartesian coordinates of conf-4 structure of [BMIM][BF₄] obtained from DFT.

C	0.15129600	0.96849300	-0.28217500
C	1.02126900	2.89600100	0.36373900
C	1.98454300	2.20850500	-0.31604800
N	1.42093300	1.00858900	-0.71112200
H	-0.53069800	0.13924800	-0.44397400
H	1.04514000	3.86509300	0.83770500
H	3.00733400	2.46395000	-0.54579800
H	1.52483200	-0.21111400	-2.40200900
C	2.08264600	-0.07773900	-1.47054600
C	2.15939300	-1.39503000	-0.69089100
H	3.08017100	0.29507600	-1.72183100
C	2.99202400	-1.32415900	0.59588900
H	2.59854600	-2.13364000	-1.37573400
H	1.14283600	-1.74638500	-0.47454800
C	3.07043200	-2.67672100	1.31437000
H	2.55803800	-0.58012000	1.27829900
H	4.00791800	-0.97382800	0.35733700
H	3.66627600	-2.60250600	2.23120000
H	2.07141800	-3.03373100	1.59064300
H	3.53311200	-3.43907600	0.67520900
N	-0.11264400	2.10331200	0.37588500
C	-1.40900500	2.45239600	0.98147500
H	-1.97602600	1.53444500	1.13850600
H	-1.21969700	2.95073500	1.93448600
H	-1.95681500	3.11606900	0.30828200
F	-2.90405600	0.19567200	-0.80197100
B	-2.57973900	-0.99345800	-0.09645900
F	-1.38209800	-1.52244300	-0.69883400
F	-2.23910700	-0.61956800	1.23642000
F	-3.59999500	-1.91707600	-0.12824800

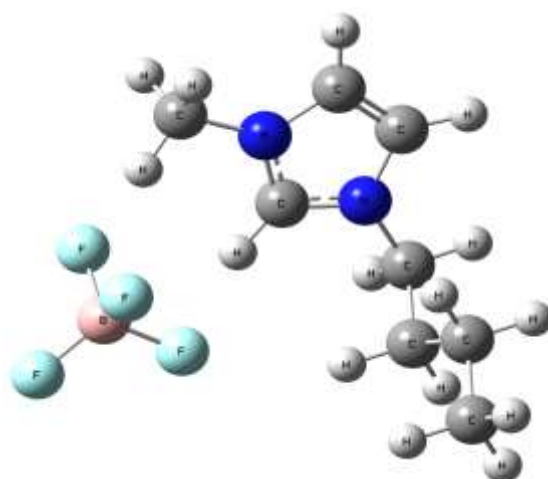
**Figure A3-4.** Structure of conf-4 in DFT with $\Delta E=3.12$ kJ/mol and $\Delta E_B=-335.74$ kJ/mol.

Table A3-5. Cartesian coordinates of conf-5 structure of [BMIM][BF₄] obtained from DFT.

C	-2.51186700	-0.06951200	0.78005800
C	-2.08641800	-1.28194700	-1.01440000
C	-0.90899300	-0.73671000	-0.58845900
N	-1.20124000	0.01757300	0.53331400
H	-3.03081900	0.40746100	1.59752800
H	-2.29643900	-1.94272100	-1.84127300
H	0.10793800	-0.84466800	-0.95841000
H	-0.57530400	0.75897000	2.37055800
C	-0.23456900	0.81453000	1.33211000
C	-0.12769200	2.27091600	0.86433600
H	0.72577000	0.30195500	1.25988600
C	0.41757700	2.45472300	-0.55880200
H	0.55082600	2.76069200	1.57596700
H	-1.10281600	2.77221200	0.96907300
C	0.62329800	3.93198600	-0.91432500
H	-0.27366700	2.00406200	-1.28524200
H	1.36487400	1.91069700	-0.64947300
H	1.00541600	4.03905100	-1.93576800
H	-0.31488700	4.49943200	-0.84684100
H	1.34820100	4.40325500	-0.23891300
N	-3.07970900	-0.85608200	-0.14693300
C	-4.49282800	-1.22668500	-0.21125800
H	-5.03149300	-0.72159400	0.59216500
H	-4.91087500	-0.91990300	-1.17322500
H	-4.59737000	-2.30804700	-0.09140000
F	1.96560700	-1.00292500	-1.29963600
B	2.54695900	-1.19211000	0.00024300
F	1.55900900	-1.83023500	0.80869600
F	3.69873600	-1.94985800	-0.08300100
F	2.79791900	0.09029100	0.55326600

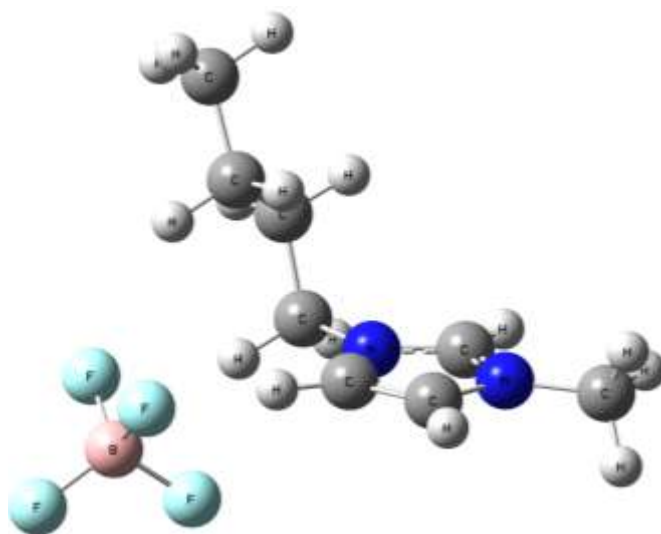
**Figure A3-5.** Structure of conf-5 in DFT with $\Delta E=31.48$ kJ/mol and $\Delta E_B=-307.37$ kJ/mol.

Table A3-6. Cartesian coordinates of conf-6 structure of [BMIM][BF₄] obtained from DFT.

C	1.11355100	-1.59742300	0.31355900
C	-0.31431300	-0.16957500	-0.58997300
C	0.90406700	0.00774400	-1.18204700
N	1.78726300	-0.89173000	-0.60854500
H	1.52812900	-2.38256200	0.92729700
H	-1.26389800	0.33335900	-0.75720100
H	1.21012200	0.68855600	-1.96096900
H	3.45857300	-2.09736600	-0.89791500
C	3.22348200	-1.02869000	-0.91190700
C	4.13169000	-0.25805700	0.05601500
H	3.35774700	-0.67729700	-1.93908600
C	3.95966300	1.26671500	0.02821300
H	5.16556600	-0.51710200	-0.21164100
H	3.97530100	-0.63485900	1.07664200
C	4.93675100	1.98337200	0.96789300
H	2.93104400	1.53149600	0.30561100
H	4.10857900	1.62850500	-0.99970600
H	4.79283100	3.06848400	0.92913400
H	4.79230800	1.66621300	2.00811700
H	5.97858600	1.77386200	0.69531700
N	-0.15610000	-1.18000400	0.34129200
C	-1.20366700	-1.70737900	1.23590000
H	-0.84655700	-2.64728100	1.66137800
H	-1.41055700	-0.97214400	2.01441800
H	-2.11821500	-1.85034700	0.65897000
F	-3.68898100	-0.78292700	-0.30704800
B	-3.63701800	0.61404400	-0.02214300
F	-2.90638400	1.23953700	-1.08057900
F	-4.90333700	1.15154900	0.09936700
F	-2.87907000	0.78519200	1.17328400

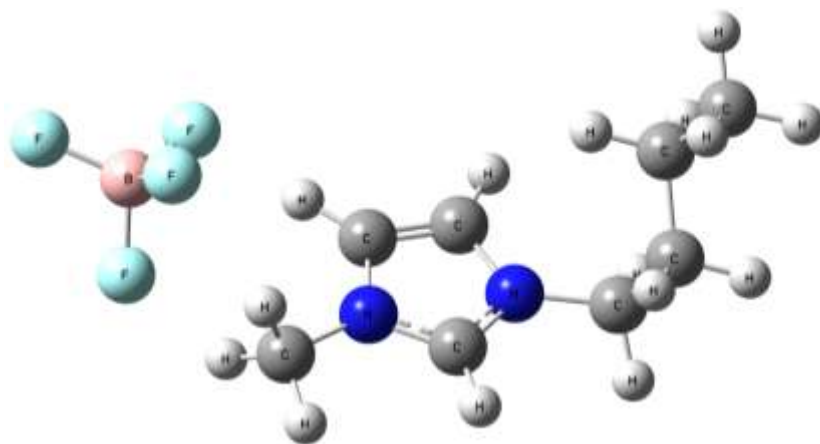
**Figure A3-6.** Structure of conf-6 in DFT with $\Delta E=32.02$ kJ/mol and $\Delta E_B=-306.84$ kJ/mol.

Table A3-7. Cartesian coordinates of conf-7 structure of [BMIM][BF₄] obtained from DFT.

C	2.53198100	-0.87488200	-0.00379400
C	0.56544400	-1.86669400	-0.21680000
C	0.50099600	-0.66232000	-0.85489100
N	1.73596100	-0.06047500	-0.71179900
H	3.55833700	-0.67849500	0.26543000
H	-0.21819000	-2.59172500	-0.05680200
H	-0.34883900	-0.17734000	-1.32190700
H	3.15343500	1.27032800	-1.44950800
C	2.09438500	1.29668500	-1.17403800
C	1.82207500	2.38789100	-0.12880500
H	1.51574100	1.47313100	-2.08486800
C	0.33977200	2.62241700	0.19568600
H	2.26439400	3.31185500	-0.52870900
H	2.38132300	2.15306400	0.78898200
C	0.14260200	3.77196500	1.19057400
H	-0.12218600	1.71497000	0.60060800
H	-0.20238500	2.84580400	-0.73359400
H	-0.92165100	3.91436900	1.40446600
H	0.64657700	3.56516100	2.14374100
H	0.53910600	4.71850000	0.79961600
N	1.84027900	-1.98260700	0.30511400
C	2.33797700	-3.11656600	1.08469000
H	3.36835600	-2.92043700	1.38599500
H	1.71669400	-3.24450100	1.97423800
H	2.30263200	-4.02421000	0.47746300
F	-2.33797300	-1.81357800	-0.29768700
B	-2.63450500	-0.44601400	-0.02087200
F	-2.25966100	0.32013000	-1.17337500
F	-3.97721800	-0.27401400	0.26684700
F	-1.81469000	-0.02696100	1.06313400

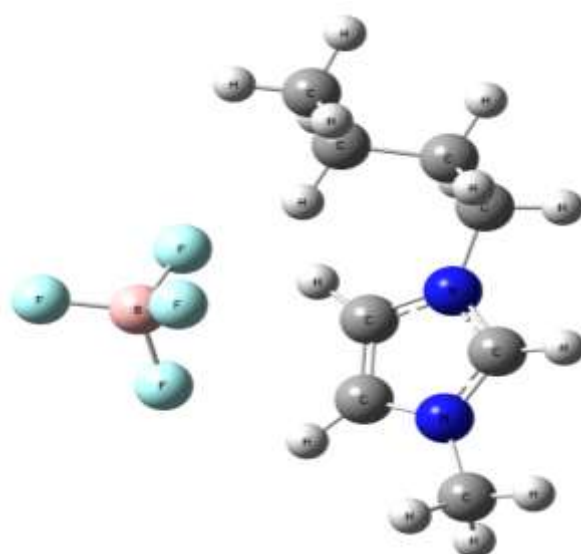
**Figure A3-7.** Structure of conf-7 in DFT with $\Delta E=38.32$ kJ/mol and $\Delta E_B=-300.54$ kJ/mol.

Table A3-8. Literature¹⁻² calculated FT-IR bands of bulk [BMIM][BF₄].

IR assignments	Experimental (cm ⁻¹)	Calculated (cm ⁻¹)	Reference
Higher frequency region			
Ring $\nu(\text{C4-C5H})_{\text{asym}}$ (s)	3162	3277	2
	3163	3162	1
Ring $\nu(\text{C2H})_{\text{sym}}$ (s)	3122	3257	2
	3123	3132	1
Ring $\nu(\text{CH}_3)_{\text{asym}}$ (vs)		3158	2
	3105	3030	1
Butyl $\nu(\text{HC1HH})_{\text{sym}}$ (s),	2965	3084	2
$\nu(\text{HC2H})_{\text{asym}}$ (w)	2966	2983	1
Ring $\nu(\text{CH}_3)_{\text{sym}}$ (vs)	2939	3059	2
	2942		1
Butyl $\nu(\text{HC1H})_{\text{sym}}$, $\nu(\text{HC2H})_{\text{sym}}$,		3040	2
	2877	2888	1
$\nu(\text{HC3H})_{\text{asym}}$, $\nu(\text{HC4HH})_{\text{sym}}$			
Lower frequency region			
Ring in plane asym stretch (vs),	1576	1607	2
	1568	1566	1
Ring $\delta(\text{C2H})$ (vs),			
Ring CH_3 $\delta(\text{HCH})$ scissoring (s),			
Ring $\nu(\text{C2-N})$ (s)			
Ring $\delta(\text{CH}_3)$ wagging (vs),	1467	1484	2
	1459	1468	1
Butyl $\delta(\text{HC1H})$ scissoring (w)			
Ring in plane asym stretch (vs),	1454	1455	2
		1457	1
Butyl $\delta(\text{HC1H})$ twisting (vs),			
Ring in plane sym stretch (s),	1431	1421	2
		1398	1
Butyl $\delta(\text{C1H})$, $\delta(\text{C2H})$, $\delta(\text{C3H})$ (s),			
Ring $\delta(\text{CH}_3)$ wagging (s)			
Butyl $\delta(\text{C1H})$, $\delta(\text{C2H})$, $\delta(\text{C3H})$ (s),		1387	2
Ring $\nu(\text{N-Bu})$ (m),	1339	1334	1
Ring in plane $\delta(\text{CH})$ (vs)	1300	1282	1

Ring $\delta(\text{C2H})$, $\delta(\text{C4H})$, $\delta(\text{C5H})$ (vs)		1181	2
Ring in plane asym stretch (s), Ring $\nu(\text{C-N})$	1285	1254	1
$\nu(\text{BF}_4)$ (vw)			
$\nu(\text{BF}_4)$ (vs),	1173	1209	2
Ring CH_3 $\delta(\text{CH})$ wagging (s),	1213	1214	1
Ring $\delta(\text{C2H})$, $\delta(\text{C4H})$, $\delta(\text{C5H})$ (m)			
Ring $\delta(\text{HC4C5H})$ scissoring (vs),		1125	2
	1172	1148	1
Ring CH_3 $\delta(\text{CH})$ (s),			
Butyl $\nu(\text{CCCC})_{\text{asym}}$ (m)			
$\nu(\text{BF}_4)_{\text{asym}}$ (vs),	1024	1019	2
Ring in plane sym stretch (w),	1074	1069	1
Ring $\delta(\text{C4H-C5H})$ (w)			
Butyl $\delta(\text{HC1H})$ wagging (s),		995	2
$\delta(\text{HC2H})$ twisting (s), $\delta(\text{HC3H})$	1037	1039	1
twisting (s), $\delta(\text{HC4H})$ (m), Ring in			
plane sym stretch (w),			
$\nu(\text{BF}_4)_{\text{asym}}$ (vw)			
$\nu(\text{BF}_4)_{\text{asym}}$ (vs),		975	2
Ring $\delta(\text{C2H})$ (vs),	1019	1006	1
Butyl $\delta(\text{HC4H})$ (m)			
$\nu(\text{BF}_4)_{\text{asym}}$ (vs), Butyl $\delta(\text{HC1H})$		966	2
rocking (vs),	992	983	1
$\delta(\text{HC2H})$ wagging (s), $\delta(\text{HC3H})$			
wagging (s), $\delta(\text{HC1H})$ rocking (m)			

*Level of theory applied are B3LYP/6-31GD) and B3LYP/6-311+G(2d,p) for ref. 1 and ref. 2, respectively.

A3-3. Scanning Electron Microscopy coupled with Energy-Dispersive X-Ray Spectroscopy (SEM/EDX)

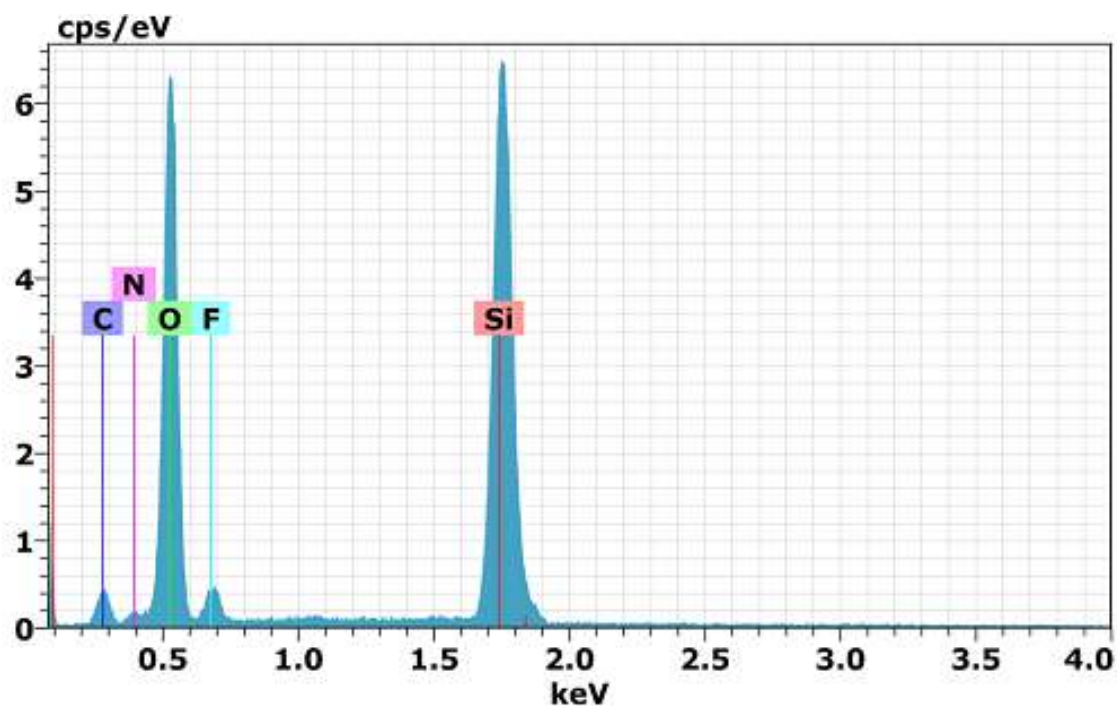


Figure A3-8. EDX spectra of SiO₂-supported [BMIM][BF₄].

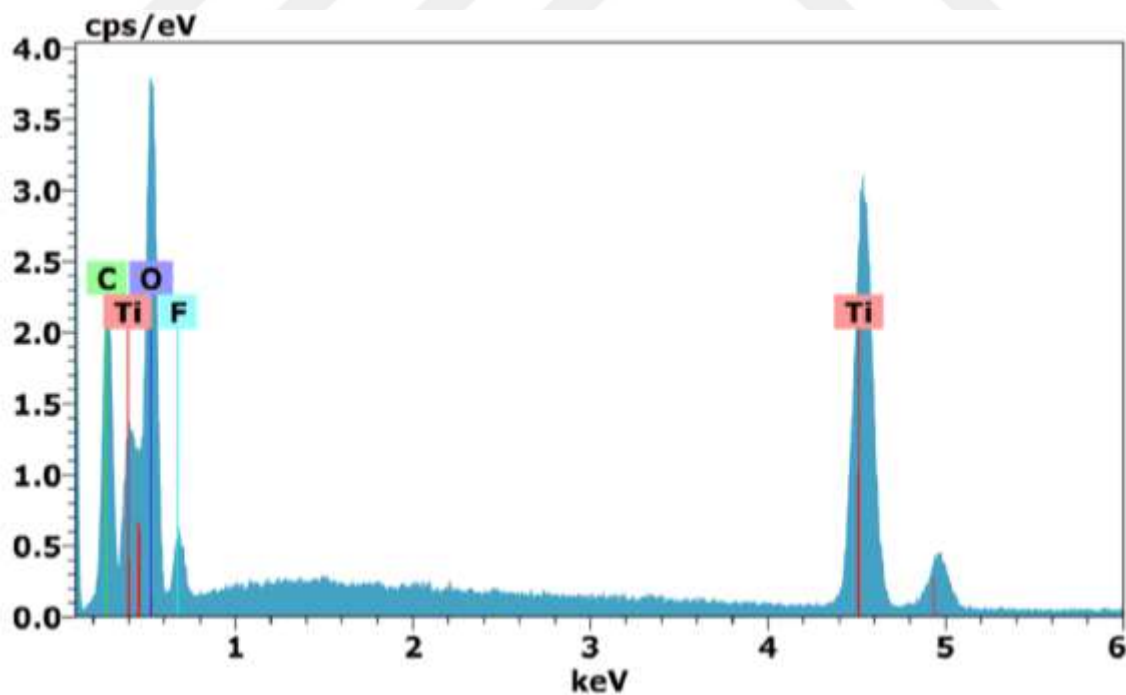


Figure A3-9. EDX spectra of TiO₂-supported [BMIM][BF₄].

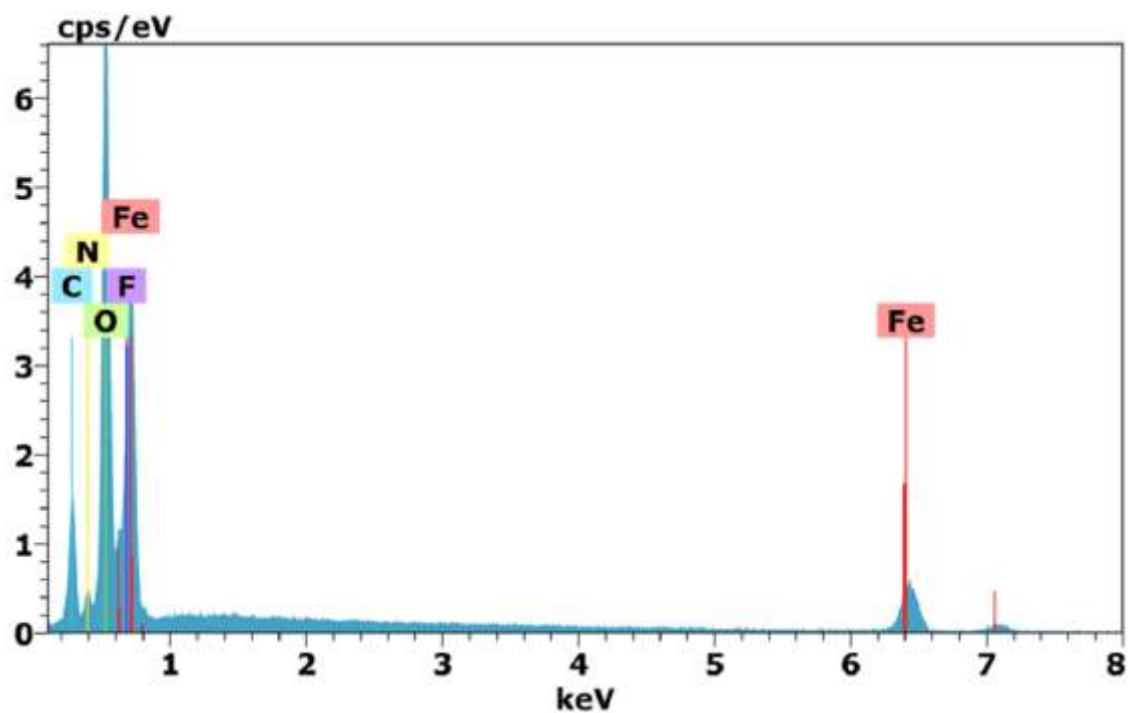


Figure A3-10. EDX spectra of Fe_2O_3 -supported $[\text{BMIM}][\text{BF}_4]$.

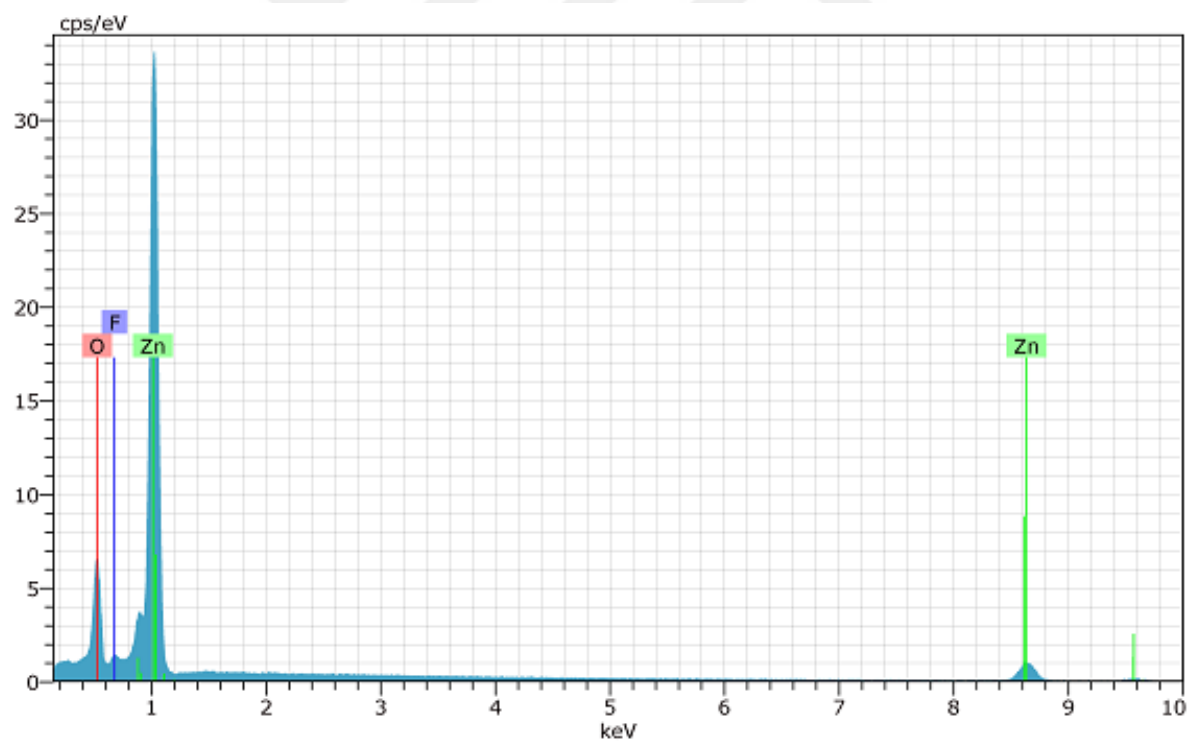


Figure A3-11. EDX spectra of ZnO -supported $[\text{BMIM}][\text{BF}_4]$.

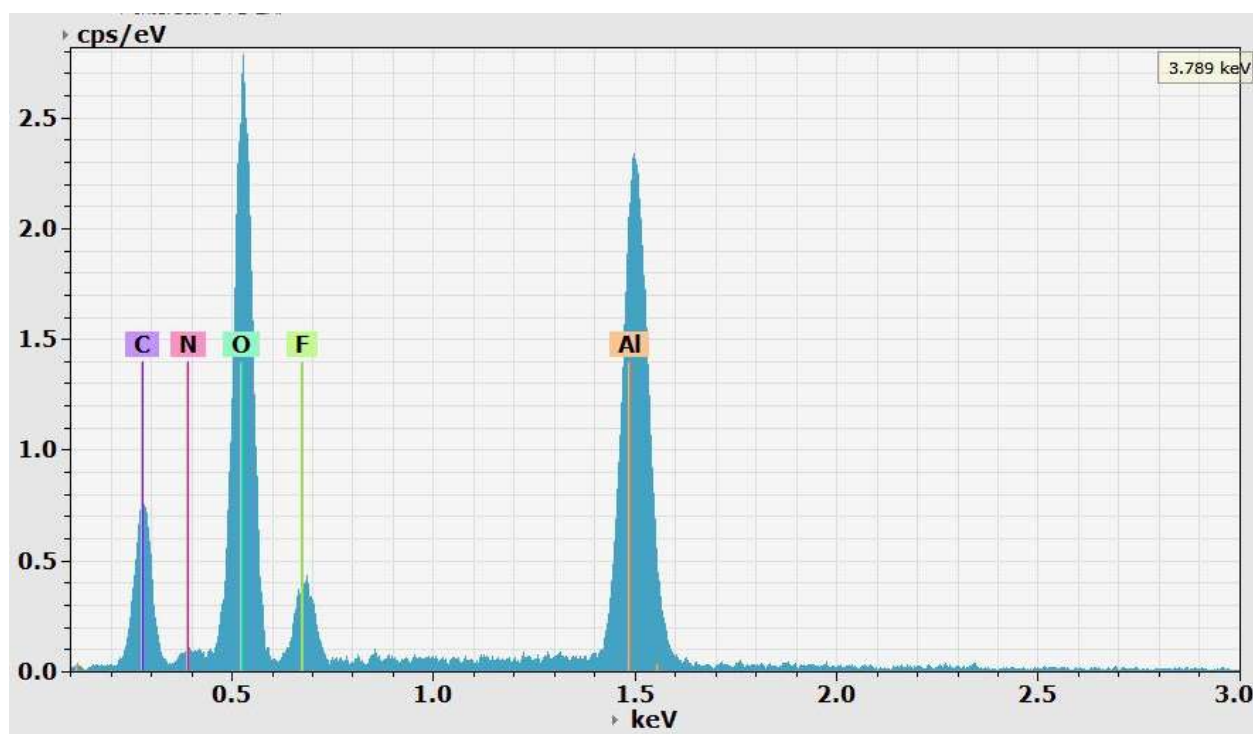


Figure A3-12. EDX spectra of γ - Al_2O_3 -supported [BMIM][BF_4].

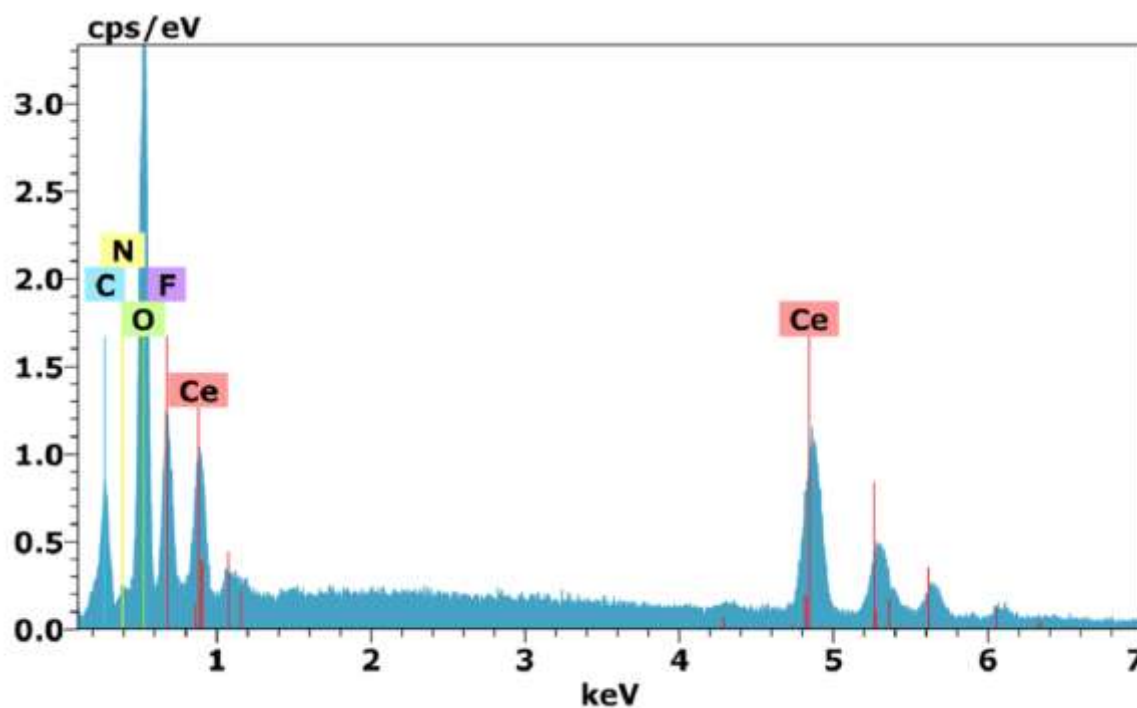


Figure A3-13. EDX spectra of CeO_2 -supported [BMIM][BF_4].

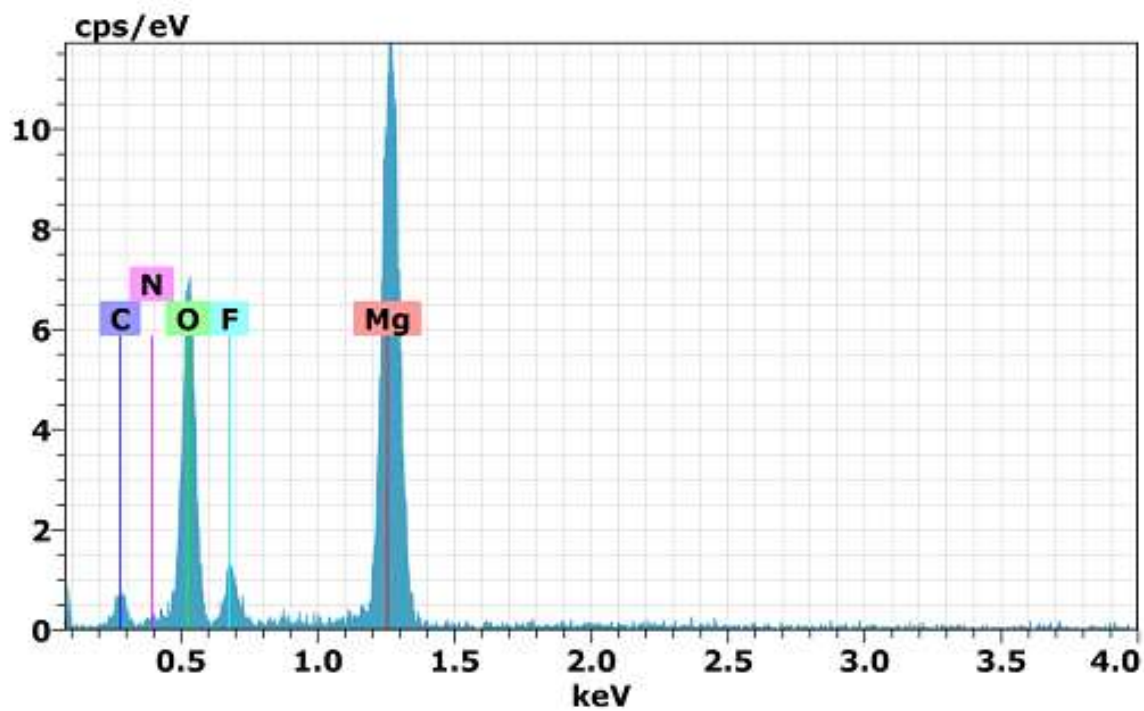


Figure A3-14. EDX spectra of MgO-supported [BMIM][BF₄].

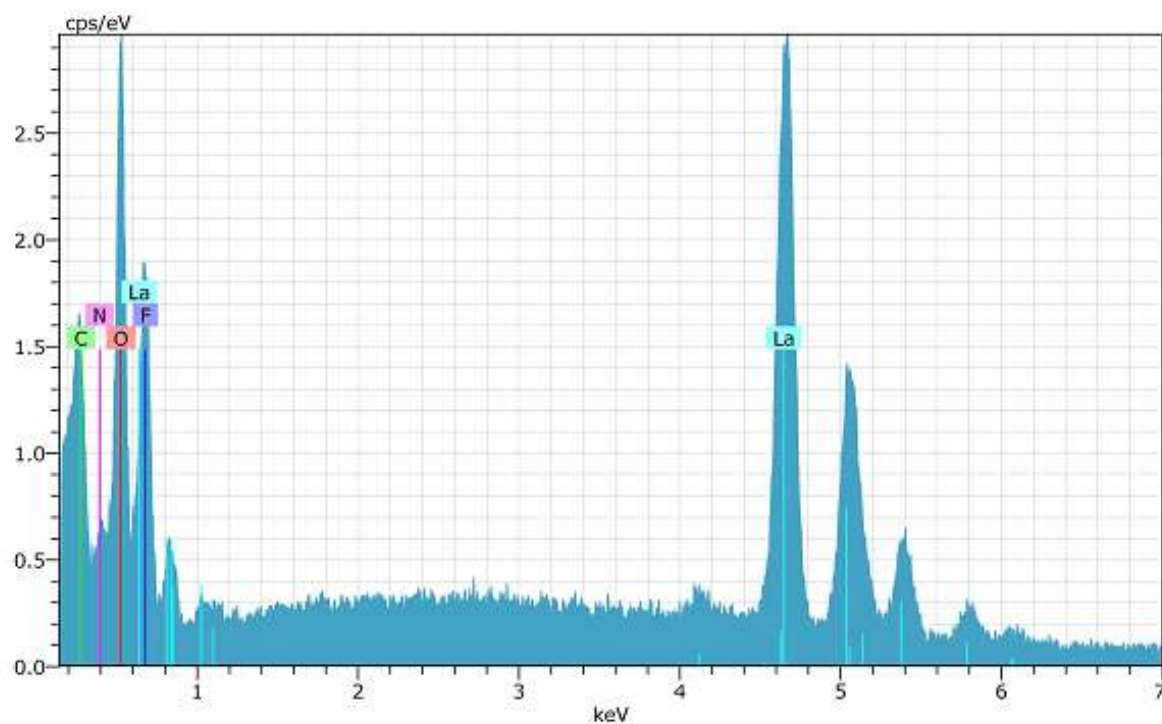


Figure A3-15. EDX spectra of La₂O₃supported [BMIM][BF₄].

Table A3-9. IL loading amount on metal-oxides. These values are calculated by using integrals of. EDX spectra area of each supported IL.

Supported IL	Calculated IL loading (%)
[BMIM][BF ₄]/SiO ₂	14.6
[BMIM][BF ₄]/TiO ₂	11.2
[BMIM][BF ₄]/Fe ₂ O ₃	6.8
[BMIM][BF ₄]/ZnO	11.9
[BMIM][BF ₄]/ γ -Al ₂ O ₃	9.7
[BMIM][BF ₄]/CeO ₂	1.4
[BMIM][BF ₄]/MgO	14.9
[BMIM][BF ₄]/La ₂ O ₃	16.8

A3-4. Braunaauer-Emmett-Teller (BET) Surface Area Analysis and Barrett-Joyner-Halenda (BJH) Pore Size and Volume Analysis Results

a) For SiO₂,

BET Surface Area Report

BET Surface Area: 331.1175 $\pm$ 2.6125 m²/g

Slope: 0.013074 $\pm$ 0.000102 g/cm³ STP

Y-Intercept: 0.000073 $\pm$ 0.000020 g/cm³ STP

C: 179.933091

Qm: 76.0630 cm³/g STP

Correlation Coefficient: 0.9997575

Molecular Cross-Sectional Area: 0.1620 nm²

Relative Pressure (p/p ^o)	Quantity Adsorbed (cm ³ /g STP)	1/[Q(p ^o p - 1)]
0.048648422	69.5840	0.000735
0.078375926	76.2398	0.001115
0.109431616	81.6103	0.001506
0.133297819	85.1822	0.001806
0.161417981	89.0510	0.002162
0.189894278	92.7377	0.002528
0.218820927	96.3347	0.002908
0.247285548	99.8110	0.003291
0.276512379	103.3686	0.003697
0.305498450	106.9358	0.004114

Pore Volume

BJH Adsorption cumulative volume of pores
between 17.000 Å and 3000.000 Å width: 1.193179 cm³/g

BJH Desorption cumulative volume of pores
between 17.000 Å and 3000.000 Å width: 1.204990 cm³/g

b) For SiO₂-supported [BMIM][BF₄],

BET Surface Area Report

BET Surface Area: 194.0477 ± 0.8094 m²/g

Slope: 0.021943 ± 0.000092 g/cm³ STP

Y-Intercept: 0.000491 ± 0.000018 g/cm³ STP

C: 45.724125

Qm: 44.5759 cm³/g STP

Correlation Coefficient: 0.9999299

Molecular Cross-Sectional Area: 0.1620 nm²

Relative Pressure (p/p ⁰)	Quantity Adsorbed (cm ³ /g STP)	1/[Q(p ⁰ /p - 1)]
0.048443005	33.6294	0.001514
0.076540230	37.9639	0.002183
0.114282649	42.6293	0.003027
0.132785623	44.6722	0.003428
0.160526058	47.5352	0.004023
0.187995940	50.2206	0.004610
0.216050744	52.8452	0.005215
0.244498493	55.4613	0.005835
0.272396430	57.9636	0.006459
0.301273245	60.5708	0.007119

Pore Volume

BJH Adsorption cumulative volume of pores
between 17.000 Å and 3000.000 Å width: 0.880142 cm³/g

BJH Desorption cumulative volume of pores
between 17.000 Å and 3000.000 Å width: 0.880027 cm³/g

c) For TiO₂,**BET Surface Area Report**BET Surface Area: 10.9724 ± 0.0575 m²/gSlope: 0.393707 ± 0.002041 g/cm³ STPY-Intercept: 0.003033 ± 0.000390 g/cm³ STP

C: 130.820885

Qm: 2.5205 cm³/g STP

Correlation Coefficient: 0.9997716

Molecular Cross-Sectional Area: 0.1620 nm²

Relative Pressure (p/p ⁰)	Quantity Adsorbed (cm ³ /g STP)	1/[Q(p ⁰ /p - 1)]
0.050319230	2.2865	0.023173
0.064057828	2.3819	0.028734
0.077935407	2.4704	0.034214
0.091844008	2.5513	0.039640
0.105757078	2.6285	0.044994
0.119648811	2.7054	0.050236
0.133524455	2.7753	0.055525
0.147217918	2.8460	0.060659
0.161129741	2.9069	0.066077
0.174913313	2.9717	0.071339
0.188815706	3.0382	0.076612
0.202669491	3.0994	0.082011
0.217039999	3.1616	0.087678
0.230818107	3.2229	0.093111
0.244752132	3.2739	0.098984
0.258665076	3.3304	0.104768
0.272562757	3.3856	0.110670
0.286067826	3.4372	0.116576
0.300391665	3.4928	0.122930

Pore Volume

BJH Adsorption cumulative volume of pores

between 17.000 Å and 3000.000 Å width: 0.011627 cm³/g

BJH Desorption cumulative volume of pores

between 17.000 Å and 3000.000 Å width: 0.013342 cm³/g

d) For TiO₂-supported [BMIM][BF₄],

BET Surface Area Report

BET Surface Area: 3.9040 ± 0.0711 m²/g
 Slope: 1.093276 ± 0.019938 g/cm³ STP
 Y-Intercept: 0.021787 ± 0.003808 g/cm³ STP
 C: 51.179478
 Qm: 0.8968 cm³/g STP
 Correlation Coefficient: 0.9971849
 Molecular Cross-Sectional Area: 0.1620 nm²

Relative Pressure (p/p ^o)	Quantity Adsorbed (cm ³ /g STP)	1/[Q(p ^o p - 1)]
0.050063549	0.6446	0.081758
0.064042593	0.7021	0.097452
0.078022698	0.7548	0.112122
0.091876622	0.8038	0.125872
0.105844398	0.8484	0.139533
0.119657287	0.8920	0.152376
0.133448426	0.9218	0.167069
0.147498848	0.9683	0.178685
0.161293694	0.9905	0.194150
0.175271279	1.0281	0.206703
0.189160116	1.0589	0.220322
0.202697823	1.0778	0.235888
0.216906494	1.1081	0.249971
0.230398923	1.1177	0.267837
0.244733629	1.1298	0.286809
0.258551913	1.1422	0.305309
0.272395897	1.1611	0.322439
0.286373208	1.1695	0.343140
0.300213757	1.1740	0.365438

Pore Volume

BJH Adsorption cumulative volume of pores
 between 17.000 Å and 3000.000 Å width: 0.001821 cm³/g

BJH Desorption cumulative volume of pores
 between 17.000 Å and 3000.000 Å width: 0.002207 cm³/g

e) For Fe_2O_3 ,**BET Surface Area Report**BET Surface Area: $5.6810 \pm 0.0147 \text{ m}^2/\text{g}$ Slope: $0.760553 \pm 0.001948 \text{ g}/\text{cm}^3 \text{ STP}$ Y-Intercept: $0.005719 \pm 0.000375 \text{ g}/\text{cm}^3 \text{ STP}$

C: 133.996653

Qm: $1.3050 \text{ cm}^3/\text{g STP}$

Correlation Coefficient: 0.9999738

Molecular Cross-Sectional Area: 0.1620 nm^2

Relative Pressure (p/p^0)	Quantity Adsorbed ($\text{cm}^3/\text{g STP}$)	$1/[Q(p^0/p - 1)]$
0.050382918	1.2162	0.043625
0.077293396	1.2921	0.064833
0.105721130	1.3655	0.086573
0.133662842	1.4331	0.107655
0.161512042	1.4980	0.128590
0.189154727	1.5627	0.149280
0.216955368	1.6269	0.170304
0.244689355	1.6948	0.191151
0.272575420	1.7598	0.212929
0.300371999	1.8271	0.234979

Pore Volume

BJH Adsorption cumulative volume of pores

between $17.000 \text{ \AA}$ and $3000.000 \text{ \AA}$ width: $0.008144 \text{ cm}^3/\text{g}$

BJH Desorption cumulative volume of pores

between $17.000 \text{ \AA}$ and $3000.000 \text{ \AA}$ width: $0.008241 \text{ cm}^3/\text{g}$

f) For Fe₂O₃-supported [BMIM][BF₄],

BET Surface Area Report

BET Surface Area: 1.6988 ± 0.0177 m²/g

Slope: 2.486294 ± 0.026156 g/cm³ STP

Y-Intercept: 0.076213 ± 0.004996 g/cm³ STP

C: 33.622999

Qm: 0.3902 cm³/g STP

Correlation Coefficient: 0.9990606

Molecular Cross-Sectional Area: 0.1620 nm²

Relative Pressure (p/p ^o)	Quantity Adsorbed (cm ³ /g STP)	1/[Q(p ^o p - 1)]
0.050126181	0.2565	0.205774
0.063970284	0.2826	0.241821
0.077799750	0.3044	0.277135
0.091787059	0.3256	0.310360
0.105799568	0.3460	0.341915
0.119633174	0.3654	0.371848
0.133590533	0.3797	0.406085
0.147382184	0.3964	0.436073
0.161061820	0.4053	0.473651
0.175265955	0.4185	0.507796
0.189222216	0.4315	0.540847
0.203080735	0.4477	0.569145
0.216921031	0.4580	0.604875
0.230884761	0.4690	0.640036
0.244685554	0.4782	0.677370
0.258588399	0.4869	0.716273
0.272492372	0.4926	0.760306
0.286355323	0.5002	0.802122
0.300175775	0.5100	0.841045

Pore Volume

BJH Adsorption cumulative volume of pores

between 17.000 Å and 3000.000 Å width: 0.001024 cm³/g

BJH Desorption cumulative volume of pores

between 17.000 Å and 3000.000 Å width: 0.001288 cm³/g

g) For ZnO,

BET Surface Area ReportBET Surface Area: $4.7864 \pm 0.0131 \text{ m}^2/\text{g}$ Slope: $0.906885 \pm 0.002450 \text{ g/cm}^3 \text{ STP}$ Y-Intercept: $0.002608 \pm 0.000472 \text{ g/cm}^3 \text{ STP}$

C: 348.704482

Qm: $1.0995 \text{ cm}^3/\text{g STP}$

Correlation Coefficient: 0.9999708

Molecular Cross-Sectional Area: 0.1620 nm^2

Relative Pressure (p/p ⁰)	Quantity Adsorbed (cm ³ /g STP)	1/[Q(p ⁰ /p - 1)]
0.050077842	1.0792	0.048851
0.077888336	1.1478	0.073593
0.105952249	1.2012	0.098660
0.133660316	1.2499	0.123433
0.161496792	1.2987	0.148303
0.189293354	1.3457	0.173513
0.217010440	1.3928	0.198987
0.244876043	1.4428	0.224757
0.272653078	1.4983	0.250187
0.300303309	1.5564	0.275758

Pore Volume

BJH Adsorption cumulative volume of pores

between 17.000 Å and 3000.000 Å width: $0.006613 \text{ cm}^3/\text{g}$

BJH Desorption cumulative volume of pores

between 17.000 Å and 3000.000 Å width: $0.006671 \text{ cm}^3/\text{g}$

h) For ZnO-supported [BMIM][BF₄],

BET Surface Area Report

BET Surface Area: $0.8733 \pm 0.0393 \text{ m}^2/\text{g}$

Slope: $5.125719 \pm 0.220814 \text{ g/cm}^3 \text{ STP}$

Y-Intercept: $-0.141206 \pm 0.039751 \text{ g/cm}^3 \text{ STP}$

C: -35.299622

Qm: $0.2006 \text{ cm}^3/\text{g STP}$

Correlation Coefficient: 0.9863652

Molecular Cross-Sectional Area: 0.1620 nm^2

Relative Pressure (p/p°)	Quantity Adsorbed (cm ³ /g STP)	1/[Q(p°/p - 1)]
0.050046735	0.2621	0.200972
0.063890331	0.2701	0.252729
0.077987823	0.2826	0.299319
0.091447096	0.2895	0.347670
0.105754044	0.2965	0.398913
0.119652717	0.2946	0.461300
0.133567871	0.3010	0.512218
0.147488691	0.3030	0.571002
0.161396424	0.3033	0.634525
0.174727785	0.3083	0.686695
0.189091420	0.3030	0.769542
0.203015244	0.3043	0.837109
0.216822874	0.3045	0.909229
0.230766914	0.2992	1.002654
0.244703659	0.2946	1.099919
0.278038643	0.2849	1.351994
0.306286789	0.2779	1.588481

Pore Volume

BJH Adsorption cumulative volume of pores

between 17.000 Å and 3000.000 Å width: $0.000500 \text{ cm}^3/\text{g}$

BJH Desorption cumulative volume of pores

between 17.000 Å and 3000.000 Å width: $0.000500 \text{ cm}^3/\text{g}$

i) For γ -Al₂O₃,**BET Surface Area Report**BET Surface Area: 185.4580 ± 0.7397 m²/gSlope: 0.023102 ± 0.000092 g/cm³ STPY-Intercept: 0.000371 ± 0.000018 g/cm³ STP

C: 63.292033

Qm: 42.6027 cm³/g STP

Correlation Coefficient: 0.9998653

Molecular Cross-Sectional Area: 0.1620 nm²

Relative Pressure (p/p ⁰)	Quantity Adsorbed (cm ³ /g STP)	1/[Q(p ⁰ /p - 1)]
0.049871950	36.1549	0.001452
0.063957385	37.7523	0.001810
0.076142899	39.0036	0.002113
0.091417532	40.4769	0.002486
0.105216755	41.7470	0.002817
0.119274611	42.9844	0.003151
0.132886418	44.1665	0.003470
0.146884167	45.3691	0.003795
0.160822456	46.5472	0.004117
0.174390500	47.6902	0.004429
0.188499308	48.8880	0.004751
0.202048272	50.0483	0.005059
0.216363009	51.2916	0.005383
0.230372037	52.5156	0.005700
0.243930033	53.7228	0.006005
0.257971465	55.0051	0.006320
0.271891769	56.3063	0.006632
0.286144837	57.6702	0.006951
0.300066714	59.0437	0.007261

Pore Volume

BJH Adsorption cumulative volume of pores

between 17.000 Å and 3000.000 Å width: 0.179622 cm³/g

BJH Desorption cumulative volume of pores

between 17.000 Å and 3000.000 Å width: 0.261613 cm³/g

j) For γ -Al₂O₃-supported [BMIM][BF₄],

BET Surface Area Report

BET Surface Area: 14.0223 ± 0.0619 m²/g
 Slope: 0.301448 ± 0.001346 g/cm³ STP
 Y-Intercept: 0.009001 ± 0.000259 g/cm³ STP
 C: 34.491747
 Qm: 3.2211 cm³/g STP
 Correlation Coefficient: 0.9999202
 Molecular Cross-Sectional Area: 0.1620 nm²

Relative Pressure (p/p ^o)	Quantity Adsorbed (cm ³ /g STP)	1/[Q(p ^o /p - 1)]
0.050191954	2.2562	0.023422
0.077064657	2.5793	0.032373
0.105679883	2.8680	0.041202
0.133463748	3.1044	0.049613
0.161265587	3.3235	0.057852
0.189004591	3.5284	0.066050
0.216785936	3.7294	0.074217
0.244645140	3.9229	0.082561
0.272550118	4.1172	0.091000
0.300330927	4.3120	0.099547

Pore Volume

BJH Adsorption cumulative volume of pores
 between 17.000 Å and 3000.000 Å width: 0.060117 cm³/g

BJH Desorption cumulative volume of pores
 between 17.000 Å and 3000.000 Å width: 0.060910 cm³/g

k) For CeO₂,**BET Surface Area Report**BET Surface Area: 10.1734 ± 0.0189 m²/gSlope: 0.425264 ± 0.000780 g/cm³ STPY-Intercept: 0.002636 ± 0.000149 g/cm³ STP

C: 162.318547

Qm: 2.3370 cm³/g STP

Correlation Coefficient: 0.9999714

Molecular Cross-Sectional Area: 0.1620 nm²

Relative Pressure (p/p ^o)	Quantity Adsorbed (cm ³ /g STP)	1/[Q(p ^o /p - 1)]
0.050245263	2.2370	0.023650
0.064043258	2.3023	0.029721
0.077779550	2.3612	0.035719
0.091885892	2.4156	0.041887
0.105724068	2.4707	0.047851
0.119380543	2.5261	0.053666
0.133410418	2.5810	0.059647
0.147303092	2.6409	0.065414
0.161290803	2.6974	0.071293
0.175161246	2.7520	0.077165
0.188953599	2.8107	0.082888
0.203034663	2.8661	0.088886
0.216825853	2.9264	0.094607
0.230700937	2.9847	0.100474
0.244672002	3.0471	0.106307
0.258542282	3.1033	0.112361
0.272344502	3.1626	0.118345
0.286399683	3.2225	0.124544
0.300196141	3.2772	0.130898

Pore Volume

BJH Adsorption cumulative volume of pores

between 17.000 Å and 3000.000 Å width: 0.030284 cm³/g

BJH Desorption cumulative volume of pores

between 17.000 Å and 3000.000 Å width: 0.032077 cm³/g

l) For CeO₂-supported [BMIM][BF₄],

BET Surface Area Report

BET Surface Area: 0.6326 ± 0.0359 m²/g
 Slope: 6.577265 ± 0.383580 g/cm³ STP
 Y-Intercept: 0.304085 ± 0.070872 g/cm³ STP
 C: 22.629661
 Qm: 0.1453 cm³/g STP
 Correlation Coefficient: 0.9738534
 Molecular Cross-Sectional Area: 0.1620 nm²

Relative Pressure (p/p°)	Quantity Adsorbed (cm ³ /g STP)	1/[Q(p°/p - 1)]
0.050049864	0.0641	0.822181
0.064163190	0.0838	0.818330
0.078102064	0.0975	0.868557
0.091985458	0.1048	0.966293
0.105532362	0.1205	0.978840
0.119686903	0.1287	1.056092
0.133329554	0.1336	1.151454
0.147463164	0.1415	1.222101
0.161085405	0.1516	1.266807
0.174979473	0.1634	1.298373
0.189144524	0.1620	1.440088
0.203110204	0.1672	1.524387
0.216889334	0.1687	1.641912
0.230386228	0.1734	1.726580
0.244708810	0.1736	1.866647
0.258512543	0.1705	2.044272
0.272473055	0.1684	2.224047
0.306024810	0.1695	2.601625

Pore Volume

BJH Adsorption cumulative volume of pores
 between 17.000 Å and 3000.000 Å width: 0.009800 cm³/g

BJH Desorption cumulative volume of pores
 between 17.000 Å and 3000.000 Å width: 0.000512 cm³/g

m) For MgO,

BET Surface Area ReportBET Surface Area: $33.0554 \pm 0.0746 \text{ m}^2/\text{g}$ Slope: $0.130983 \pm 0.000292 \text{ g/cm}^3 \text{ STP}$ Y-Intercept: $0.000711 \pm 0.000056 \text{ g/cm}^3 \text{ STP}$

C: 185.315411

Qm: $7.5934 \text{ cm}^3/\text{g STP}$

Correlation Coefficient: 0.9999577

Molecular Cross-Sectional Area: 0.1620 nm^2

Relative Pressure (p/p°)	Quantity Adsorbed (cm ³ /g STP)	1/[Q(p°/p - 1)]
0.050004789	7.1859	0.007325
0.063934708	7.4580	0.009158
0.077750577	7.7095	0.010935
0.091976606	7.9049	0.012814
0.105575058	8.0939	0.014583
0.119667301	8.2999	0.016378
0.133310774	8.4719	0.018156
0.147233719	8.6534	0.019952
0.161093655	8.8215	0.021768
0.175192300	9.0067	0.023583
0.188846042	9.1726	0.025381
0.203035864	9.3651	0.027203
0.216563950	9.5332	0.028996
0.230867245	9.7350	0.030834
0.244679861	9.9115	0.032684
0.258186451	10.0972	0.034470
0.272106554	10.2797	0.036366
0.286454125	10.4687	0.038348
0.300346436	10.6451	0.040327

Pore Volume

BJH Adsorption cumulative volume of pores

between 17.000 Å and 3000.000 Å width: $0.062743 \text{ cm}^3/\text{g}$

BJH Desorption cumulative volume of pores

between 17.000 Å and 3000.000 Å width: $0.068801 \text{ cm}^3/\text{g}$

n) For MgO-supported [BMIM][BF₄],

BET Surface Area Report

BET Surface Area: 5.0858 ± 0.0236 m²/g

Slope: 0.836730 ± 0.003900 g/cm³ STP

Y-Intercept: 0.019223 ± 0.000745 g/cm³ STP

C: 44.527727

Qm: 1.1683 cm³/g STP

Correlation Coefficient: 0.9998154

Molecular Cross-Sectional Area: 0.1620 nm²

Relative Pressure (p/p°)	Quantity Adsorbed (cm ³ /g STP)	1/[Q(p°/p - 1)]
0.050204766	0.8636	0.061207
0.063927820	0.9309	0.073360
0.078012843	0.9886	0.085594
0.091870757	1.0426	0.097027
0.105534616	1.0885	0.108393
0.119638401	1.1330	0.119947
0.133469370	1.1788	0.130662
0.147433378	1.2150	0.142327
0.161363734	1.2553	0.153286
0.175146253	1.2873	0.164941
0.189134833	1.3231	0.176287
0.203029300	1.3573	0.187691
0.216521051	1.3906	0.198732
0.230747007	1.4221	0.210932
0.244747628	1.4548	0.222754
0.258549022	1.4815	0.235380
0.272048728	1.5120	0.247168
0.286320052	1.5406	0.260417
0.300257265	1.5676	0.273731

Pore Volume

BJH Adsorption cumulative volume of pores

between 17.000 Å and 3000.000 Å width: 0.006394 cm³/g

BJH Desorption cumulative volume of pores

between 17.000 Å and 3000.000 Å width: 0.007273 cm³/g

o) For La_2O_3 ,**BET Surface Area Report**BET Surface Area: $0.9869 \pm 0.0204 \text{ m}^2/\text{g}$ Slope: $4.398151 \pm 0.089765 \text{ g}/\text{cm}^3 \text{ STP}$ Y-Intercept: $0.012972 \pm 0.017148 \text{ g}/\text{cm}^3 \text{ STP}$

C: 340.062323

Qm: $0.2267 \text{ cm}^3/\text{g STP}$

Correlation Coefficient: 0.9964780

Molecular Cross-Sectional Area: 0.1620 nm^2

Relative Pressure (p/p°)	Quantity Adsorbed ($\text{cm}^3/\text{g STP}$)	$1/[Q(p^\circ/p - 1)]$
0.050265002	0.1960	0.269991
0.063849782	0.2118	0.322090
0.078062017	0.2240	0.377934
0.091883673	0.2353	0.430014
0.105779481	0.2451	0.482566
0.119658055	0.2567	0.529434
0.133543046	0.2617	0.588955
0.147539688	0.2669	0.648347
0.161393879	0.2754	0.698924
0.175318484	0.2823	0.753147
0.189100116	0.2894	0.805834
0.202713300	0.2920	0.870633
0.217030721	0.2936	0.943988
0.230674448	0.2977	1.007159
0.244761903	0.3027	1.070579
0.258477872	0.3044	1.145192
0.272537195	0.3037	1.233413
0.286316417	0.3063	1.309760
0.300329649	0.3064	1.400977

Pore Volume

BJH Adsorption cumulative volume of pores

between 17.000 Å and 3000.000 Å width: $0.001547 \text{ cm}^3/\text{g}$

BJH Desorption cumulative volume of pores

between 17.000 Å and 3000.000 Å width: $0.001649 \text{ cm}^3/\text{g}$

p) For La₂O₃-supported [BMIM][BF₄],

BET Surface Area Report

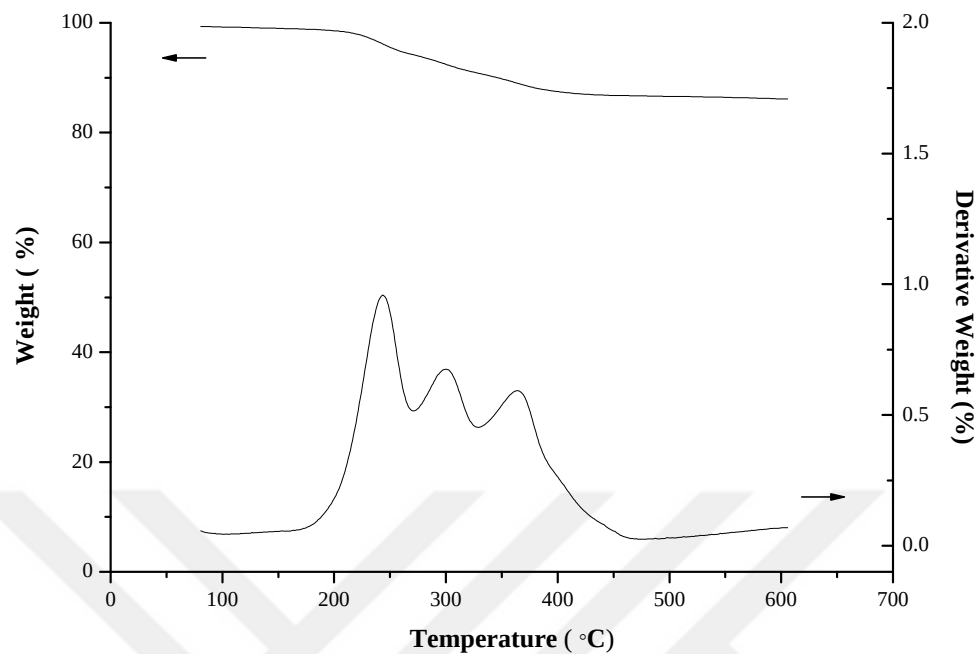
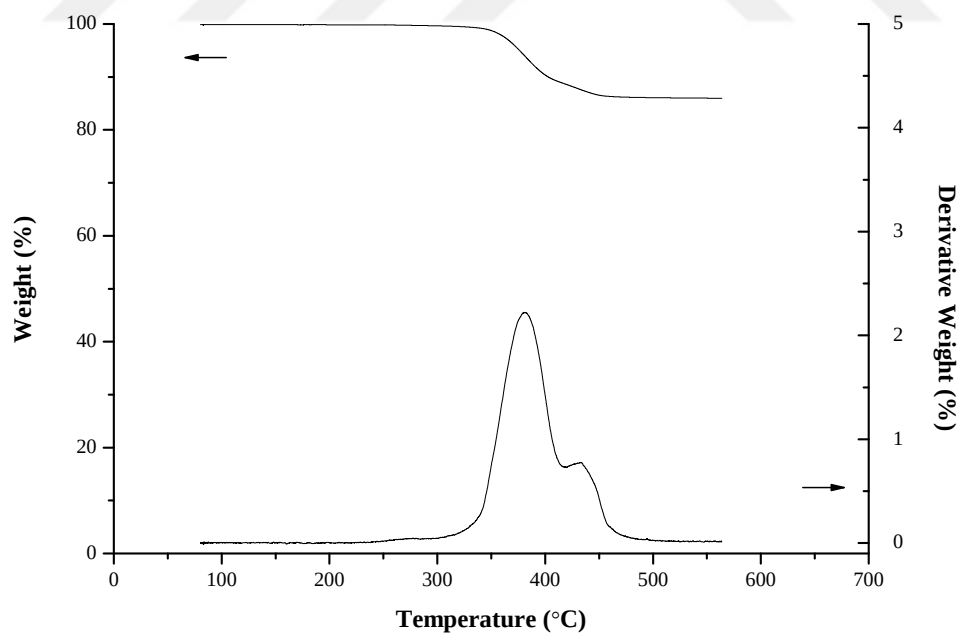
BET Surface Area: 0.9051 ± 0.0565 m²/g
 Slope: 4.997991 ± 0.290116 g/cm³ STP
 Y-Intercept: -0.188430 ± 0.076595 g/cm³ STP
 C: -25.524392
 Qm: 0.2079 cm³/g STP
 Correlation Coefficient: 0.9803767
 Molecular Cross-Sectional Area: 0.1620 nm²

Relative Pressure (p/p ⁰)	Quantity Adsorbed (cm ³ /g STP)	1/[Q(p ⁰ p - 1)]
0.034773747	0.2567	0.140329
0.046352711	0.2673	0.181854
0.057462575	0.2754	0.221372
0.077767439	0.2886	0.292149
0.105514165	0.3079	0.383156
0.133301382	0.3202	0.480291
0.161039747	0.3341	0.574457
0.189300217	0.3463	0.674237
0.216544846	0.3578	0.772551
0.244826798	0.3677	0.881678
0.271873530	0.3814	0.979079
0.300438102	0.3916	1.096582
0.478065226	0.4431	2.067000
0.610664744	0.4825	3.250991

Pore Volume

BJH Adsorption cumulative volume of pores
 between 17.000 Å and 3000.000 Å width: 0.000553 cm³/g

BJH Desorption cumulative volume of pores
 between 17.000 Å and 3000.000 Å width: 0.000512 cm³/g

A3-5. Thermogravimetric Analysis (TGA)**Figure A3-16.** TG/DTG curve of SiO₂-supported [BMIM][BF₄].**Figure A3-17.** TG/DTG curve of TiO₂-supported [BMIM][BF₄].

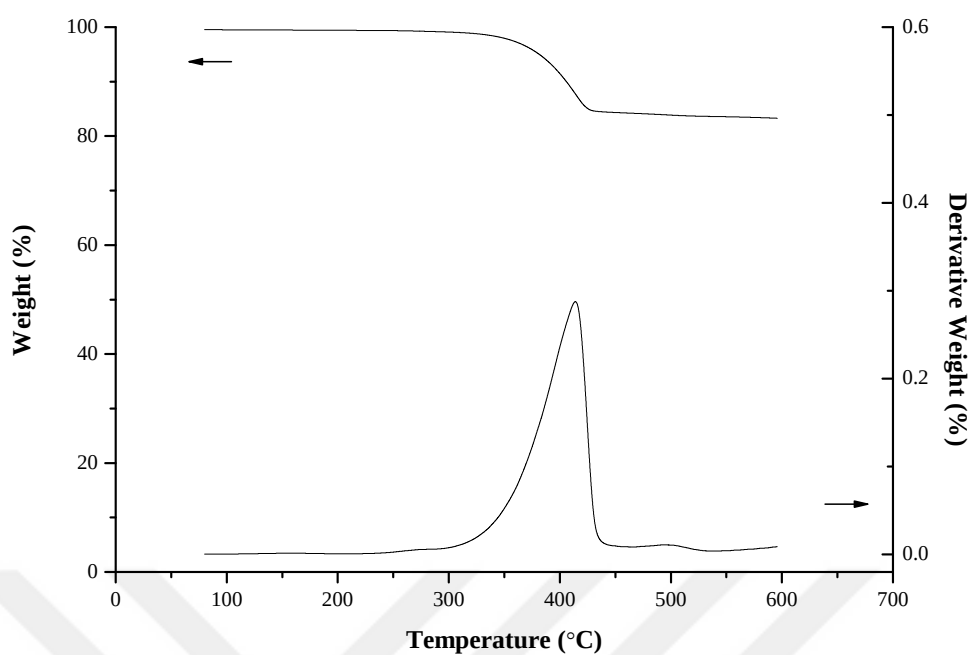


Figure A3-18. TG/DTG curve of Fe₂O₃-supported [BMIM][BF₄].

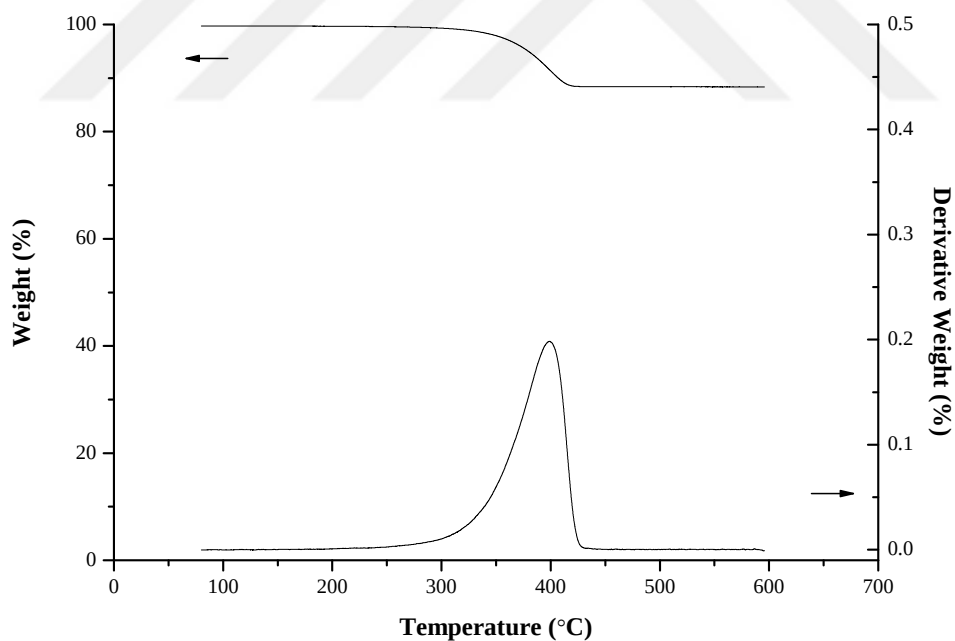


Figure A3-19. TG/DTG curve of ZnO-supported [BMIM][BF₄].

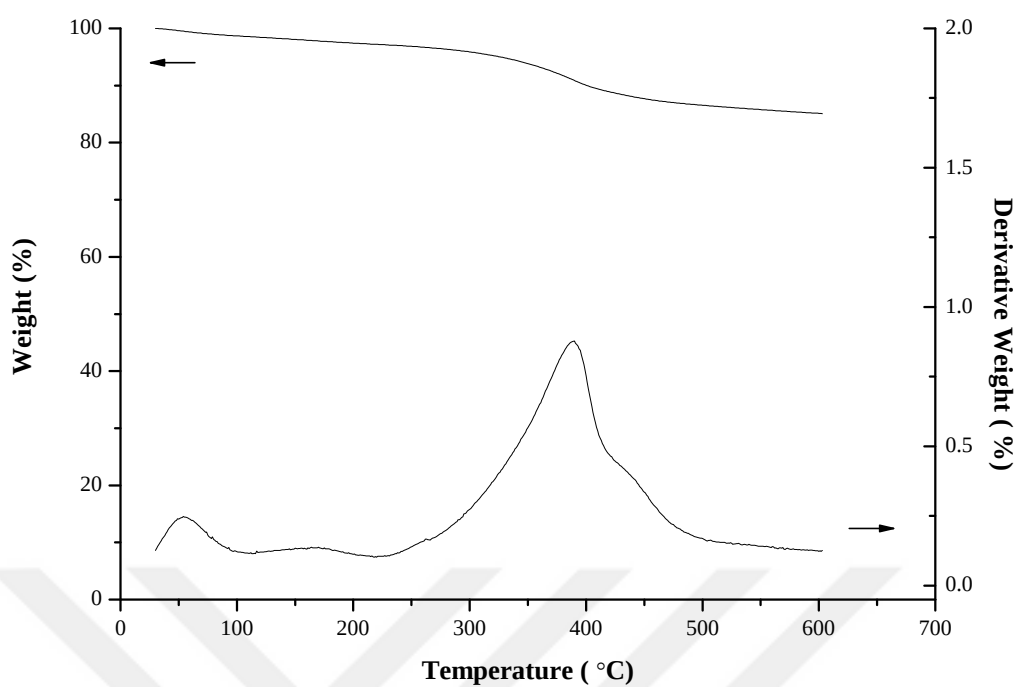


Figure A3-20. TG/DTG curve of γ -Al₂O₃-supported [BMIM][BF₄].

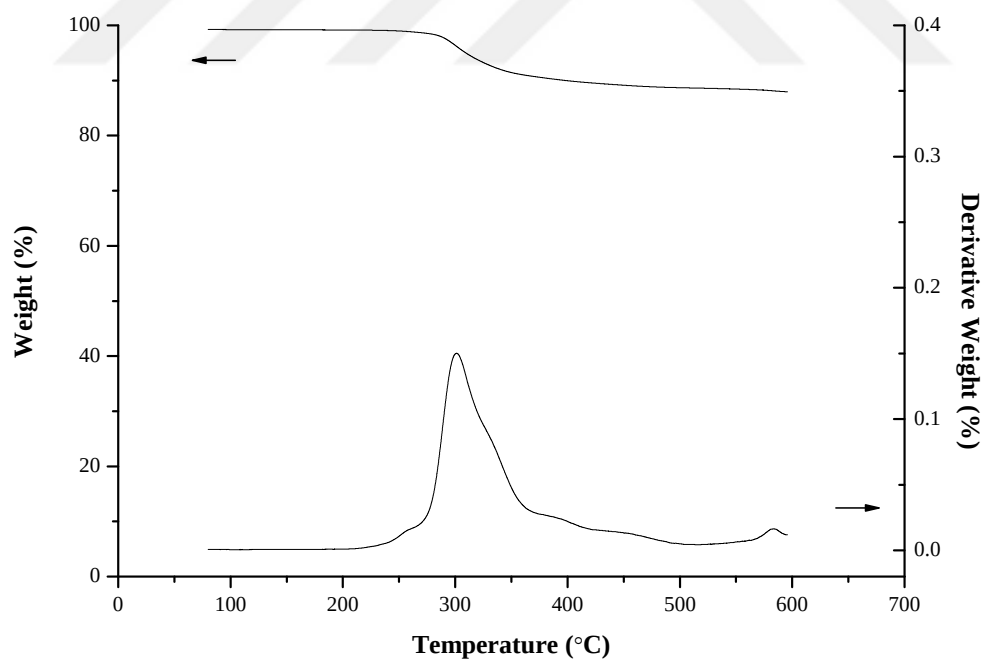


Figure A3-21. TG/DTG curve of CeO₂-supported [BMIM][BF₄].

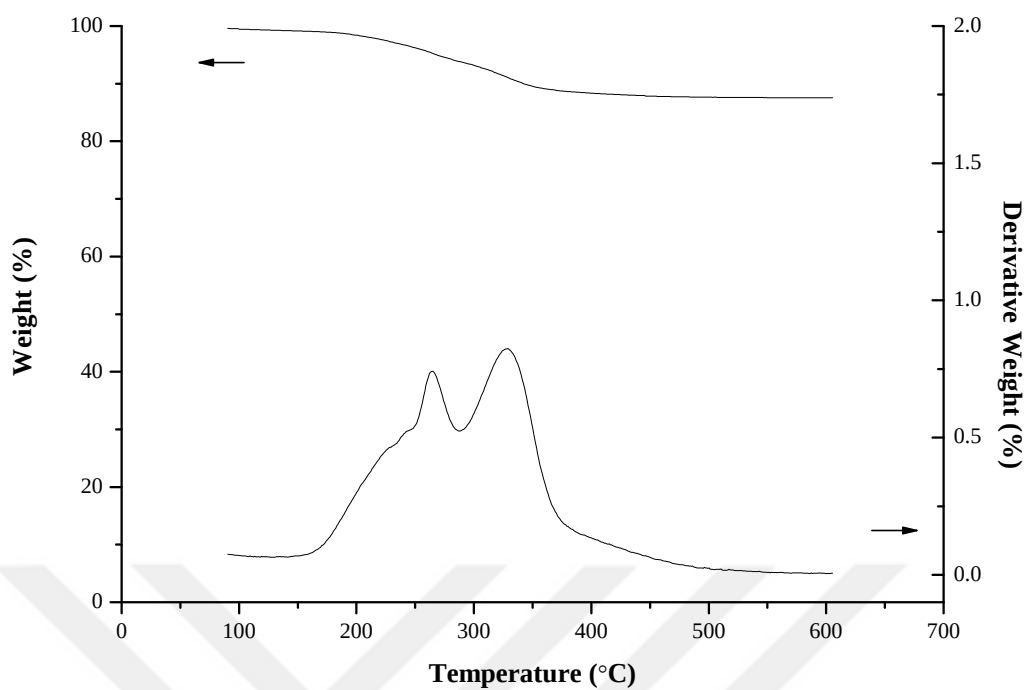


Figure A3-22. TG/DTG curve of MgO-supported [BMIM][BF₄].

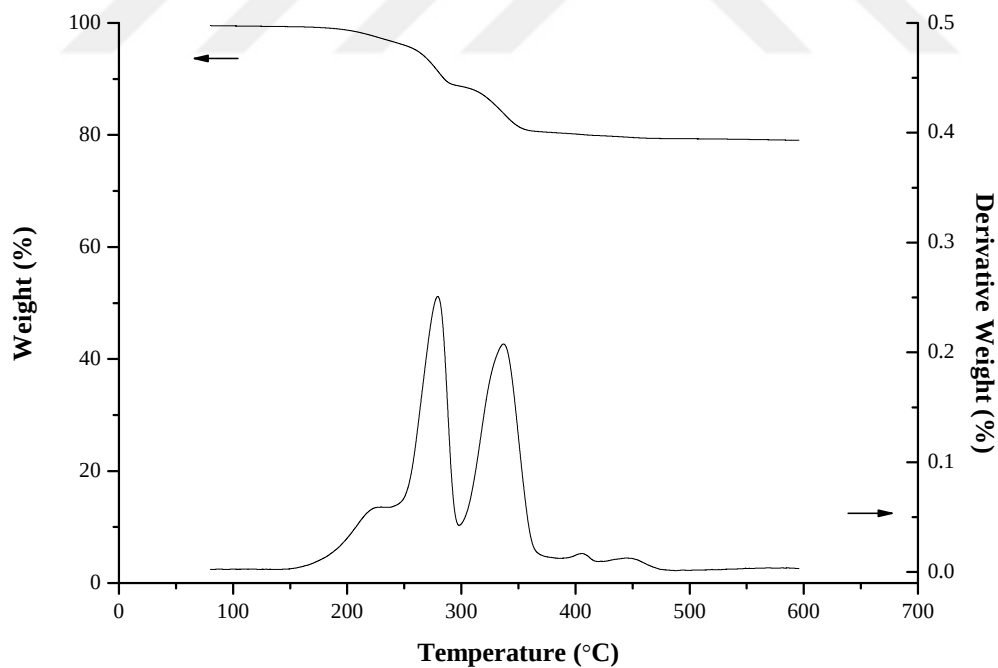
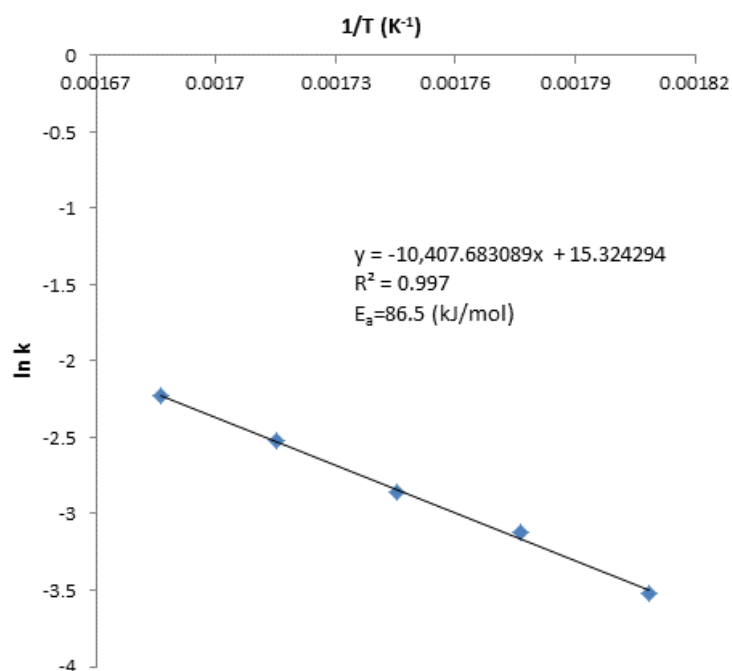
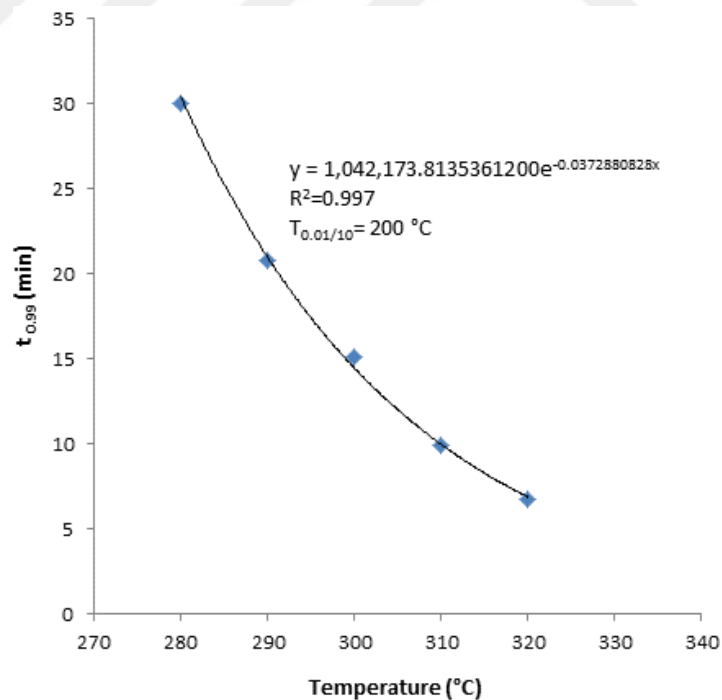


Figure A3-23. TG/DTG curve of La₂O₃-supported [BMIM][BF₄].

A3-6. Activation Energy (E_a) and $T_{0.01/10}$ Calculationsa) For SiO₂-supported [BMIM][BF₄],**Figure A3-24.** Activation energy plot for SiO₂-supported [BMIM][BF₄].**Figure A3-25.** $T_{0.01/10}$ plot for SiO₂-supported [BMIM][BF₄].

b) For TiO₂-supported [BMIM][BF₄],

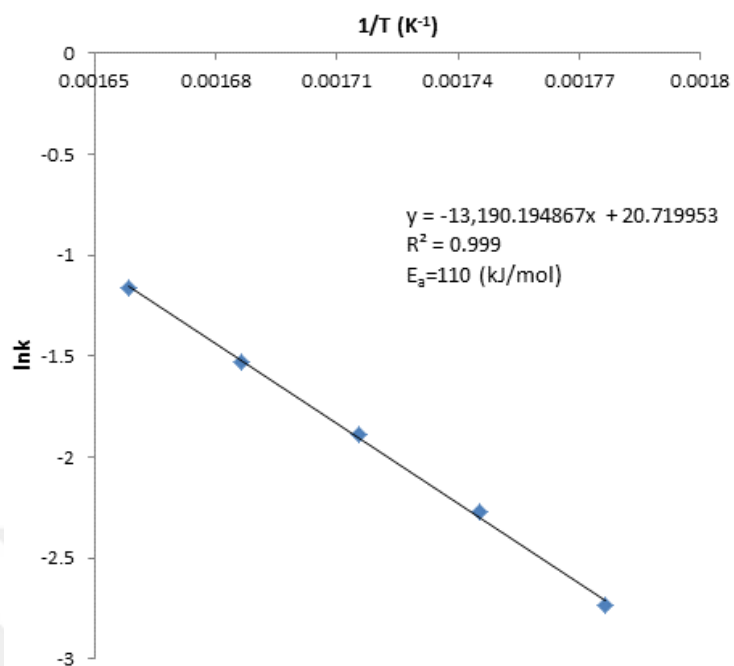


Figure A3-26. Activation energy plot for TiO₂-supported [BMIM][BF₄].

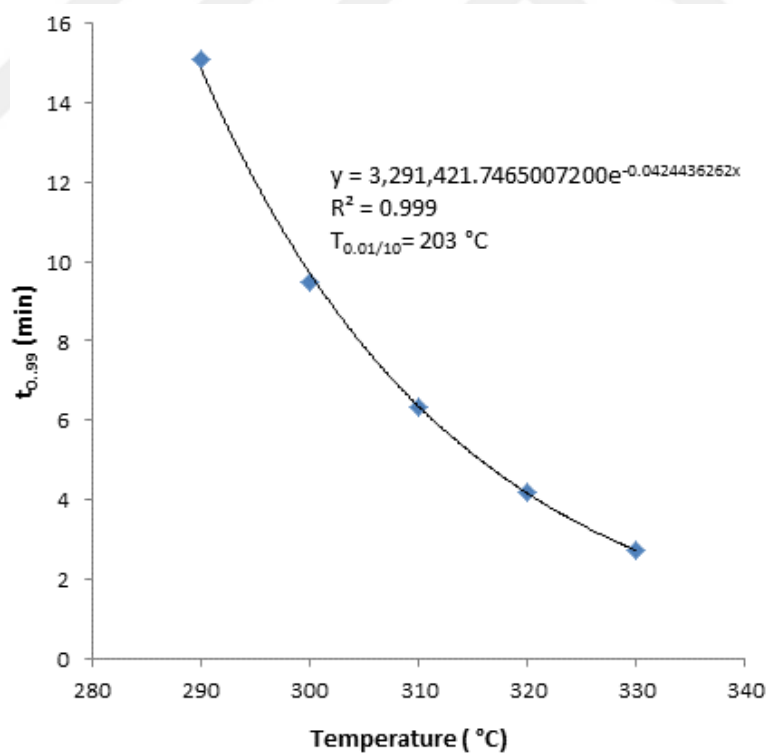


Figure A3-27. $T_{0.01/10}$ plot for TiO₂-supported [BMIM][BF₄].

c) For Fe_2O_3 -supported [BMIM][BF_4],

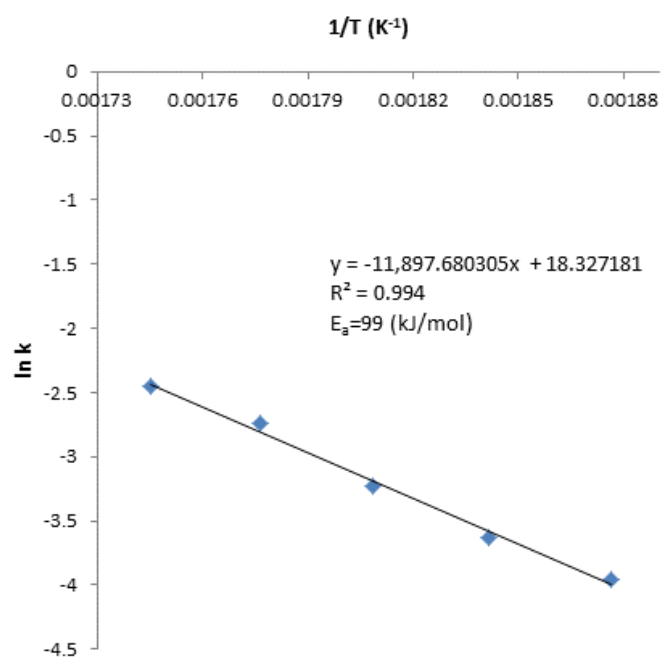


Figure A3-28. Activation energy plot for Fe_2O_3 -supported [BMIM][BF_4].

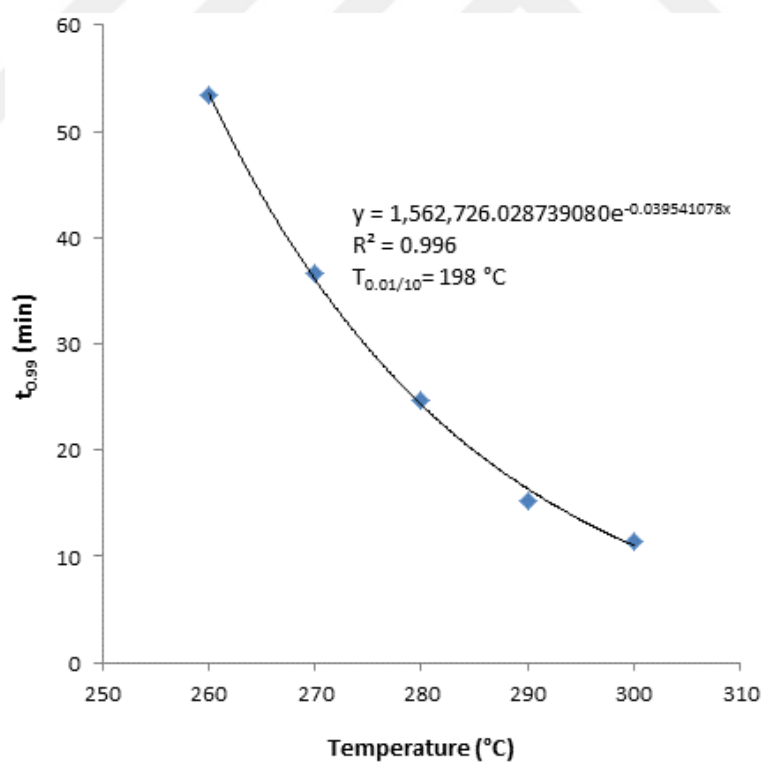


Figure A3-29. $T_{0.01/10}$ plot for Fe_2O_3 -supported [BMIM][BF_4].

d) For ZnO-supported [BMIM][BF₄],

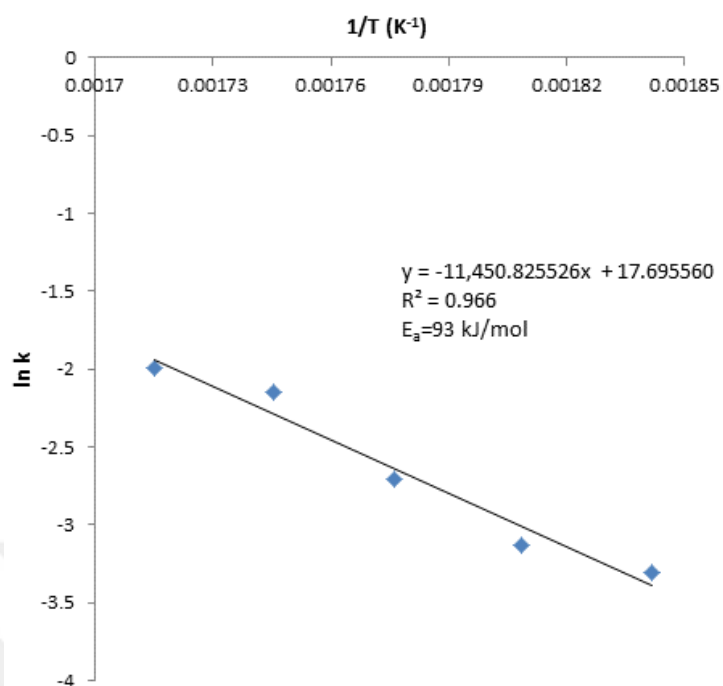


Figure A3-30. Activation energy plot for ZnO-supported [BMIM][BF₄].

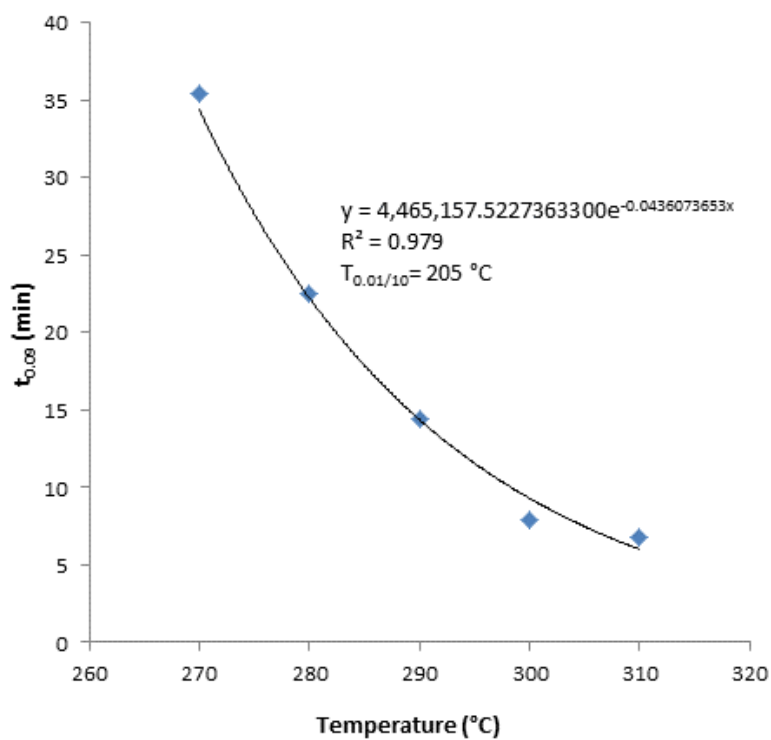


Figure A3-31. $T_{0.01/10}$ plot for ZnO-supported [BMIM][BF₄].

e) For $\gamma\text{-Al}_2\text{O}_3$ -supported [BMIM][BF₄],

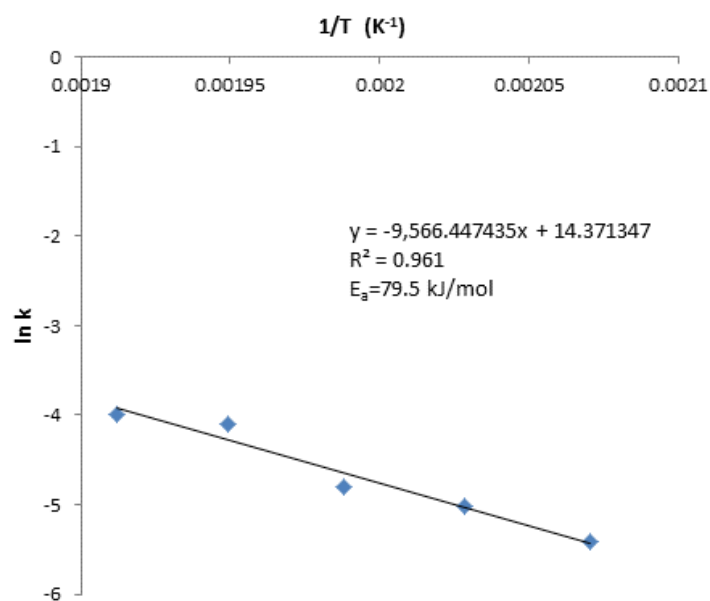


Figure A3-32. Activation energy plot for $\gamma\text{-Al}_2\text{O}_3$ -supported [BMIM][BF₄].

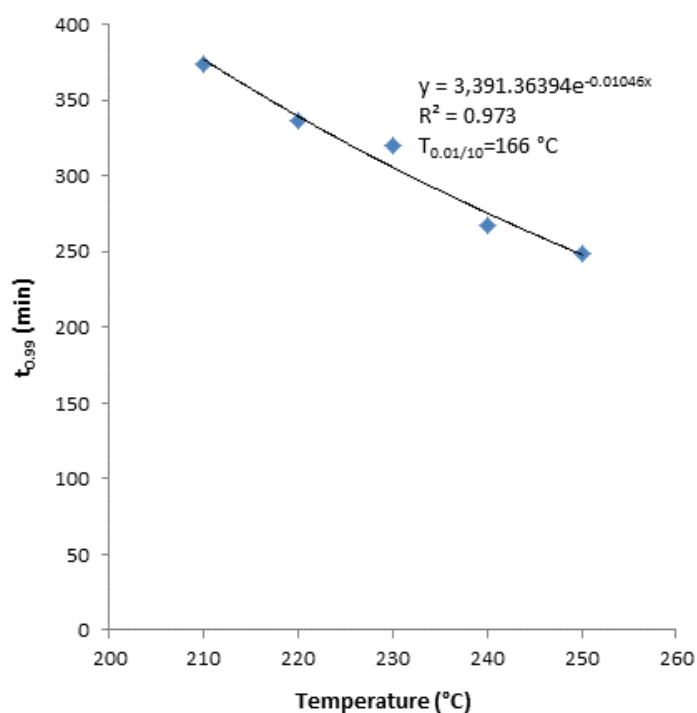


Figure A3-33. $T_{0.01/10}$ plot for $\gamma\text{-Al}_2\text{O}_3$ -supported [BMIM][BF₄].

f) For CeO₂-supported [BMIM][BF₄],

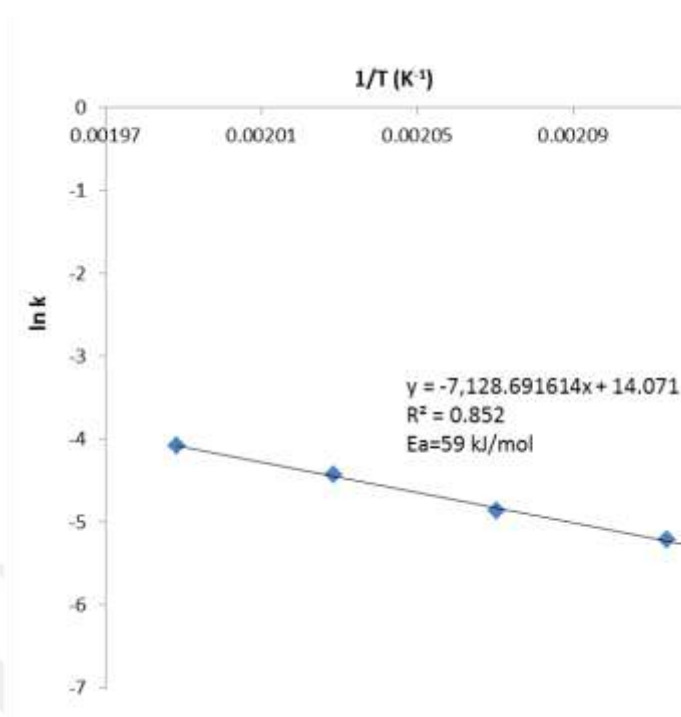


Figure A3-34. Activation energy plot for CeO₂-supported [BMIM][BF₄].

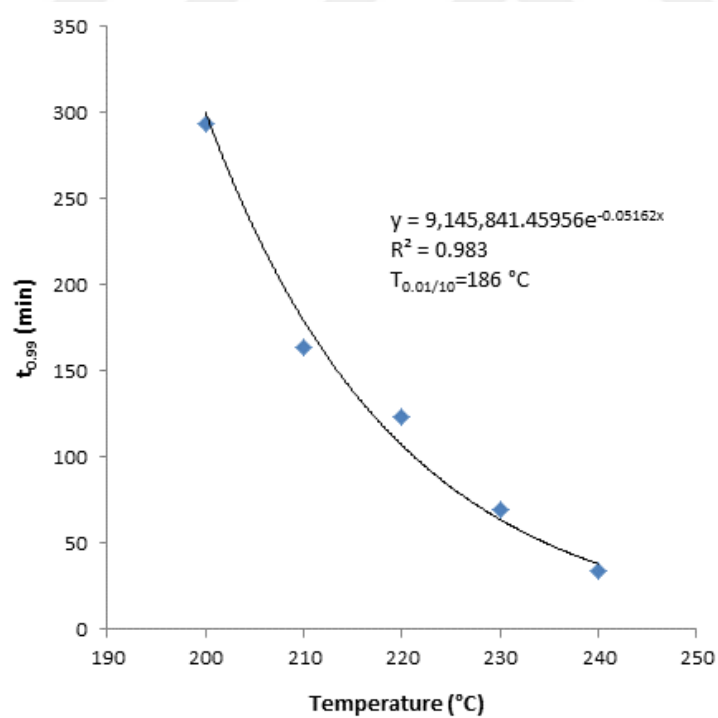


Figure A3-35. $T_{0.01/10}$ plot for CeO₂-supported [BMIM][BF₄].

g) For MgO-supported [BMIM][BF₄],

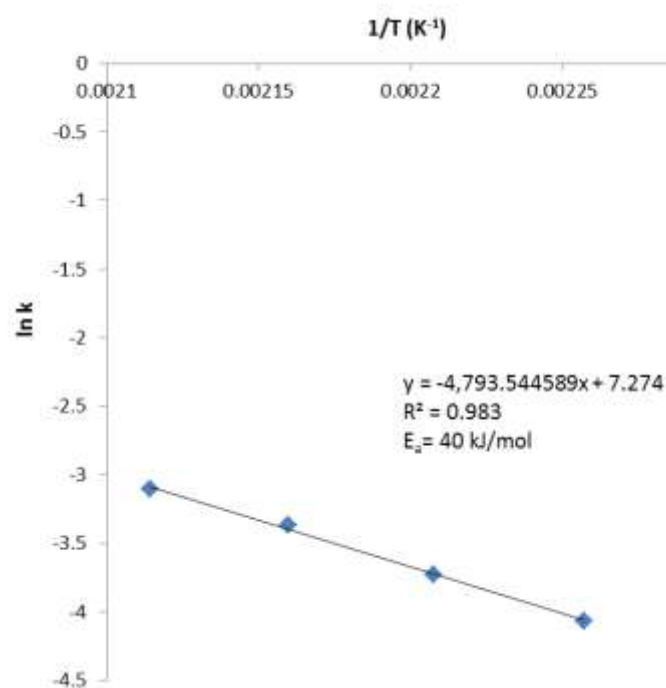


Figure A3-36. Activation energy plot for MgO-supported [BMIM][BF₄].

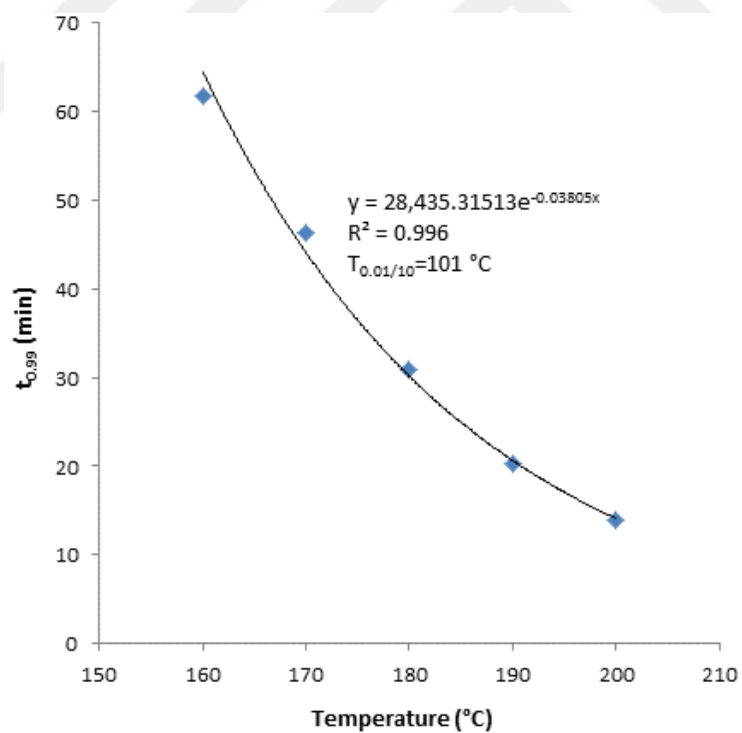


Figure A3-37. $T_{0.01/10}$ plot for MgO-supported [BMIM][BF₄].

h) For La_2O_3 -supported $[\text{BMIM}][\text{BF}_4]$,

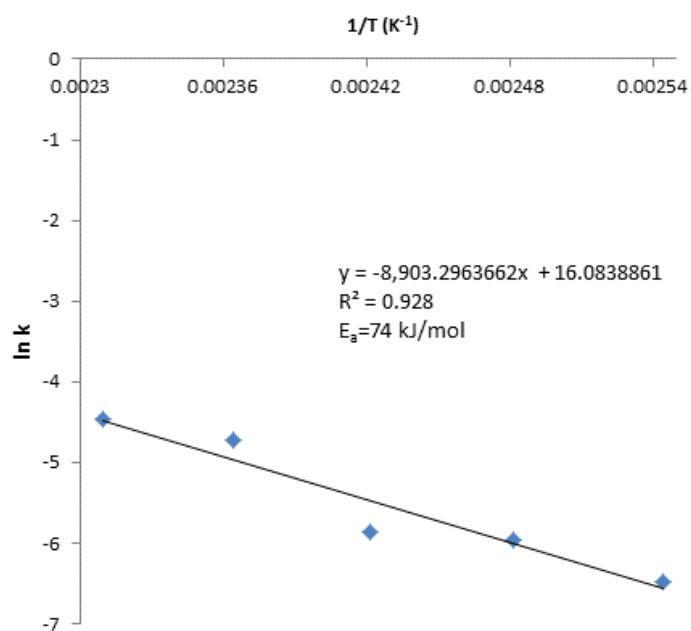


Figure A3-38. Activation energy plot for La_2O_3 -supported $[\text{BMIM}][\text{BF}_4]$.

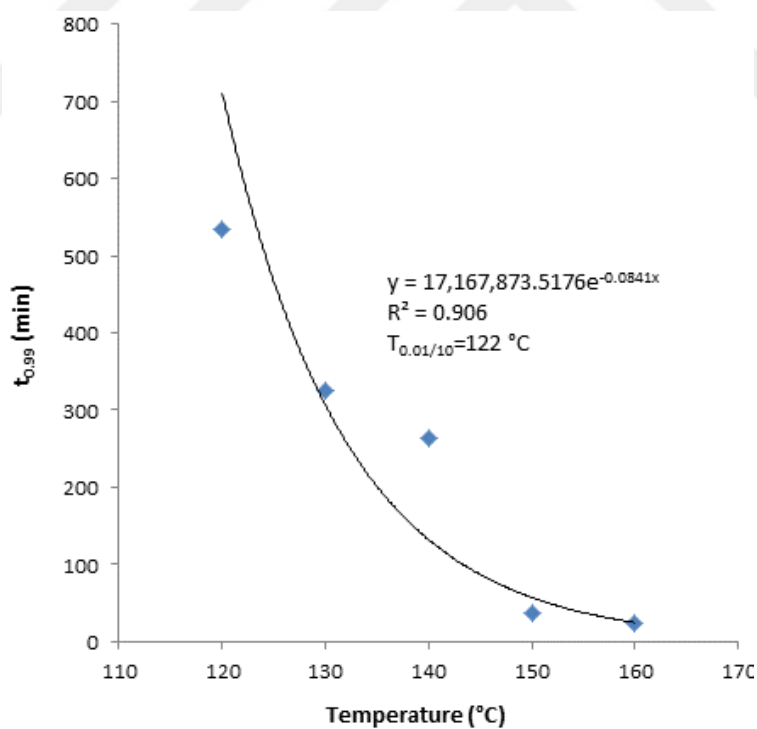


Figure A3-39. $T_{0.01/10}$ plot for La_2O_3 -supported $[\text{BMIM}][\text{BF}_4]$.

A3-7. Long-Term Thermal Stability Analysis by FT-IR

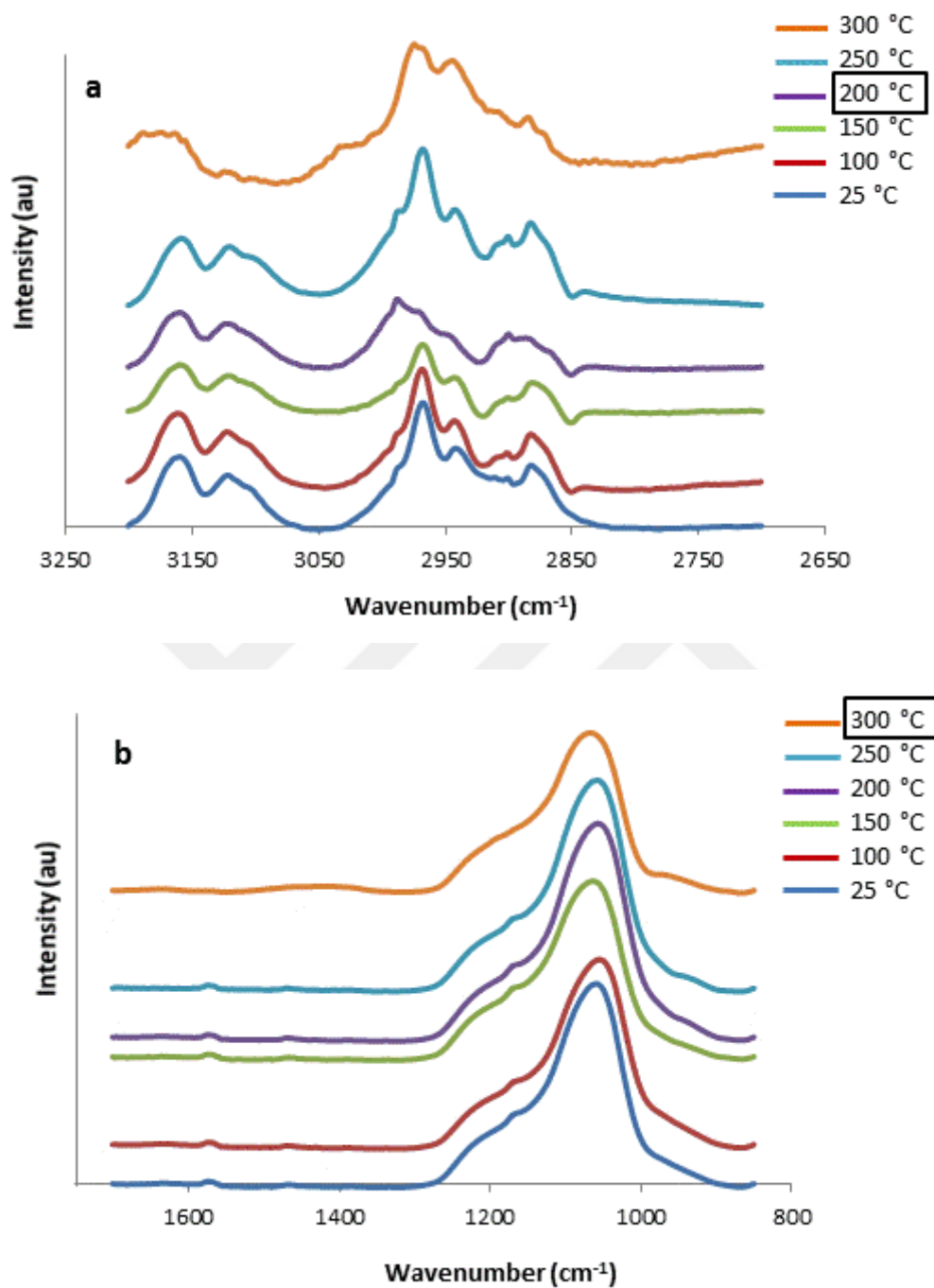


Figure A3-40. IR spectra of SiO₂-supported [BMIM][BF₄] after 6 h-treatments: room temperature, 100, 150, 200, 250, and 573 K in the region of a) 2750-3250 cm⁻¹ b) 850-1750 cm⁻¹.

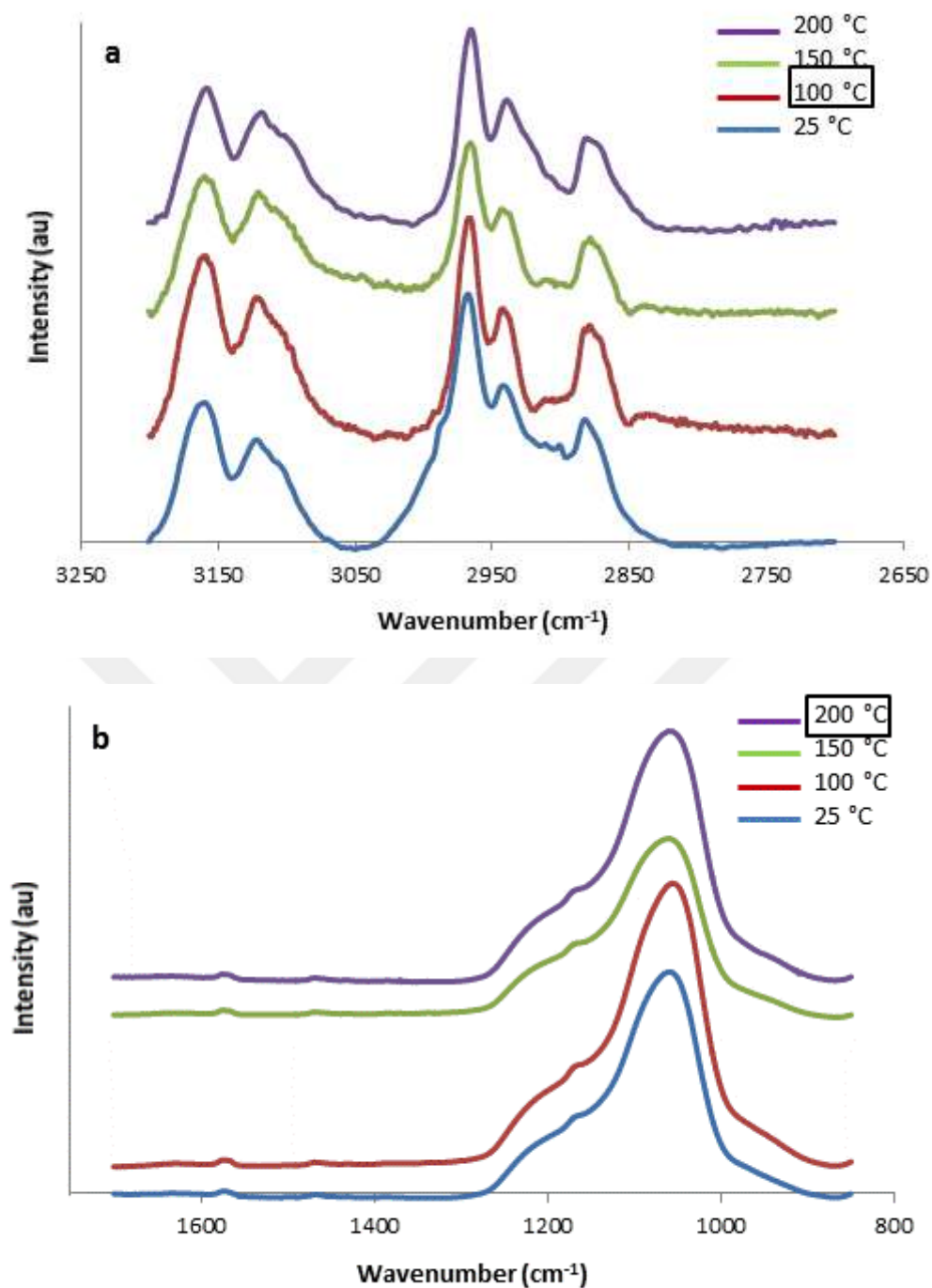


Figure A3-41. IR spectra of SiO₂-supported [BMIM][BF₄] after 10 h-treatments: room temperature, 100, 150, 200, 250, and 573 K in the region of a) 2750-3250 cm⁻¹ b) 850-1750 cm⁻¹.

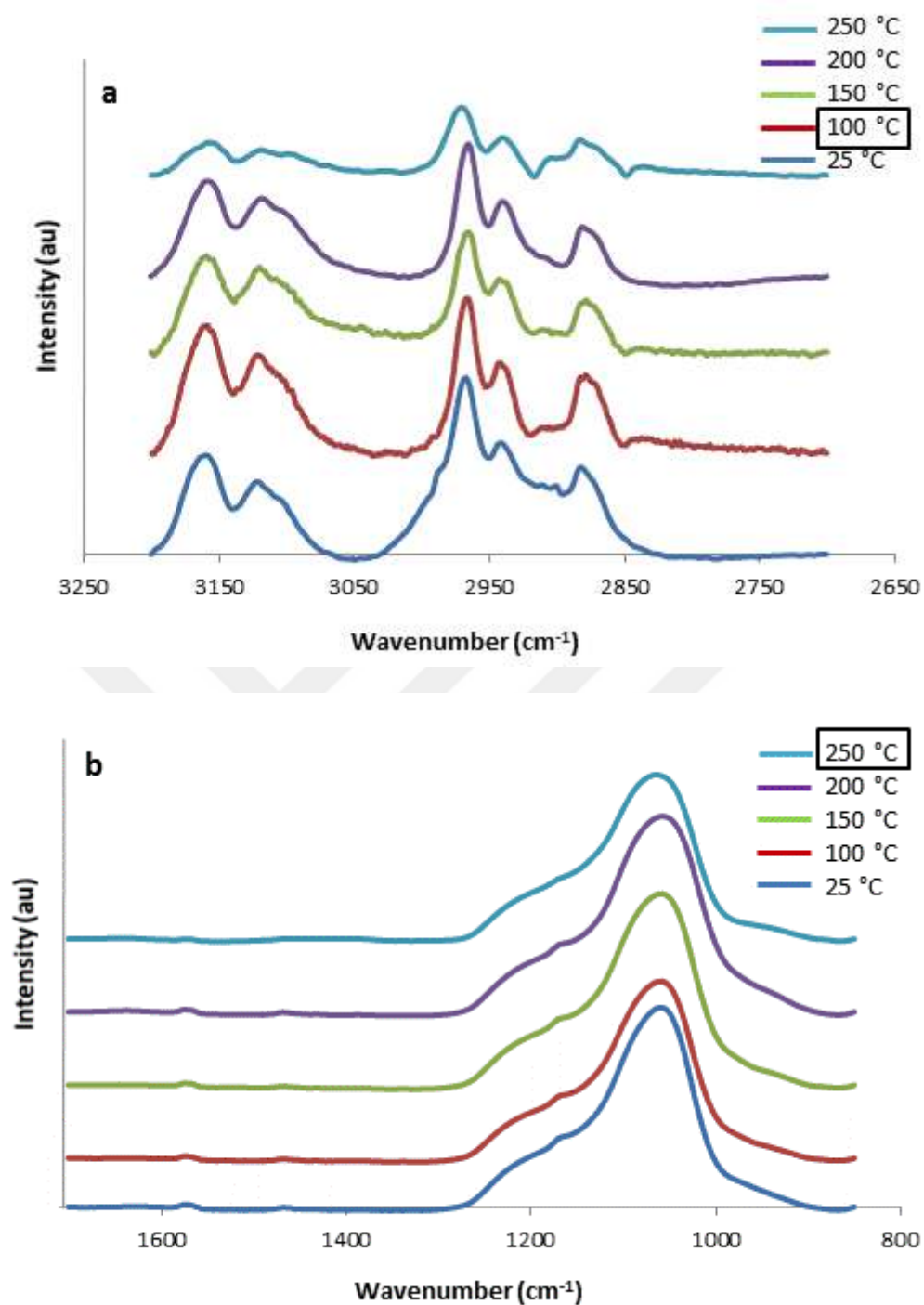


Figure A3-42. IR spectra of SiO₂-supported [BMIM][BF₄] after 24 h-treatments: room temperature, 100, 150, 200, 250, and 573 K in the region of a) 2750-3250 cm⁻¹ b) 850-1750 cm⁻¹.

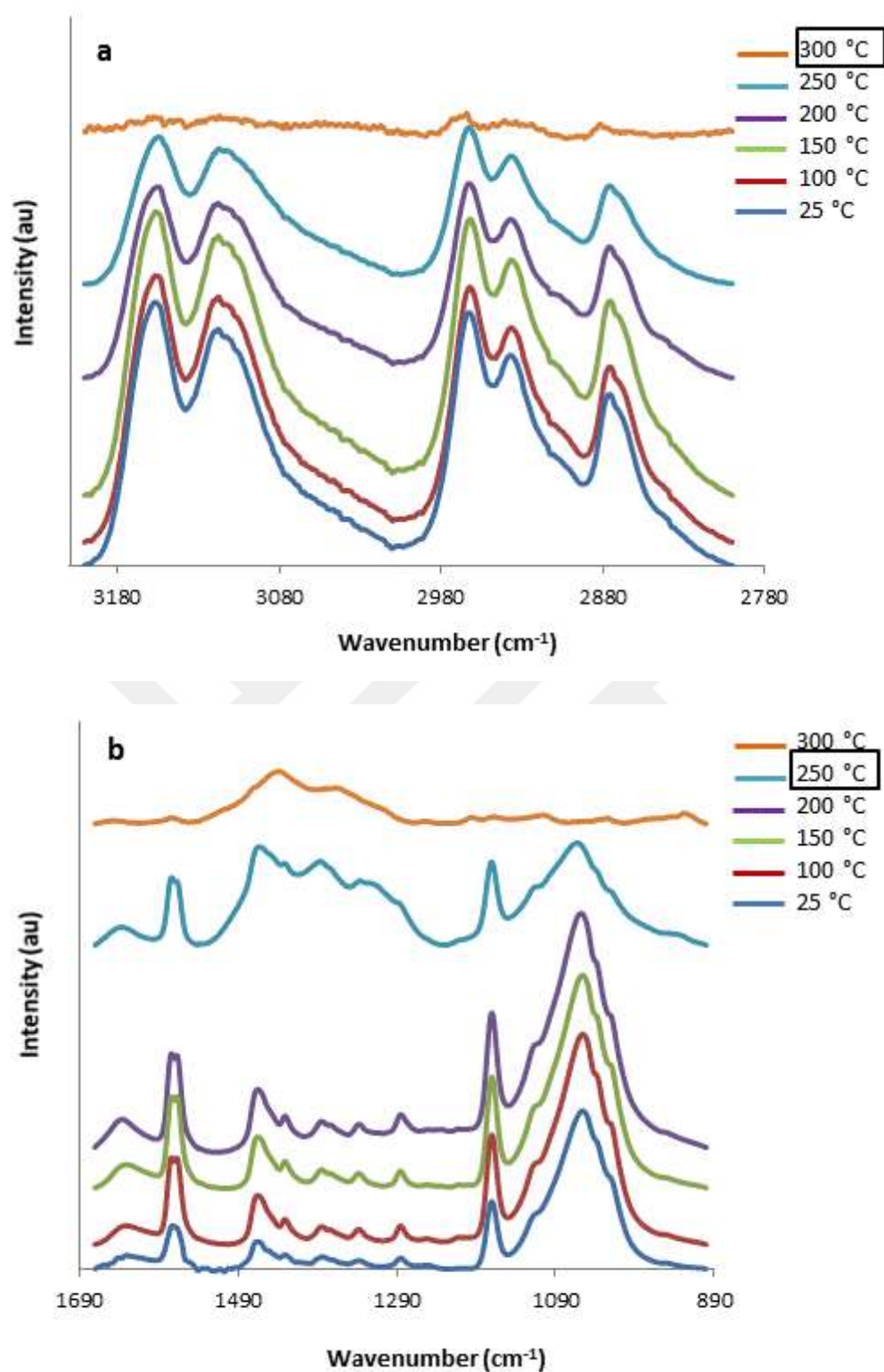


Figure A3-43. IR spectra of TiO₂-supported [BMIM][BF₄] after 6 h-treatments: room temperature, 100, 150, 200, 250, and 573 K in the region of a) 2750-3250 cm⁻¹ b) 850-1750 cm⁻¹.

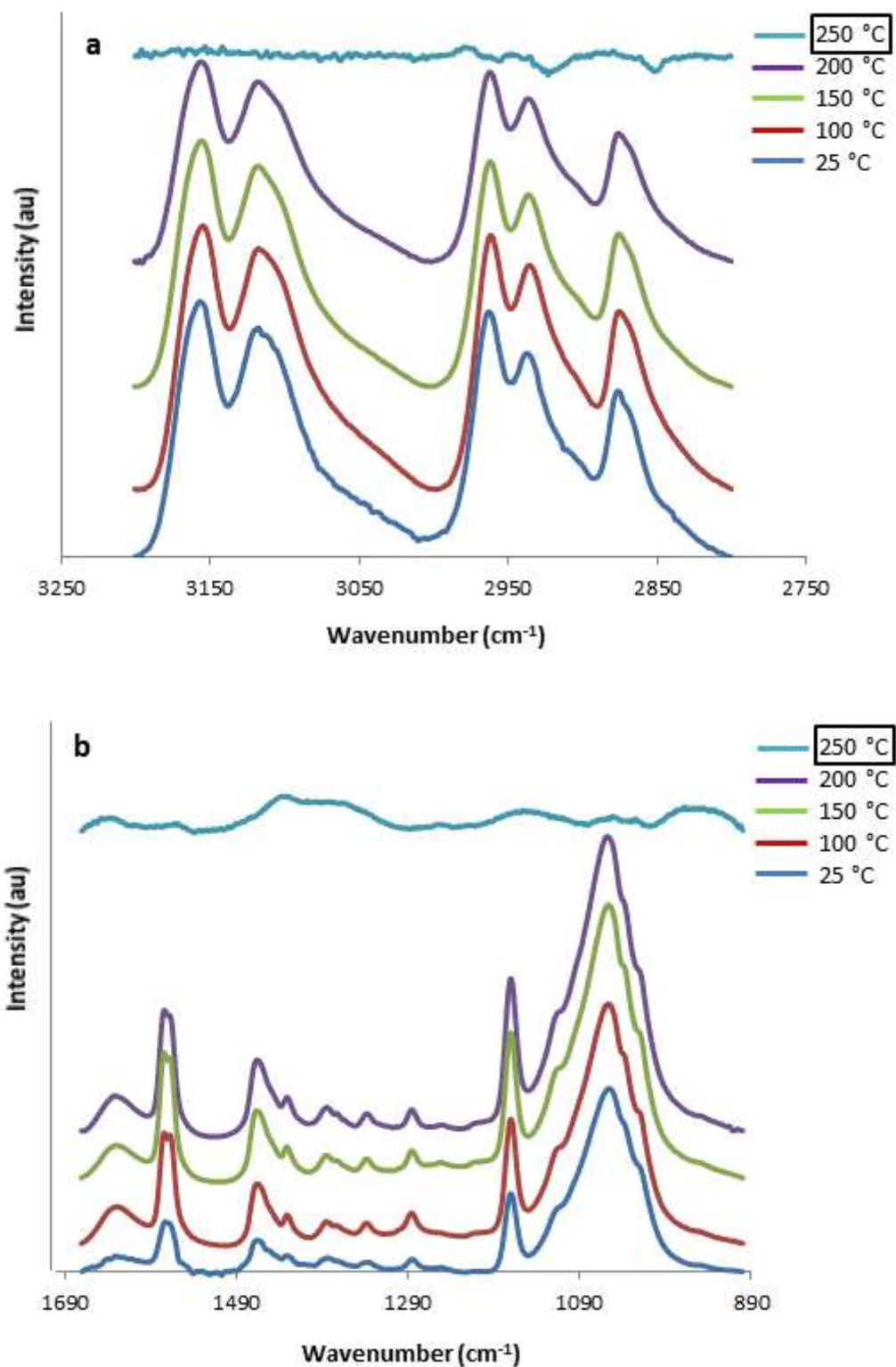


Figure A3-44. IR spectra of TiO₂-supported [BMIM][BF₄] after 10h-treatments: room temperature, 100, 150, 200, 250, and 573 K in the region of a) 2750-3250 cm⁻¹ b) 850-1750 cm⁻¹.

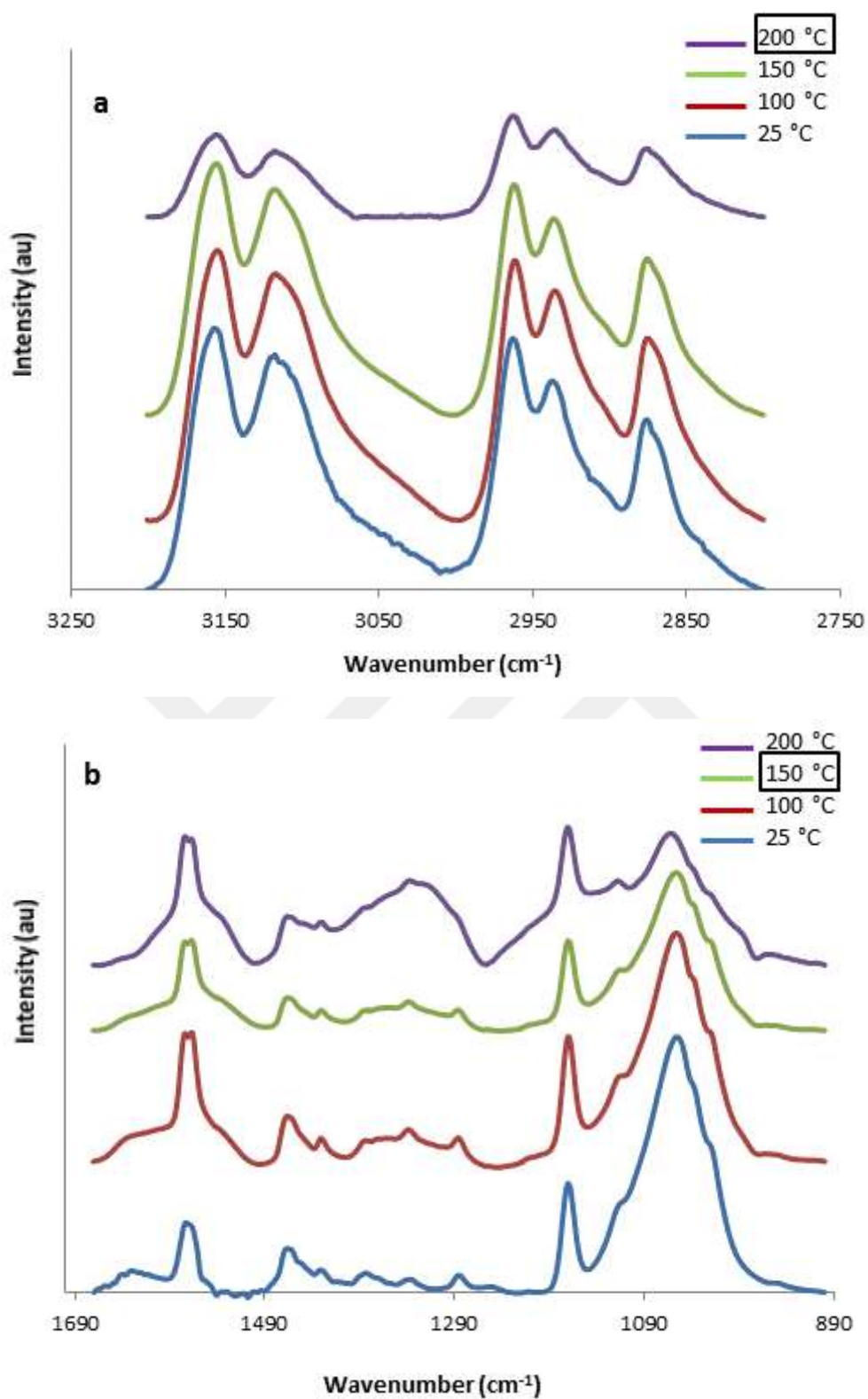


Figure A3-45. IR spectra of TiO₂-supported [BMIM][BF₄] after 24 h-treatments: room temperature, 100, 150, 200, 250, and 573 K in the region of a) 2750-3250 cm⁻¹ b) 850-1750 cm⁻¹.

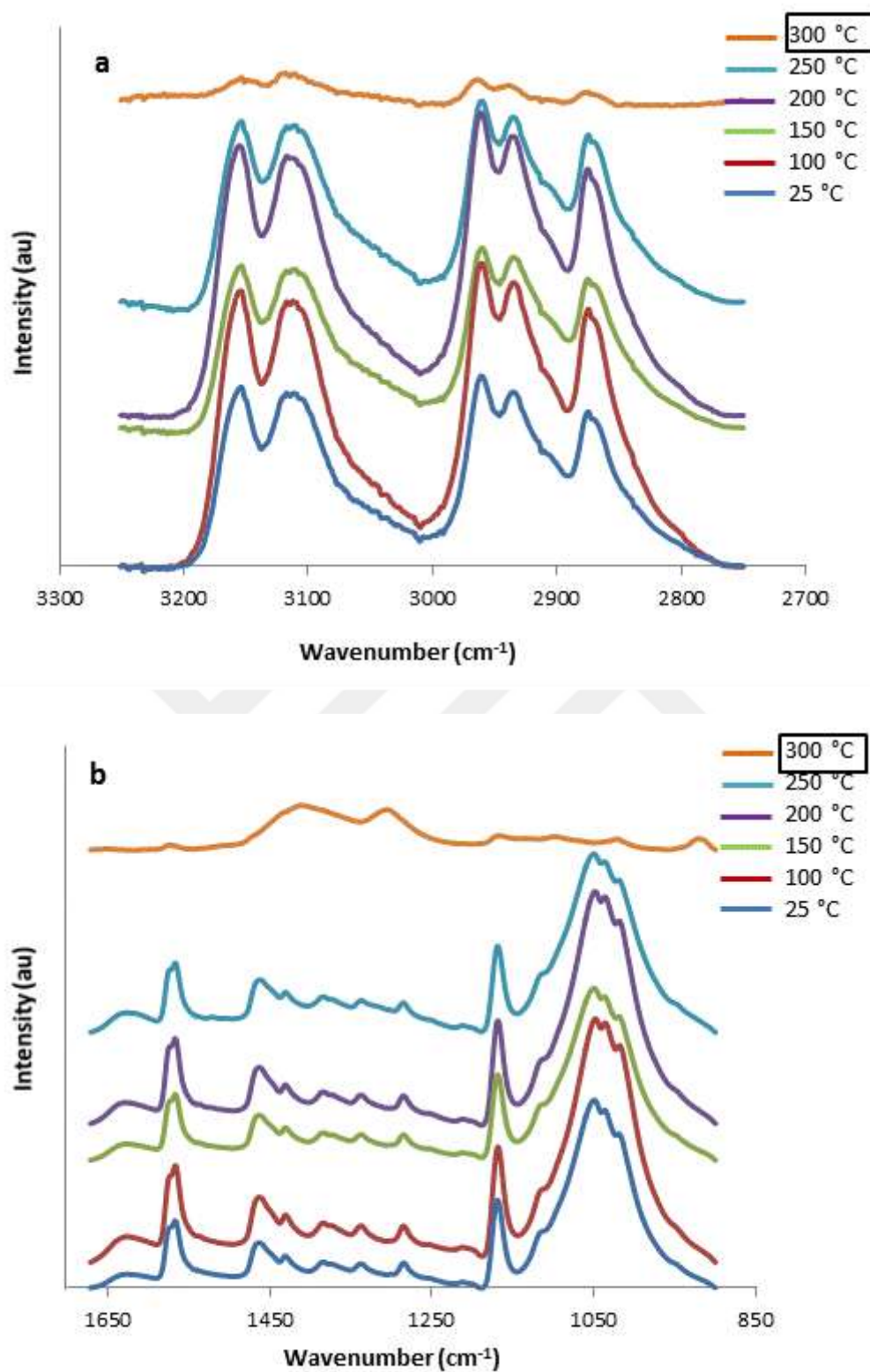


Figure A3-46. IR spectra of Fe_2O_3 -supported $[\text{BMIM}][\text{BF}_4]$ after 6 h-treatments: room temperature, 100, 150, 200, 250, and 573 K in the region of a) 2750-3250 cm^{-1} b) 850-1750 cm^{-1} .

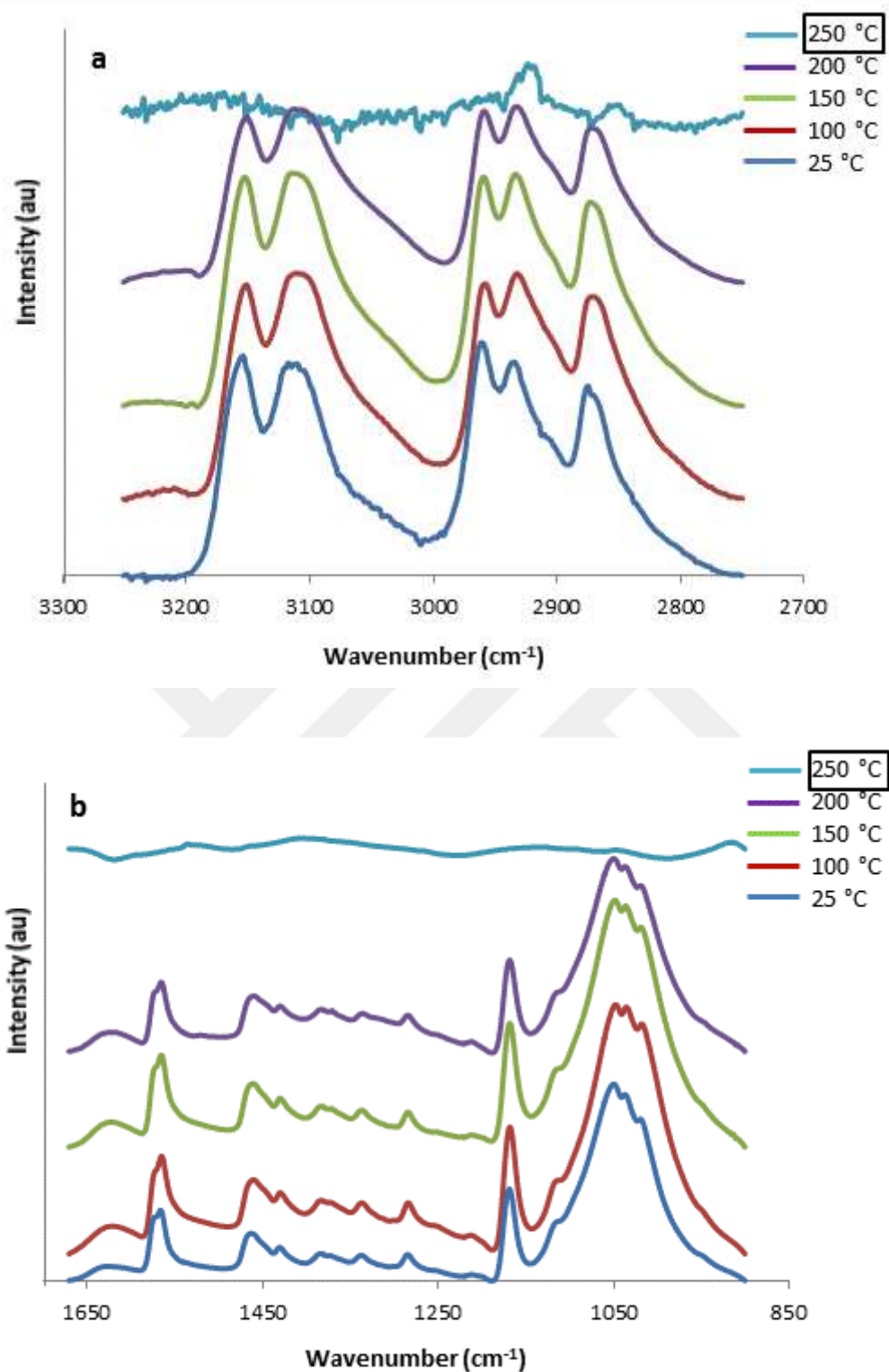


Figure A3-47. IR spectra of Fe_2O_3 -supported $[\text{BMIM}][\text{BF}_4]$ after 10 h-treatments: room temperature, 100, 150, 200, 250, and 573 K in the region of a) 2750-3250 cm^{-1} b) 850-1750 cm^{-1} .

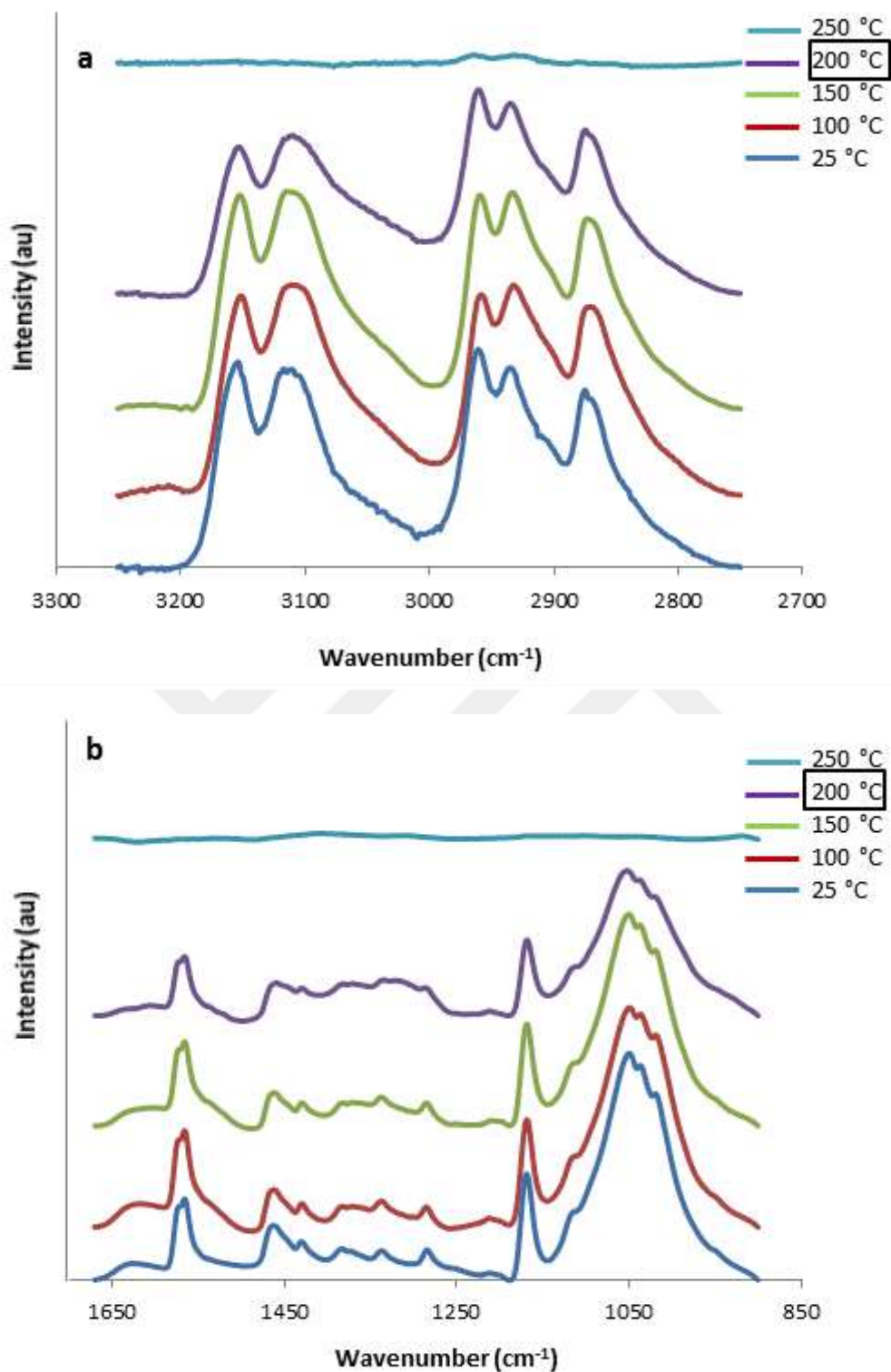


Figure A3-48. IR spectra of Fe_2O_3 -supported $[\text{BMIM}][\text{BF}_4]$ after 24 h-treatments: room temperature, 100, 150, 200, 250, and 573 K in the region of a) 2750-3250 cm^{-1} b) 850-1750 cm^{-1} .

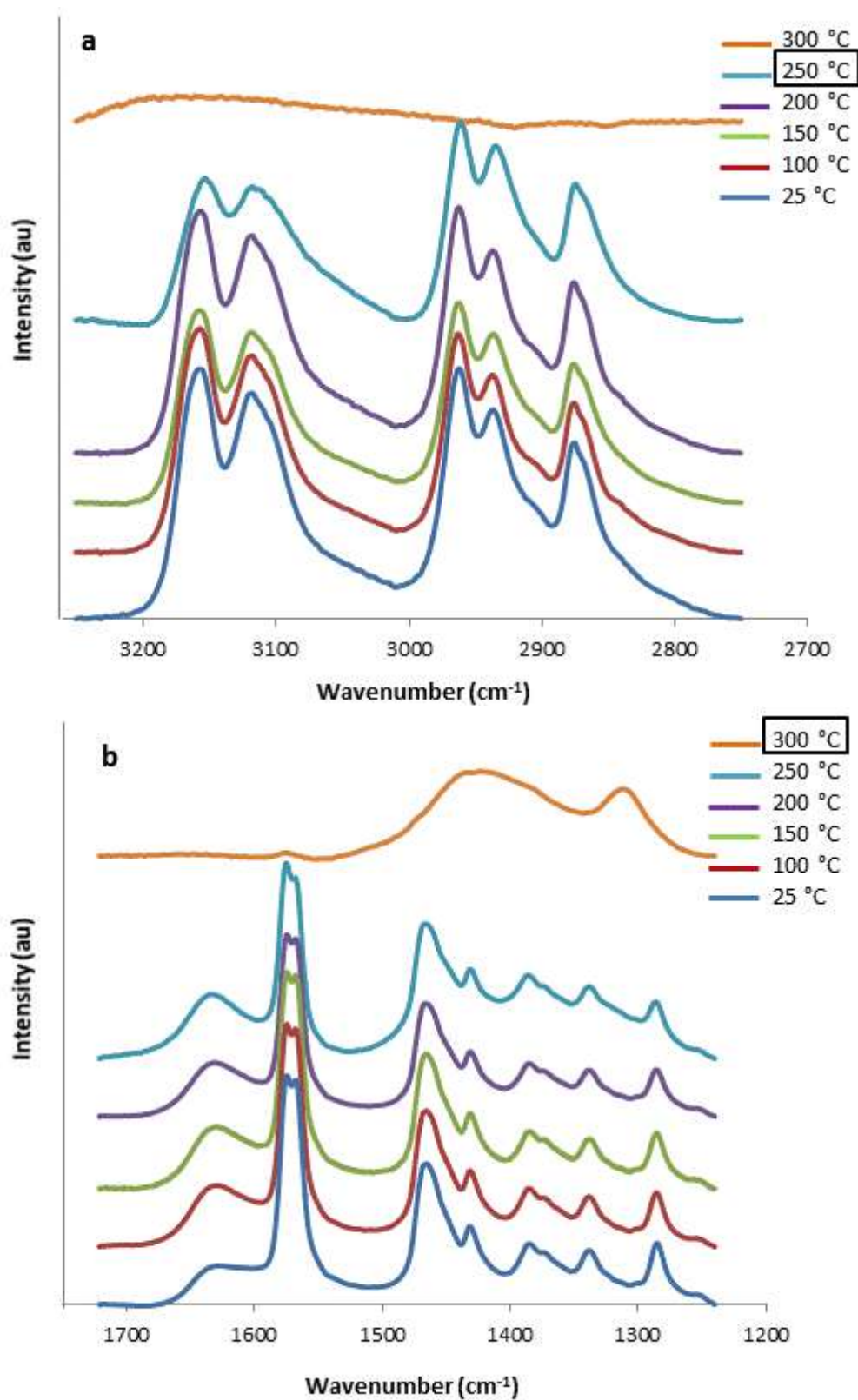


Figure A3-49. IR spectra of ZnO-supported [BMIM][BF₄] after 6 h-treatments: room temperature, 100, 150, 200, 250, and 573 K in the region of a) 2750-3250 cm⁻¹ b) 850-1750 cm⁻¹.

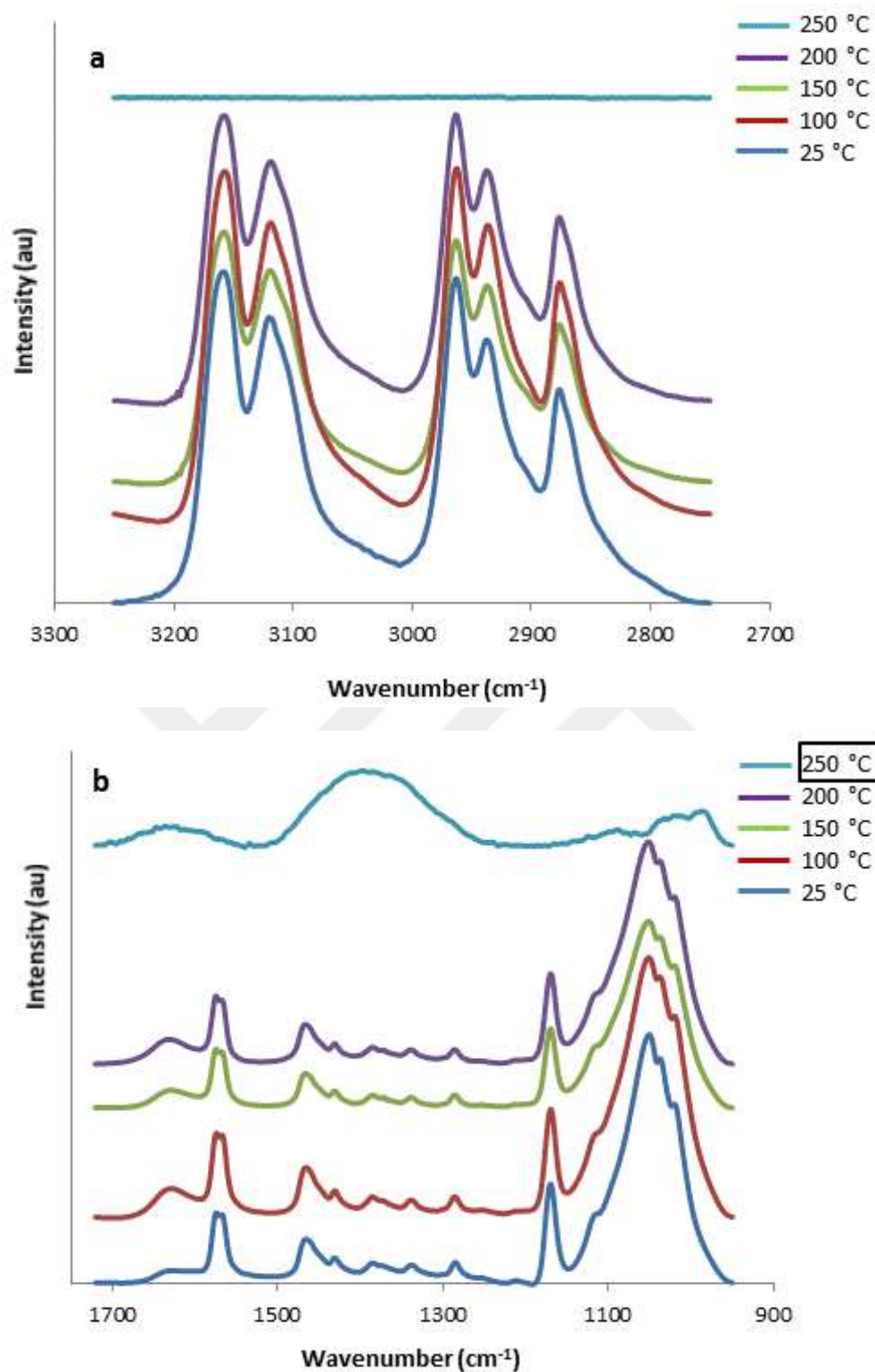


Figure A3-50. IR spectra of ZnO-supported [BMIM][BF₄] after 10 h-treatments: room temperature, 100, 150, 200, 250, and 573 K in the region of a) 2750-3250 cm⁻¹ b) 850-1750 cm⁻¹.

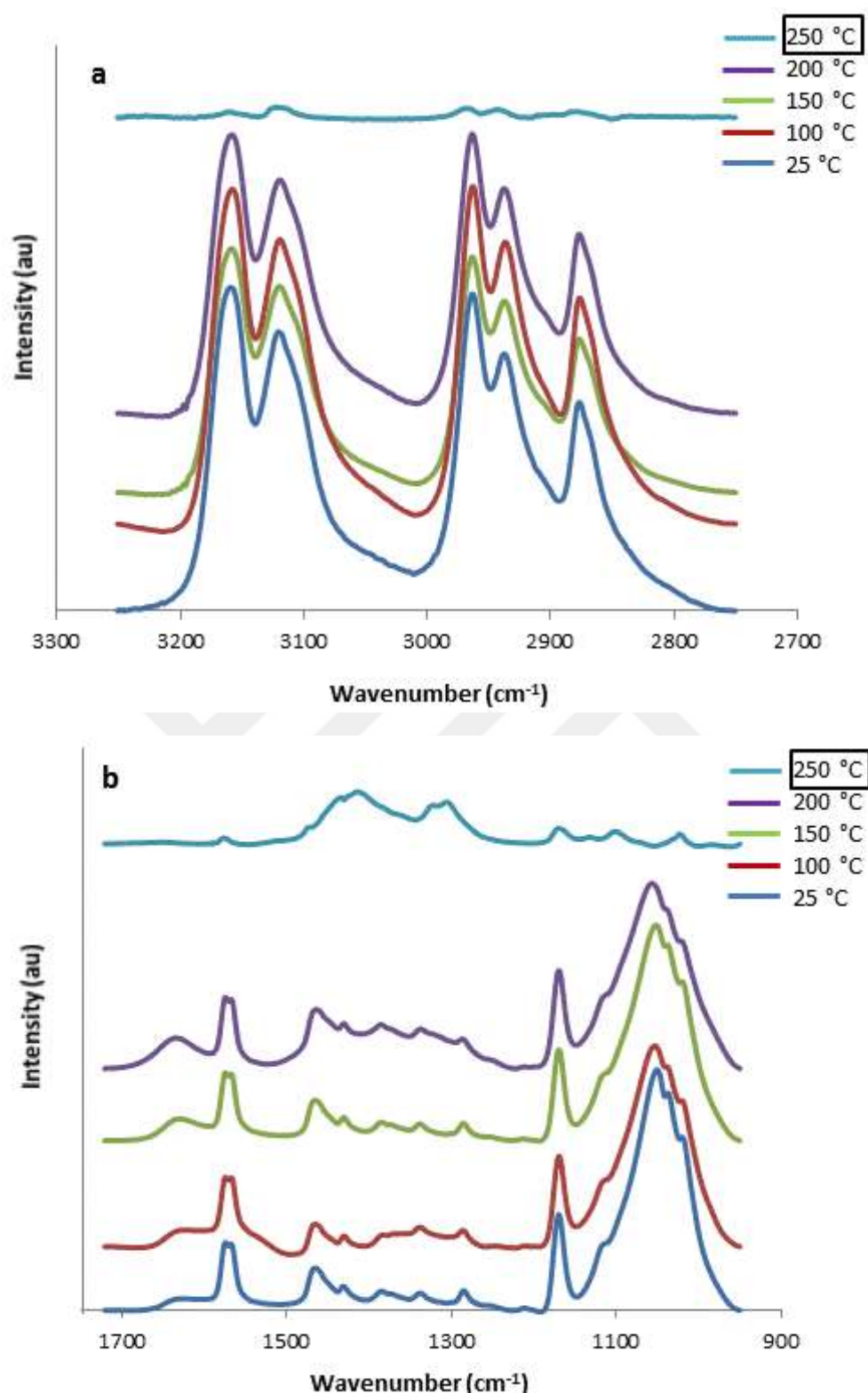


Figure A3-51. IR spectra of ZnO-supported [BMIM][BF₄] after 24 h-treatments: room temperature, 100, 150, 200, 250, and 573 K in the region of a) 2750-3250 cm⁻¹ b) 850-1750 cm⁻¹.

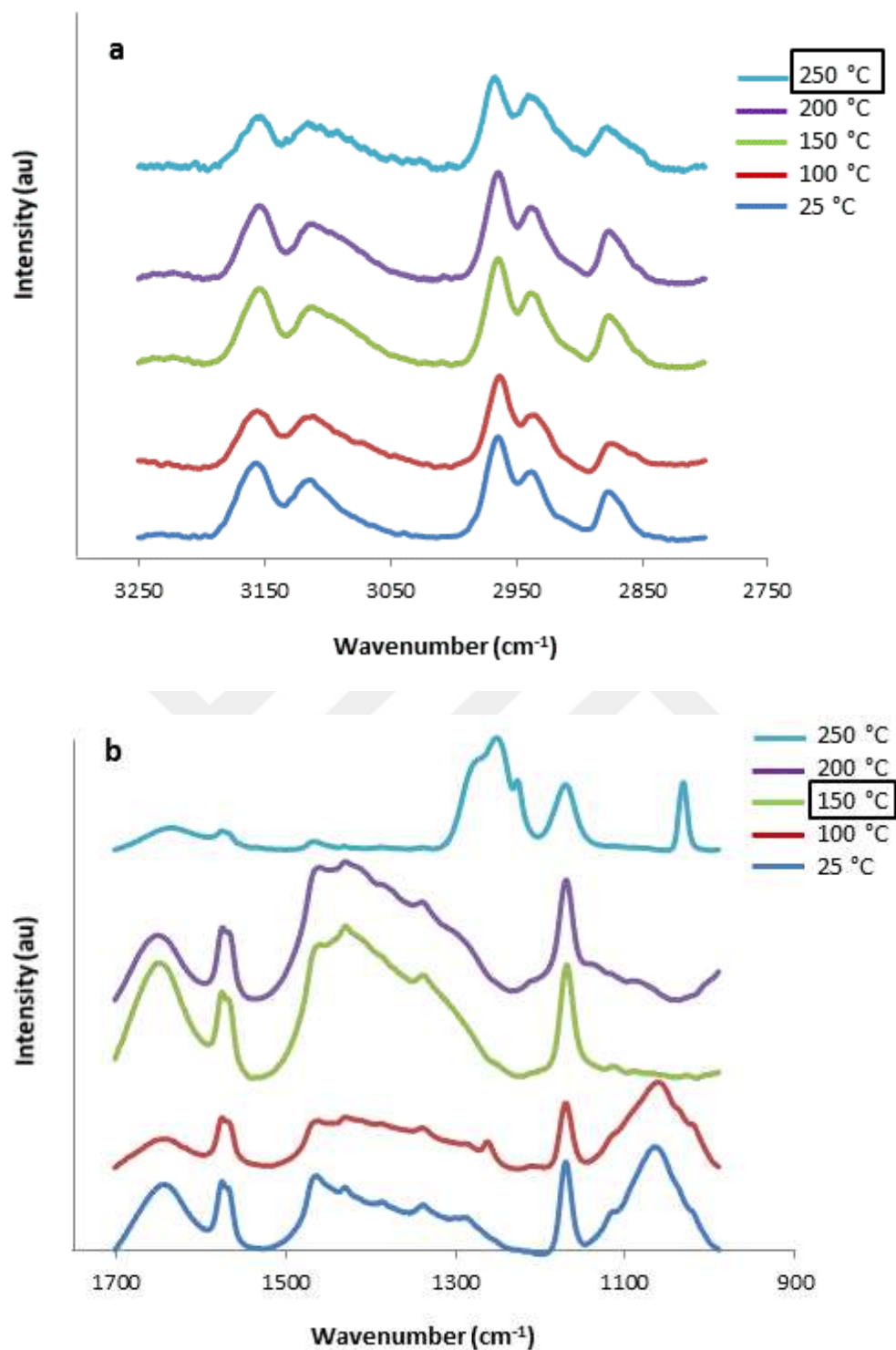


Figure A3-52. IR spectra of γ -Al₂O₃-supported [BMIM][BF₄] after 6 h-treatments: room temperature, 100, 150, 200, 250, and 573 K in the region of a) 2750-3250 cm⁻¹ b) 850-1750 cm⁻¹.

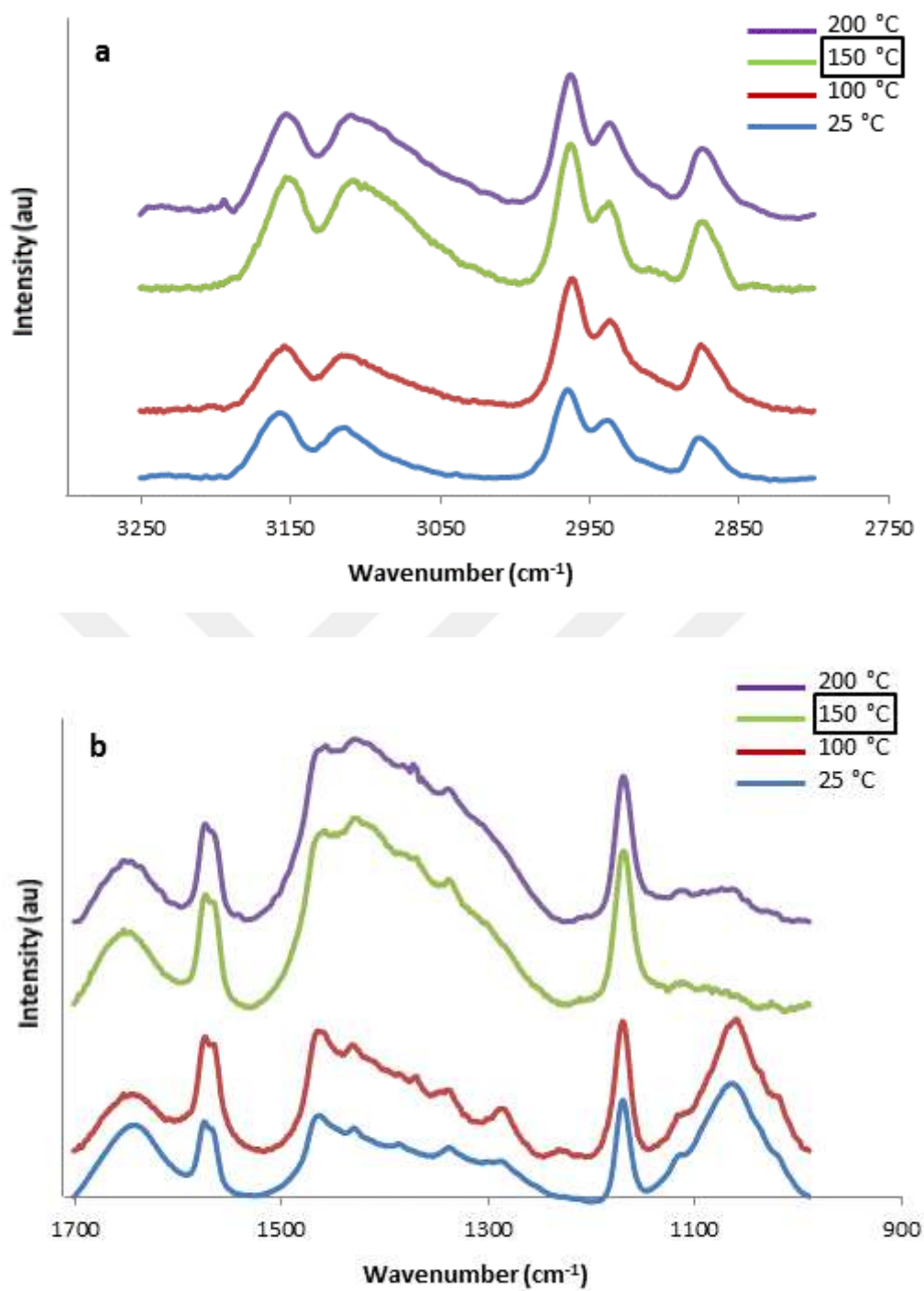


Figure A3-53. IR spectra of γ -Al₂O₃-supported [BMIM][BF₄] after 10 h-treatments: room temperature, 100, 150, 200, 250, and 573 K in the region of a) 2750-3250 cm⁻¹ b) 850-1750 cm⁻¹.

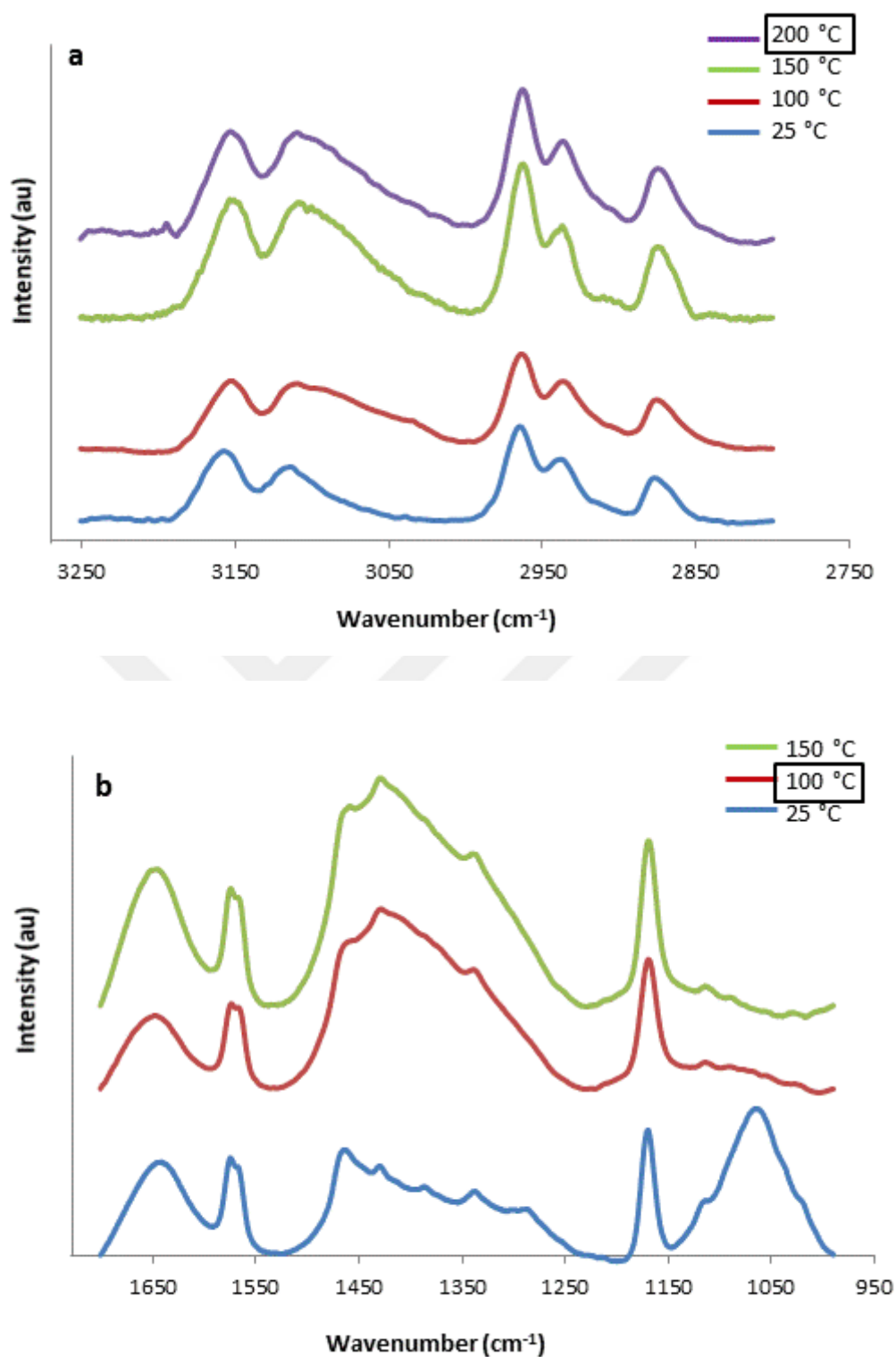


Figure A3-54. IR spectra of γ -Al₂O₃-supported [BMIM][BF₄] after 24 h-treatments: room temperature, 100, 150, 200, 250, and 573 K in the region of a) 2750-3250 cm⁻¹ b) 850-1750 cm⁻¹.

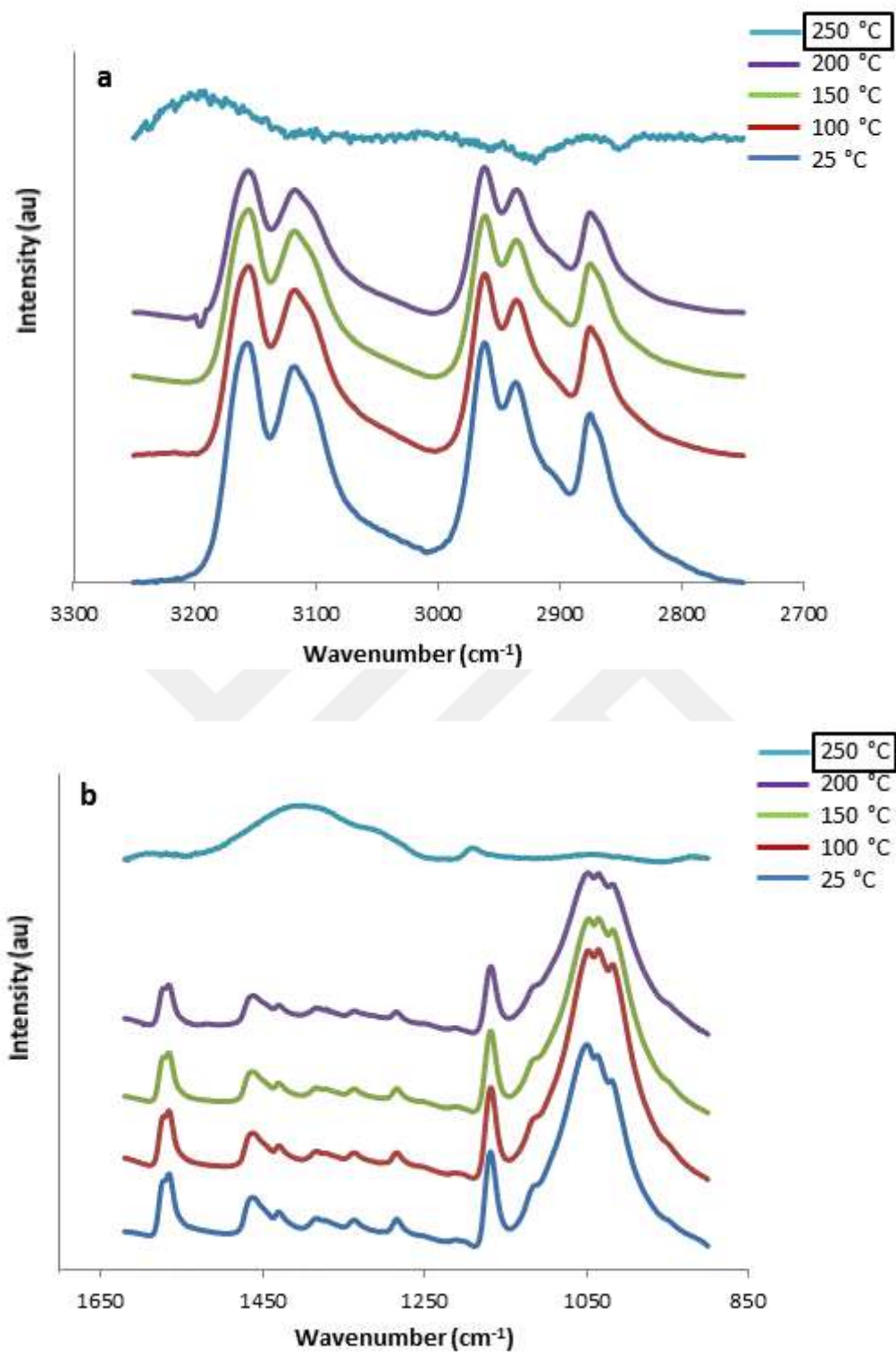


Figure A3-55. IR spectra of CeO₂-supported [BMIM][BF₄] after 10 h-treatments: room temperature, 100, 150, 200, 250, and 573 K in the region of a) 2750-3250 cm⁻¹ b) 850-1750 cm⁻¹.

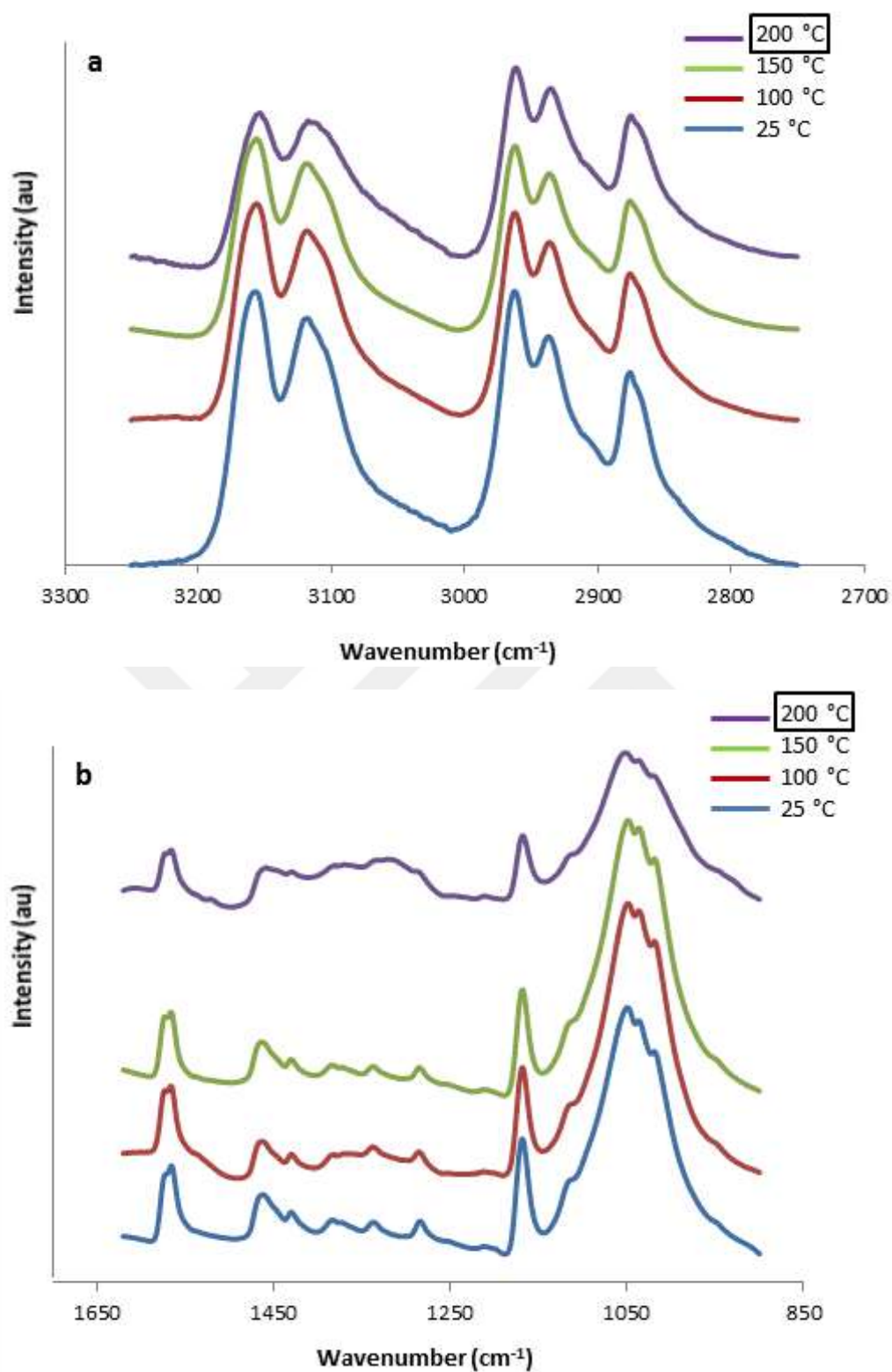


Figure A3-56. IR spectra of CeO₂-supported [BMIM][BF₄] after 24 h-treatments: room temperature, 100, 150, 200, 250, and 573 K in the region of a) 2750-3250 cm⁻¹ b) 850-1750 cm⁻¹.

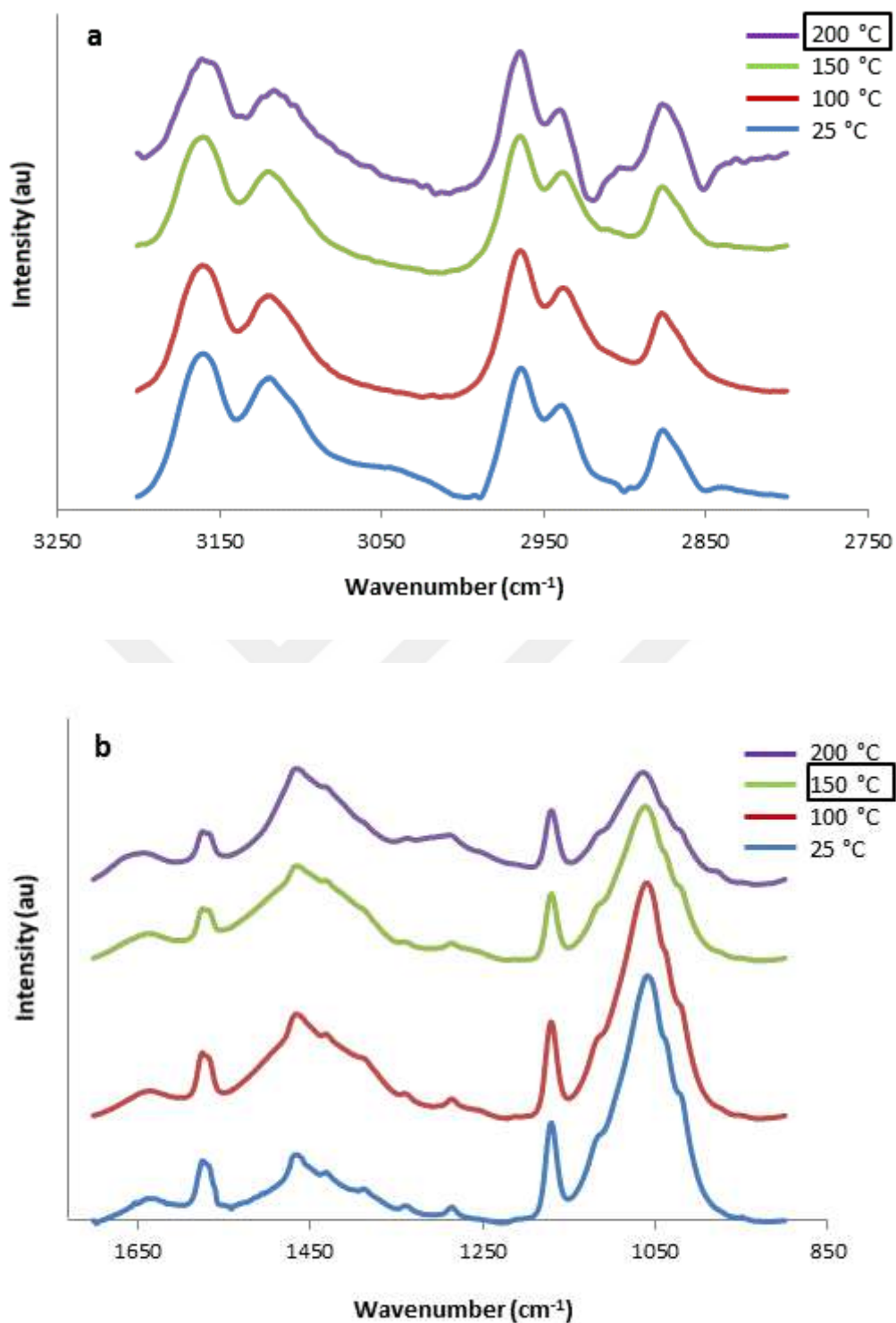


Figure A3-57. IR spectra of MgO-supported [BMIM][BF₄] after 6 h-treatments: room temperature, 100, 150, 200, 250, and 573 K in the region of a) 2750-3250 cm⁻¹ b) 850-1750 cm⁻¹.

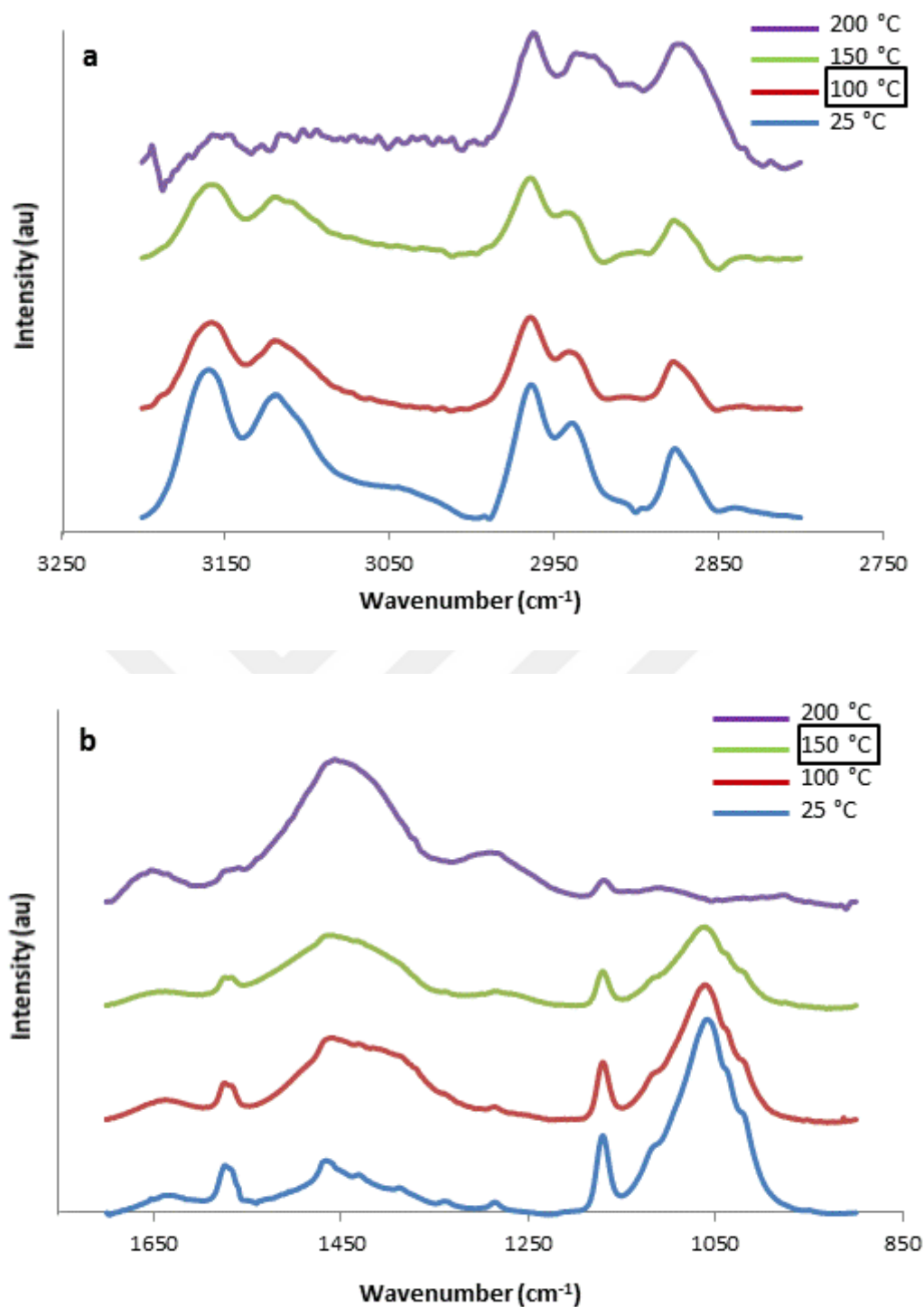


Figure A3-58. IR spectra of MgO-supported [BMIM][BF₄] after 10 h-treatments: room temperature, 100, 150, 200, 250, and 573 K in the region of a) 2750-3250 cm^{-1} b) 850-1750 cm^{-1} .

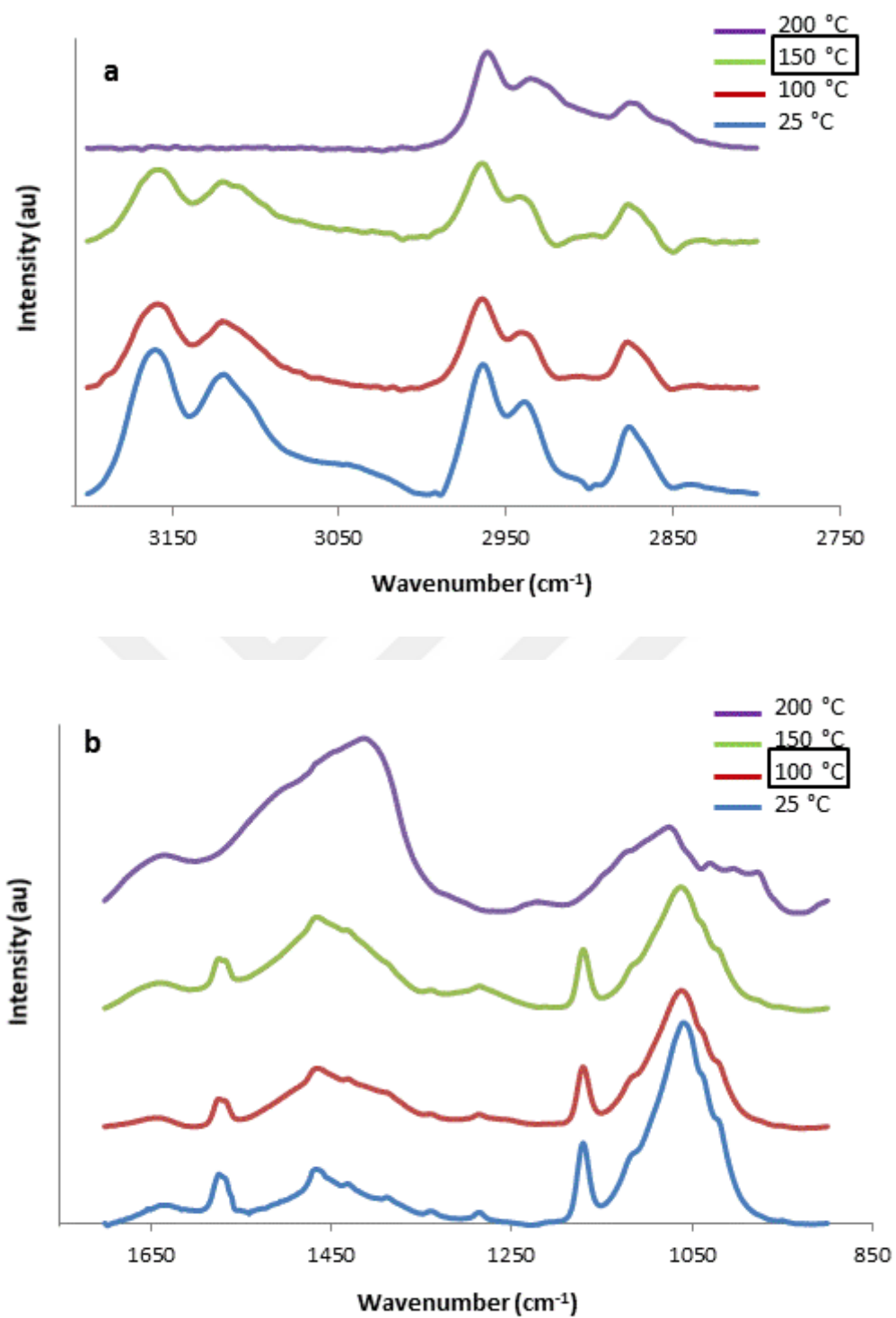


Figure A3-59. IR spectra of MgO-supported [BMIM][BF₄] after 24 h-treatments: room temperature, 100, 150, 200, 250, and 573 K in the region of a) 2750–3250 cm^{-1} b) 850–1750 cm^{-1} .

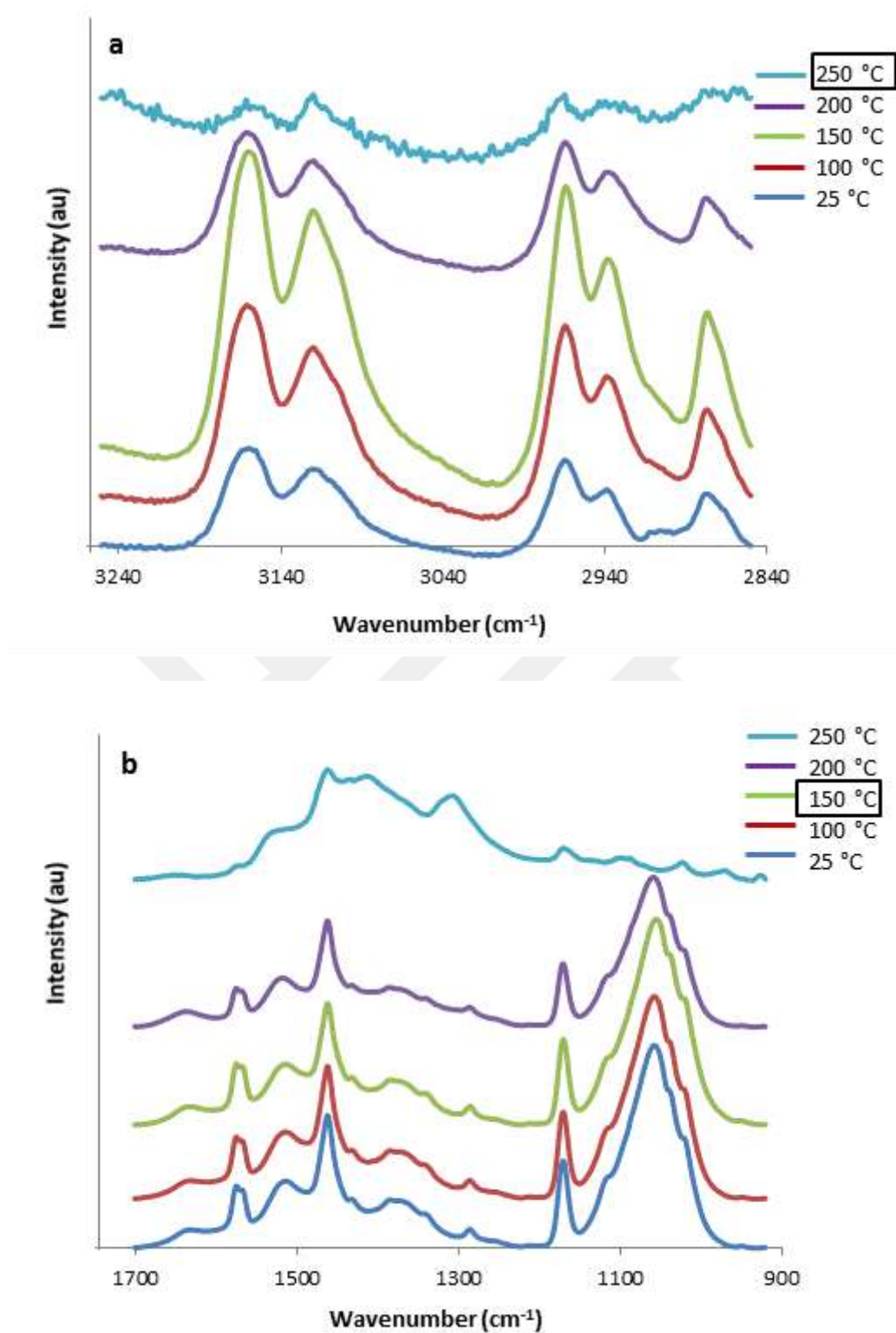


Figure A3-60. IR spectra of La_2O_3 -supported $[\text{BMIM}][\text{BF}_4]$ after 6 h-treatments: room temperature, 100, 150, 200, 250, and 573 K in the region of a) 2750-3250 cm^{-1} b) 850-1750 cm^{-1} .

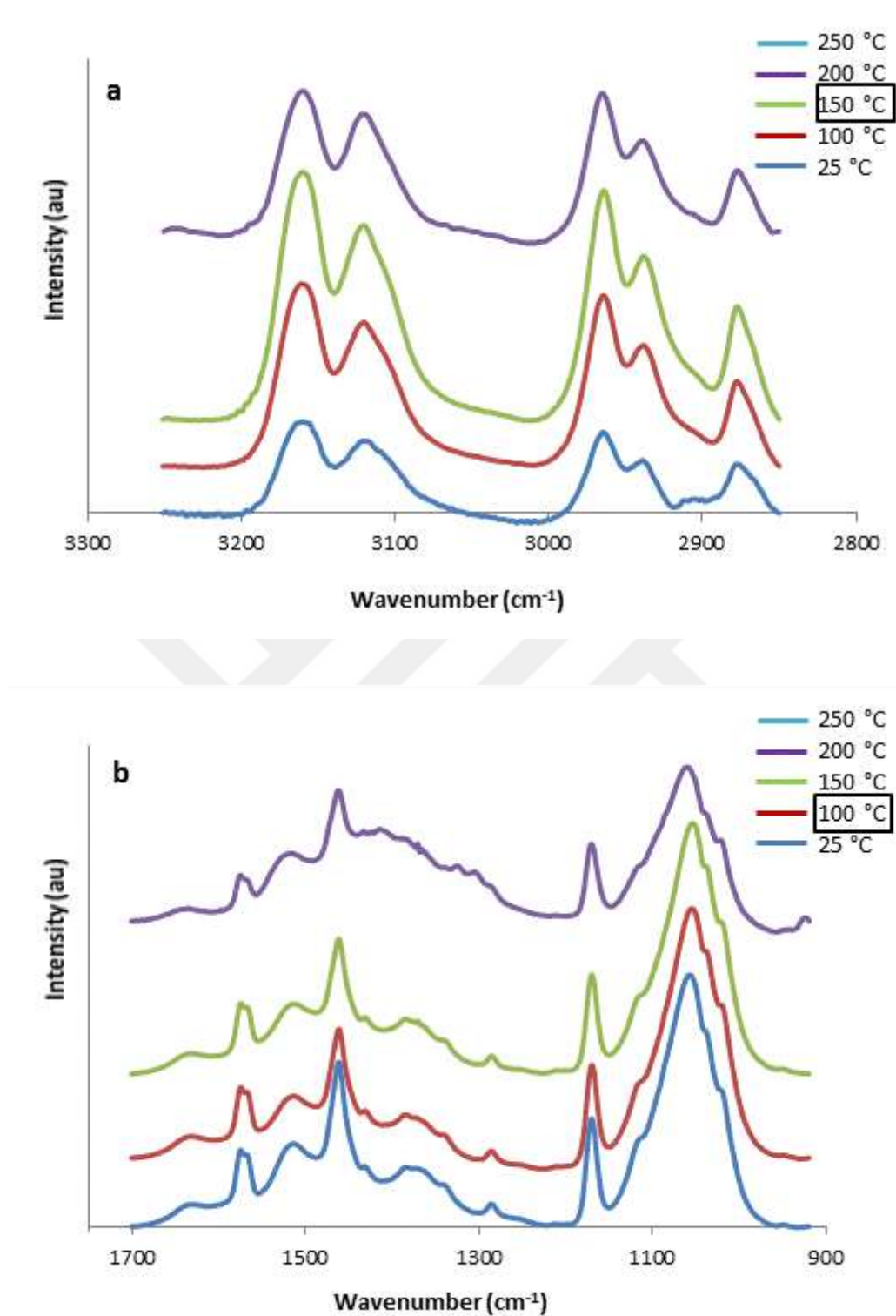


Figure A3-61. IR spectra of La_2O_3 -supported $[\text{BMIM}][\text{BF}_4]$ after 10 h-treatments: room temperature, 100, 150, 200, 250, and 573 K in the region of a) 2750-3250 cm^{-1} b) 850-1750 cm^{-1} .

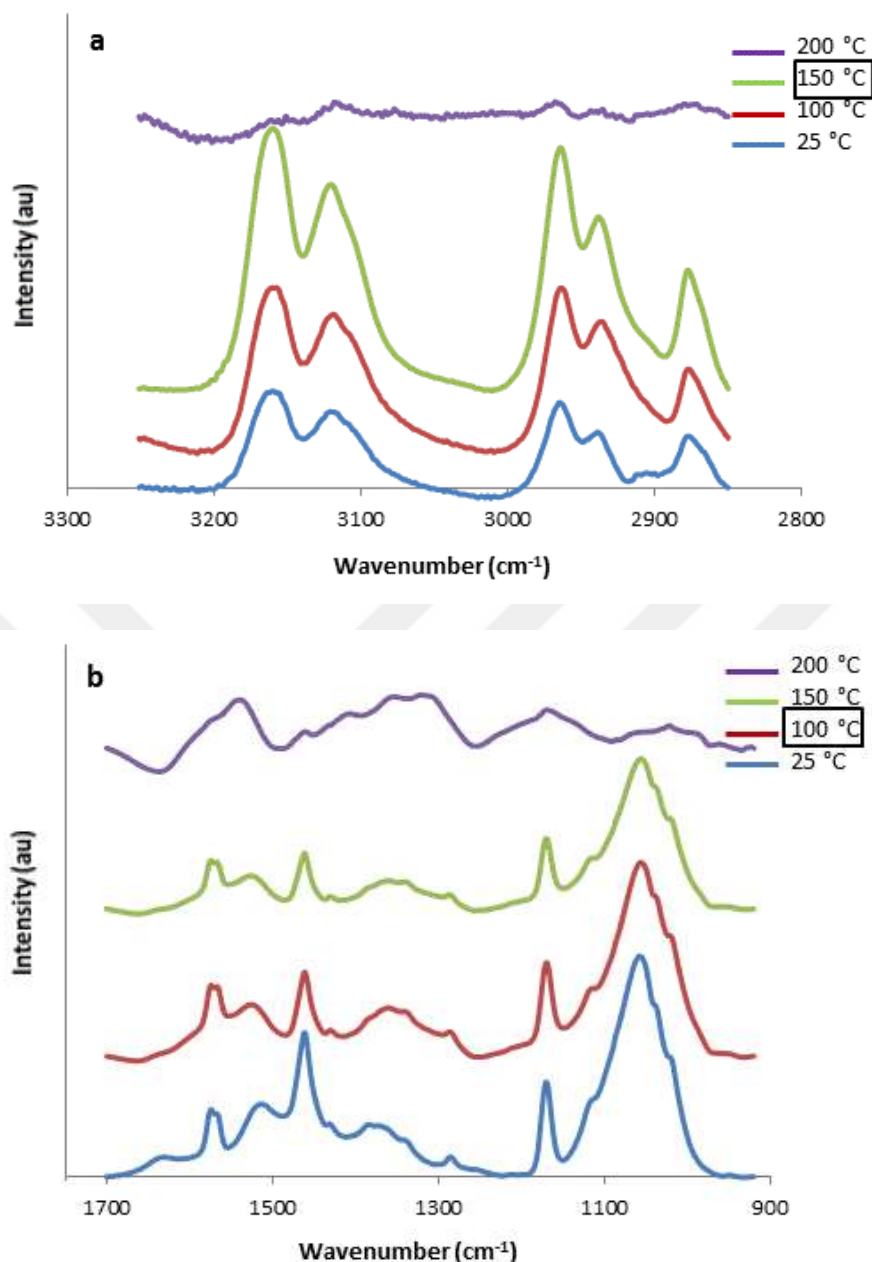


Figure A3-62. IR spectra of La₂O₃-supported [BMIM][BF₄] after 24 h-treatments: room temperature, 100, 150, 200, 250, and 573 K in region of A) 2750-3250 cm⁻¹ B) 850-1750 cm⁻¹.

A3-8. References

1. S. A. Katsyuba, E. E. Zvereva, A. Vidiš, P. J. Dyson, Application of Density Functional Theory and Vibrational Spectroscopy Toward the Rational Design of Ionic Liquids. *The Journal of Physical Chemistry A*, **2007**, 111, 352-370.
2. N. E. Heimer, et al., Vibrational spectra of imidazolium tetrafluoroborate ionic liquids. *Journal of Molecular Liquids*, **2006**, 124, 84-95.

Appendix A4

Supplementary Materials for Effects of Interionic Interactions in 1,3-Dialkylimidazolium Ionic Liquids on the Electronic Structure of Metal Sites in Solid Catalysts with Ionic Liquid Layer (SCILL)

*This chapter has been published in *Journal of Molecular Liquids* **2016**, 216, 293 by authors M. Babucci and A. Uzun. The original manuscript has been rearranged to conform to the format requirements of the dissertation.

A4-1. Fourier Transform IR (FTIR) Spectroscopy

Stretching vibrations of carbonyl groups, $\nu(\text{CO})$, of the metal oxide supported $\text{Ir}(\text{CO})_2$ complexes were utilized to probe the electronic environment on iridium centers. $\nu(\text{CO})_{\text{sym}}$ and $\nu(\text{CO})_{\text{asym}}$ of IL-coated $\text{Ir}(\text{CO})_2(\text{acac})$ on $\gamma\text{-Al}_2\text{O}_3$ are plotted.

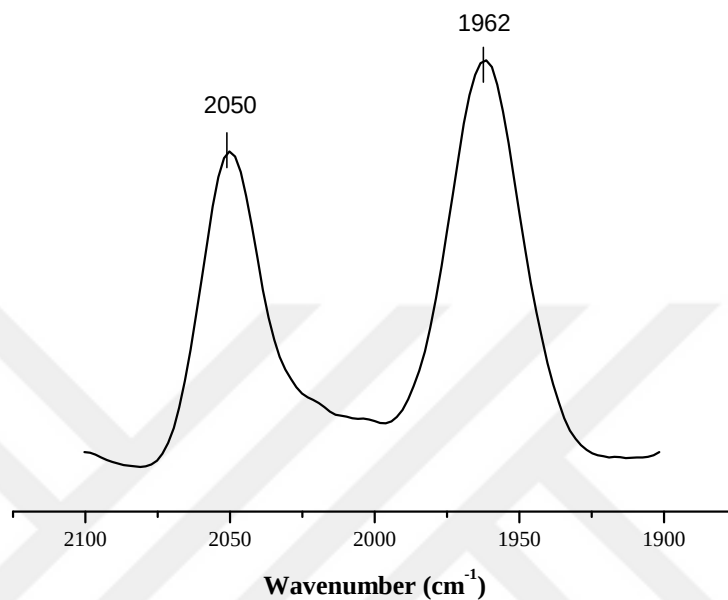


Figure A4-1. $\nu(\text{CO})$ of [EMIM][DEP] coated $\text{Ir}(\text{CO})_2/\gamma\text{-Al}_2\text{O}_3$.

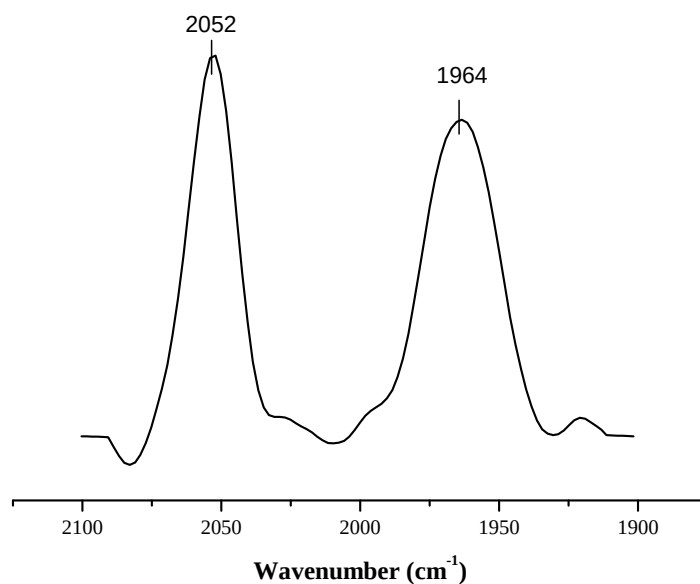


Figure A4-2. $\nu(\text{CO})$ of [EMIM][LAC] coated $\text{Ir}(\text{CO})_2/\gamma\text{-Al}_2\text{O}_3$.

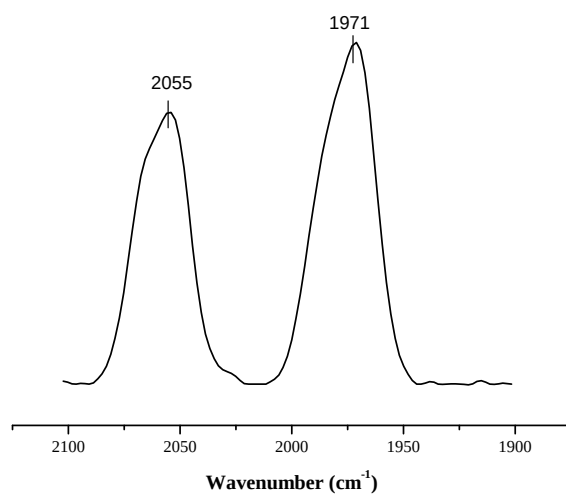


Figure A4-3. $\nu(\text{CO})$ of [EMIM][MSO₄] coated Ir(CO)₂/γ-Al₂O₃.

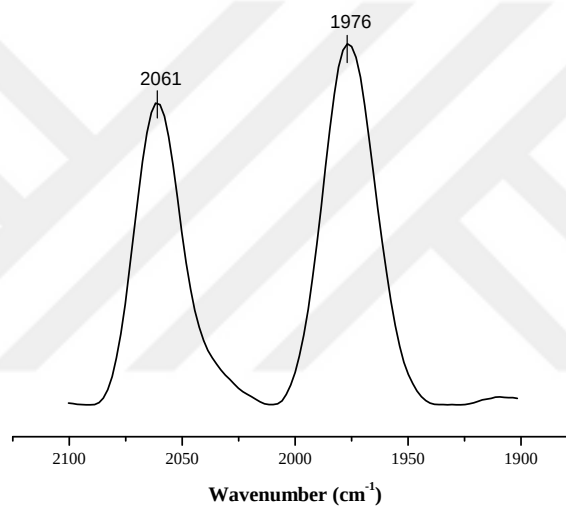


Figure A4-4. $\nu(\text{CO})$ of [EMIM][TfO] coated Ir(CO)₂/γ-Al₂O₃.

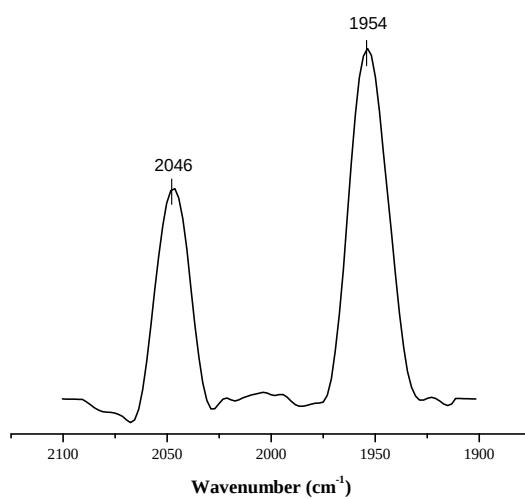


Figure A4-5. $\nu(\text{CO})$ of [BMIM][Ac] coated Ir(CO)₂/γ-Al₂O₃.

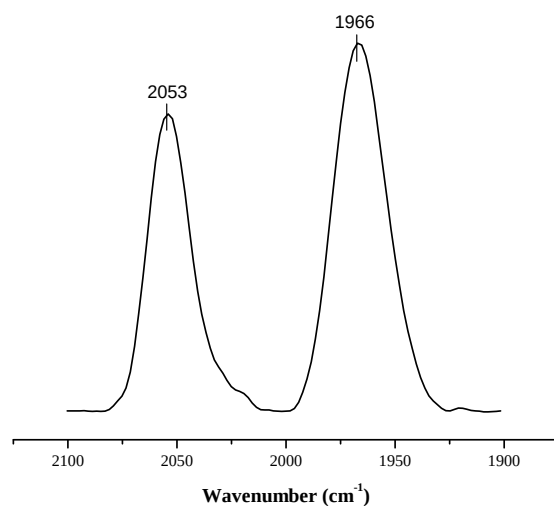


Figure A4-6. $\nu(\text{CO})$ of [BMIM][TFA] coated $\text{Ir}(\text{CO})_2/\gamma\text{-Al}_2\text{O}_3$.

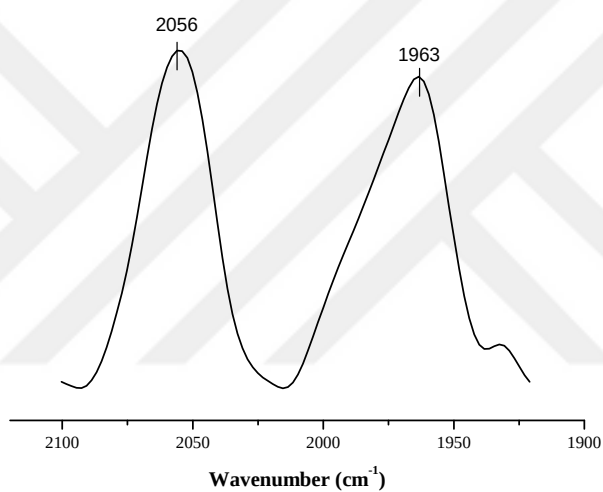


Figure A4-7. $\nu(\text{CO})$ of [BMIM][TOS] coated $\text{Ir}(\text{CO})_2/\gamma\text{-Al}_2\text{O}_3$.

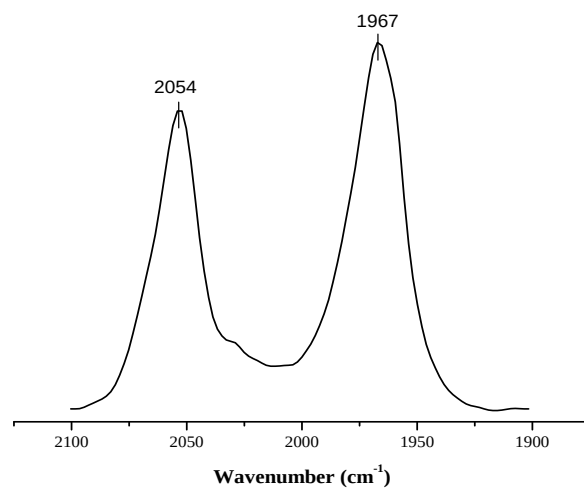


Figure A4-8. $\nu(\text{CO})$ of [BMIM][HSO₄] coated $\text{Ir}(\text{CO})_2/\gamma\text{-Al}_2\text{O}_3$.

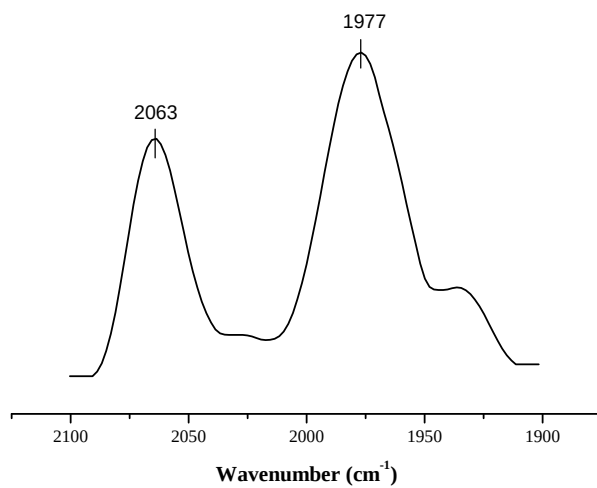


Figure A4-9. $\nu(\text{CO})$ of [BMIM][NTf₂] coated Ir(CO)₂/γ-Al₂O₃.

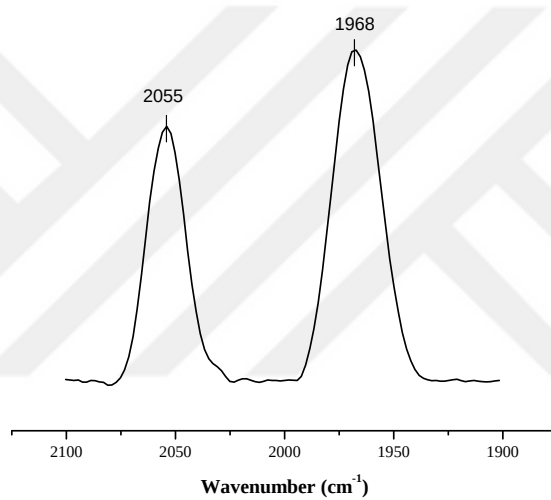


Figure A4-10. $\nu(\text{CO})$ of [BMIM][OS] coated Ir(CO)₂/γ-Al₂O₃.

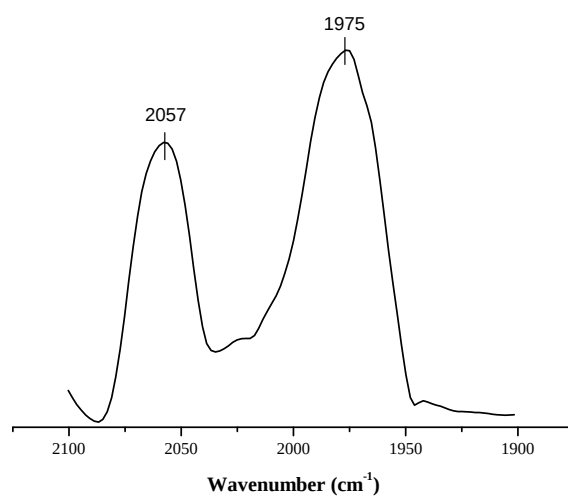


Figure A4-11. $\nu(\text{CO})$ of [DMIM][MSO₄] coated Ir(CO)₂/γ-Al₂O₃.

IL loading effect on $\nu(\text{CO})_{\text{sym}}$ of IL-coated $\text{Ir}(\text{CO})_2/\gamma\text{-Al}_2\text{O}_3$ was studied by using 20 wt.% and 40 wt.% IL loadings.

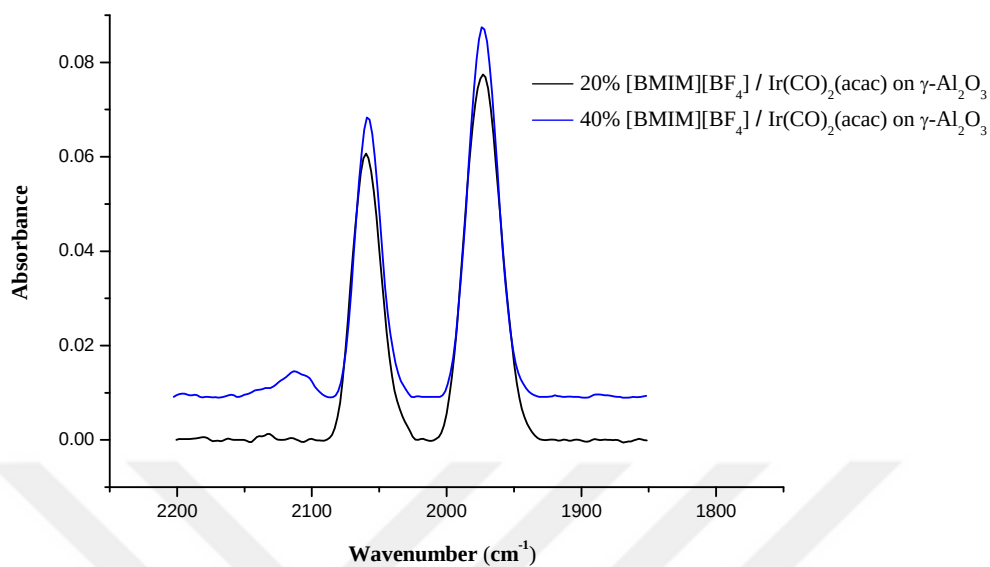


Figure A4-12. 20 wt.% [BMIM][BF₄] (black) and 40 wt.% [BMIM][BF₄] (blue) coated $\text{Ir}(\text{CO})_2/\gamma\text{-Al}_2\text{O}_3$.

The shift of antisymmetric vibrational frequency of CO with changing $\nu(\text{C2H})$ of fourteen individual ILs was plotted (Figure A4-13).

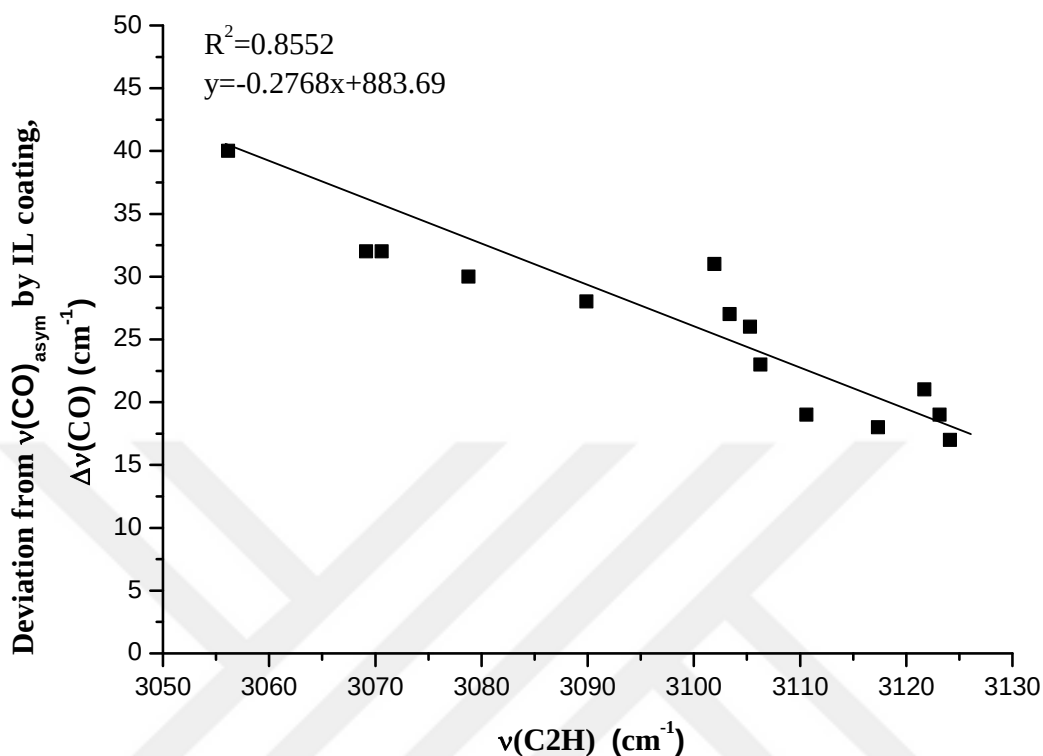


Figure A4-13. Variation of red shift amount in $\nu(\text{CO})_{\text{asym}}$ values when coated with IL as a function of $\nu(\text{C2H})$ of bulk ILs ($\nu(\text{C2H})$ values are provided in Table 1).

Approximate thickness of the IL layer on the $[\text{BMIM}][\text{BF}_4]$ coated $\text{Ir}(\text{CO})_2/\gamma\text{-Al}_2\text{O}_3$ was estimated by dividing the difference between pore volumes of uncoated ($0.44 \times 10^{-6} \text{ m}^3/\text{g}$) and IL-coated ($0.19 \times 10^{-6} \text{ m}^3/\text{g}$) $\text{Ir}(\text{CO})_2/\gamma\text{-Al}_2\text{O}_3$ samples into the surface area of uncoated sample ($190.31 \text{ m}^2/\text{g}$). Calculated thickness from BET was 1.3 nm. Expected IL-layer thickness value for $[\text{BMIM}][\text{BF}_4]$ coated $\text{Ir}(\text{CO})_2/\gamma\text{-Al}_2\text{O}_3$ was obtained by using the density of IL ($1.17 \times 10^6 \text{ g/m}^3$) and surface area of uncoated $\text{Ir}(\text{CO})_2/\gamma\text{-Al}_2\text{O}_3$, assuming a uniform IL dispersion (20 wt.% loading) over $\text{Ir}(\text{CO})_2/\gamma\text{-Al}_2\text{O}_3$. Expected IL-layer thickness was approximately 1 nm, consistent with the value from BET calculations and indicates single to a few layers of IL.

A4-2. Brunauer–Emmett–Teller (BET) Pore Volume and Surface Area Analysisa) For Ir(CO)₂ on γ -Al₂O₃,

BET Surface Area Report

BET Surface Area: 190.3008 ± 0.4988 m²/g
 Slope: 0.022636 ± 0.000059 g/cm³ STP
 Y-Intercept: 0.000239 ± 0.000011 g/cm³ STP
 C: 95.534179
 Qm: 43.7152 cm³/g STP
 Correlation Coefficient: 0.9999729
 Molecular Cross-Sectional Area: 0.1620 nm²

Relative Pressure (p/p ^o)	Quantity Adsorbed (cm ³ /g STP)	1/[Q(p ^o p - 1)]
0.049170953	38.4877	0.001344
0.076356457	41.7632	0.001979
0.102467214	44.3666	0.002573
0.133294876	47.1315	0.003263
0.160826622	49.4459	0.003876
0.189098798	51.7463	0.004507
0.216619302	53.9501	0.005125
0.244549099	56.1889	0.005761
0.273163030	58.5195	0.006422
0.300744008	60.8107	0.007073

b) For 20 wt.% [BMIM][BF₄]-coated Ir(CO)₂ on γ -Al₂O₃,

BET Surface Area Report

BET Surface Area: 69.9860 ± 0.2315 m²/g
 Slope: 0.060749 ± 0.000202 g/cm³ STP
 Y-Intercept: 0.001452 ± 0.000039 g/cm³ STP
 C: 42.842070
 Qm: 16.0769 cm³/g STP
 Correlation Coefficient: 0.9999558
 Molecular Cross-Sectional Area: 0.1620 nm²

Relative Pressure (p/p ^o)	Quantity Adsorbed (cm ³ /g STP)	1/[Q(p ^o p - 1)]
0.049830604	11.8899	0.004411
0.077911738	13.5582	0.006232
0.104389346	14.8418	0.007853
0.133220264	16.0475	0.009578
0.161436132	17.1030	0.011256
0.188729402	18.0609	0.012881
0.216975193	18.9870	0.014594
0.244719033	19.9123	0.016272
0.272083314	20.8014	0.017969
0.299723593	21.6993	0.019724

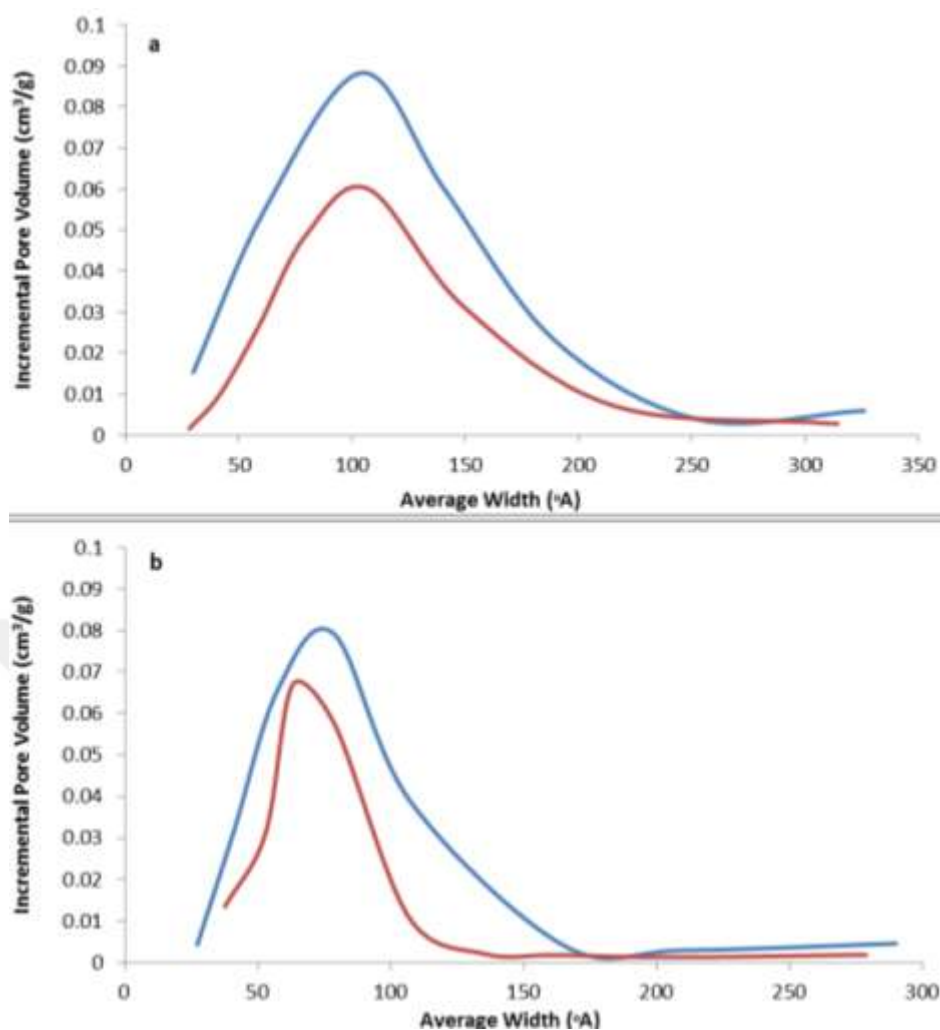


Figure A4-14. A) Adsorption B) desorption pore size distribution of uncoated Ir(CO)₂/γ-Al₂O₃ (blue) and [BMIM][BF₄]-coated Ir(CO)₂/γ-Al₂O₃ (red).

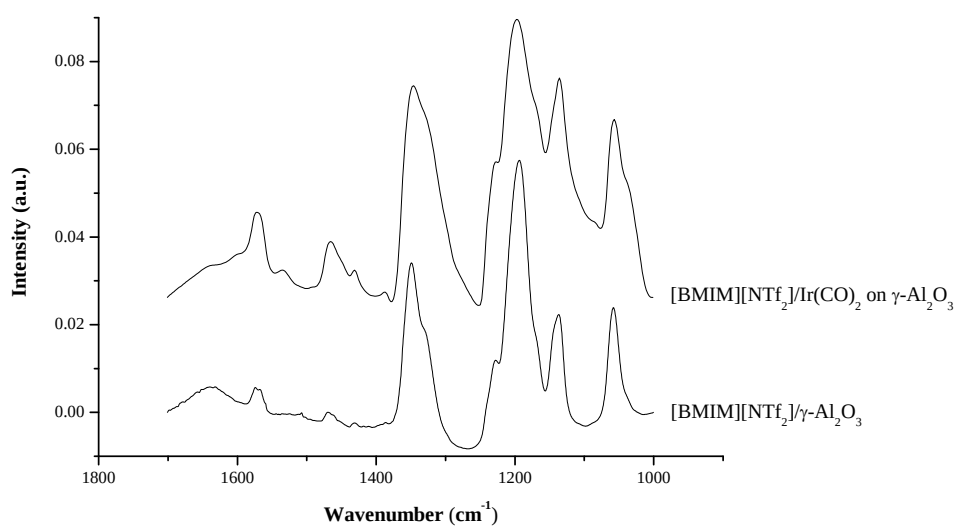


Figure A4-15. IR spectra of [BMIM][NTf₂]/γ-Al₂O₃ and [BMIM][NTf₂]-coated Ir(CO)₂/γ-Al₂O₃ in the region of 1000-1800 cm⁻¹.

Appendix A5

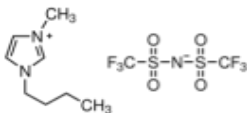
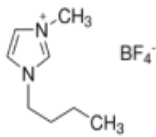
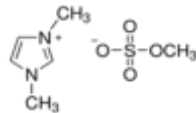
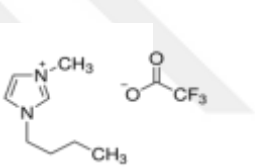
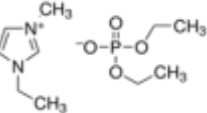
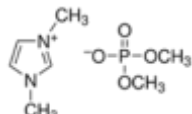
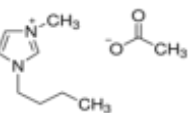
Supplementary Materials for Tuning the Selectivity of Single-Site Supported Metal Catalysts with Ionic Liquids

*This chapter has been published in *ACS Catalysis* **2017**, 2, 6969 by authors M. Babucci, C. Y. Fang, A. S. Hoffman, S. R. Bare, B. C. Gates and A. Uzun. The original manuscript has been rearranged to conform to the format requirements of the dissertation.

A5-1. Materials

A list of 1,3-dialkylimidazolium ILs used in this work is provided in Table A5-1.

Table A5-1. Names, abbreviations, and structures of the ILs.

IL Name	Abbreviation	IL Structure
1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	[BMIM][NTf ₂]	
1-Butyl-3-methylimidazolium tetrafluoroborate	[BMIM][BF ₄]	
1,3-Dimethylimidazolium methyl sulfate	[DMIM][MSO ₄]	
1-Butyl-3-methylimidazolium trifluoroacetate	[BMIM][TFA]	
1-Ethyl-3-methylimidazolium diethyl phosphate	[EMIM][DEP]	
1,3-Dimethylimidazolium dimethyl phosphate	[DMIM][DMP]	
1-Butyl-3-methylimidazolium acetate	[BMIM][Ac]	

A5-2. Fourier Transform IR (FTIR) Spectroscopy

IR spectra given in Figure A5-1A indicate that the hydroxyl groups characterized by bands at 3587 and 3693 cm^{-1} belonging to $\gamma\text{-Al}_2\text{O}_3$ were consumed during the sample synthesis. This decrease in intensity of the IR bands suggests the reaction of the precursor with these acidic hydroxyl groups. Moreover, in Figure A5-1-B, the presence of two distinct $\nu(\text{CO})$ bands, at 1994 and 2074 cm^{-1} , attributed to $\nu(\text{CO})_{\text{asym}}$ and $\nu(\text{CO})_{\text{sym}}$, respectively, in the as-prepared sample confirms the presence of iridium *gem*-dicarbonyl groups. These fingerprints were shifted from those observed in $\text{Ir}(\text{CO})_2(\text{acac})$ mixed with KBr (1987 and 2049 cm^{-1}), indicating that the supported complex is a species different from the precursor. Moreover, in the 1300-1700 cm^{-1} region, mostly showing the IR bands of acetylacetonate, the IR spectrum of the supported iridium complex (Figure A5-1C) includes bands at 1365, 1404, 1460, 1533, and 1608 cm^{-1} . These bands are assigned to $\delta_s(\text{CH}_3)$, $\nu_{\text{asm}}(\text{CO})_{\text{ring}}$, $\delta_{\text{as}}(\text{CH})$, $\nu_{\text{as}}(\text{CCC})_{\text{ring}}$, and $\nu_{\text{sym}}(\text{CO})_{\text{ring}}$, respectively, indicating the IR bands of Hacac adsorbed on $\gamma\text{-Al}_2\text{O}_3$ rather than those of the precursor (1365, 1382, and 1531 cm^{-1}).¹⁻² Thus, we conclude that leaving of the acac ligand from the precursor $\text{Ir}(\text{CO})_2(\text{acac})$ results in the chemisorption of the remaining $\text{Ir}(\text{CO})_2$ complex onto the support. Therefore, we infer that site-isolated iridium *gem*-dicarbonyl complexes were formed.

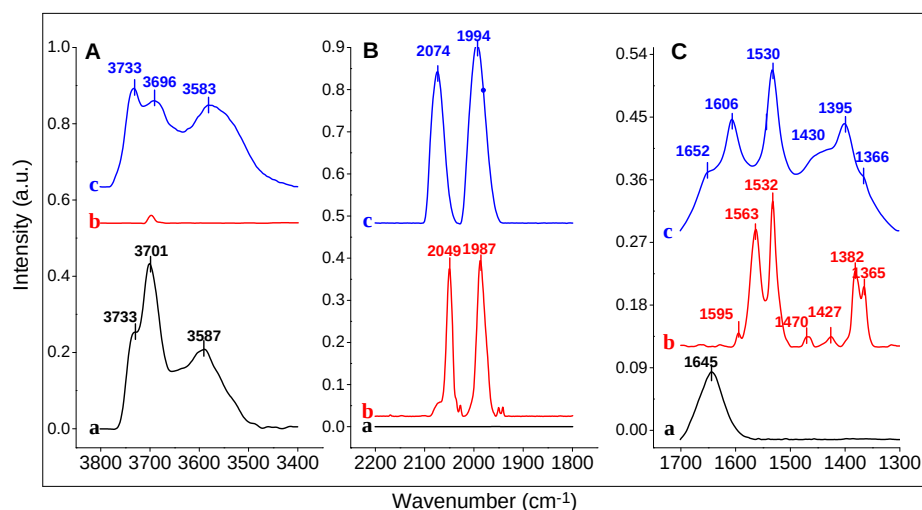


Figure A5-1. IR spectra of calcined γ -Al₂O₃ A), precursor Ir(CO)₂(acac) mixed with KBr B) catalyst C): in the region of A) 3400–3800 cm⁻¹; B) 1800–2200 cm⁻¹; C) 1300–1700 cm⁻¹.

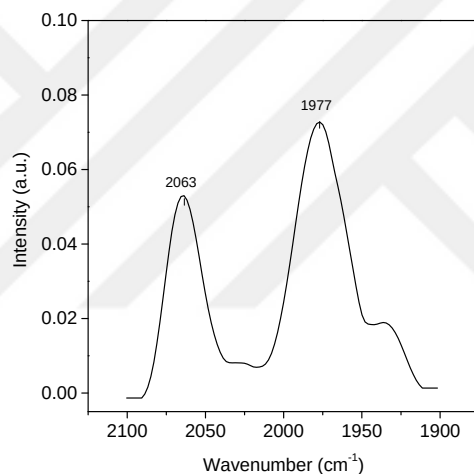


Figure A5-2. IR spectra characterizing [BMIM][NTf₂]-coated Ir(CO)₂/γ-Al₂O₃ in the region of 1900–2100 cm⁻¹.

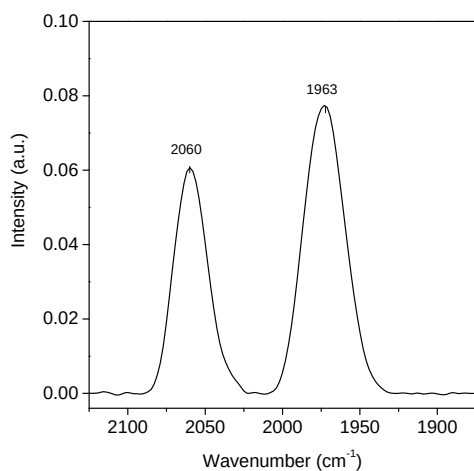


Figure A5-3. IR spectra characterizing [BMIM][BF₄]-coated Ir(CO)₂/γ-Al₂O₃ in the region of 1900–2100 cm⁻¹.

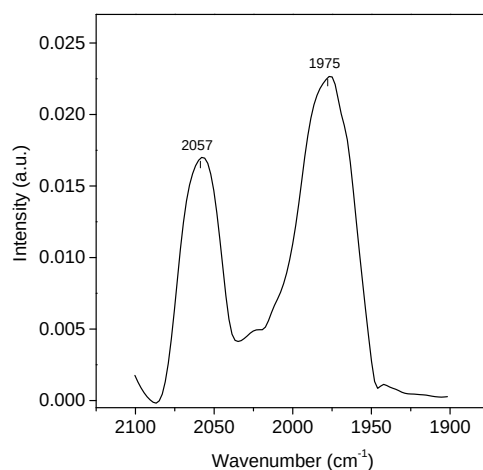


Figure A5-4. IR spectra characterizing [DMIM][MSO₄]-coated Ir(CO)₂/γ-Al₂O₃ in the region of 1900-2100 cm⁻¹.

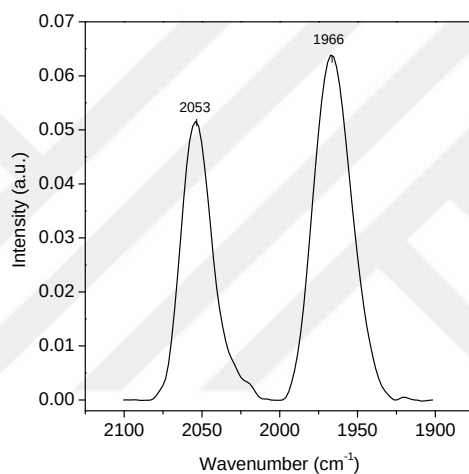


Figure A5-5. IR spectra characterizing [BMIM][TFA]-coated Ir(CO)₂/γ-Al₂O₃ in the region of 1900-2100 cm⁻¹.

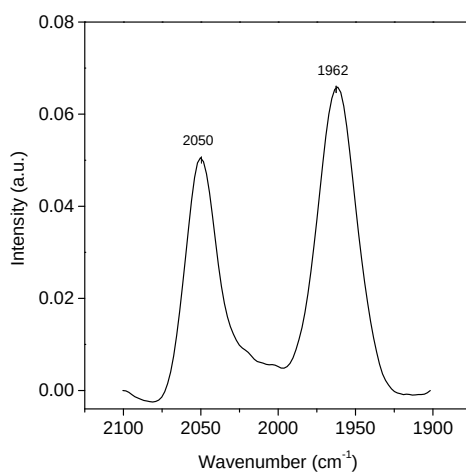


Figure A5-6. IR spectra characterizing [EMIM][DEP]-coated Ir(CO)₂/γ-Al₂O₃ in the region of 1900-2100 cm⁻¹.

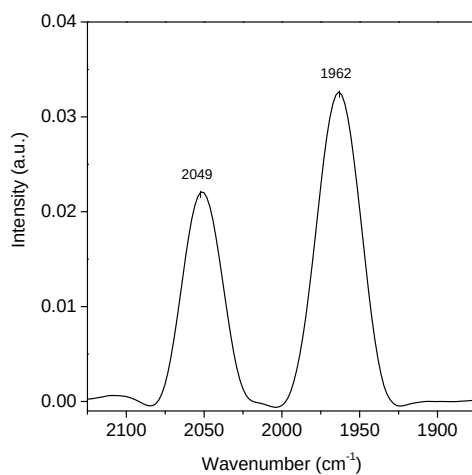


Figure A5-7. IR spectra characterizing [DMIM][DMP]-coated Ir(CO)₂/γ-Al₂O₃ in the region of 1900-2100 cm⁻¹.

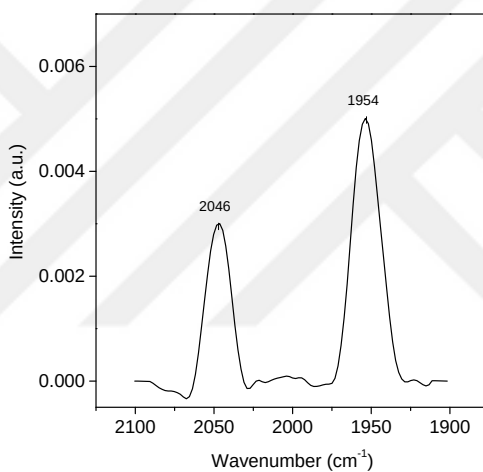


Figure A5-8. IR spectra characterizing [BMIM][Ac]-coated Ir(CO)₂/γ-Al₂O₃ in the region of 1900-2100 cm⁻¹.

A5-2-1. High-Energy Resolution Fluorescence Detection X-Ray Absorption Near Edge Structure (HERFD XANES) Measurements

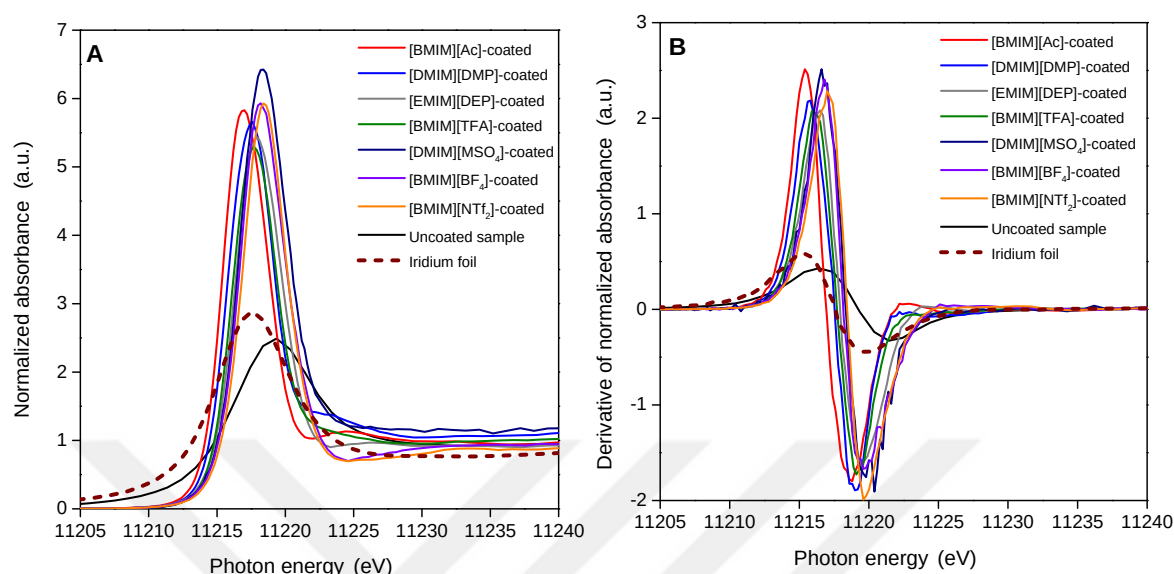


Figure A5-9. A, Normalized HERFD XANES spectra at the Ir L_{III} edge characterizing Ir(CO)₂/γ-Al₂O₃ complexes coated with various 1,3-dialkylimidazolium ILs (full names of ILs are provided in Table S1, given above). B, Derivatives of the normalized HERFD XANES spectra showing the edge energy positions. For comparison, the spectrum of iridium foil (measured in transmission mode) is provided (dashed brown line).

Table A5-2. $\nu(\text{C2H})$ of individual ILs; $\nu(\text{CO})$ bands and edge energy on uncoated and coated Ir(CO)₂/γ-Al₂O₃ complexes.

IL-coated supported Ir(CO) ₂ complexes	$\nu(\text{C2H})$ (cm ⁻¹)	$\nu(\text{CO})_{\text{sym}}$ (cm ⁻¹)	$\nu(\text{CO})_{\text{asym}}$ (cm ⁻¹)	Edge Energy (eV)
Uncoated sample	-	2074	1994	11217.9
[BMIM][NTf ₂]	3124	2063	1977	11217.0
[BMIM][BF ₄]	3122	2060	1973	11216.8
[DMIM][MSO ₄]	3111	2057	1975	11216.6
[BMIM][TFA]	3090	2053	1966	11216.0
[EMIM][DEP]	3071	2050	1962	11216.1
[DMIM][DMP]	3069	2049	1962	11215.8
[BMIM][Ac]	3056	2046	1954	11215.4

A5-3. Catalyst Performance Measurements

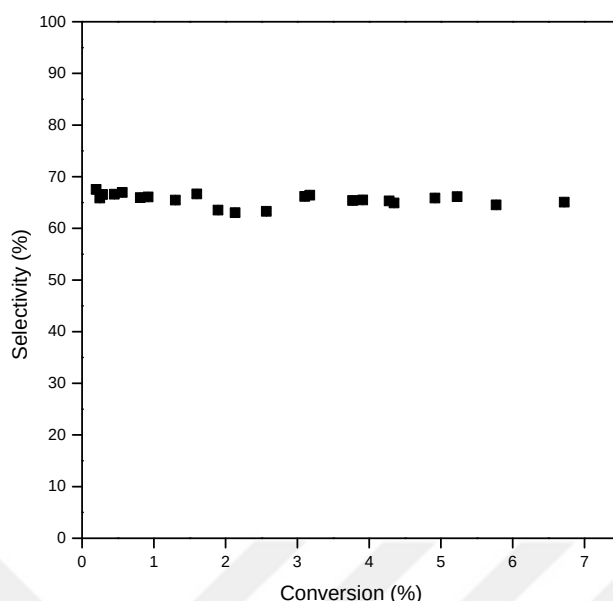


Figure A5-10. Change in total butene selectivity with BD conversion on a representative catalyst, [EMIM][DEP]-coated $\text{Ir}(\text{CO})_2/\gamma\text{-Al}_2\text{O}_3$.

A5-3-1. Characterization of Samples Before and After 1,3-Butadiene Hydrogenation

When $\gamma\text{-Al}_2\text{O}_3$ -supported iridium dicarbonyl was exposed to flowing ethene (50 vol% in balance He) at 373 K, changes in IR spectra were observed. In 1900-2100 cm^{-1} region, the intensity of $\nu_{\text{asym}}(\text{CO})$ at 1994 cm^{-1} decreased slightly with appearance of two new bands at 2027 and 2047 cm^{-1} . These new bands are assigned to $\text{Ir}(\text{CO})(\text{C}_2\text{H}_4)$ and $\text{Ir}(\text{CO})(\text{C}_2\text{H}_4)_2$, respectively.²⁻³ IR spectra given in Figure A5-9 show changes after BD hydrogenation as well. In the region of 500-1750 cm^{-1} of uncoated species, the peak at 937 cm^{-1} disappeared with the appearance of four new bands, at 1040, 1121, 1223, and 1258 cm^{-1} , assigned to BD and methyl groups physisorbed on iridium. Moreover in the 2800-3800 cm^{-1} region, the band at 3583 cm^{-1} assigned to acidic hydroxyl groups vanished. Instead, the presence of the bands at 2855, 2927, and 2955 cm^{-1} confirm the adsorption of butane $\nu(\text{CH}_2)$, 1-B or T2B/C2B ($\nu_{\text{asym}}(\text{CH}_2)$) and isobutylene or methyl, respectively.⁴

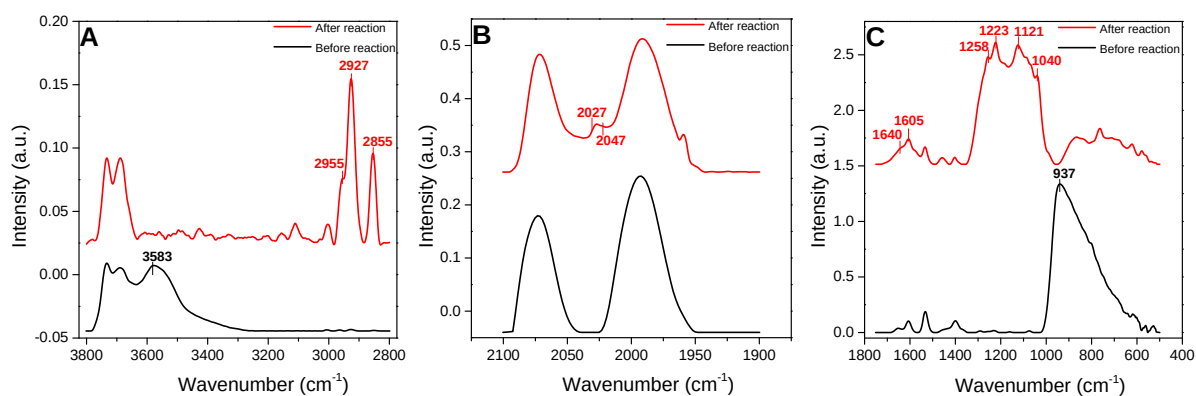


Figure A5-11. IR spectra of uncoated $\text{Ir(CO)}_2/\gamma\text{-Al}_2\text{O}_3$ before (black) and after (red) 1,3-butadiene hydrogenation in the region of A) 2800–3800 cm^{-1} ; B) 1900–2100 cm^{-1} ; C) 500–1750 cm^{-1} .

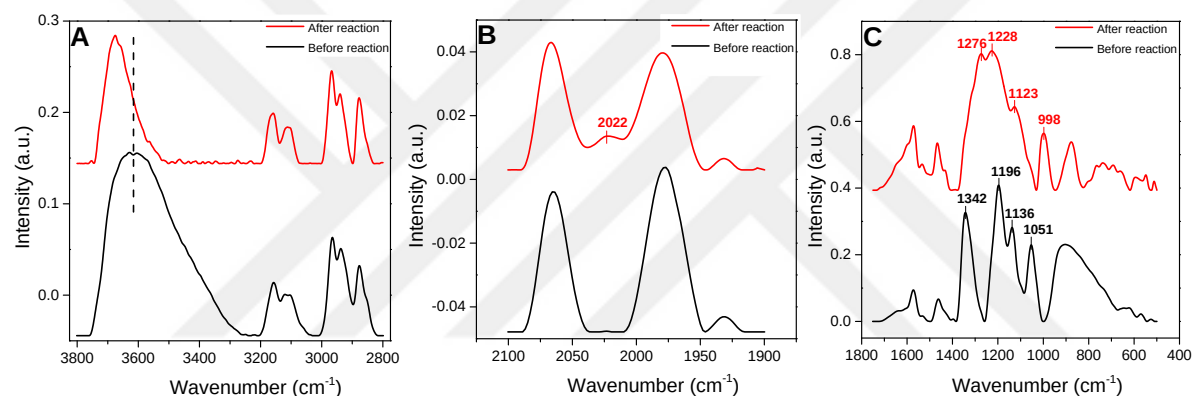


Figure A5-12. IR spectra of [BMIM][NTf₂]-coated $\text{Ir(CO)}_2/\gamma\text{-Al}_2\text{O}_3$ before (black) and after (red) 1,3-butadiene hydrogenation in the region of A) 2800–3800 cm^{-1} ; B) 1900–2100 cm^{-1} ; C) 500–1750 cm^{-1} .

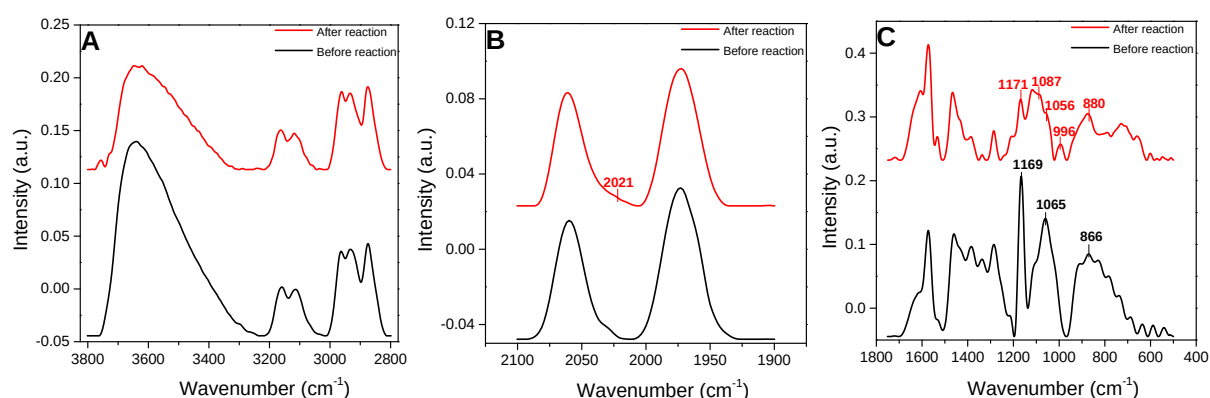


Figure A5-13. IR spectra of [BMIM][BF₄]-coated $\text{Ir(CO)}_2/\gamma\text{-Al}_2\text{O}_3$ before (black) and after (red) 1,3-butadiene hydrogenation in the region of A) 2800–3800 cm^{-1} ; B) 1900–2100 cm^{-1} ; C) 500–1750 cm^{-1} .

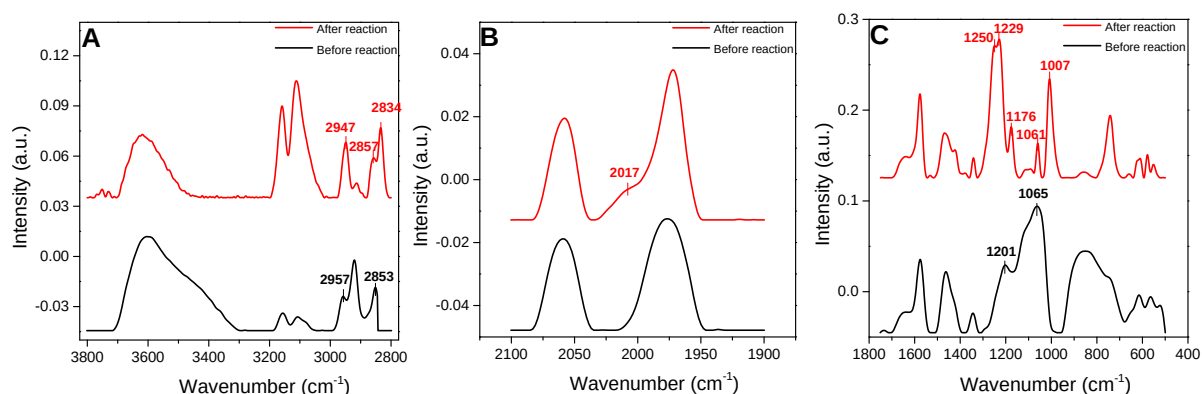


Figure A5-14. IR spectra of [DMIM][MSO₄]-coated Ir(CO)₂/γ-Al₂O₃ before (black) and after (red) 1,3-butadiene hydrogenation in the region of A) 2800–3800 cm⁻¹; B) 1900–2100 cm⁻¹; C) 500–1750 cm⁻¹.

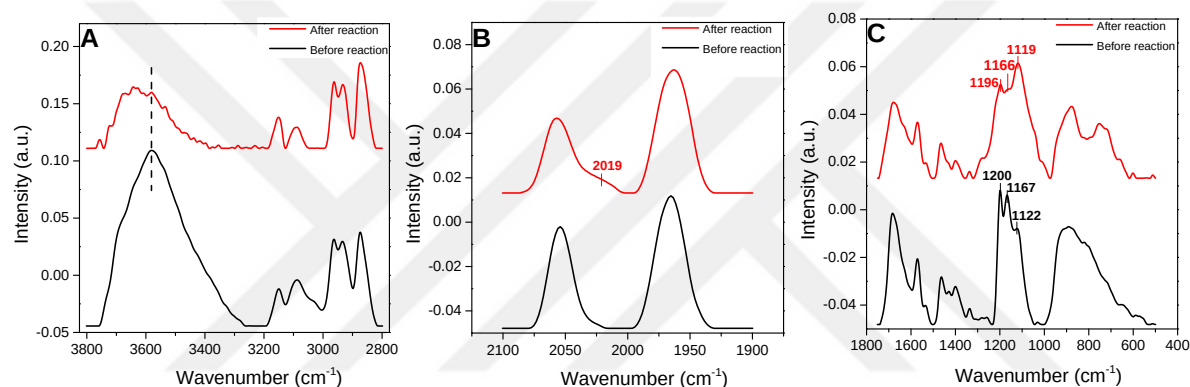


Figure A5-15. IR spectra of [BMIM][TFA]-coated Ir(CO)₂/γ-Al₂O₃ before (black) and after (red) 1,3-butadiene hydrogenation in the region of A) 2800–3800 cm⁻¹; B) 1900–2100 cm⁻¹; C) 500–1750 cm⁻¹.

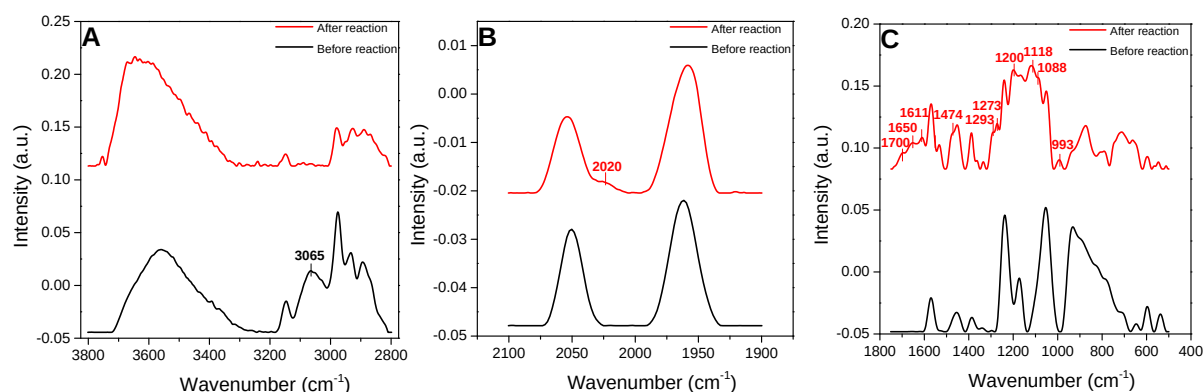


Figure A5-16. IR spectra of [EMIM][DEP]-coated Ir(CO)₂/γ-Al₂O₃ before (black) and after (red) 1,3-butadiene hydrogenation in the region of A) 2800–3800 cm⁻¹; B) 1900–2100 cm⁻¹; C) 500–1750 cm⁻¹.

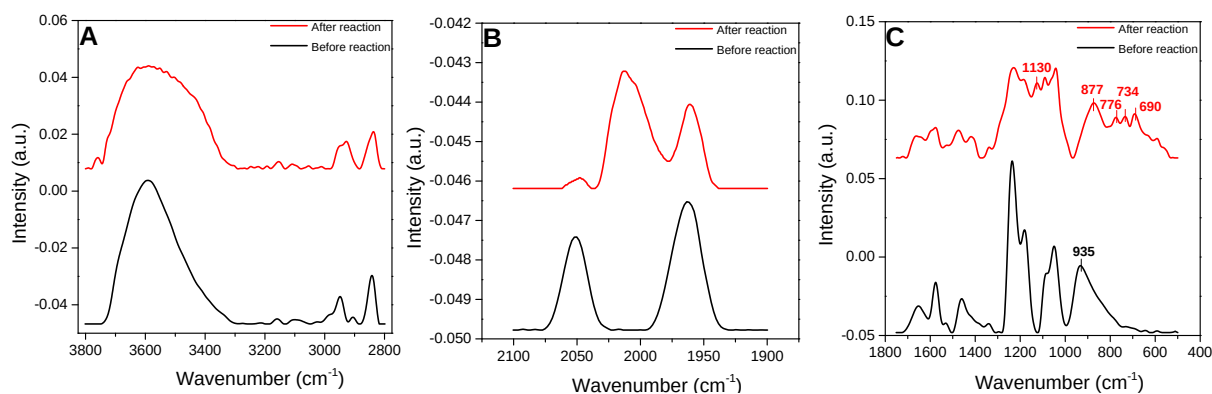


Figure A5-17. IR spectra of [DMIM][DMP]-coated $\text{Ir(CO)}_2/\gamma\text{-Al}_2\text{O}_3$ before (black) and after (red) 1,3-butadiene hydrogenation in the region of A) 2800–3800 cm^{-1} ; B) 1900–2100 cm^{-1} ; C) 500–1750 cm^{-1} .

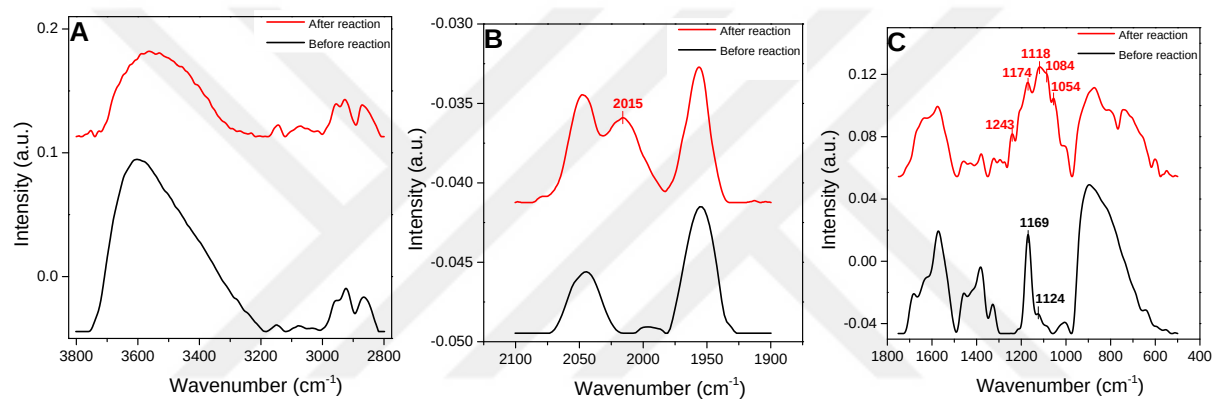


Figure A5-18. IR spectra of [BMIM][Ac]-coated $\text{Ir(CO)}_2/\gamma\text{-Al}_2\text{O}_3$ before (black) and after (red) 1,3-butadiene hydrogenation in the region of A) 2800–3800 cm^{-1} ; B) 1900–2100 cm^{-1} ; C) 500–1750 cm^{-1} .

Table A5-3. Selectivities and TOF values for partial hydrogenation of BD at 333 K and 1 bar (BD:H₂ = 1:2, molar) on uncoated and IL-coated ethene-treated Ir(CO)₂ complexes supported on γ -Al₂O₃.

IL-coated supported Ir(CO) ₂ complexes	Selectivity for hydrogenation of 1,3-butadiene at 333 K (%)					TOF (s ⁻¹)	Conversion (%)
	B	T2B	1B	C2B	Total butenes		
Uncoated sample	49	15	24	13	51	0.00838	1.42
[BMIM][NTf ₂]	39	18	32	11	61	0.00436	1.26
[BMIM][BF ₄]	38	17	31	14	62	0.00126	0.82
[DMIM][MSO ₄]	35	20	29	16	65	0.00129	0.95
[BMIM][TFA]	36	20	28	17	64	0.00085	0.91
[EMIM][DEP]	34	20	34	13	66	0.00145	0.78
[DMIM][DMP]	27	19	44	10	73	0.00213	1.02
[BMIM][Ac]	22	22	42	14	78	0.00121	0.86

A5-4. Conductor-Like Screening Model for Realistic Solvents (COSMO-RS) Calculations

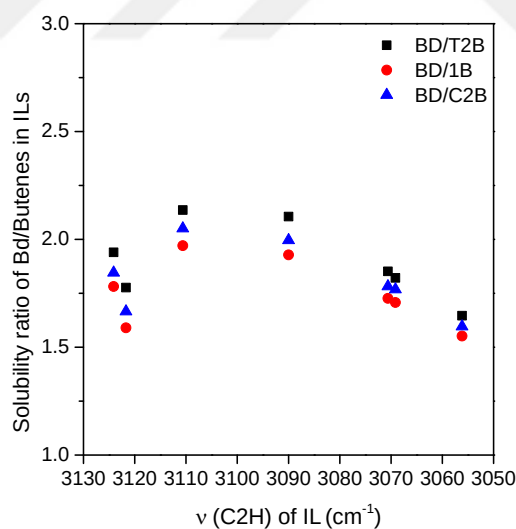


Figure A5-19. Solubility ratios of BD relative to those of individual butene isomers in ILs as a function of ν (C2H) of corresponding IL.

Table A5-4. Capacity of individual components (BD, T2B, 1B, C2B, B, and H₂) in ILs at 333 K determined by COSMO-RS calculations.

IL-coated supported Ir(CO) ₂ complexes	Solubility of each component in IL at 333 K (capacity, mol/mol)					
	BD	T2B	1B	C2B	B	H ₂
[BMIM][NTf ₂]	0.90	0.46	0.50	0.49	0.23	1.95
[BMIM][BF ₄]	0.24	0.13	0.15	0.14	0.06	1.20
[DMIM][MSO ₄]	0.80	0.38	0.41	0.39	0.20	1.65
[BMIM][TFA]	0.50	0.24	0.26	0.25	0.12	1.46
[EMIM][DEP]	0.68	0.37	0.39	0.38	0.21	1.75
[DMIM][DMP]	1.04	0.57	0.61	0.59	0.33	1.95
[BMIM][Ac]	0.72	0.44	0.47	0.45	0.27	1.75

A5-5. References

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2. J. Lu, C. Aydin, N. D. Browning, B. C. Gates, Oxide- and Zeolite-Supported Isostructural Ir(C₂H₄)₂ Complexes: Molecular-Level Observations of Electronic Effects of Supports as Ligands. *Langmuir*, **2012**, 28, 12806-12815.
3. C. Martinez-Macias, M. Chen, D. A. Dixon, B. C. Gates, Single-Site Zeolite-Anchored Organoiridium Carbonyl Complexes: Characterization of Structure and Reactivity by Spectroscopy and Computational Chemistry. *Chemistry – A European Journal*, **2015**, 21, 11825-11835.
4. A. Ravi, N. Sheppard, Infrared spectra of hydrocarbons adsorbed on silica-supported metals. IV. Butenes on iridium. *Journal of Physical Chemistry*, **1972**, 76, 2699-2703.

Appendix A6

Supplementary Materials for

Controlling the catalytic activity and selectivity for partial
hydrogenation by tuning the environment around the active
sites in supported Ir complexes

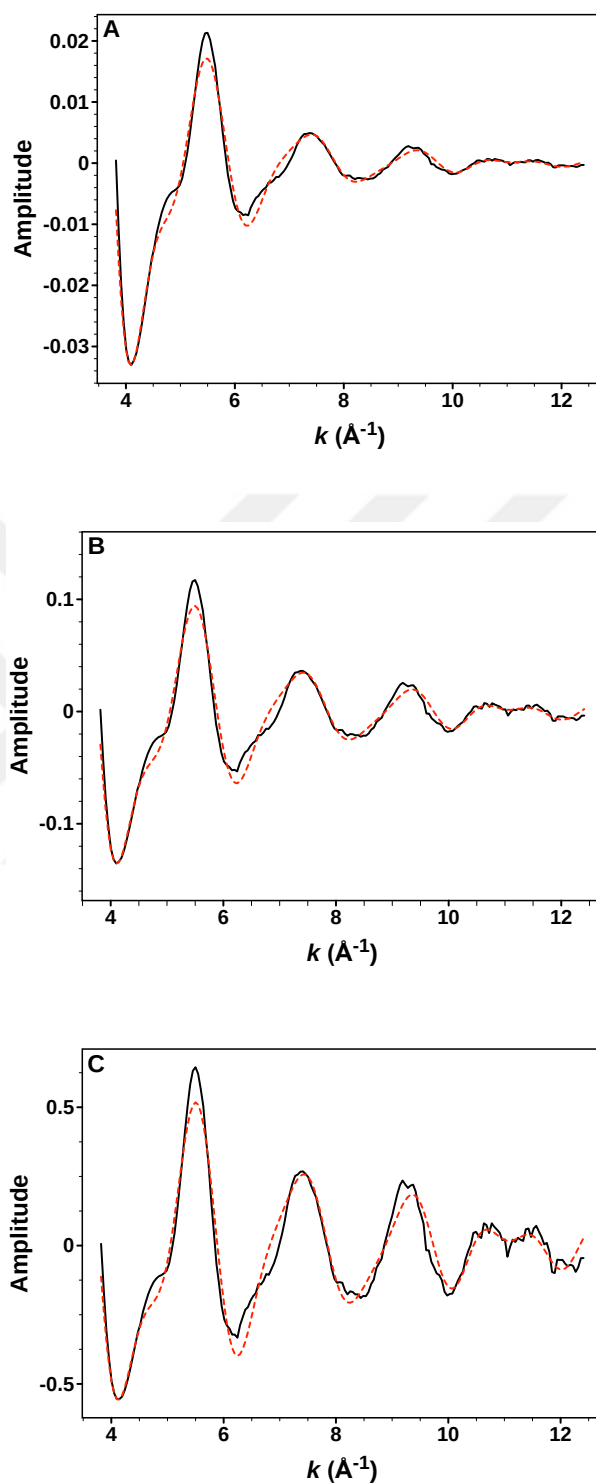
A6-1. Extended X-Ray Absorption Fine Structure (EXAFS) Results of Uncoated Samples

Figure A6-1. Results of EXAFS analysis characterizing the sample formed by the reaction of $\text{Ir}(\text{CO})_2(\text{acac})$ with SiO_2 calcined in flowing O_2 at 793 K. EXAFS function, χ (solid line), and calculated contribution (dotted line) (A, unweighted; B, k^1 -weighted; and C, k^2 -weighted).

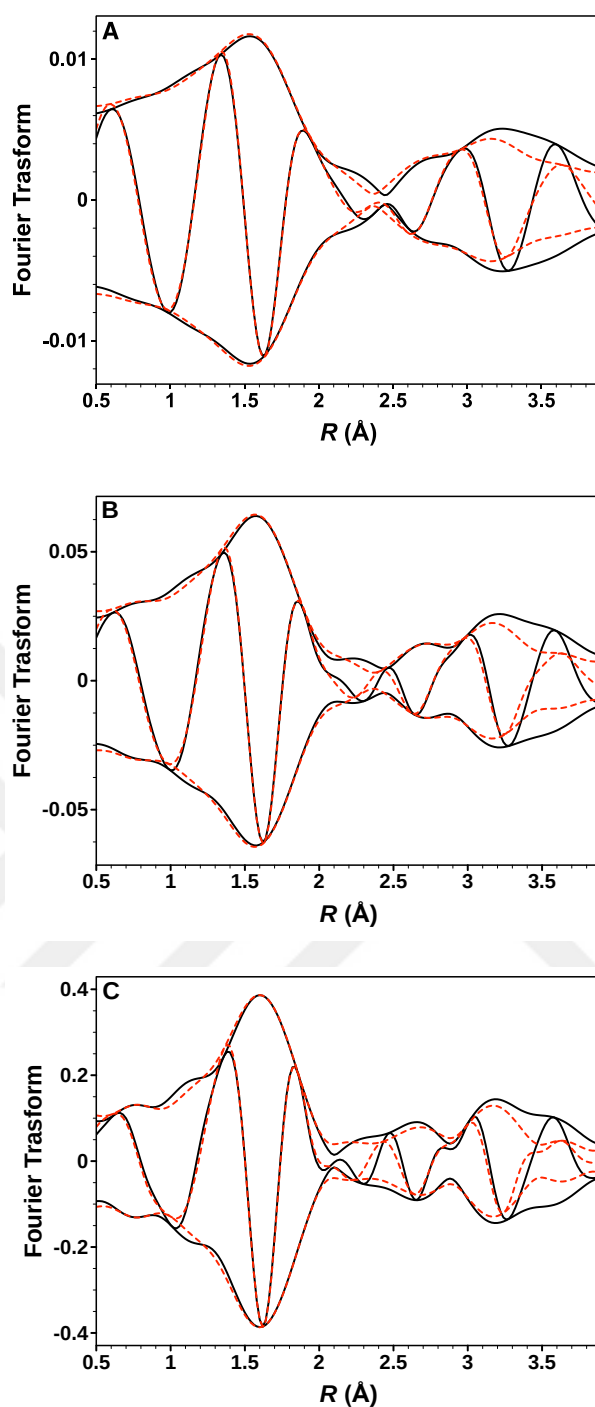


Figure A6-2. Results of EXAFS analysis characterizing the sample formed by the reaction of $\text{Ir}(\text{CO})_2(\text{acac})$ with SiO_2 calcined in flowing O_2 at 793 K. Imaginary part and magnitude of the Fourier transform of data (solid line), and calculated contribution (dotted line) (A, unweighted; B, k^1 -weighted; and C, k^2 -weighted).

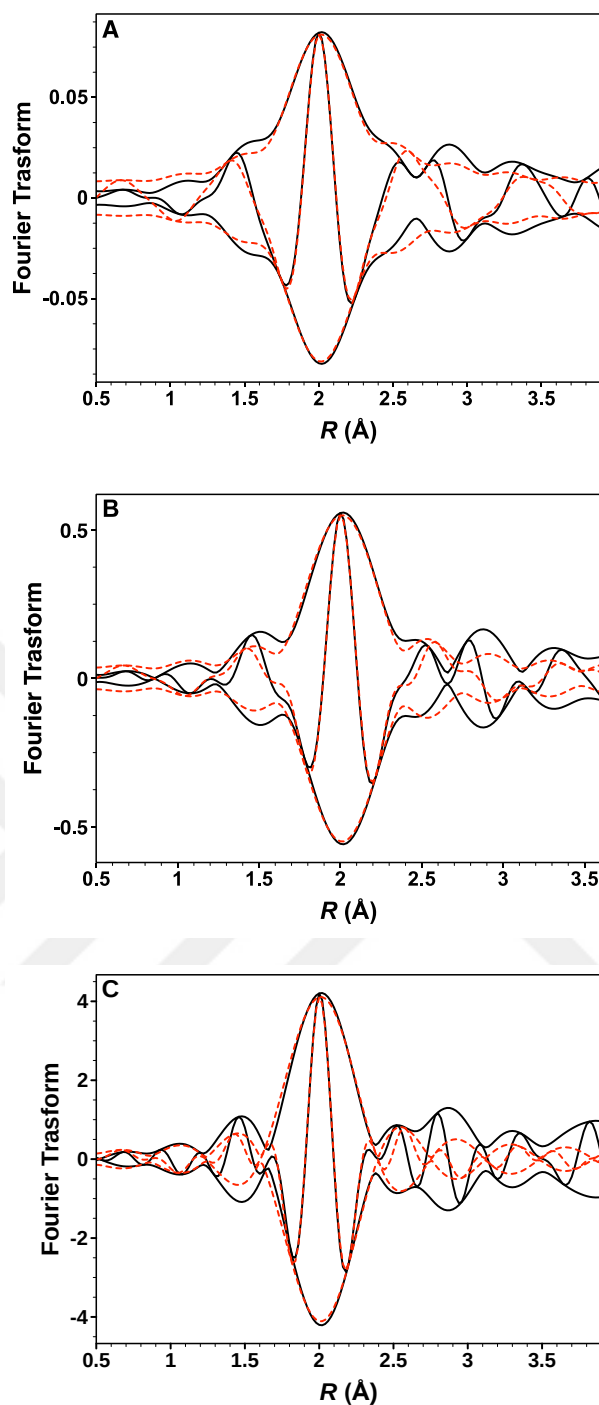


Figure A6-3. Imaginary part and magnitude of phase- and amplitude-corrected Fourier transform (A, unweighted; B, k^1 -weighted; and C, k^2 -weighted) of raw data minus calculated Ir–O_s, Ir–O_{CO} and Ir–Si contribution (solid line) and calculated Ir–C_{CO} contribution (dotted line) characterizing the sample formed by the reaction of Ir(CO)₂(acac) with SiO₂ calcined in flowing O₂ at 793 K.

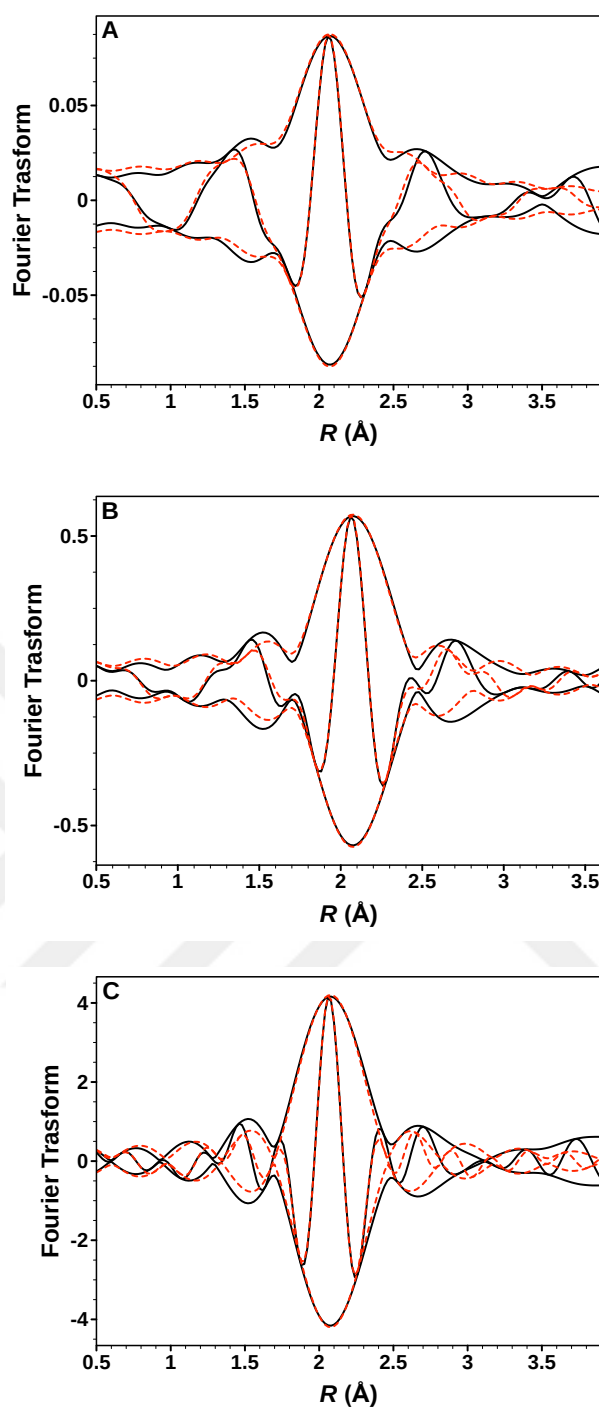


Figure A6-4. Imaginary part and magnitude of phase- and amplitude-corrected Fourier transform (A, unweighted; B, k^1 -weighted; and C, k^2 -weighted) of raw data minus calculated Ir–C_{CO}, Ir–O_{CO} and Ir–Si contribution (solid line) and calculated Ir–O_s contribution (dotted line) characterizing the sample formed by the reaction of Ir(CO)₂(acac) with SiO₂ calcined in flowing O₂ at 793 K.

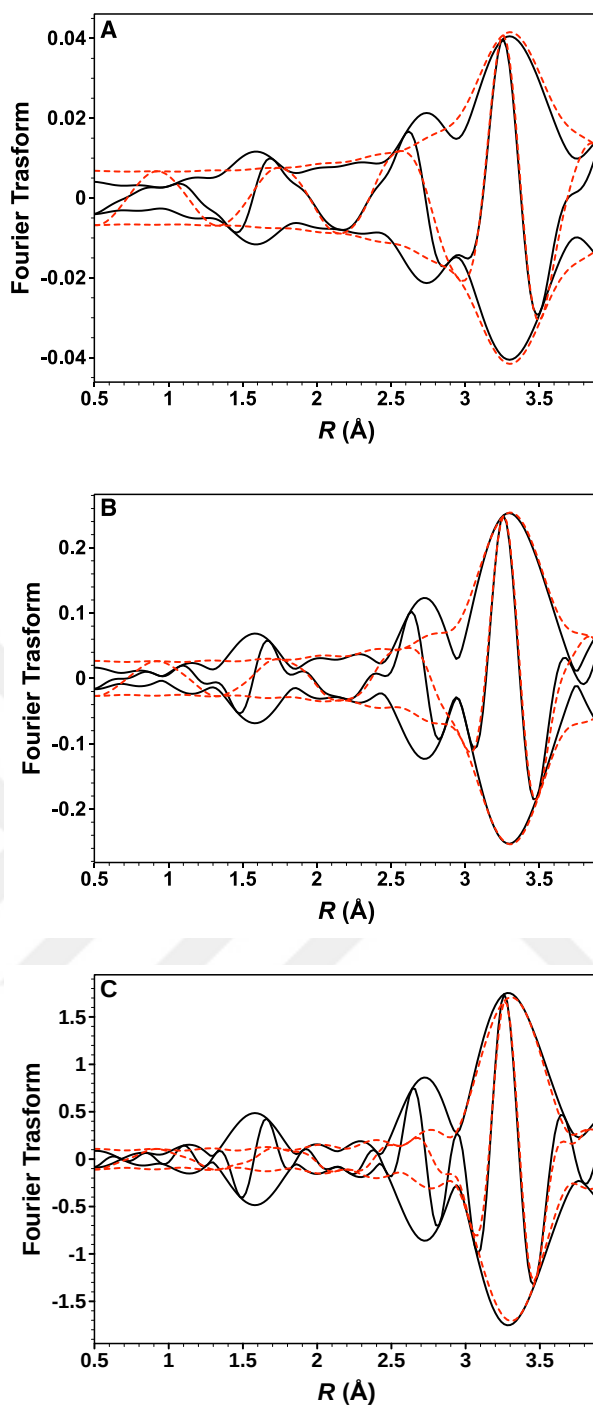


Figure A6-5. Imaginary part and magnitude of phase- and amplitude-corrected Fourier transform (A, unweighted; B, k^1 -weighted; and C, k^2 -weighted) of raw data minus calculated Ir-CO, Ir-O_s and Ir-Si contribution (solid line) and calculated Ir-OCO contribution (dotted line) characterizing the sample formed by the reaction of Ir(CO)₂(acac) with SiO₂ calcined in flowing O₂ at 793 K.

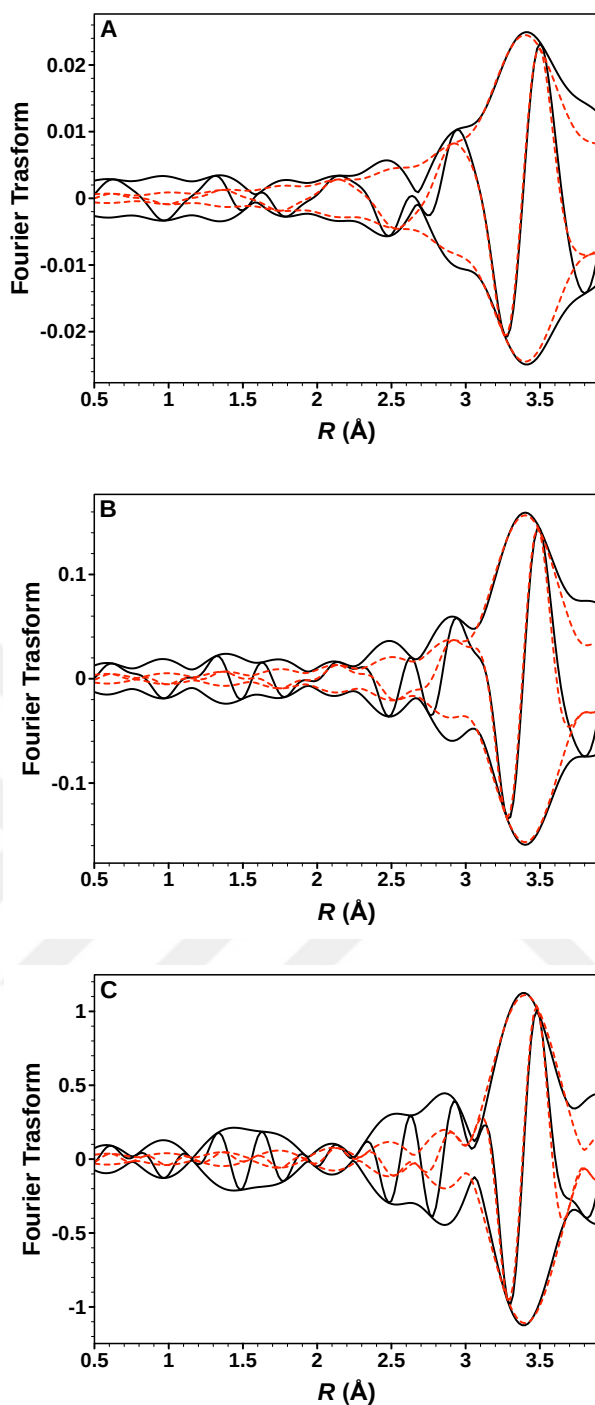


Figure A6-6. Imaginary part and magnitude of phase- and amplitude-corrected Fourier transform (A, unweighted; B, k^1 -weighted; and C, k^2 -weighted) of raw data minus calculated Ir-CO, Ir-O_s and Ir-O_{Co} contribution (solid line) and calculated Ir-Si contribution (dotted line) characterizing the sample formed by the reaction of Ir(CO)₂(acac) with SiO₂ calcined in flowing O₂ at 793 K.

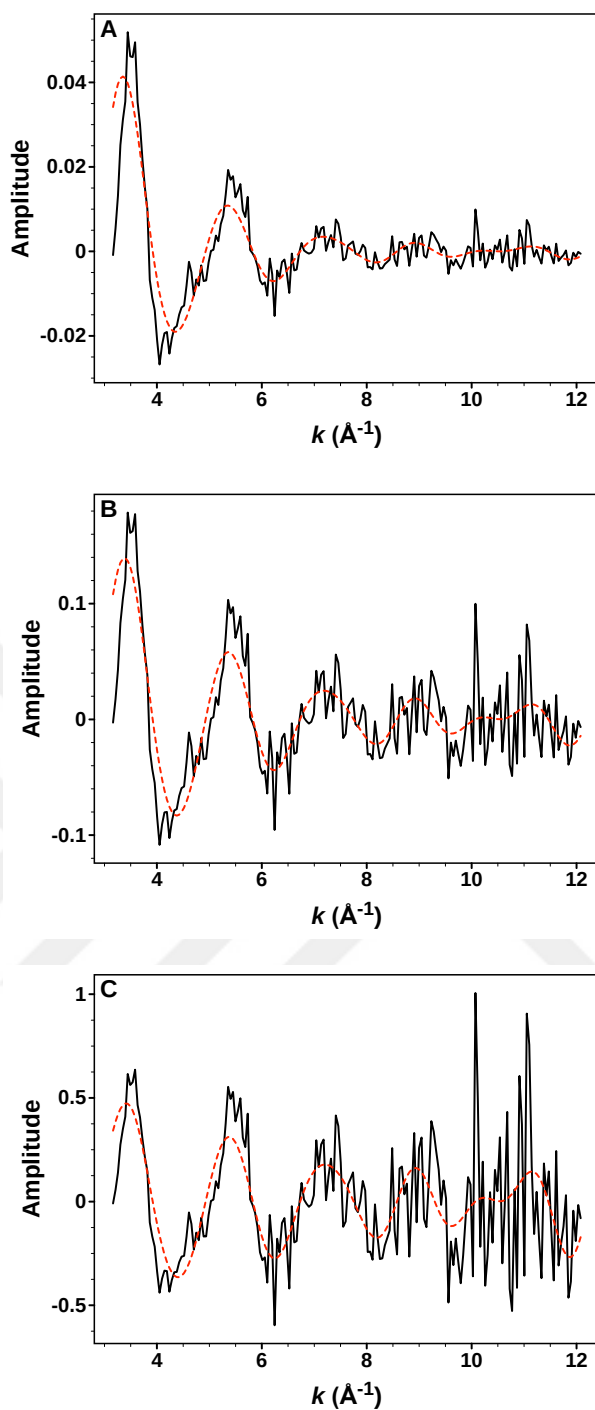


Figure A6-7. Results of EXAFS analysis characterizing the sample formed by the reaction of $\text{Ir}(\text{CO})_2(\text{acac})$ with TiO_2 calcined in flowing O_2 at 673 K. EXAFS function, χ (solid line), and calculated contribution (dotted line) (A, unweighted; B, k^1 -weighted; and C, k^2 -weighted).

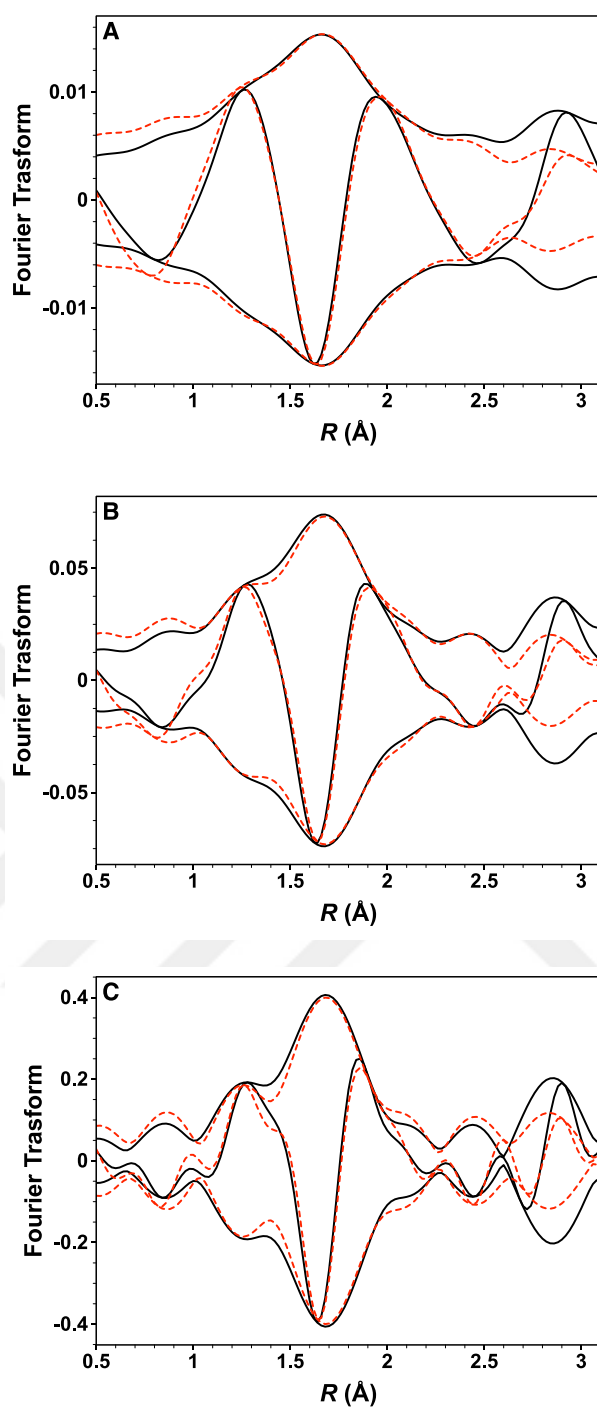


Figure A6-8. Results of EXAFS analysis characterizing the sample formed by the reaction of $\text{Ir}(\text{CO})_2(\text{acac})$ with TiO_2 calcined in flowing O_2 at 673 K. Imaginary part and magnitude of the Fourier transform of data (solid line), and calculated contribution (dotted line) (A, unweighted; B, k^1 -weighted; and C, k^2 -weighted).

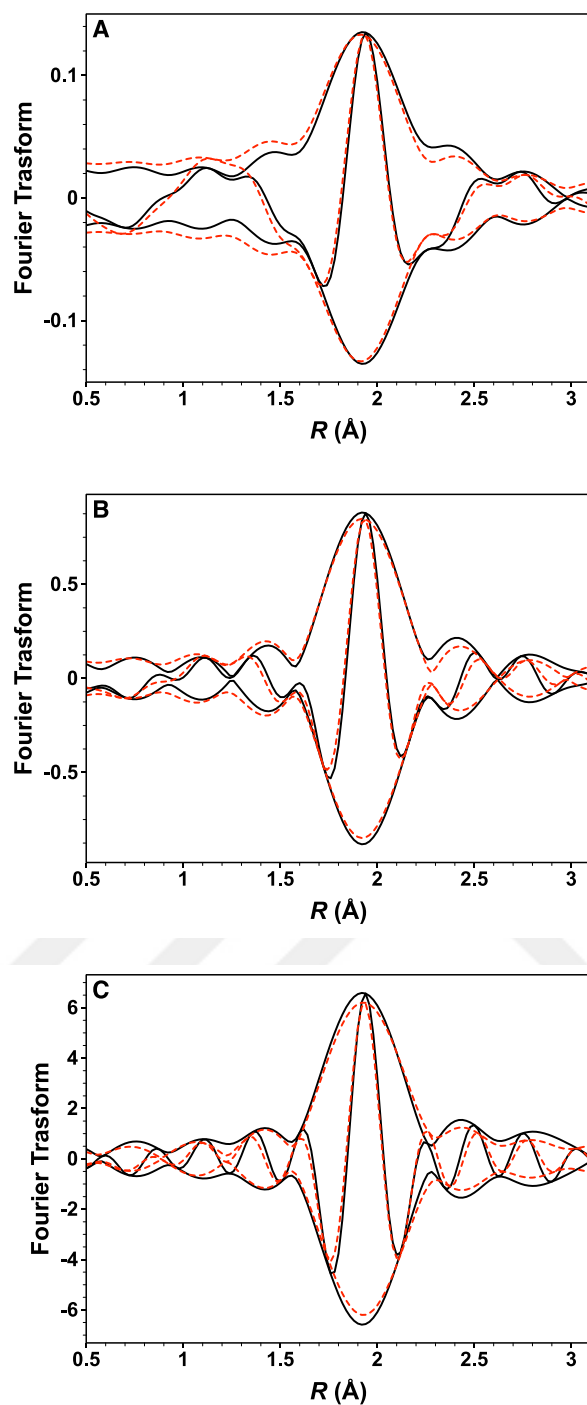


Figure A6-9. Imaginary part and magnitude of phase- and amplitude-corrected Fourier transform (A, unweighted; B, k^1 -weighted; and C, k^2 -weighted) of raw data minus calculated Ir-O_s, Ir-O_{cO} and Ir-Ti contribution (solid line) and calculated Ir-C_{cO} contribution (dotted line) characterizing the sample formed by the reaction of Ir(CO)₂(acac) with TiO₂ calcined in flowing O₂ at 673 K.

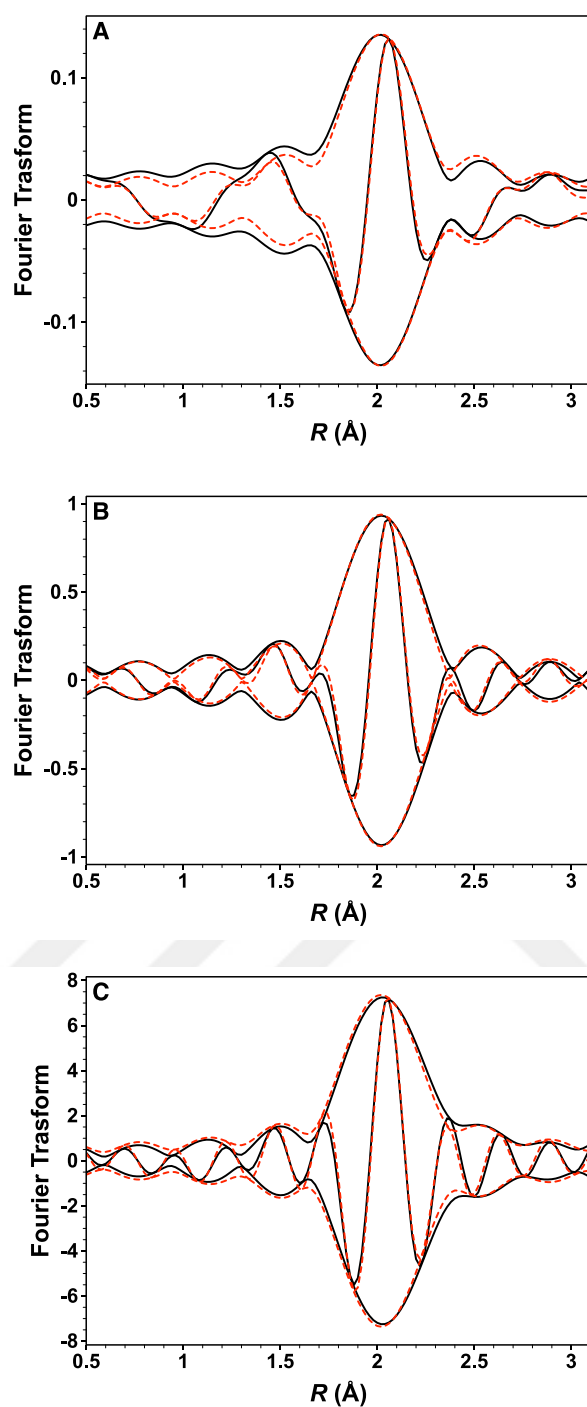


Figure A6-10. Imaginary part and magnitude of phase- and amplitude-corrected Fourier transform (A, unweighted; B, k^1 -weighted; and C, k^2 -weighted) of raw data minus calculated Ir-CO, Ir-O_{CO} and Ir-Ti contribution (solid line) and calculated Ir-O_s contribution (dotted line) characterizing the sample formed by the reaction of Ir(CO)₂(acac) with TiO₂ calcined in flowing O₂ at 673 K.

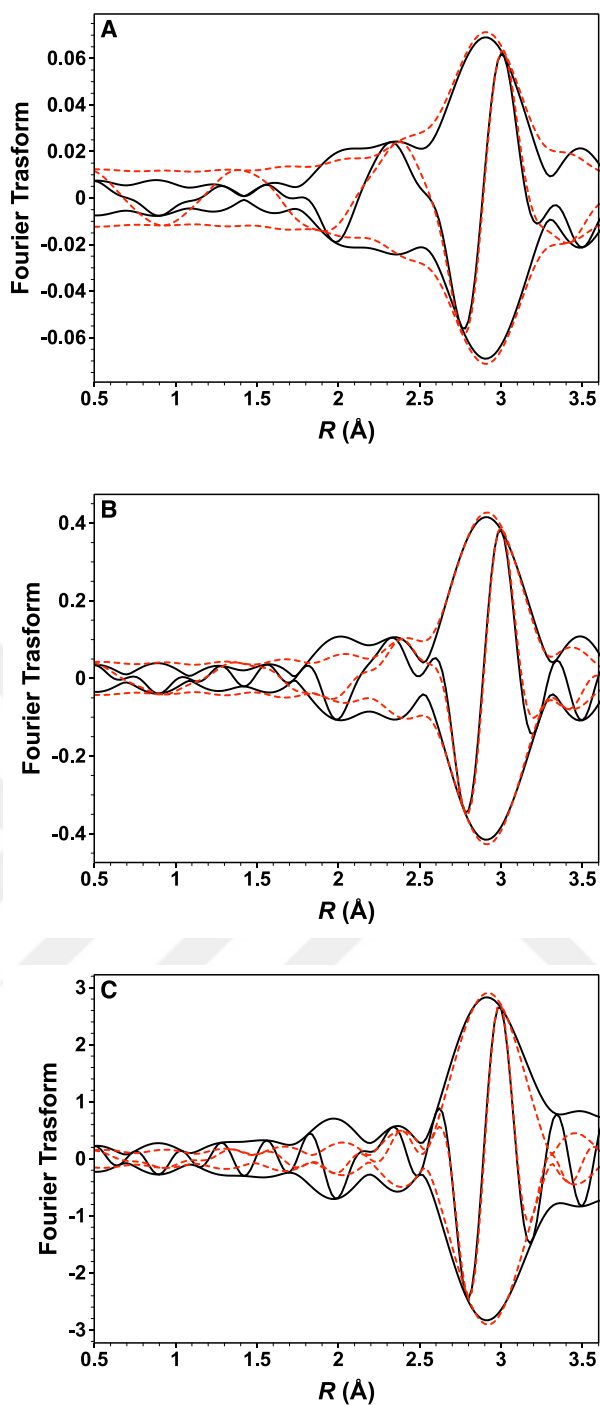


Figure A6-11. Imaginary part and magnitude of phase- and amplitude-corrected Fourier transform (A, unweighted; B, k^1 -weighted; and C, k^2 -weighted) of raw data minus calculated Ir–O_s, Ir–O_{CO} and Ir–Ti contribution (solid line) and calculated Ir–O_{CO} contribution (dotted line) characterizing the sample formed by the reaction of Ir(CO)₂(acac) with TiO₂ calcined in flowing O₂ at 673 K.

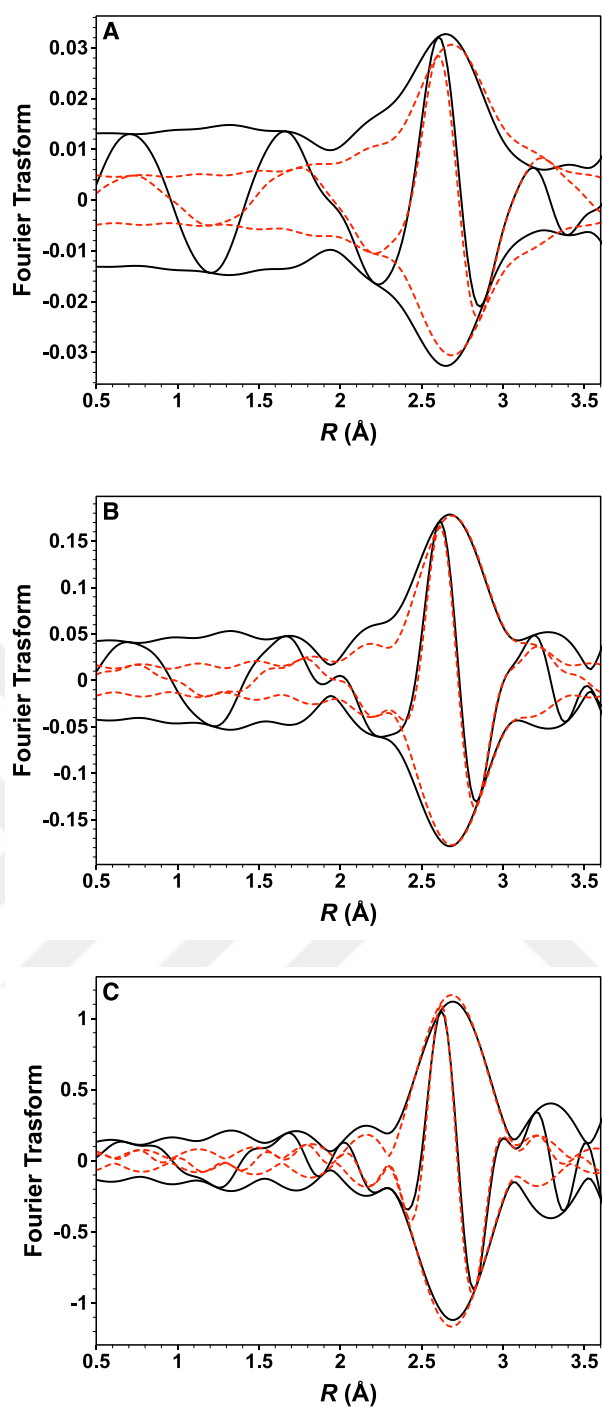


Figure A6-12. Imaginary part and magnitude of phase- and amplitude-corrected Fourier transform (A, unweighted; B, k^1 -weighted; and C, k^2 -weighted) of raw data minus calculated Ir–O_s, Ir–C_{CO} and Ir–O_{CO} contribution (solid line) and calculated Ir–Ti contribution (dotted line) characterizing the sample formed by the reaction of Ir(CO)₂(acac) with TiO₂ calcined in flowing O₂ at 673 K.

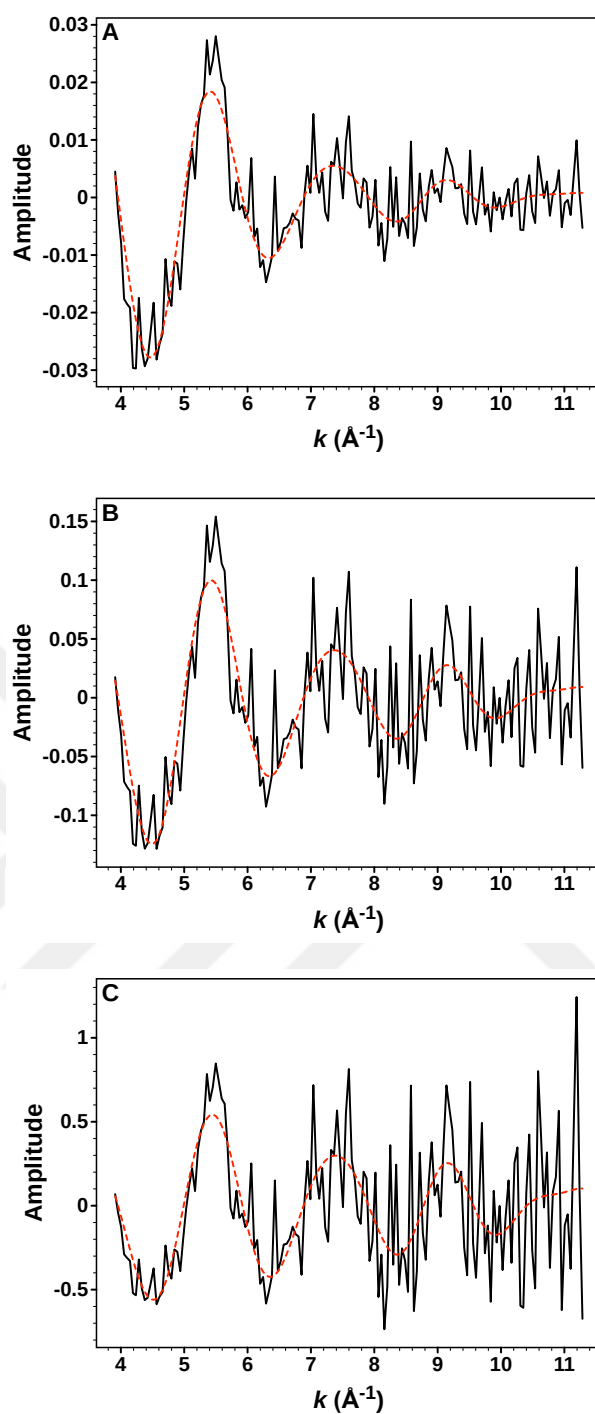


Figure A6-13. Results of EXAFS analysis characterizing the sample formed by the reaction of $\text{Ir}(\text{CO})_2(\text{acac})$ with Fe_2O_3 calcined in flowing O_2 at 773 K. EXAFS function, χ (solid line), and calculated contribution (dotted line) (A, unweighted; B, k^1 -weighted; and C, k^2 -weighted).

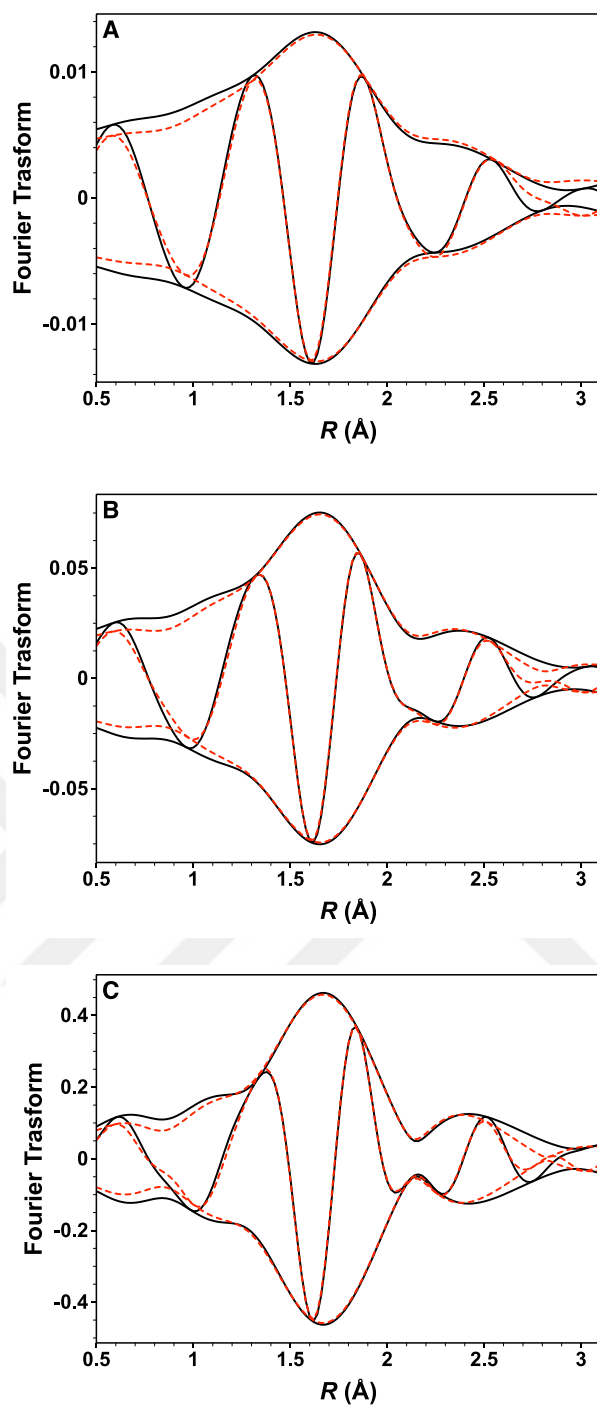


Figure A6-14. Results of EXAFS analysis characterizing the sample formed by the reaction of $\text{Ir}(\text{CO})_2(\text{acac})$ with Fe_2O_3 calcined in flowing O_2 at 773 K. EXAFS function, χ (solid line), and calculated contribution (dotted line) (A, unweighted; B, k^1 -weighted; and C, k^2 -weighted).

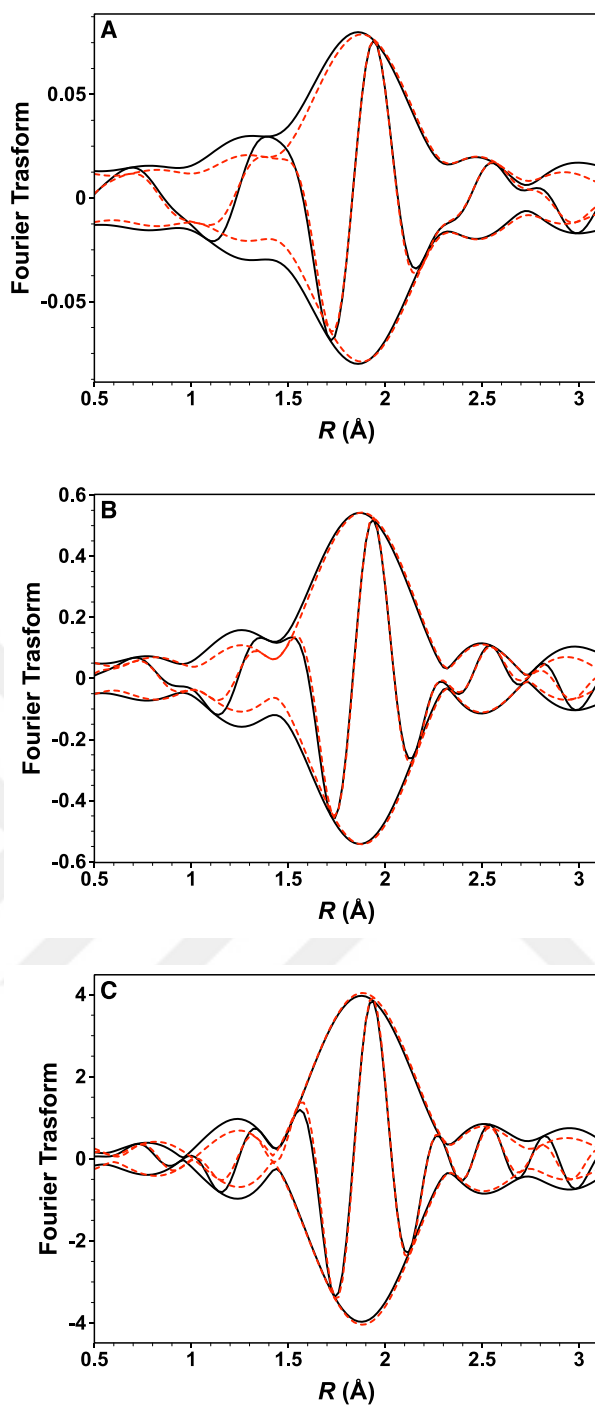


Figure A6-15. Imaginary part and magnitude of phase- and amplitude-corrected Fourier transform (A, unweighted; B, k^1 -weighted; and C, k^2 -weighted) of raw data minus calculated Ir-O_s, Ir-O_{CO} and Ir-Fe contribution (solid line) and calculated Ir-C_{CO} contribution (dotted line) characterizing the sample formed by the reaction of Ir(CO)₂(acac) with Fe₂O₃ calcined in flowing O₂ at 773 K.

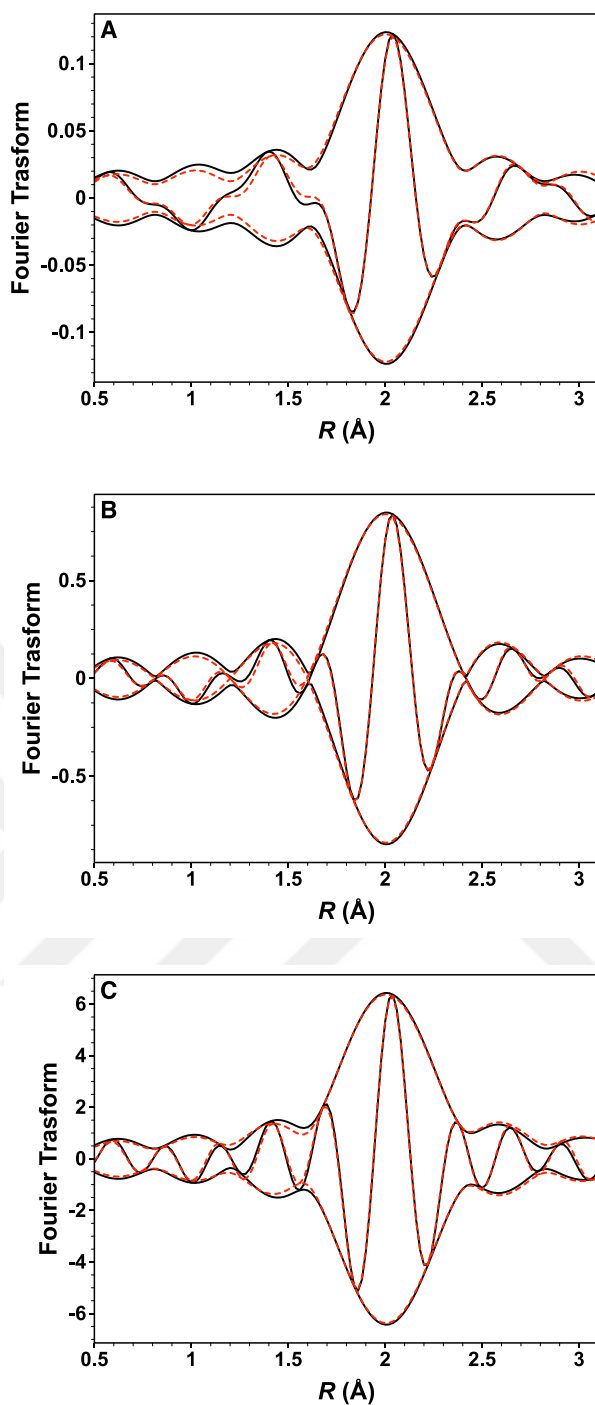


Figure A6-16. Imaginary part and magnitude of phase- and amplitude-corrected Fourier transform (A, unweighted; B, k^1 -weighted; and C, k^2 -weighted) of raw data minus calculated Ir–C_{CO}, Ir–O_{CO} and Ir–Fe contribution (solid line) and calculated Ir–O_s contribution (dotted line) characterizing the sample formed by the reaction of Ir(CO)₂(acac) with Fe₂O₃ calcined in flowing O₂ at 773 K.

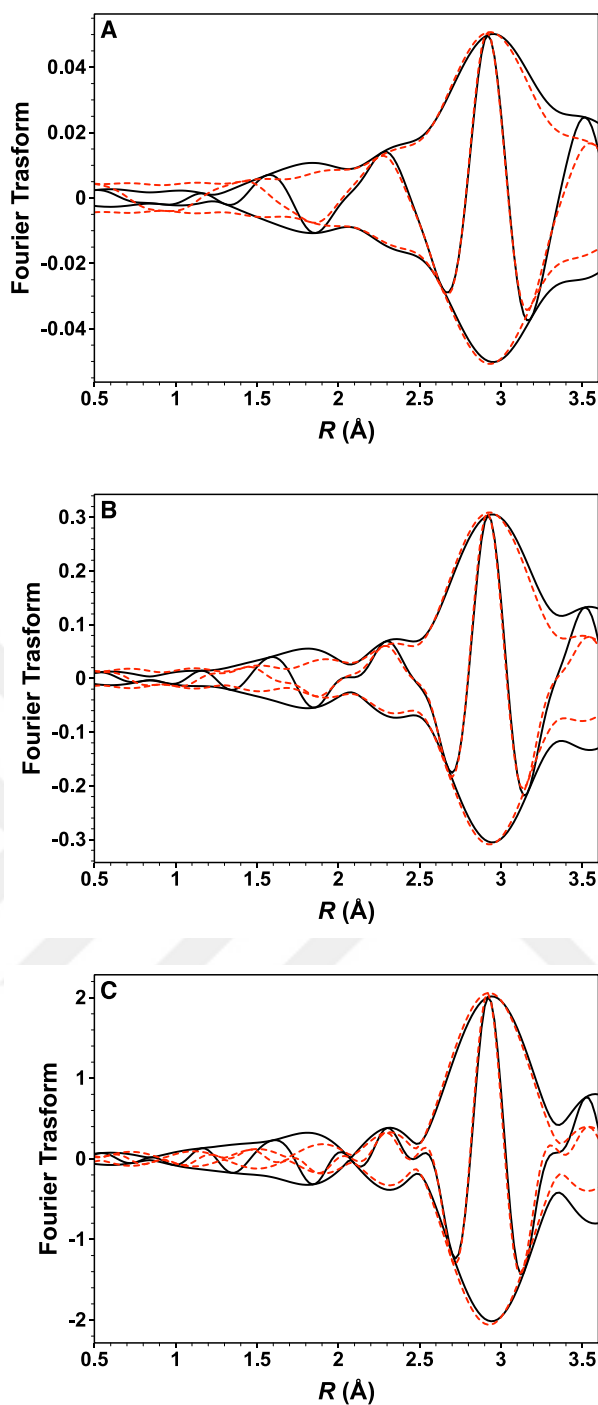


Figure A6-17. Imaginary part and magnitude of phase- and amplitude-corrected Fourier transform (A, unweighted; B, k^1 -weighted; and C, k^2 -weighted) of raw data minus calculated Ir-CO, Ir-O_s and Ir-Fe contribution (solid line) and calculated Ir-O_{co} contribution (dotted line) characterizing the sample formed by the reaction of Ir(CO)₂(acac) with Fe₂O₃ calcined in flowing O₂ at 773 K.

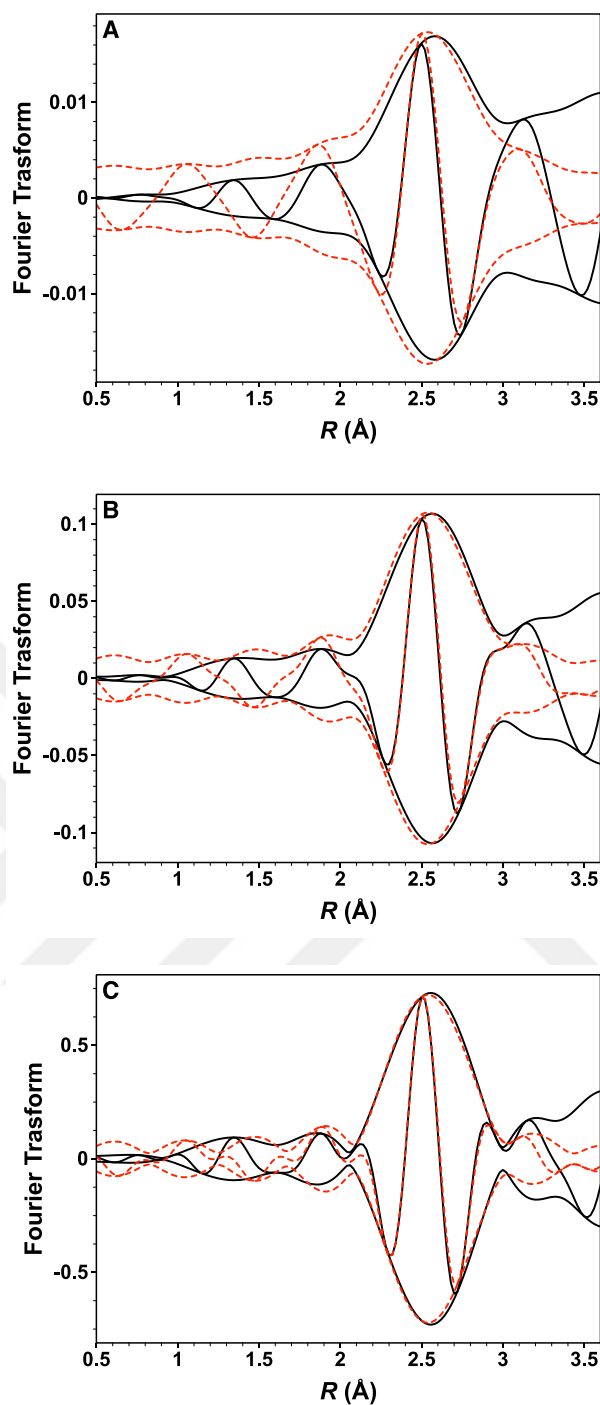


Figure A6-18. Imaginary part and magnitude of phase- and amplitude-corrected Fourier transform (A, unweighted; B, k^1 -weighted; and C, k^2 -weighted) of raw data minus calculated Ir-CO, Ir-O_s and Ir-OCO contribution (solid line) and calculated Ir-Fe contribution (dotted line) characterizing the sample formed by the reaction of Ir(CO)₂(acac) with Fe₂O₃ calcined in flowing O₂ at 773 K.

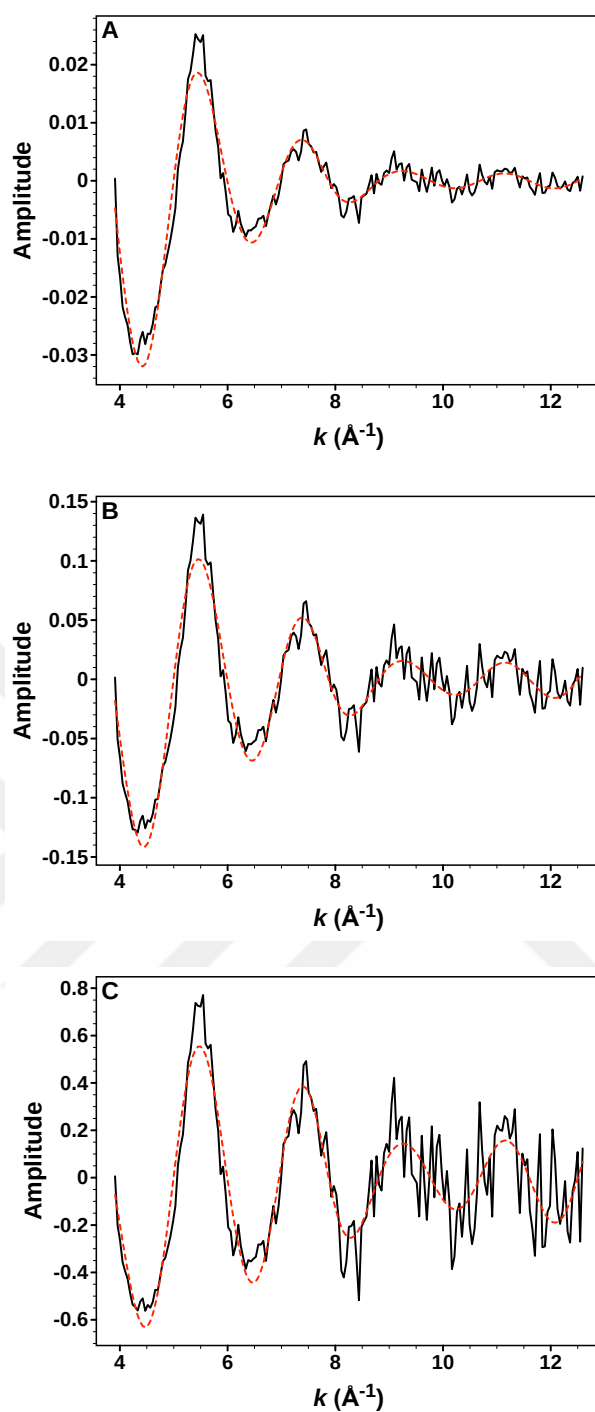


Figure A6-19. Results of EXAFS analysis characterizing the sample formed by the reaction of $\text{Ir}(\text{CO})_2(\text{acac})$ with CeO_2 calcined in flowing O_2 at 673 K. EXAFS function, χ (solid line), and calculated contribution (dotted line) (A, unweighted; B, k^1 -weighted; and C, k^2 -weighted).

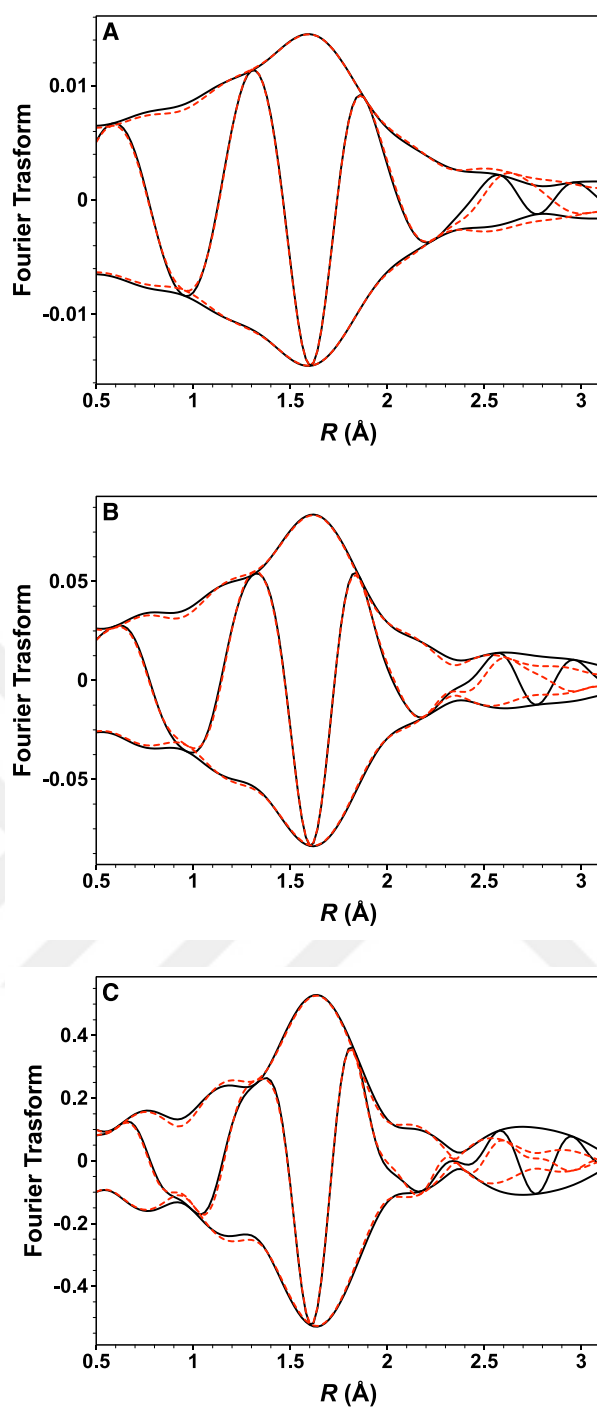


Figure A6-20. Results of EXAFS analysis characterizing the sample formed by the reaction of $\text{Ir}(\text{CO})_2(\text{acac})$ with CeO_2 calcined in flowing O_2 at 673 K. Imaginary part and magnitude of the Fourier transform of data (solid line), and calculated contribution (dotted line) (A, unweighted; B, k^1 -weighted; and C, k^2 -weighted).

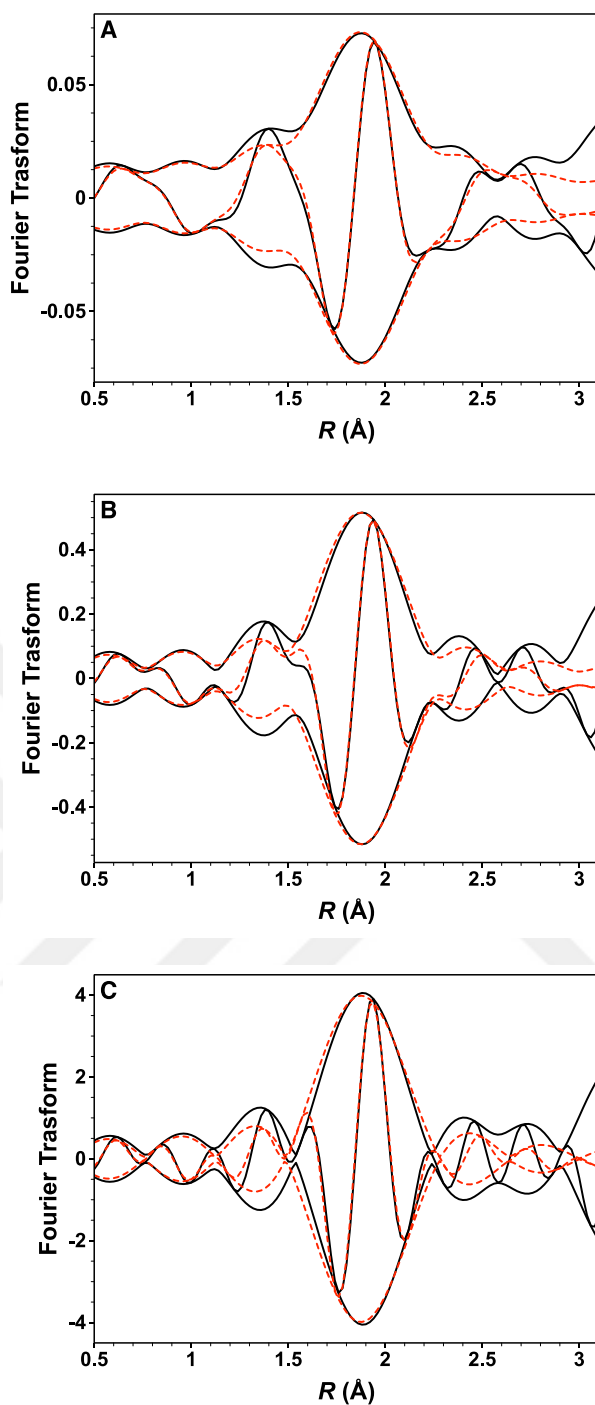


Figure A6-21. Imaginary part and magnitude of phase- and amplitude-corrected Fourier transform (A, unweighted; B, k^1 -weighted; and C, k^2 -weighted) of raw data minus calculated Ir–O_s, Ir–O_{CO} and Ir–Ce contribution (solid line) and calculated Ir–C_{CO} contribution (dotted line) characterizing the sample formed by the reaction of Ir(CO)₂(acac) with CeO₂ calcined in flowing O₂ at 673 K.

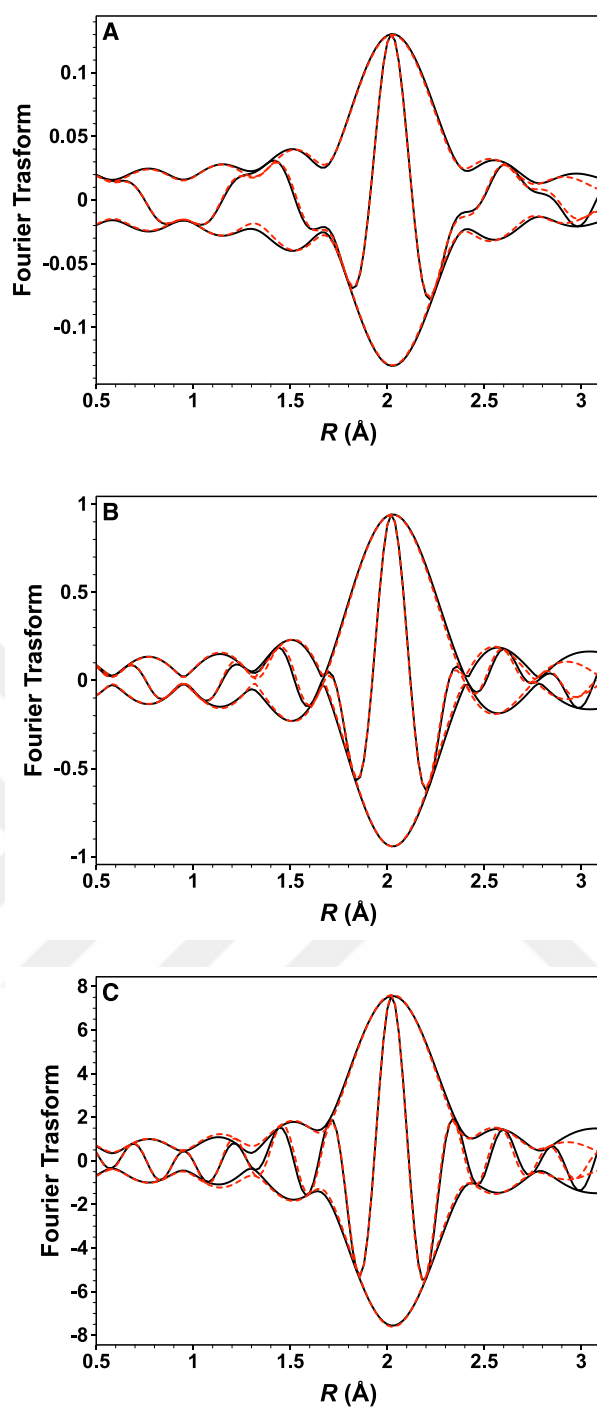


Figure A6-22. Imaginary part and magnitude of phase- and amplitude-corrected Fourier transform (A, unweighted; B, k^1 -weighted; and C, k^2 -weighted) of raw data minus calculated Ir–C_{CO}, Ir–O_{CO} and Ir–Ce contribution (solid line) and calculated Ir–O_s contribution (dotted line) characterizing the sample formed by the reaction of Ir(CO)₂(acac) with CeO₂ calcined in flowing O₂ at 673 K.

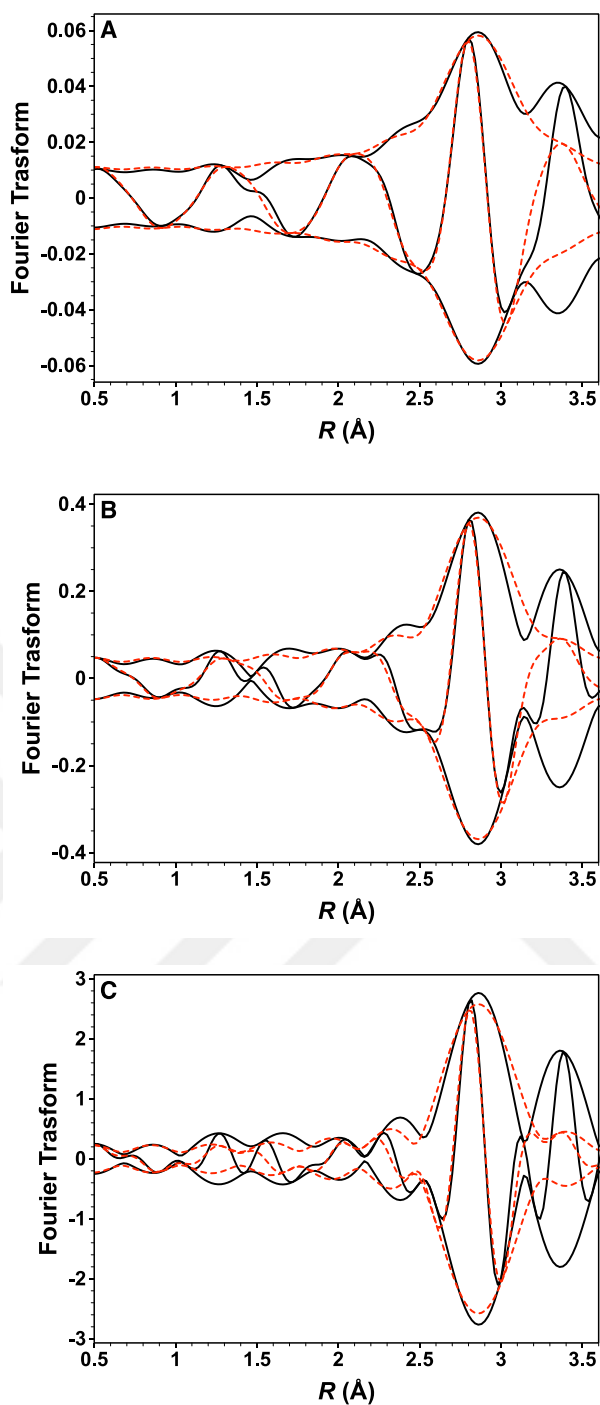


Figure A6-23. Imaginary part and magnitude of phase- and amplitude-corrected Fourier transform (A, unweighted; B, k^1 -weighted; and C, k^2 -weighted) of raw data minus calculated Ir-CO, Ir-O_s and Ir-Ce contribution (solid line) and calculated Ir-O-CO contribution (dotted line) characterizing the sample formed by the reaction of Ir(CO)₂(acac) with CeO₂ calcined in flowing O₂ at 673 K.

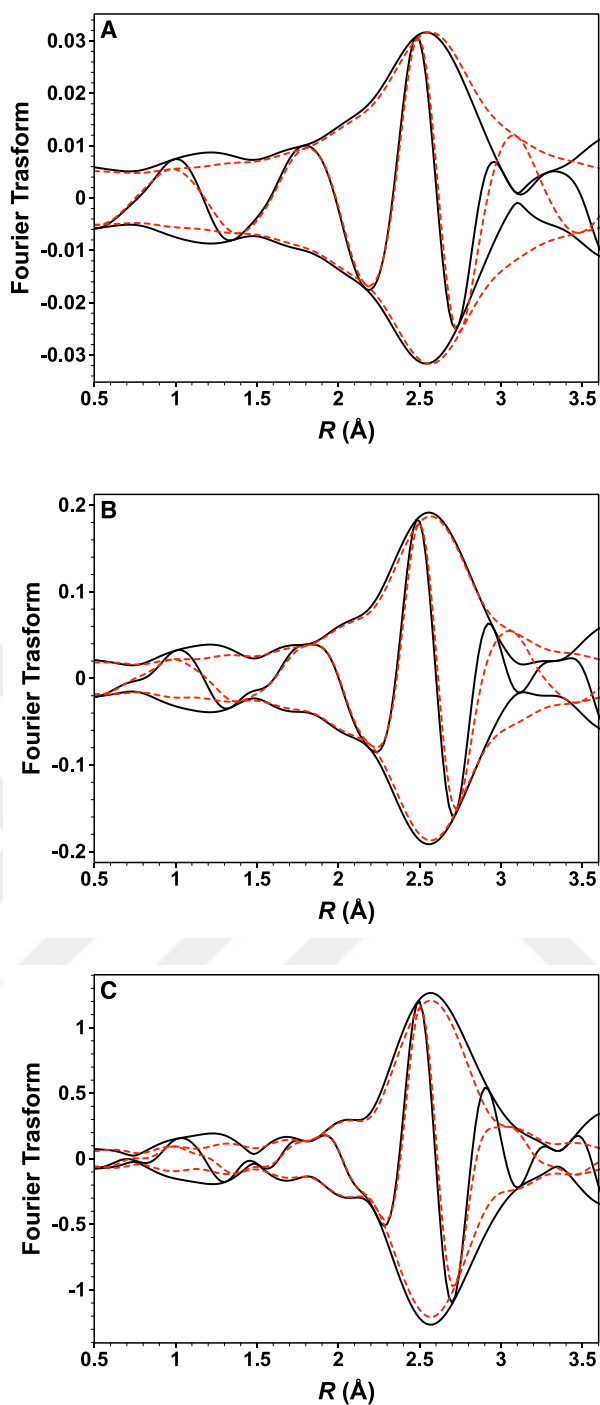


Figure A6-24. Imaginary part and magnitude of phase- and amplitude-corrected Fourier transform (A, unweighted; B, k^1 -weighted; and C, k^2 -weighted) of raw data minus calculated Ir-CO, Ir-O_s and Ir-OCO contribution (solid line) and calculated Ir-Ce contribution (dotted line) characterizing the sample formed by the reaction of Ir(CO)₂(acac) with CeO₂ calcined in flowing O₂ at 673 K.

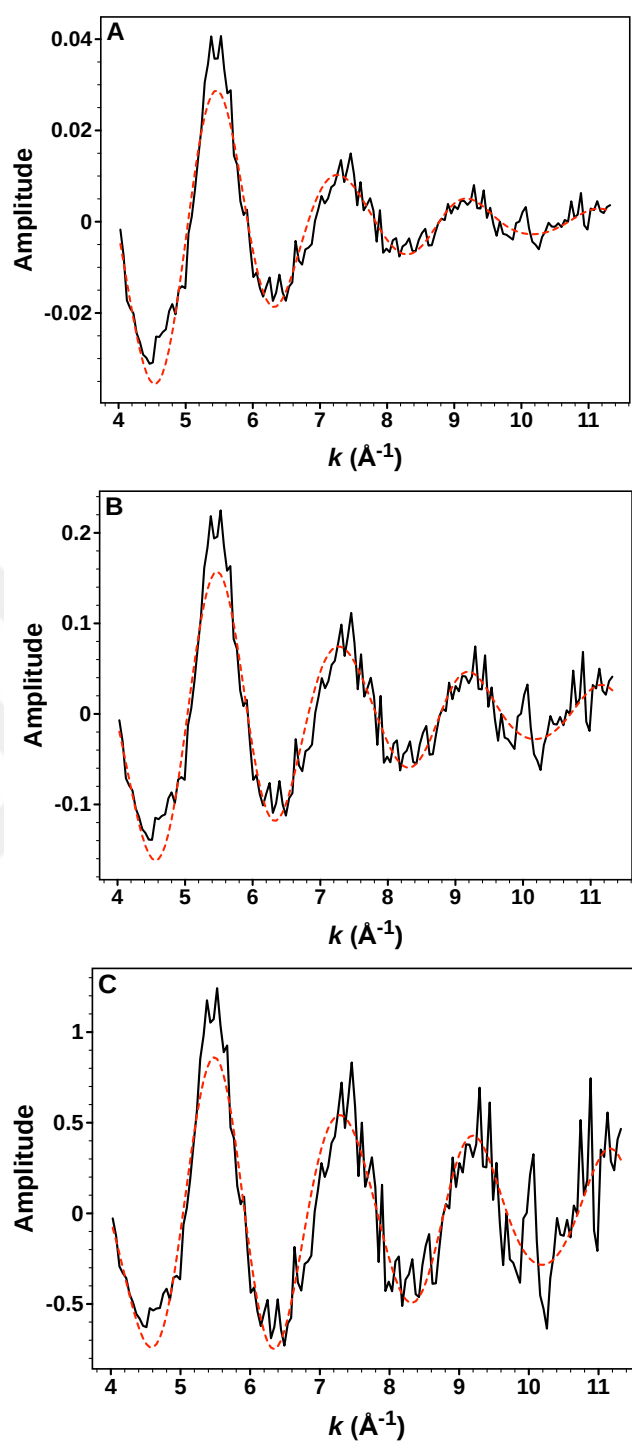


Figure A6-25. Results of EXAFS analysis characterizing the sample formed by the reaction of $\text{Ir}(\text{CO})_2(\text{acac})$ with MgO calcined in flowing O_2 at 973 K. EXAFS function, χ (solid line), and calculated contribution (dotted line) (A, unweighted; B, k^1 -weighted; and C, k^2 -weighted).

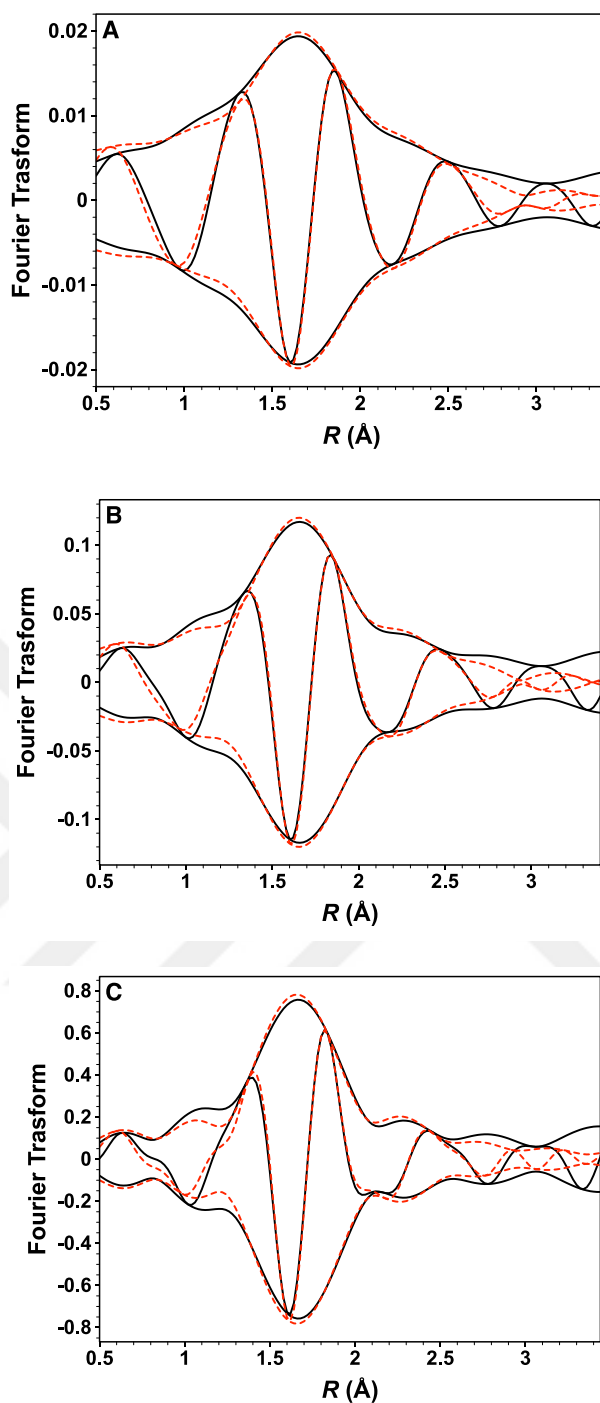


Figure A6-26. Results of EXAFS analysis characterizing the sample formed by the reaction of $\text{Ir}(\text{CO})_2(\text{acac})$ with MgO calcined in flowing O_2 at 973 K. EXAFS function, χ (solid line), and calculated contribution (dotted line) (A, unweighted; B, k^1 -weighted; and C, k^2 -weighted).

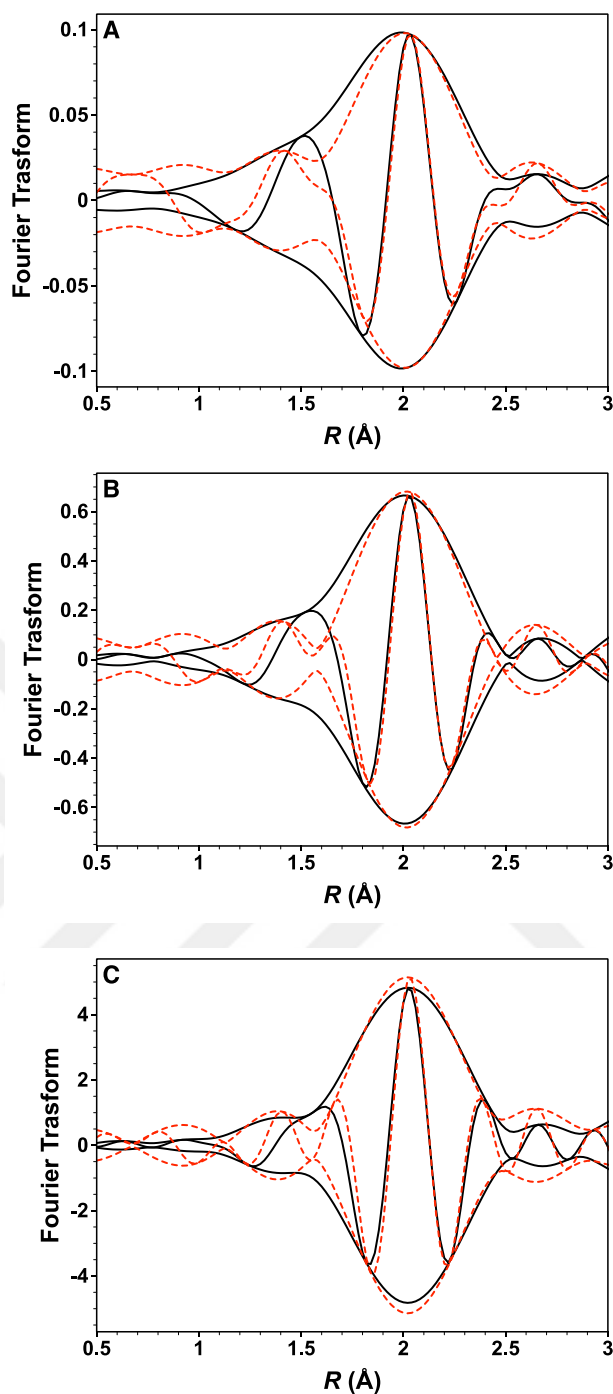


Figure A6-27. Imaginary part and magnitude of phase- and amplitude-corrected Fourier transform (A, unweighted; B, k^1 -weighted; and C, k^2 -weighted) of raw data minus calculated Ir-O_s, Ir-O_{CO} and Ir-Mg contribution (solid line) and calculated Ir-C_{CO} contribution (dotted line) characterizing the sample formed by the reaction of Ir(CO)₂(acac) with MgO calcined in flowing O₂ at 973 K.

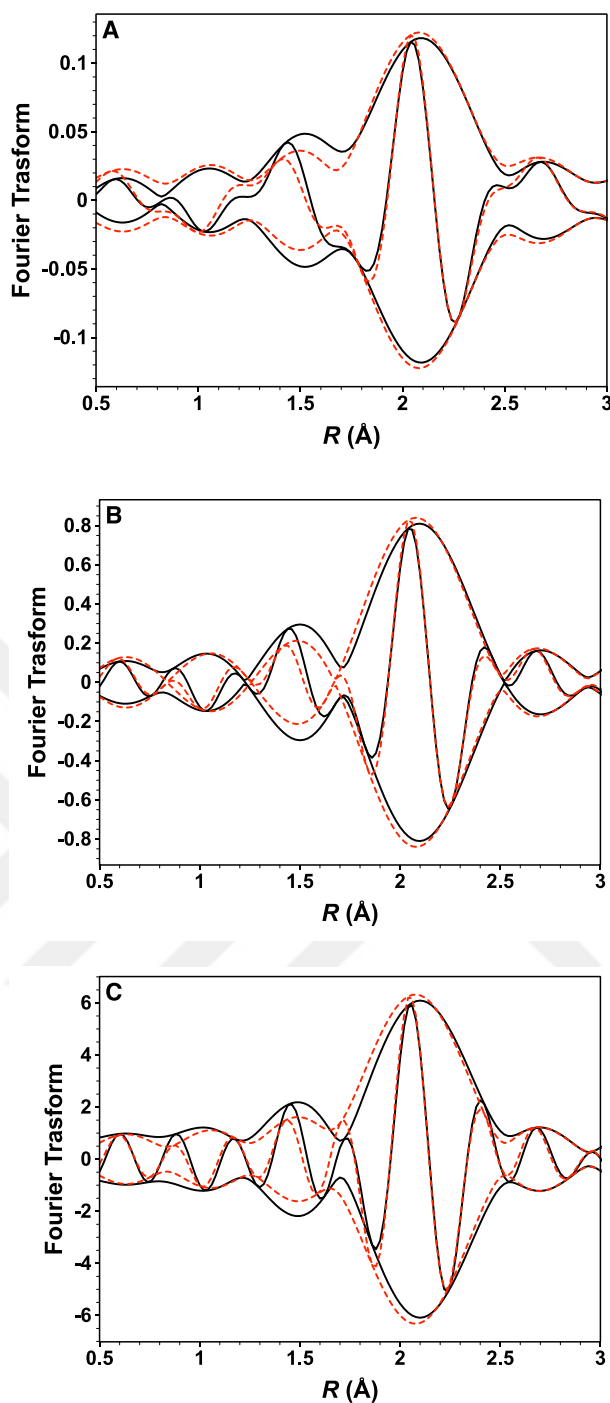


Figure A6-28. Imaginary part and magnitude of phase- and amplitude-corrected Fourier transform (A, unweighted; B, k^1 -weighted; and C, k^2 -weighted) of raw data minus calculated Ir–C_{CO}, Ir–O_{CO} and Ir–Mg contribution (solid line) and calculated Ir–O_s contribution (dotted line) characterizing the sample formed by the reaction of Ir(CO)₂(acac) with MgO calcined in flowing O₂ at 973 K.

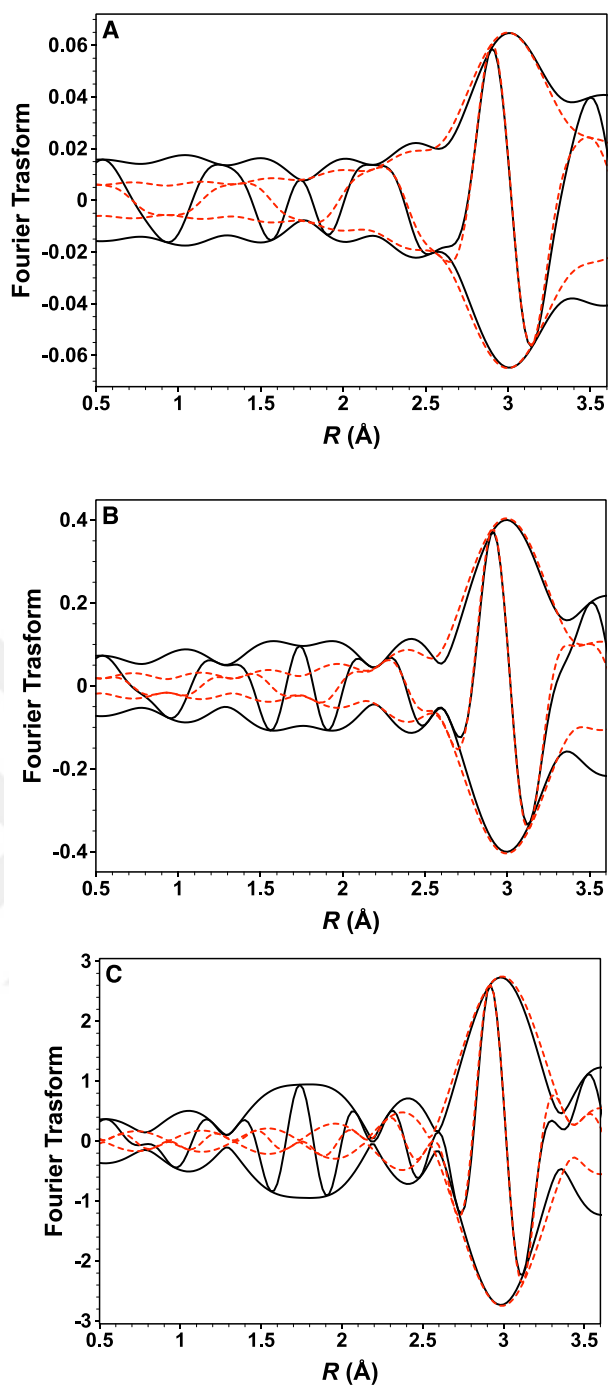


Figure A6-29. Imaginary part and magnitude of phase- and amplitude-corrected Fourier transform (A, unweighted; B, k^1 -weighted; and C, k^2 -weighted) of raw data minus calculated Ir-CO, Ir-O_s and Ir-Mg contribution (solid line) and calculated Ir-OCO contribution (dotted line) characterizing the sample formed by the reaction of Ir(CO)₂(acac) with MgO calcined in flowing O₂ at 973 K.

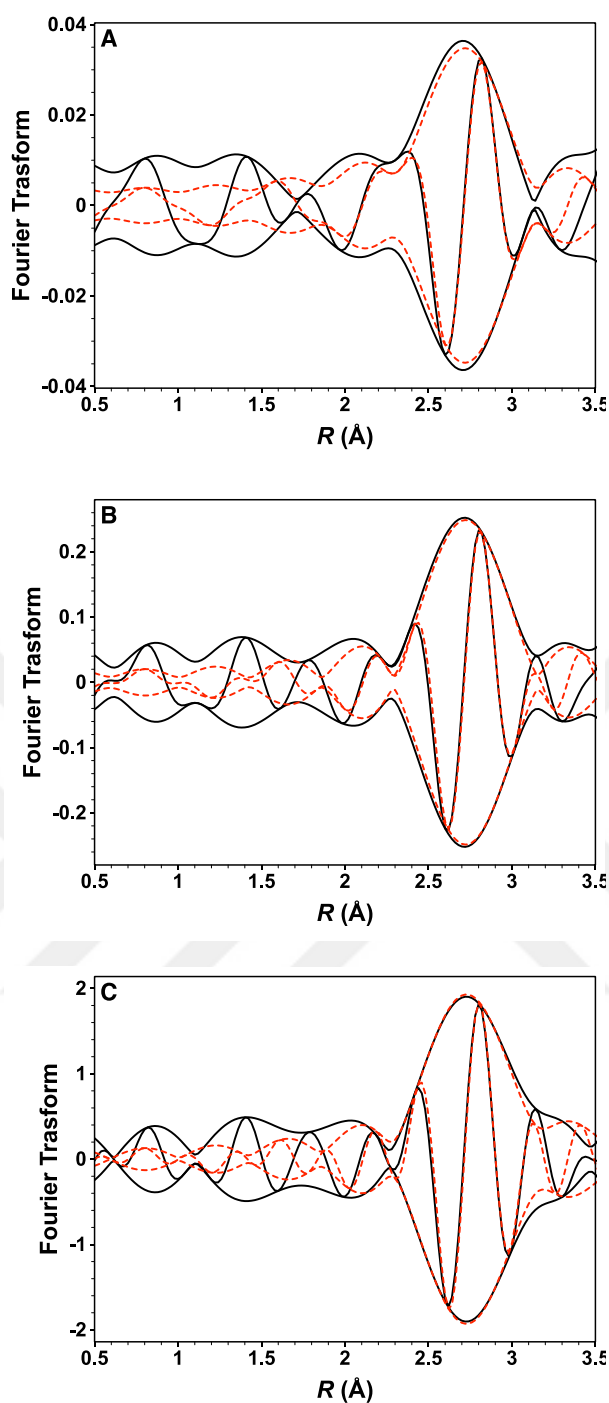


Figure A6-30. Imaginary part and magnitude of phase- and amplitude-corrected Fourier transform (A, unweighted; B, k^1 -weighted; and C, k^2 -weighted) of raw data minus calculated Ir-CO, Ir-O_s and Ir-O_{CO} contribution (solid line) and calculated Ir-Mg contribution (dotted line) characterizing the sample formed by the reaction of Ir(CO)₂(acac) with MgO calcined in flowing O₂ at 973 K.

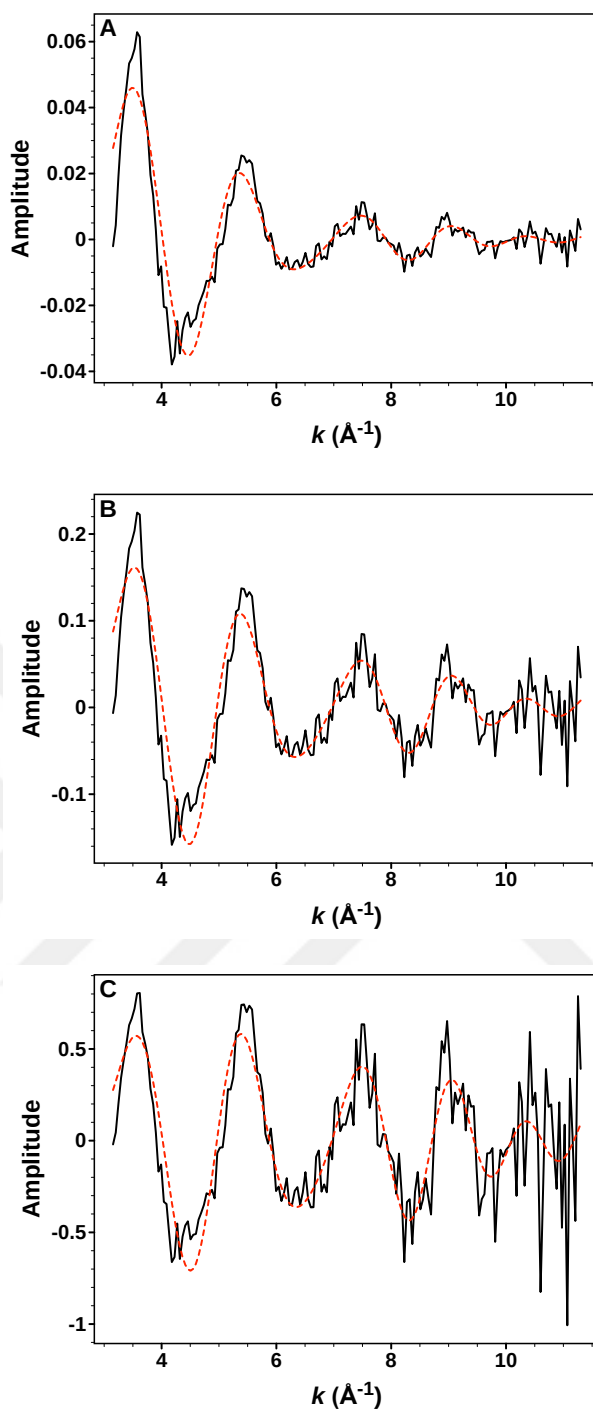


Figure A6-31. Results of EXAFS analysis characterizing the sample formed by the reaction of $\text{Ir}(\text{CO})_2(\text{acac})$ with La_2O_3 calcined in flowing O_2 at 873 K. EXAFS function, χ (solid line), and calculated contribution (dotted line) (A, unweighted; B, k^1 -weighted; and C, k^2 -weighted).

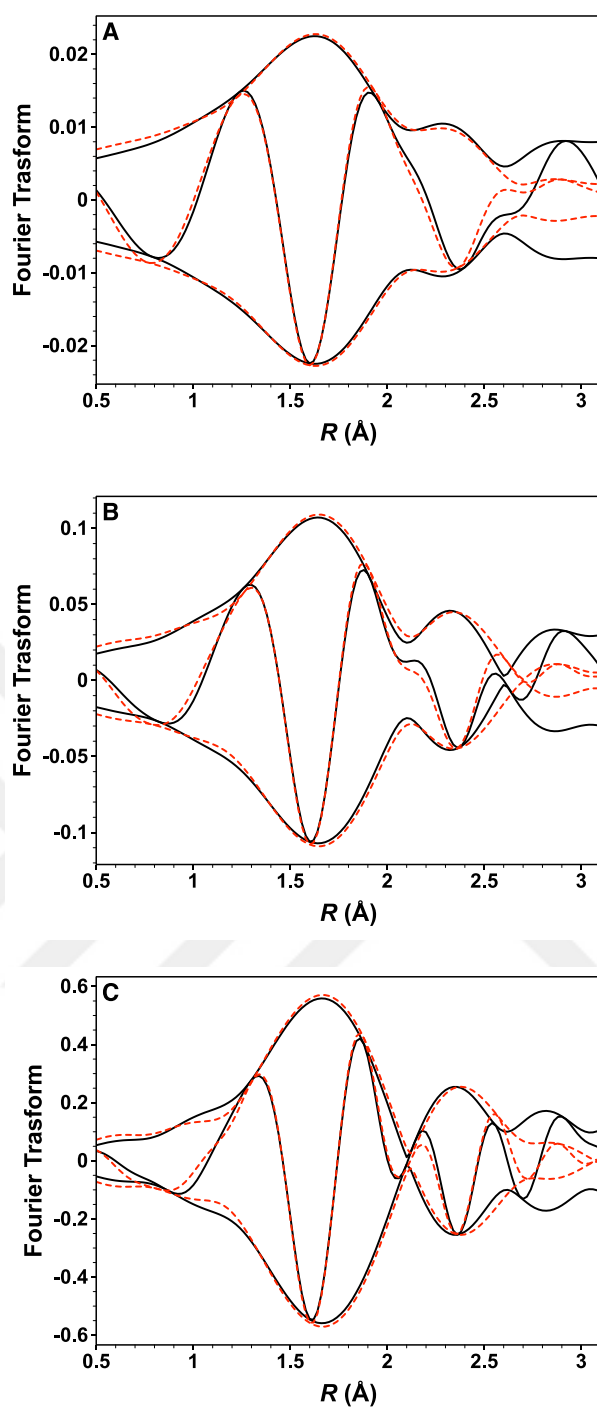


Figure A6-32. Results of EXAFS analysis characterizing the sample formed by the reaction of $\text{Ir}(\text{CO})_2(\text{acac})$ with La_2O_3 calcined in flowing O_2 at 873 K. EXAFS function, χ (solid line), and calculated contribution (dotted line) (A, unweighted; B, k^1 -weighted; and C, k^2 -weighted).

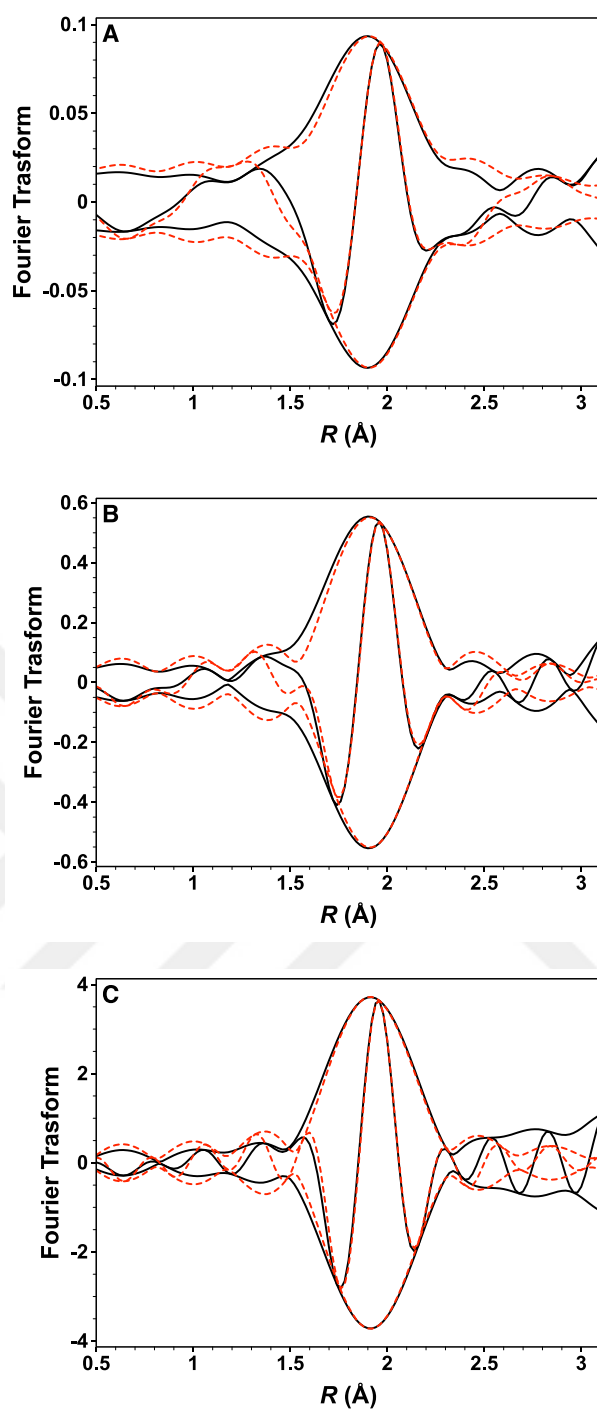


Figure A6-33. Imaginary part and magnitude of phase- and amplitude-corrected Fourier transform (A, unweighted; B, k^1 -weighted; and C, k^2 -weighted) of raw data minus calculated Ir–O_s, Ir–O_{CO} and Ir–O_I contribution (solid line) and calculated Ir–C_{CO} contribution (dotted line) characterizing the sample formed by the reaction of Ir(CO)₂(acac) with La₂O₃ calcined in flowing O₂ at 873 K.

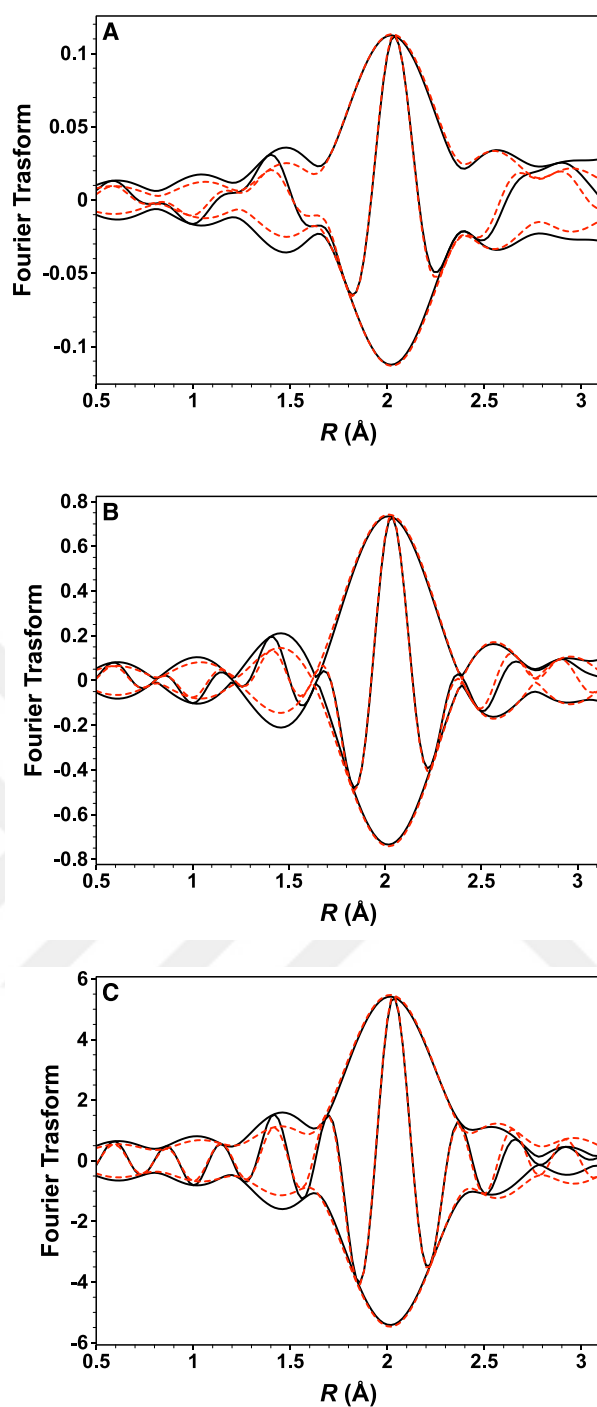


Figure A6-34. Imaginary part and magnitude of phase- and amplitude-corrected Fourier transform (A, unweighted; B, k^1 -weighted; and C, k^2 -weighted) of raw data minus calculated Ir-CO, Ir-O_{CO} and Ir-O_I contribution (solid line) and calculated Ir-O_s contribution (dotted line) characterizing the sample formed by the reaction of Ir(CO)₂(acac) with La₂O₃ calcined in flowing O₂ at 873 K.

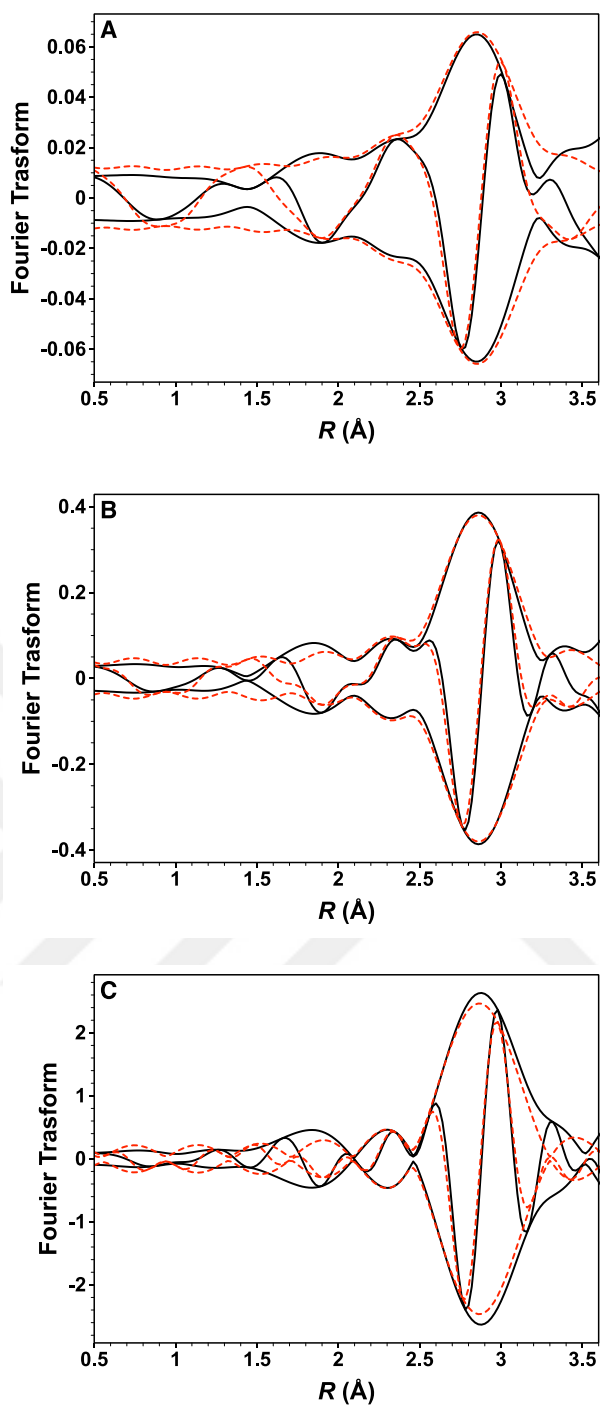


Figure A6-35. Imaginary part and magnitude of phase- and amplitude-corrected Fourier transform (A, unweighted; B, k^1 -weighted; and C, k^2 -weighted) of raw data minus calculated Ir-CO, Ir-O_s and Ir-O_l contribution (solid line) and calculated Ir-OCO contribution (dotted line) characterizing the sample formed by the reaction of Ir(CO)₂(acac) with La₂O₃ calcined in flowing O₂ at 873 K.

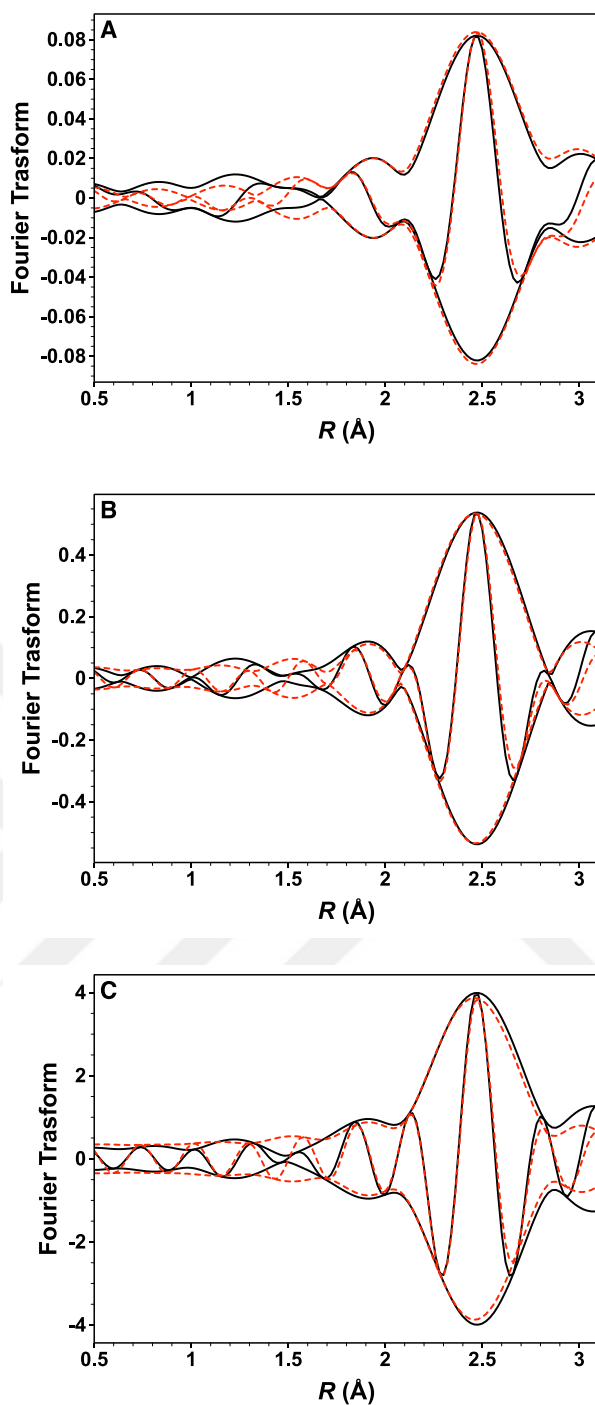


Figure A6-36. Imaginary part and magnitude of phase- and amplitude-corrected Fourier transform (A, unweighted; B, k^1 -weighted; and C, k^2 -weighted) of raw data minus calculated Ir-CO, Ir-O_s and Ir-O_{CO} contribution (solid line) and calculated Ir-O₁ contribution (dotted line) characterizing the sample formed by the reaction of Ir(CO)₂(acac) with La₂O₃ calcined in flowing O₂ at 873 K.

Table A6-1. Goodness of fit parameters and variance between data and EXAFS fits for each supported Ir(CO)₂ complexes.

Sample	Goodness of fit ^a	k^0 - weighted variance ^b (%)	k^{fit} - weighted variance ^b (%)	Variance in R space, ^{b, c} with a k^1 weighting (%)	
				Imaginary	Absolute
Ir(CO) ₂ /SiO ₂ ($\Delta k = 3.82 - 12.43 \text{ \AA}^{-1}$)	4.82	2.53	2.53	0.75	0.62
Ir(CO) ₂ /TiO ₂ ($\Delta k = 3.17 - 12.10 \text{ \AA}^{-1}$)	6.38	28.50	28.50	4.48	2.97
Ir(CO) ₂ /Fe ₂ O ₃ ($\Delta k = 3.92 - 11.30 \text{ \AA}^{-1}$)	1.88	21.0	21.0	1.55	0.40
Ir(CO) ₂ /CeO ₂ ($\Delta k = 3.92 - 12.60 \text{ \AA}^{-1}$)	3.85	5.60	5.60	2.29	0.18
Ir(CO) ₂ /MgO ($\Delta k = 4.02 - 11.30 \text{ \AA}^{-1}$)	3.13	8.94	8.94	4.86	1.89
Ir(CO) ₂ /La ₂ O ₃ ($\Delta k = 3.15 - 11.30 \text{ \AA}^{-1}$)	8.65	18.10	18.10	4.61	3.65

^a Goodness of fit values are calculated by XDAP as follows:

$$goodness\ of\ fit = \frac{\nu}{NPTS(\nu - N_{free})} \sum_{i=1}^{NPTS} \left(\frac{\chi_{exp,i} - \chi_{model,i}}{\sigma_{exp,i}} \right)^2$$

^b Variance between the k -weighted Fourier transform of the data and the fit over the fitting range (1.0–5.0 Å) was calculated by XDAP as follows:

$$k^n\ variance = \frac{\int [k^n(\chi_{model}(k) - \chi_{exp}(k))]^2 dk}{\int [k^n \chi_{exp}(k)]^2 dk} \times 100$$

^c Variance in R space is calculated by XDAP as follows:

$$k^n\ variance = \frac{\int [k^n(FT_{model}(R) - FT_{exp}(R))]^2 dR}{\int [k^n FT_{exp}(R)]^2 dR} \times 100$$

A6-2. Fourier Transform Infrared Spectroscopy (IR) Results

A6-2-1. Evidence of Atomically Dispersed Iridium Complexes Supported On Metal Oxides

Figure A6-37 present the IR spectra of the samples. The bands in 1300–1700 cm^{-1} region (given in Table A6-2) represent acetylacetone (Hacac) formed by the reaction of precursor acac ligands with support hydroxyl groups, forming structures similar to those obtained when Hacac is adsorbed on metal oxides.¹ The 1800–2200 cm^{-1} region of the IR spectrum of the precursor includes bands at 2049 and 1985 cm^{-1} characterizing the symmetric ($\nu_{\text{sym}}(\text{CO})$) and asymmetric ($\nu_{\text{asym}}(\text{CO})$) stretches of the CO ligands (Figure A6-37 and Table A6-2). The weak bands at 2029 and 1950 cm^{-1} represent natural-abundance ^{13}CO .² Spectra of the supported iridium complexes indicate distinct bands similar to those of the precursor $\text{Ir}(\text{CO})_2(\text{acac})$, assigned to the symmetric ($\nu_{\text{sym}}(\text{CO})$) and asymmetric ($\nu_{\text{asym}}(\text{CO})$) stretches of the CO ligands. We observed no bridging CO bands that would have indicated the presence of iridium clusters (which would have appeared in the range of 1850 to 1950 cm^{-1}).³ Thus, the IR data match the EXAFS data (Table 1) and show that $\text{Ir}(\text{CO})_2$ complexes were bonded to the metal oxides in the absence of detectable iridium clusters.⁴⁻⁵ Moreover, shoulders at 2028 and 2036 cm^{-1} in the spectra of the Fe_2O_3 - and CeO_2 -supported samples, respectively, indicate iridium carbonyls on minority surface sites.^{2,6}

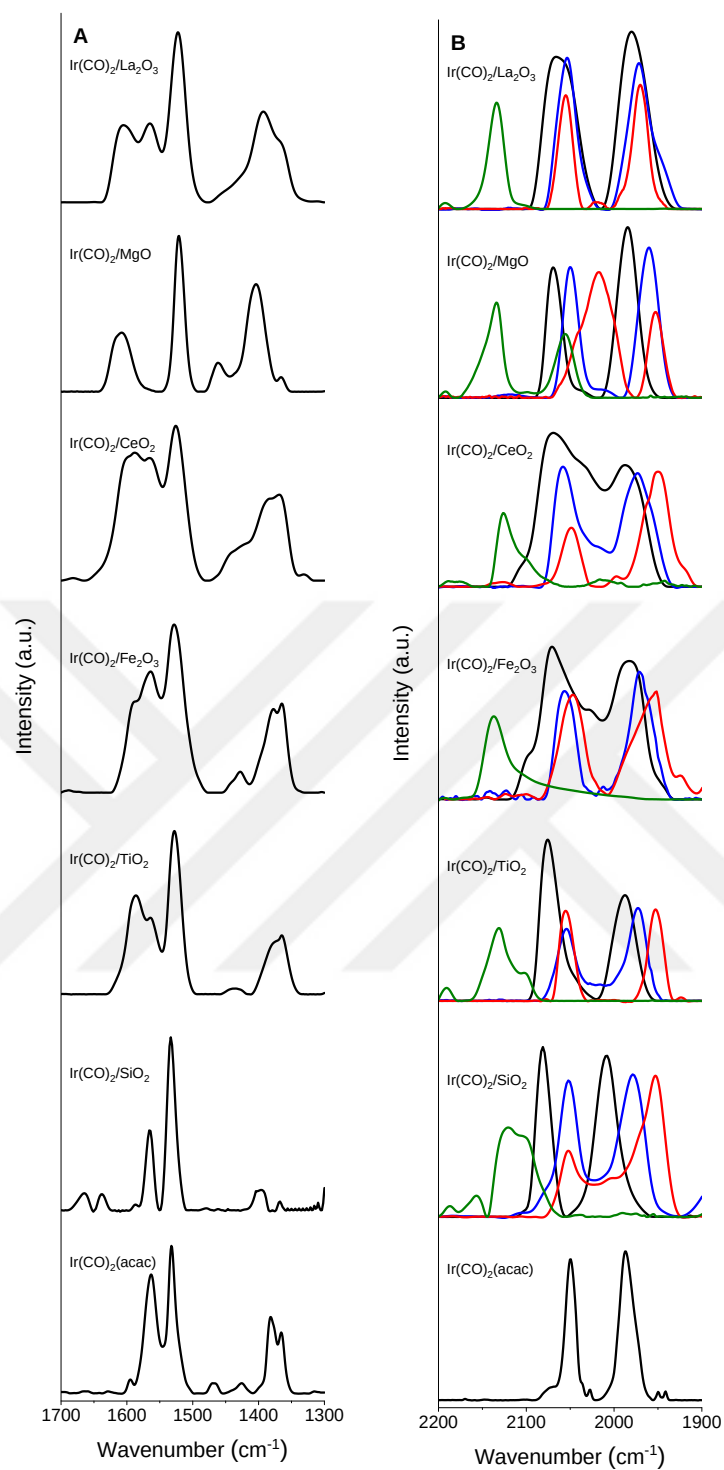
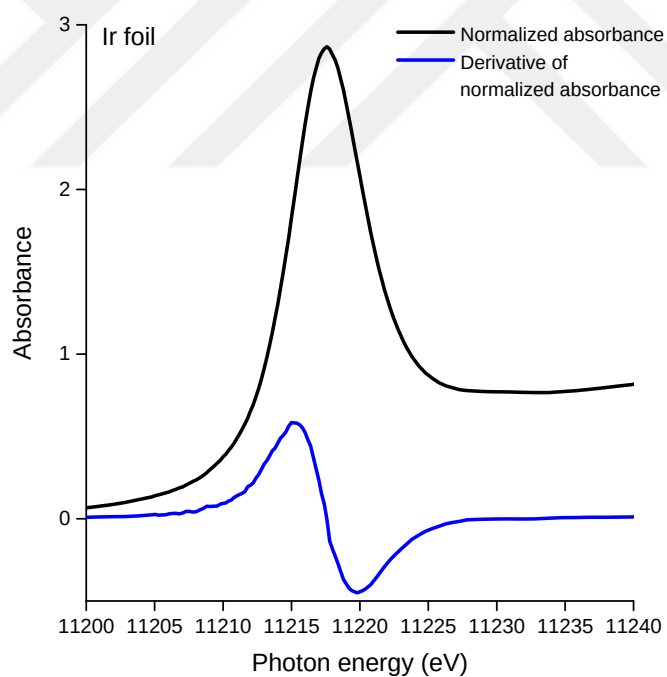


Figure A6-37. IR spectra of uncoated (black) and IL-coated ([BMIM][BF₄] (blue), [BMIM][Ac] (red), and [CPMIM][DCA] (green)) Ir(CO)₂ complexes supported on SiO₂, TiO₂, Fe₂O₃, CeO₂, MgO, and La₂O₃ in the region of A) 1300–1700 cm⁻¹ and B) 1800–2200 cm⁻¹.

Table A6-2. IR band positions of uncoated iridium complexes on various supports and the precursor in the acac region (1300–1700 cm⁻¹).

Sample	Frequencies of IR bands in 1300–1700 cm ⁻¹ region (cm ⁻¹)				
	$\delta_{\text{asym}}(\text{CH}_3)$	$\nu_{\text{asym}}(\text{CO})_{\text{rin}}$	$\delta_{\text{asym}}(\text{CH})$	$\nu_{\text{asym}}(\text{CCC})_{\text{rin}}$	$\nu_{\text{sym}}(\text{CO})_{\text{ring}}$
Ir(CO) ₂ (acac)	1365	1382	1427	1532	1563
Ir(CO) ₂ /SiO ₂	1372	1396	1432	1535	1569
Ir(CO) ₂ /TiO ₂	1365	1388	1436	1528	1559
Ir(CO) ₂ /Fe ₂ O ₃	1362	1393	1430	1527	1561
Ir(CO) ₂ /CeO ₂	1365	1386	1441	1525	1559
Ir(CO) ₂ /MgO	1365	1404	1460	1541	1568
Ir(CO) ₂ /La ₂ O ₃	1361	1393	1450	1540	1568

A6-3. X-Ray Absorption Near Edge Structure (XANES) Results**Figure A6-3.** Normalized (black) and derivative of normalized (blue) XANES spectra at the Ir L_{III} edge characterizing iridium foil.

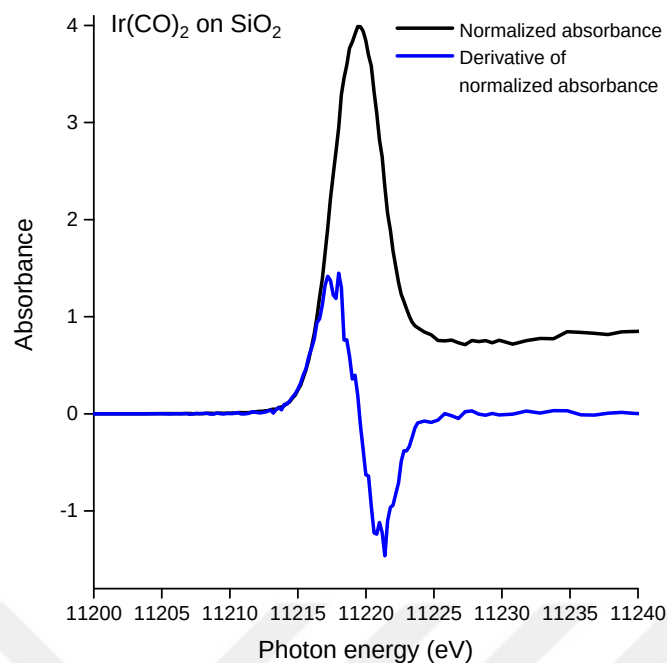


Figure A6-4. Normalized (black) and derivative of normalized (blue) XANES spectra at the Ir L_{III} edge characterizing uncoated Ir(CO)₂ complexes on SiO₂.

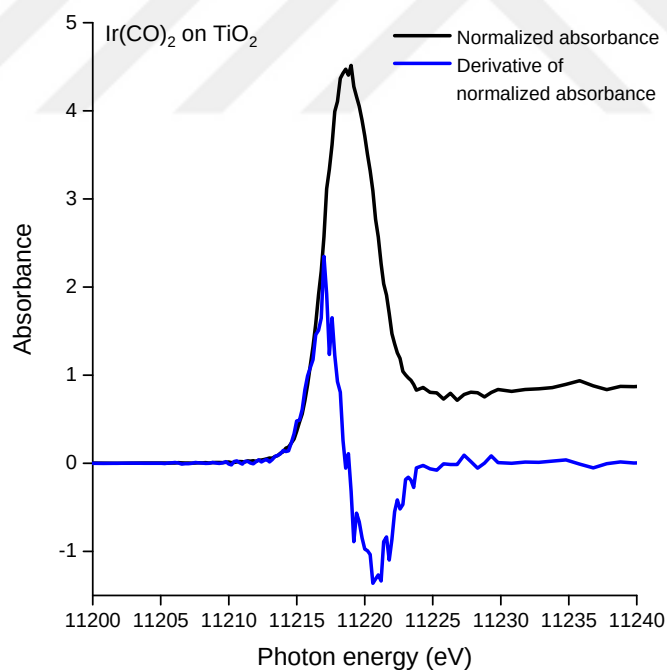


Figure A6-40. Normalized (black) and derivative of normalized (blue) XANES spectra at the Ir L_{III} edge characterizing uncoated Ir(CO)₂ complexes on TiO₂.

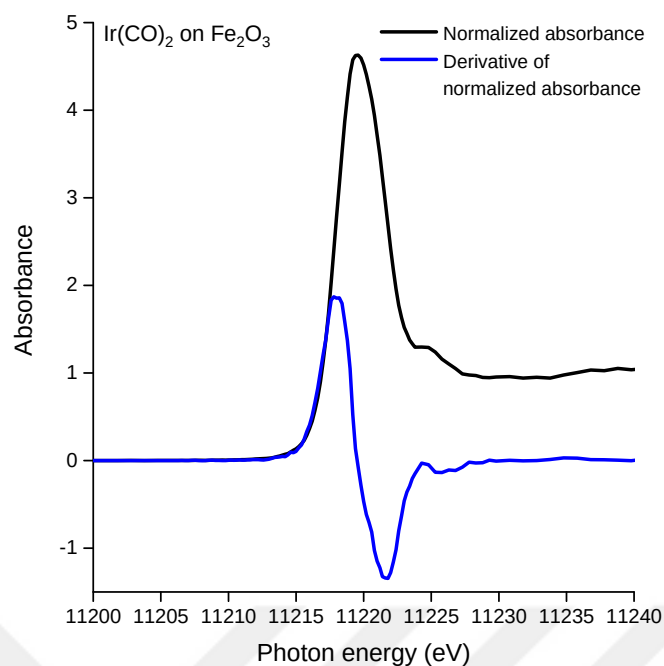


Figure A6-41. Normalized (black) and derivative of normalized (blue) XANES spectra at the Ir L_{III} edge characterizing uncoated Ir(CO)₂ complexes on Fe₂O₃.

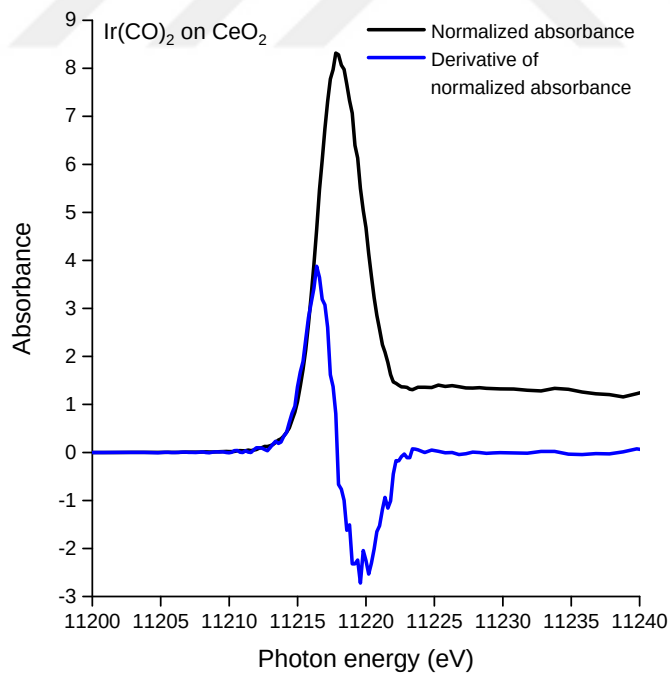


Figure A6-52. Normalized (black) and derivative of normalized (blue) XANES spectra at the Ir L_{III} edge characterizing uncoated Ir(CO)₂ complexes on CeO₂.

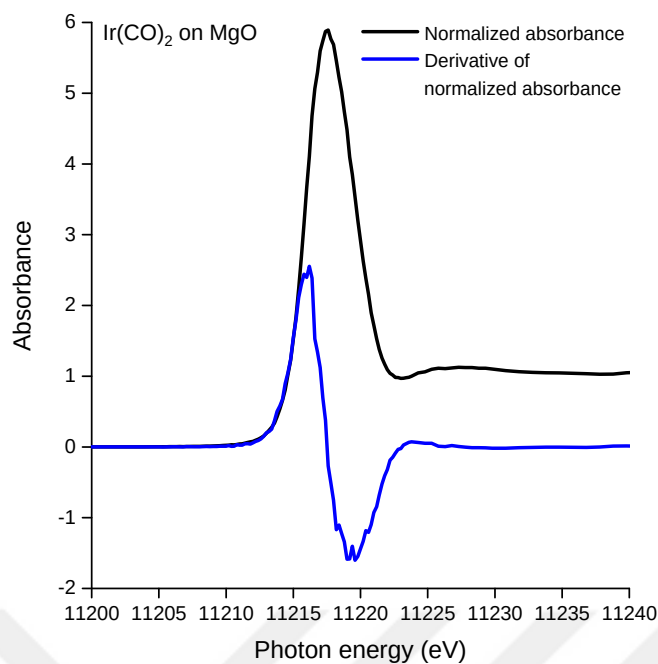


Figure A6-43. Normalized (black) and derivative of normalized (blue) XANES spectra at the Ir L_{III} edge characterizing uncoated Ir(CO)₂ complexes on MgO.

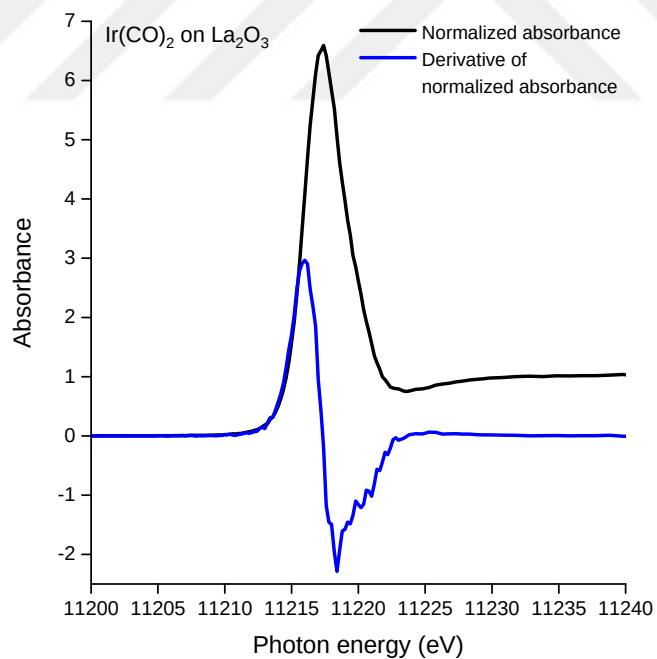


Figure A6-44. Normalized (black) and derivative of normalized (blue) XANES spectra at the Ir L_{III} edge characterizing uncoated Ir(CO)₂ complexes on La₂O₃.

Table A6-3. Ir L_{III} edge energies of uncoated, [BMIM][BF₄]-coated, [BMIM][Ac]-coated, and [CPMIM][DCA]-coated supported Ir(CO)₂ complexes.

Supported Ir(CO) ₂ Complex	Ir L _{III} edge energy (eV)
Ir(CO) ₂ /SiO ₂	11218.0
Ir(CO) ₂ /TiO ₂	11217.0
Ir(CO) ₂ /Fe ₂ O ₃	11217.5
Ir(CO) ₂ /CeO ₂	11216.4
Ir(CO) ₂ /MgO	11216.2
Ir(CO) ₂ /La ₂ O ₃	11216.0

A6-4. Scanning Electron Microscopy Coupled with Energy-Dispersive X-ray Spectroscopy (SEM/EDX) Analysis

A6-4-1. Uniform Distribution of IL Molecules

The IL loadings of the samples, prepared by bringing each supported iridium complex in contact with the respective IL and then adding excess calcined support to absorb the excess IL, were set to 20 wt% (and the corresponding Ir loading was 0.4 wt%). To get an indication of the uniformity of the IL coatings on the scale of SEM/EDX images, we collected data for a representative [BMIM][BF₄]-coated sample set (Figure A6-45); the distribution of fluorine atoms on the scale of the images confirms that the IL was distributed uniformly over the surface. Assuming that this result can be generalized, the average spacing of the Ir atoms was estimated in the range of 1–3 nm, depending on the support's surface area. SEM/EDX images (Table A6-4 and Figures A6-46 to A6-51) indicate that the IL loadings ranged from 8–25 wt% in the respective imaged regions. Accordingly, these Ir and IL loadings correspond to approximately 45 ± 3 IL molecules per Ir site with a maximum of a few molecular layers of IL layer. We infer that these values are sufficient to ensure the availability of at least one IL

molecule in the vicinity of each Ir center assuming a uniform Ir site distribution over the supports.

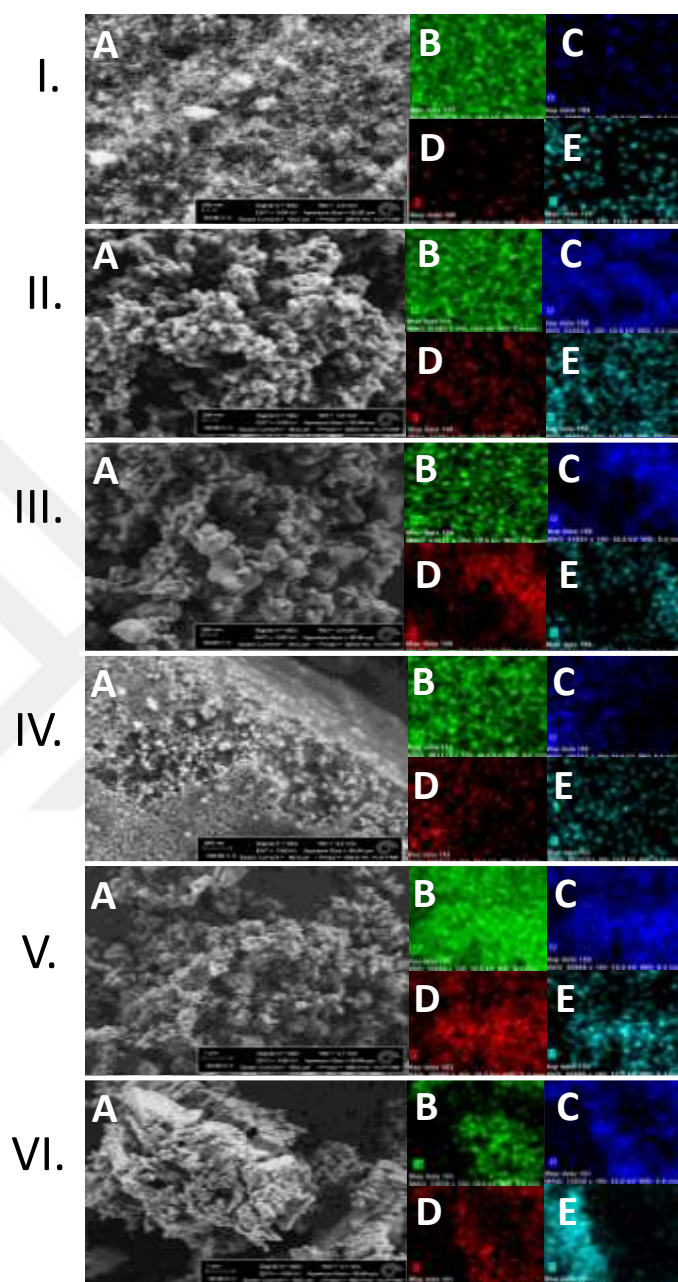


Figure A6-45. SEM images characterizing a representative sample set of [BMIM][BF₄]-coated Ir(CO)₂ complexes supported on various metal oxides: SiO₂ (IA), TiO₂ (IIA), Fe₂O₃ (IIIA), CeO₂ (IVA), MgO (VA), La₂O₃ (VIA). EDX map showing the distribution of the individual elements Si (IB), Ti (IIB), Fe (IIIB), Ce (IVB), Mg (VIB), La (VIIB), O (IC, IIC, IIIC, IVC, VC, VIC), F (ID, IID, IIID, IVD, VD, VID), and C (IE, IIE, IIIE, IVE, VE, VIE).

EDX spectra of IL-coated supported Ir(CO)₂ complexes are given in Figures A6-58 to A6-S63.

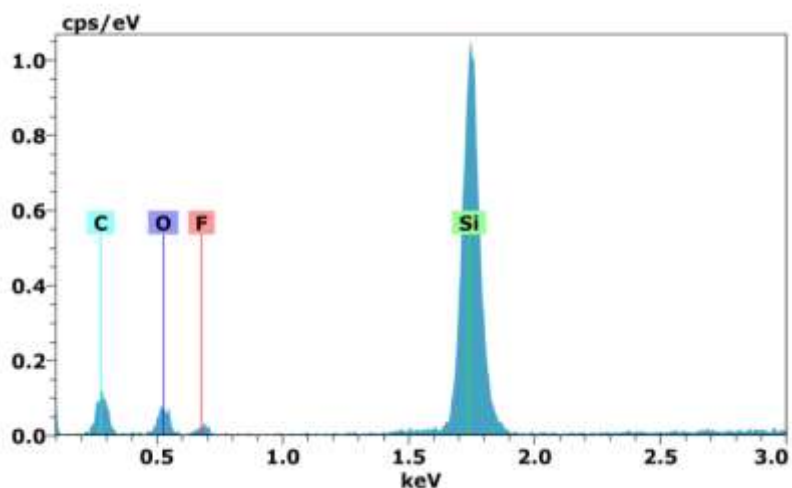


Figure A6-46. EDX spectra of [BMIM][BF₄]-coated Ir(CO)₂/SiO₂.

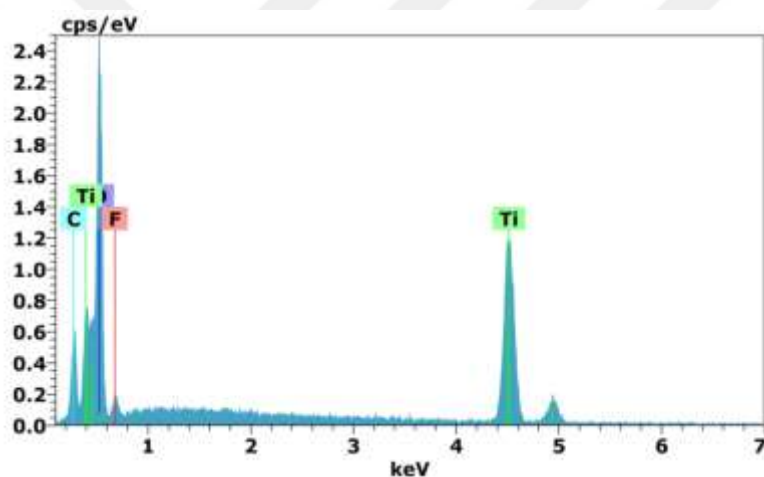


Figure A6-47. EDX spectra of [BMIM][BF₄]-coated Ir(CO)₂/TiO₂.

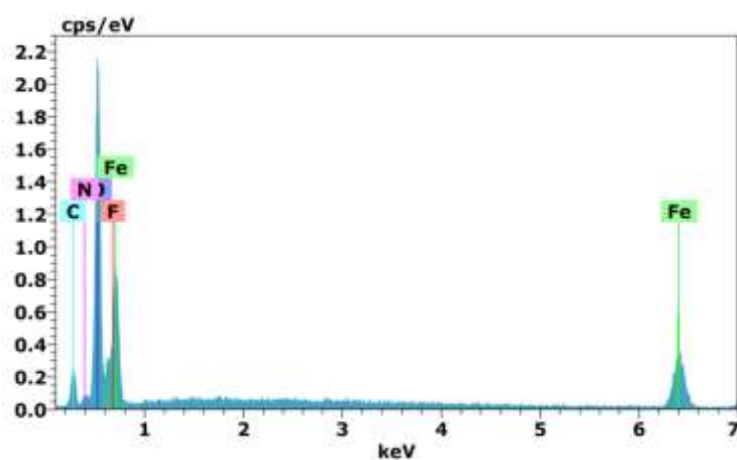


Figure A6-48. EDX spectra of [BMIM][BF₄]-coated Ir(CO)₂/Fe₂O₃.

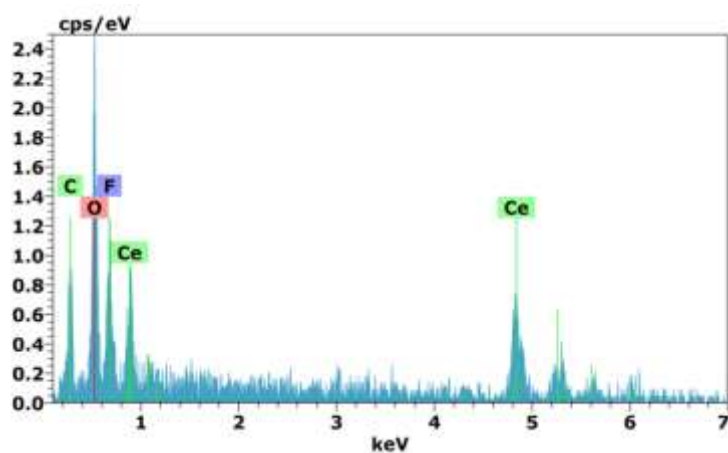


Figure A6-49. EDX spectra of [BMIM][BF₄]-coated Ir(CO)₂/CeO₂.

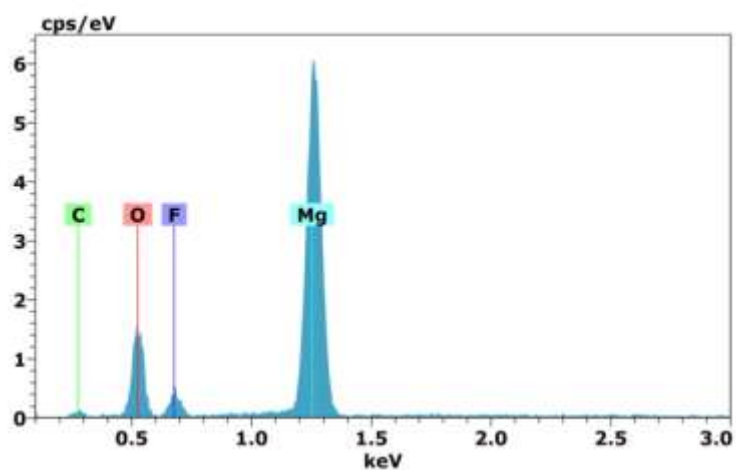


Figure A6-50. EDX spectra of [BMIM][BF₄]-coated Ir(CO)₂/MgO.

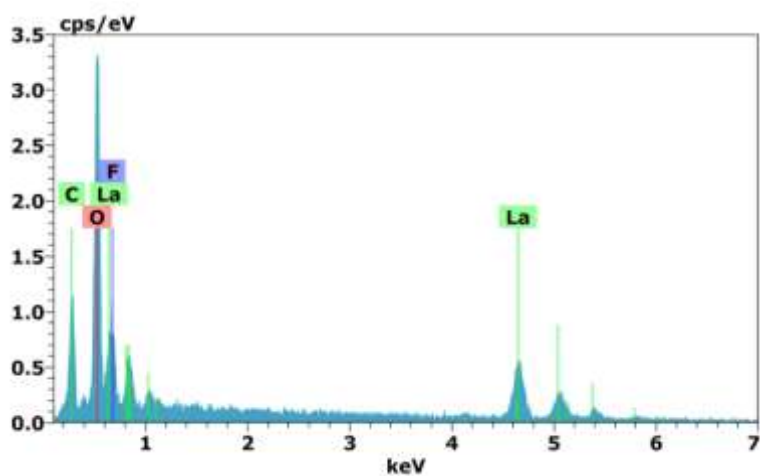


Figure A6-51. EDX spectra of [BMIM][BF₄]-coated Ir(CO)₂/La₂O₃.

Table A6-4. [BMIM][BF₄] loading amount on supported Ir(CO)₂ complexes. These values are calculated by using integrals of EDX spectra area of each sample.

Samples	Calculated IL loading (%)
[BMIM][BF ₄]-coated Ir(CO) ₂ /SiO ₂	23
[BMIM][BF ₄]-coated Ir(CO) ₂ /TiO ₂	18
[BMIM][BF ₄]-coated Ir(CO) ₂ /Fe ₂ O ₃	8
[BMIM][BF ₄]-coated Ir(CO) ₂ /CeO ₂	16
[BMIM][BF ₄]-coated Ir(CO) ₂ /MgO	22
[BMIM][BF ₄]-coated Ir(CO) ₂ /La ₂ O ₃	24

A6-5. IR Evidence of Atomically Dispersed Supported Iridium Complexes After IL Coating

IR spectra comparing the features of the uncoated and IL-coated samples along with those of the bulk ILs are shown in Figure A6-37 and Figures A6-52 to A6-54. The data confirm presence of the IL and show that the supported complexes were still present as site-isolated iridium *gem*-dicarbonyls. The spectra of the IL-coated samples, like those of the uncoated samples, are characterized by two distinct carbonyl stretching bands of the supported iridium species.

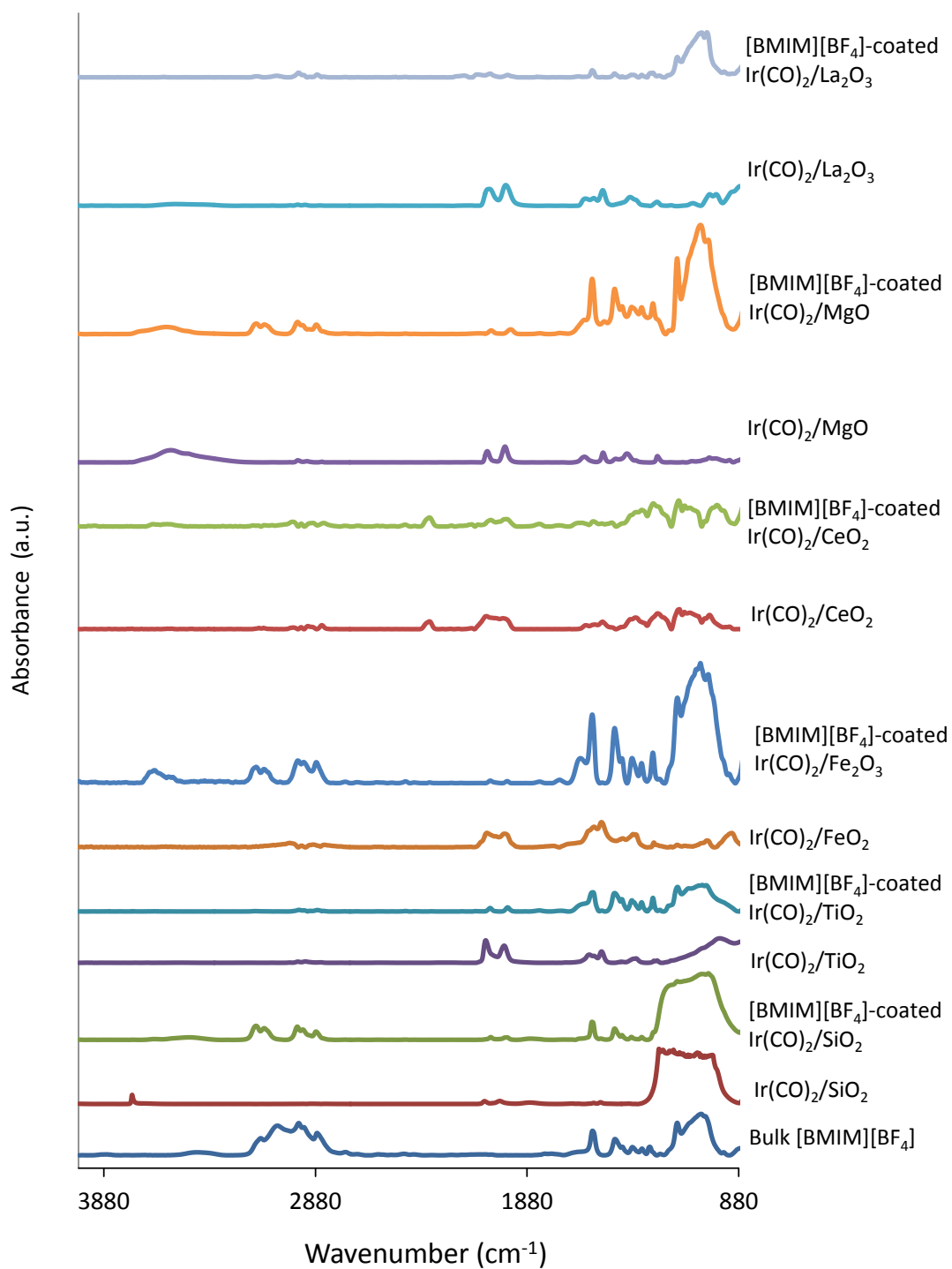


Figure A6-6. IR data comparing the structural features of bulk [BMIM][BF₄] with those of coated and uncoated Ir(CO)₂ complexes prepared on different supports.

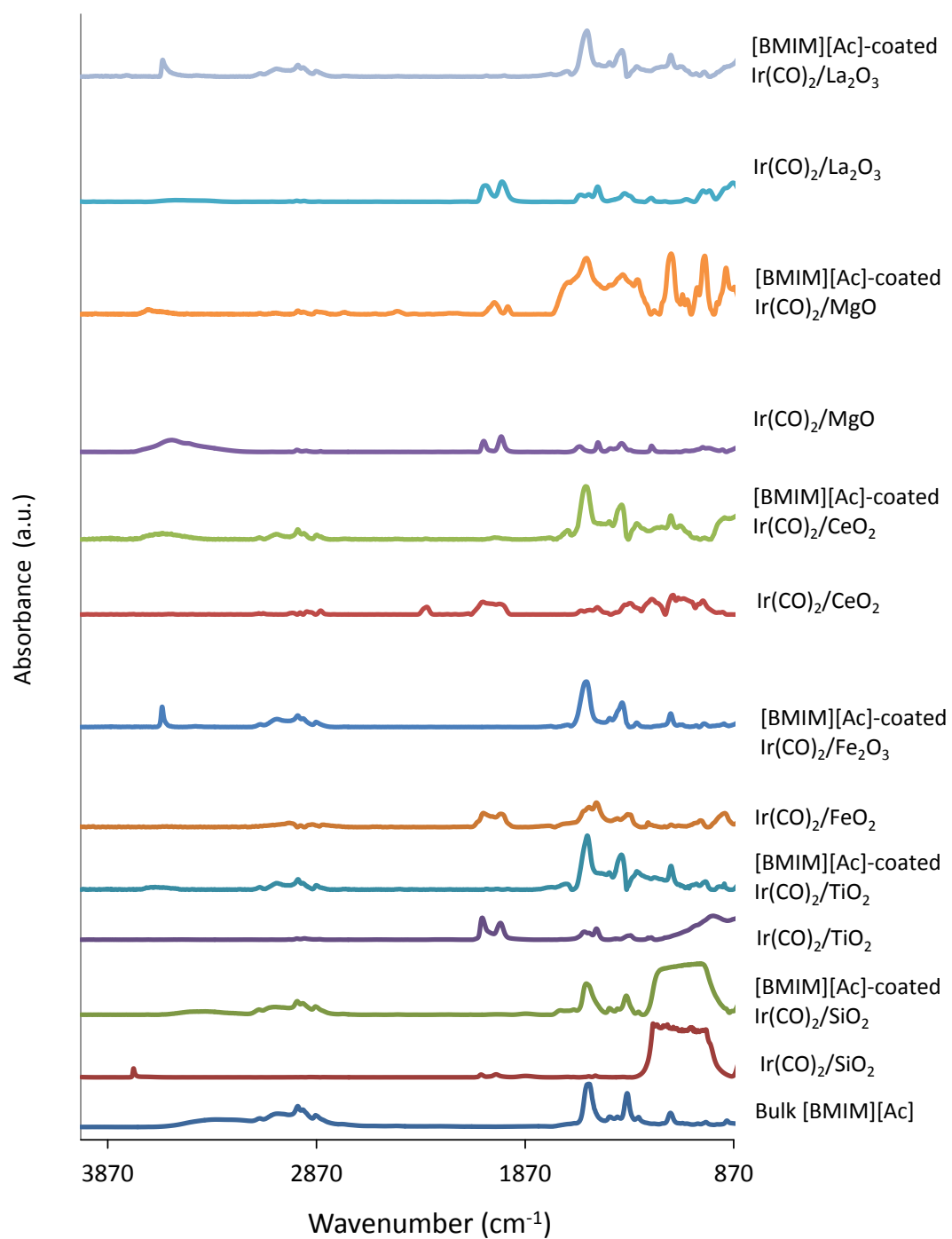


Figure A6-53. IR data comparing the structural features of bulk [BMIM][Ac] with those of coated and uncoated $\text{Ir}(\text{CO})_2$ complexes prepared on different supports.

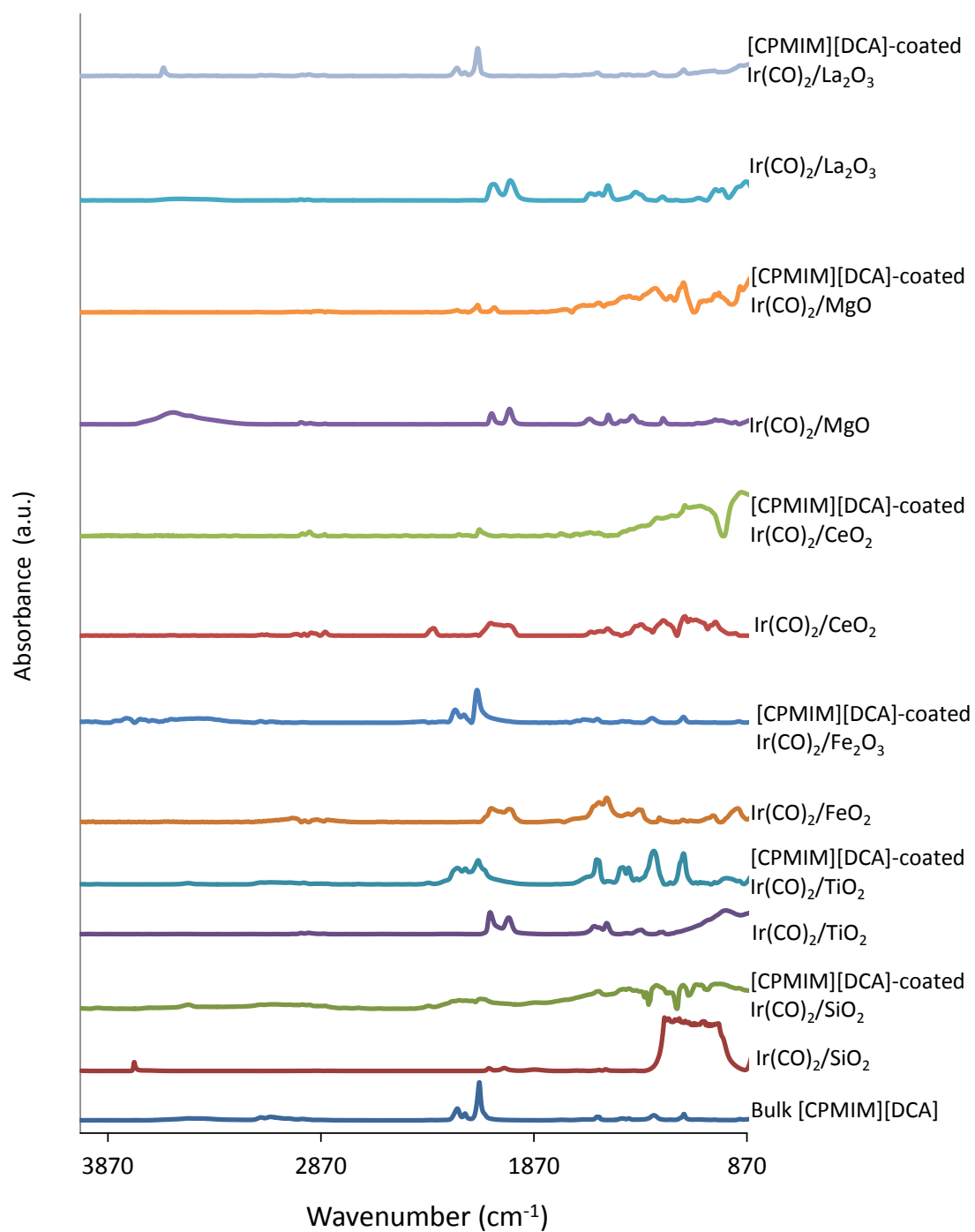


Figure A6-7. IR data comparing the structural features of bulk [CPMIM][DCA] with those of coated and uncoated $\text{Ir}(\text{CO})_2$ complexes prepared on different supports.

A6-6. Evidence Confirming Iridium Complexes Remained Bonded to Supports in the Presence of ILs

To rule out the possibility that the iridium complex was removed from the surface and dissolved in the IL coating, we washed some IL-coated samples in methanol and checked the IR spectra of the filtrates and the washed samples. No vibrational bands associated with iridium carbonyls were detected in the filtrates, and the spectra of the washed samples still indicated the presence of the iridium carbonyls (although the peak positions and shapes were changed by the treatments, as illustrated in Figure A6-55 for a representative sample [BMIM][BF₄]-coated Ir(CO)₂/MgO). These results show that the iridium complexes remained bonded to the support even after the samples were coated with the ILs and did not dissolve in the IL.

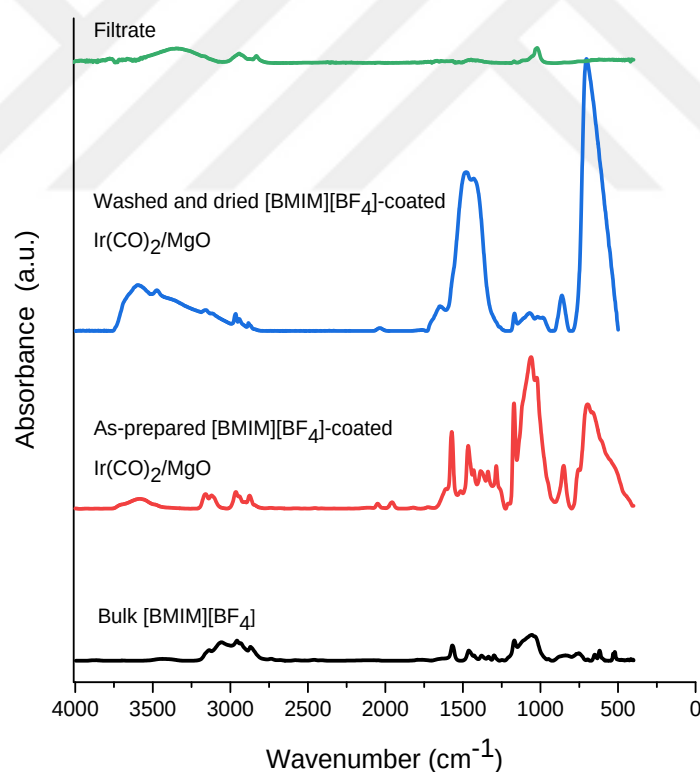


Figure A6-558. IR spectra characterizing the [BMIM][BF₄]-coated Ir(CO)₂/MgO sample before and after washing with methanol: Bulk [BMIM][BF₄] (black); as-prepared [BMIM][BF₄]-coated Ir(CO)₂/MgO (red); washed (in methanol) and dried (at 353 K in air) [BMIM][BF₄]-coated Ir(CO)₂/MgO (blue); and the filtrate of washing (green).

A6-7. Catalyst Performance Measurements

Each catalyst was first activated by removal of one of the CO ligands per each Ir atom by treatment in flowing ethylene at 373 K; this treatment incorporated ethylene ligands in place of CO, which is a strong catalytic reaction inhibitor,⁷ as reported for similar metal carbonyl complexes supported on metal oxides and zeolites.⁷⁻⁸

IR spectra recorded before and after ethylene exposure (Figures A6-56 to A6-78), indicate changes in the intensities and positions of the $\nu(\text{CO})$ bands as well as the formation of new bands, but none indicating the formation of carbonyls bonded to neighboring iridium centers, which would have indicated iridium cluster formation.⁹ New bands located between the two carbonyl stretching bands are consistent with the partial replacement of CO with ethylene.⁷⁻⁸ For example, in the spectrum of the TiO_2 -supported iridium complex coated with [BMIM][BF₄], the intensity of the $\nu_{\text{asym}}(\text{CO})$ band at 1988 cm^{-1} decreased slightly relative to that of the $\nu_{\text{sym}}(\text{CO})$ band, accompanied by the appearance of two new bands, at 2030 and 2048 cm^{-1} , assigned to $\text{Ir}(\text{CO})(\text{C}_2\text{H}_4)$ and $\text{Ir}(\text{CO})(\text{C}_2\text{H}_4)_2$, respectively.^{5,10} The areas of the $\nu(\text{CO})$ bands indicate that the supported complexes were converted into mixtures of $\text{Ir}(\text{CO})_2$ (~74%), $\text{Ir}(\text{CO})(\text{C}_2\text{H}_4)$ (~16%), and $\text{Ir}(\text{CO})(\text{C}_2\text{H}_4)_2$ (~10%) on TiO_2 , for example. Data characterizing other samples indicate the presence of mixtures of $\text{Ir}(\text{CO})_2$, $\text{Ir}(\text{CO})(\text{C}_2\text{H}_4)$, and $\text{Ir}(\text{CO})(\text{C}_2\text{H}_4)_2$ in varying concentrations (Table A6-5).

Table A6-5. Relative concentrations (%) of the supported $\text{Ir}(\text{CO})_2$, $\text{Ir}(\text{CO})(\text{C}_2\text{H}_4)$, and $\text{Ir}(\text{CO})(\text{C}_2\text{H}_4)_2$ species formed by treatment of the IL-coated and uncoated supported $\text{Ir}(\text{CO})_2$

complexes in flowing C₂H₄ at 373 K and their corresponding $\nu(\text{CO})$ values given in parentheses in units of cm⁻¹.

Supported Complex	Ir(CO) ₂	Percentages of species after ethylene treatment (%) with corresponding $\nu_{\text{sym}}(\text{CO})$ and $\nu_{\text{asym}}(\text{CO})$ (cm ⁻¹) band positions		
		Ir(CO) ₂ *	Ir(CO)(C ₂ H ₄)	Ir(CO)(C ₂ H ₄) ₂ **
Ir(CO) ₂ /SiO ₂		78 (2081, 2008)	22 (2045)	ND
Ir(CO) ₂ /TiO ₂		74 (2076, 1988)	16 (2030)	10 (2048)
Ir(CO) ₂ /Fe ₂ O ₃		55 (2073, 1979)	41 (2034)	4 (2052)
Ir(CO) ₂ /CeO ₂		68 (2071, 2057)	16 (2029)	16 (2041)
Ir(CO) ₂ /MgO		75 (2069, 1985)	17 (2032)	8 (2056)
Ir(CO) ₂ /La ₂ O ₃		68 (2066, 1977)	23 (2020)	9 (2051)
[BMIM][BF ₄]-coated		71 (2052, 1981)	29 (2031)	ND
[BMIM][BF ₄]-coated		64 (2055, 1971)	23 (2027)	13 (2041)
[BMIM][BF ₄]-coated		59 (2056, 1969)	41 (2024)	ND
[BMIM][BF ₄]-coated		86 (2057, 1974)	12 (2021)	2 (2042)
[BMIM][BF ₄]-coated		49 (2058, 1960)	51 (2024)	ND
[BMIM][BF ₄]-coated		61 (2055, 1972)	39 (2018)	ND
[BMIM][Ac]-coated		81 (2049, 1953)	19 (2039)	ND
[BMIM][Ac]-coated		57 (2052, 1962)	43 (2018)	ND
[BMIM][Ac]-coated		83 (2053, 1947)	17 (2021)	ND
[BMIM][Ac]-coated		47 (2050, 1966)	38 (2027)	15 (2038)
[BMIM][Ac]-coated		75 (2056, 1956)	25 (2008)	ND
[BMIM][Ac]-coated		95 (2053, 1970)	5 (2019)	ND
[CPMIM][DCA]-coated		93 (2098, 1974)	7 (2035)	ND
[CPMIM][DCA]-coated		91 (2084, 1956)	9 (2023)	ND
[CPMIM][DCA]-coated		96 (2081, 1973)	4 (2032)	ND
[CPMIM][DCA]-coated		89 (2074, 1963)	ND	11 (2045)
[CPMIM][DCA]-coated		76 (2064, 1959)	24 (2015)	ND
[CPMIM][DCA]-coated		88 (2061, 1973)	12 (2020)	ND

*Value calculated on the basis of sum of the intensities of $\nu_{\text{sym}}(\text{CO})$ and $\nu_{\text{asym}}(\text{CO})$.

**ND: not detected.

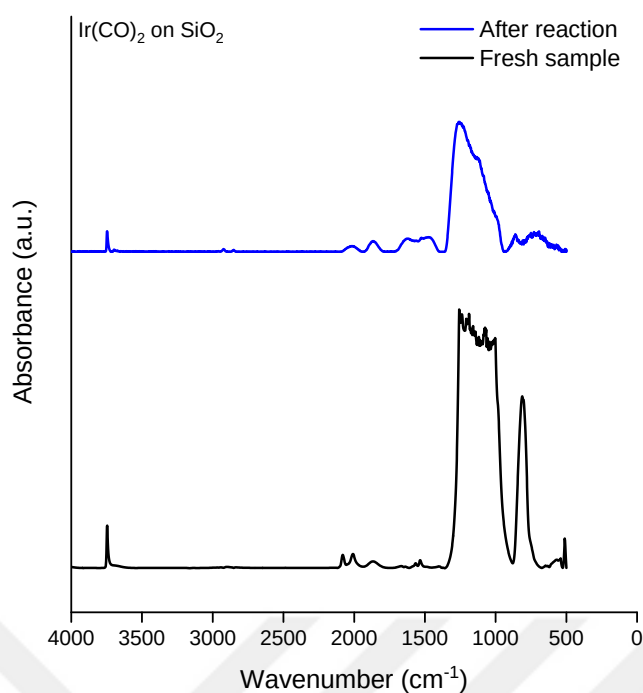


Figure A6-56. IR spectra of uncoated Ir(CO)₂ complexes on SiO₂ before (black) and after (blue) ethylene exposure.

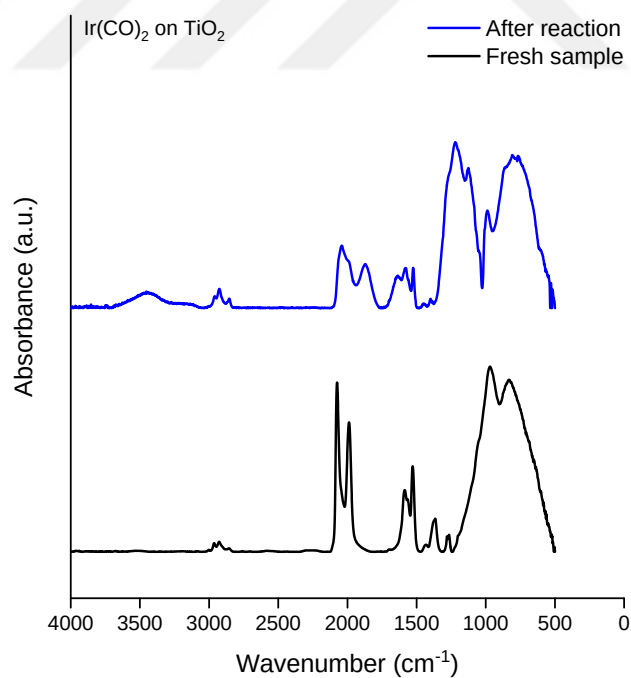


Figure A6-57. IR spectra of uncoated Ir(CO)₂ complexes on TiO₂ before (black) and after (blue) ethylene exposure.

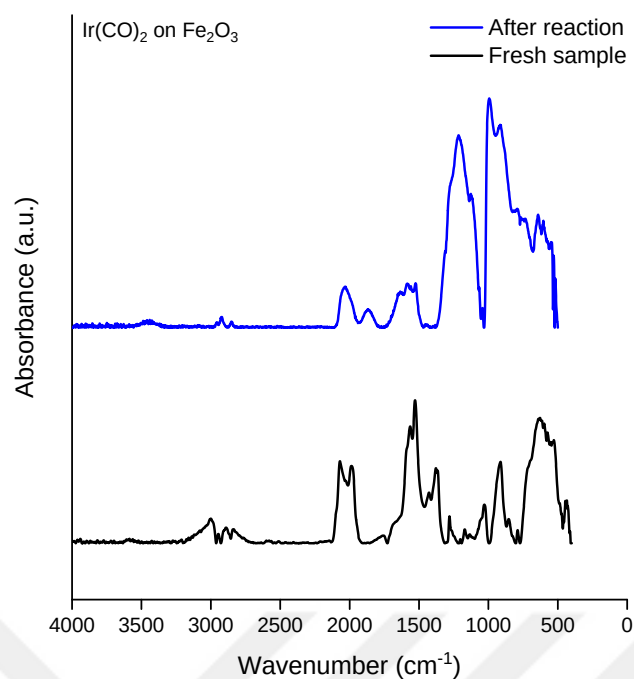


Figure A6-58. IR spectra of uncoated Ir(CO)_2 complexes on Fe_2O_3 before (black) and after (blue) ethylene exposure.

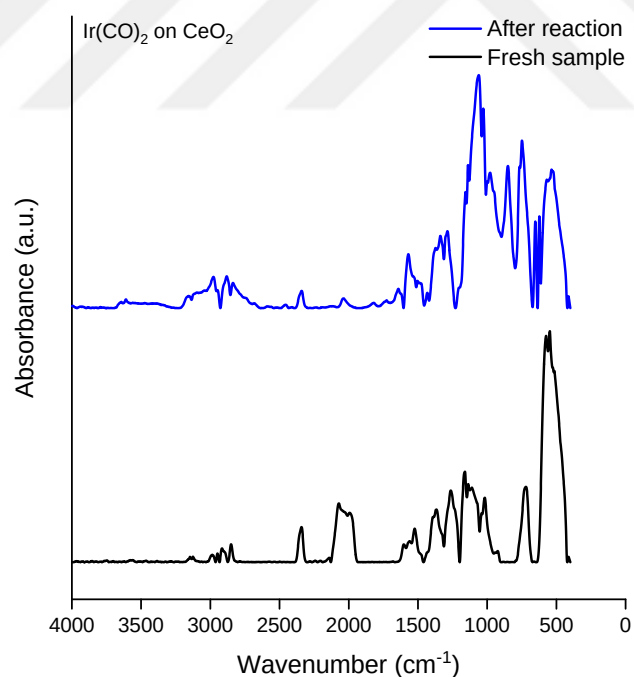


Figure A6-59. IR spectra of uncoated Ir(CO)_2 complexes on CeO_2 before (black) and after (blue) ethylene exposure.

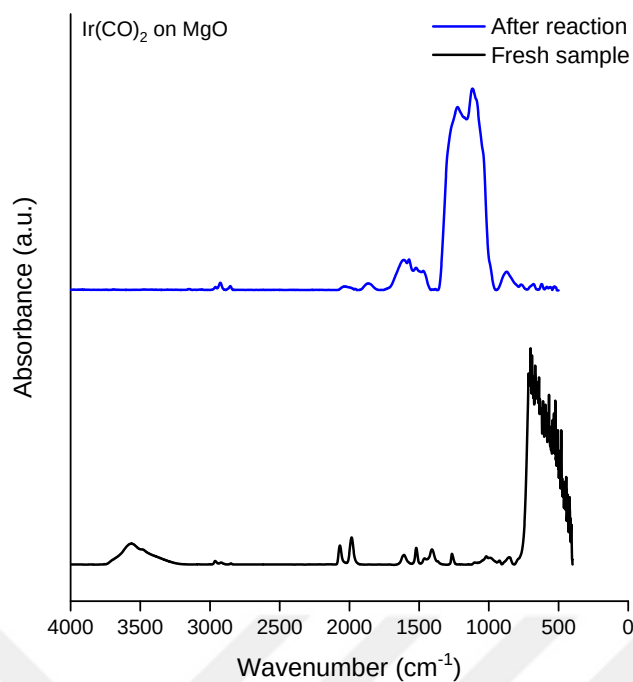


Figure A6-60. IR spectra of uncoated Ir(CO)₂ complexes on MgO before (black) and after (blue) ethylene exposure.

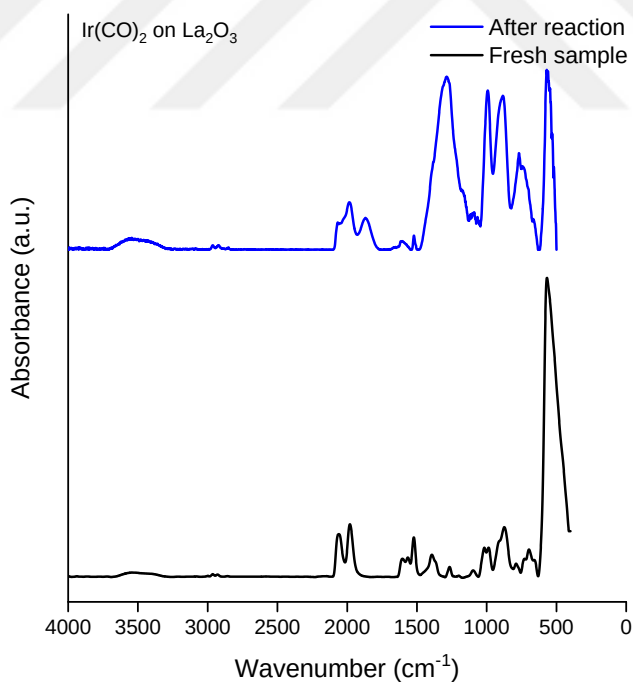


Figure A6-61. IR spectra of uncoated Ir(CO)₂ complexes on La₂O₃ before (black) and after (blue) ethylene exposure.

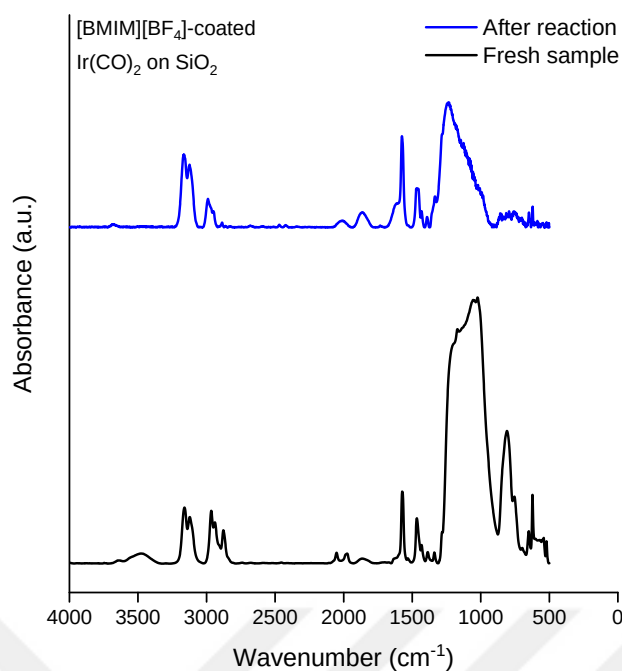


Figure A6-62. IR spectra of [BMIM][BF₄]-coated Ir(CO)₂ complexes on SiO₂ before (black) and after (blue) ethylene exposure.

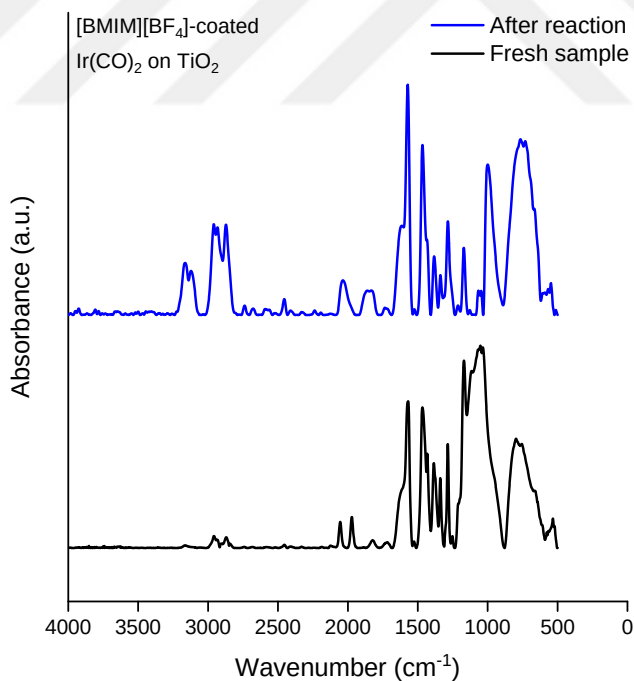


Figure A6-63. IR spectra of [BMIM][BF₄]-coated Ir(CO)₂ complexes on TiO₂ before (black) and after (blue) ethylene exposure.

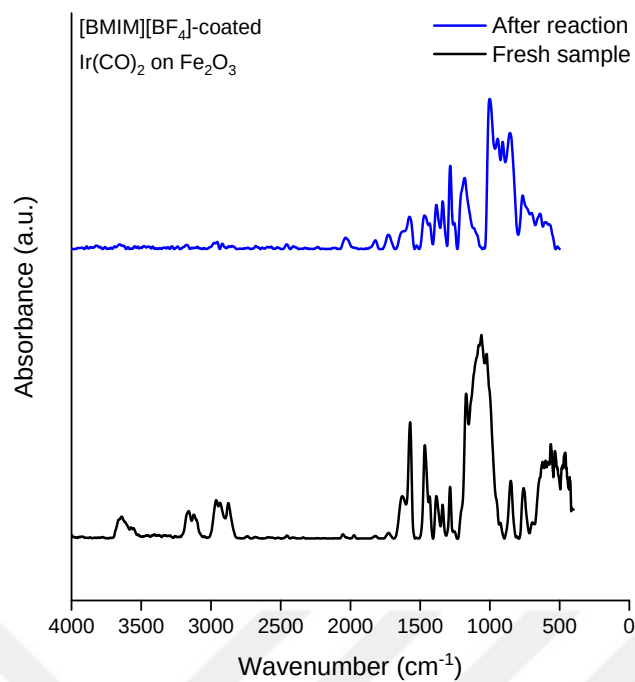


Figure A6-64. IR spectra of [BMIM][BF₄]-coated Ir(CO)₂ complexes on Fe₂O₃ before (black) and after (blue) ethylene exposure.

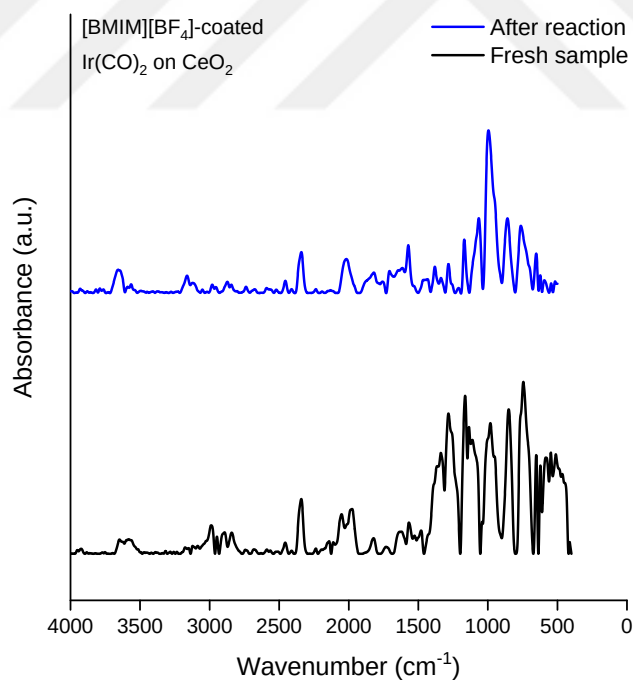


Figure A6-65. IR spectra of [BMIM][BF₄]-coated Ir(CO)₂ complexes on CeO₂ before (black) and after (blue) ethylene exposure.

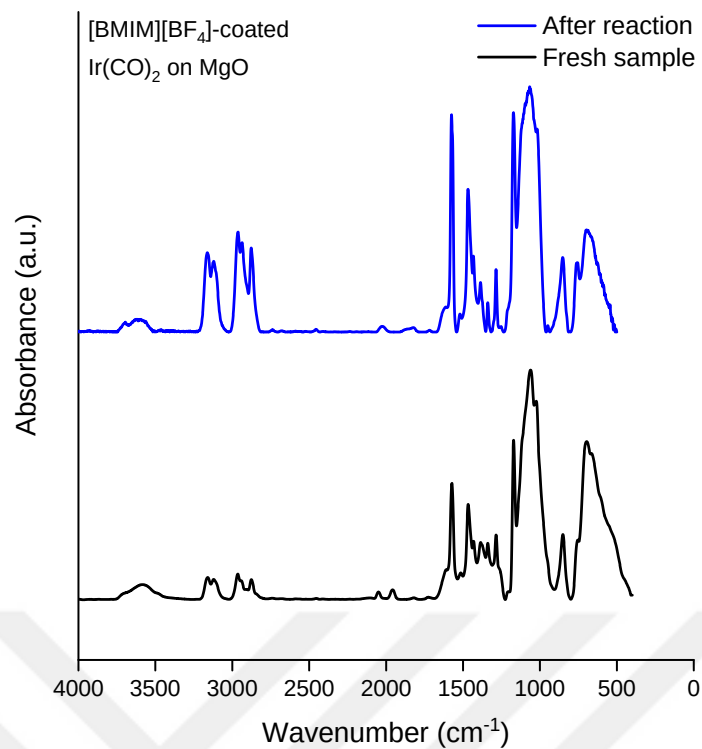


Figure A6-66. IR spectra of [BMIM][BF₄]-coated Ir(CO)₂ complexes on MgO before (black) and after (blue) ethylene exposure.

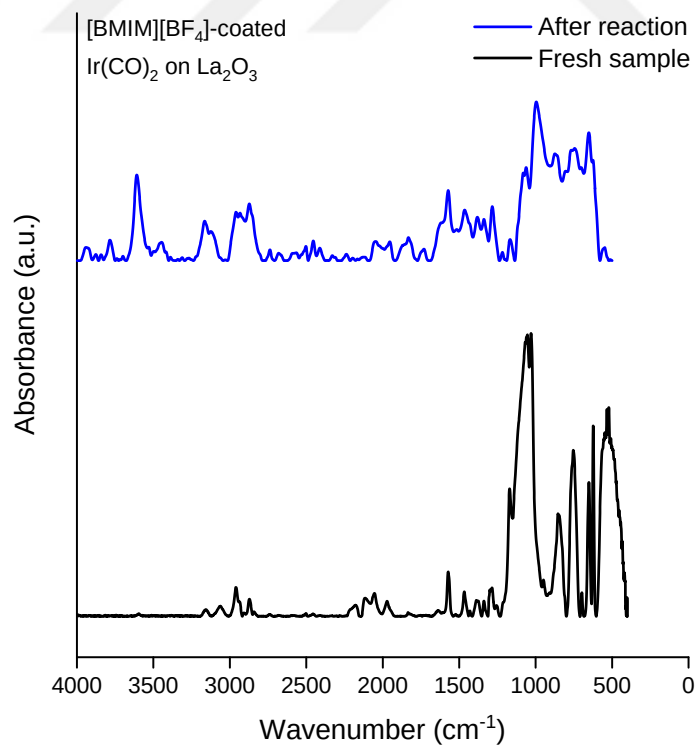


Figure A6-67. IR spectra of [BMIM][BF₄]-coated Ir(CO)₂ complexes on La₂O₃ before (black) and after (blue) ethylene exposure.

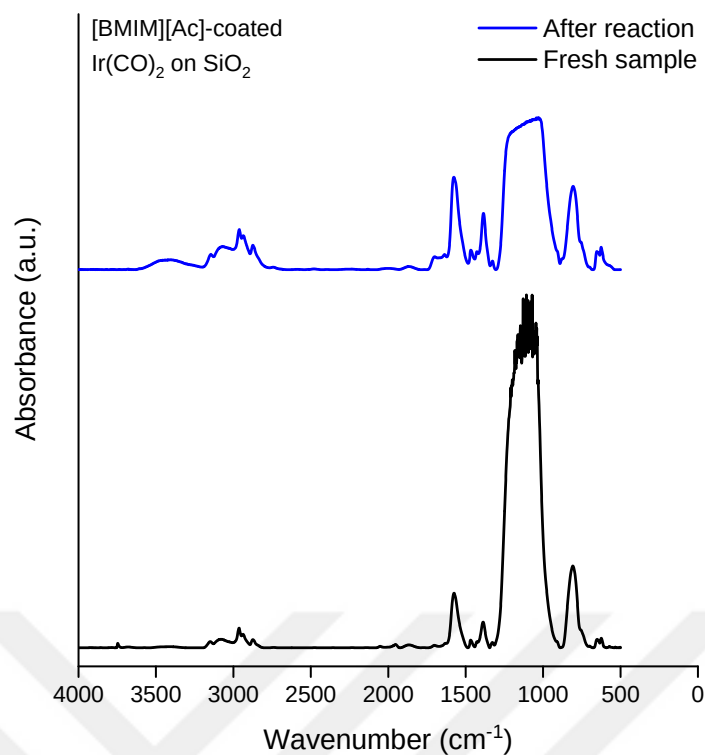


Figure A6-68. IR spectra of [BMIM][Ac]-coated Ir(CO)₂ complexes on SiO₂ before (black) and after (blue) ethylene exposure.

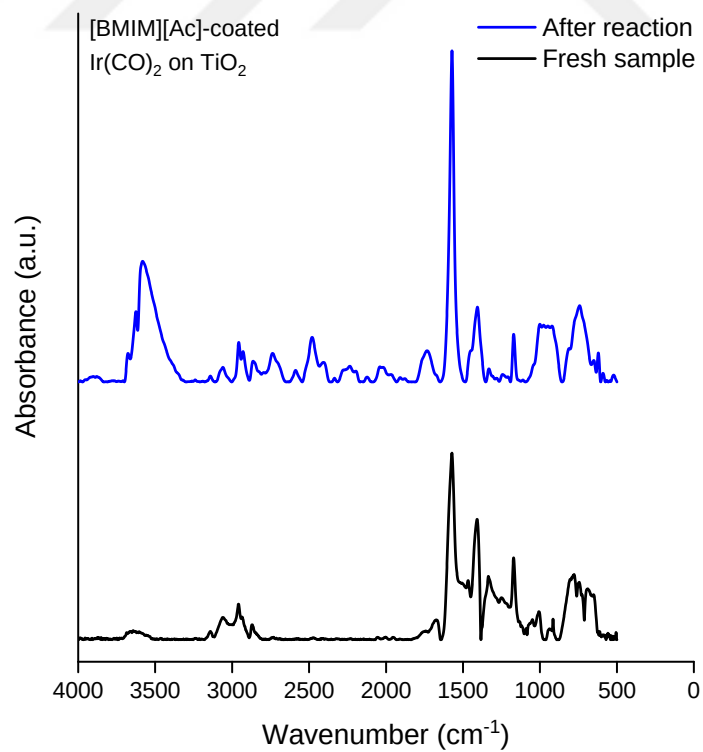


Figure A6-69. IR spectra of [BMIM][Ac]-coated Ir(CO)₂ complexes on TiO₂ before (black) and after (blue) ethylene exposure.

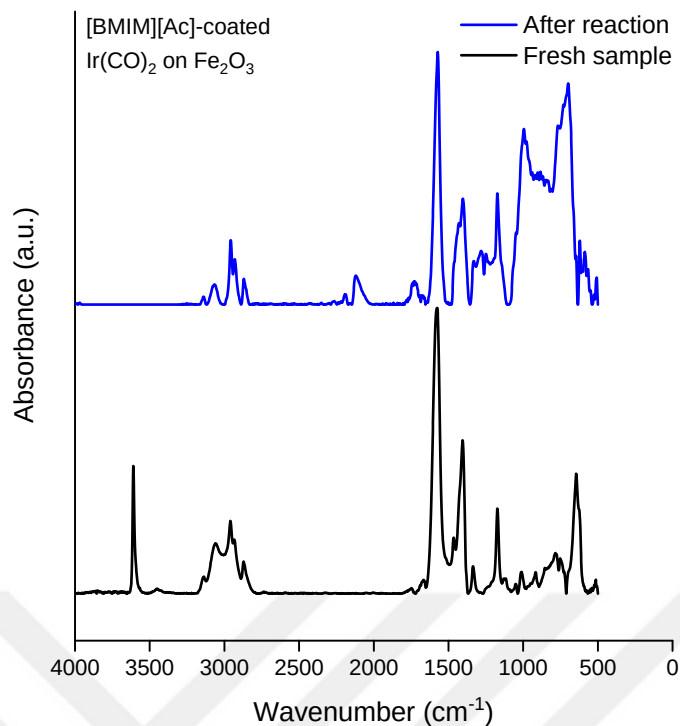


Figure A6-70. IR spectra of [BMIM][Ac]-coated Ir(CO)₂ complexes on Fe₂O₃ before (black) and after (blue) ethylene exposure.

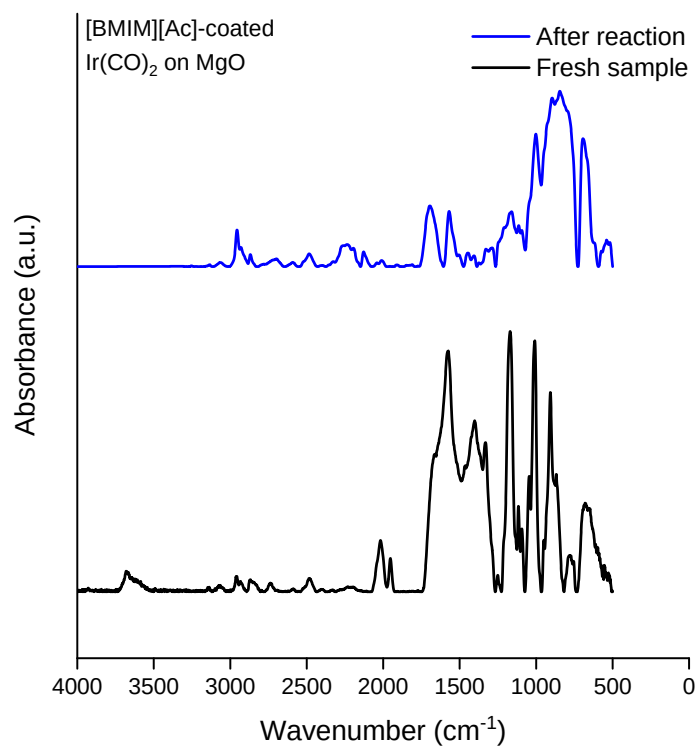


Figure A6-71. IR spectra of [BMIM][Ac]-coated Ir(CO)₂ complexes on MgO before (black) and after (blue) ethylene exposure.

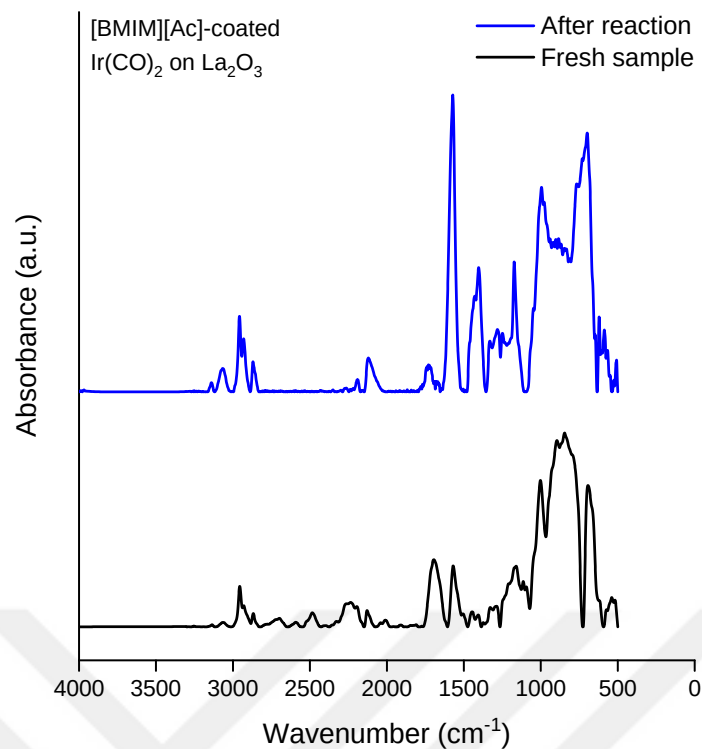


Figure A6-72. IR spectra of [BMIM][Ac]-coated Ir(CO)₂ complexes on La₂O₃ before (black) and after (blue) ethylene exposure.

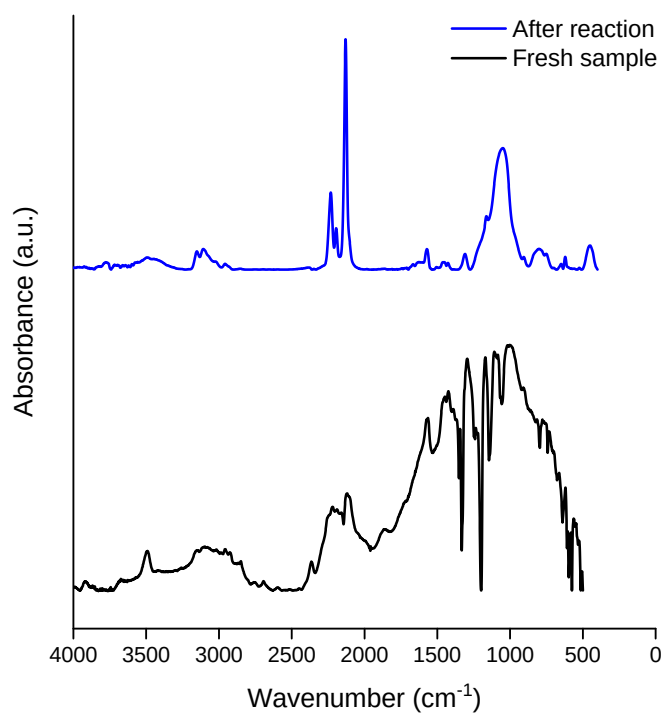


Figure A6-73. IR spectra of [CPMIM][DCA]-coated Ir(CO)₂ complexes on SiO₂ before (black) and after (blue) ethylene exposure.

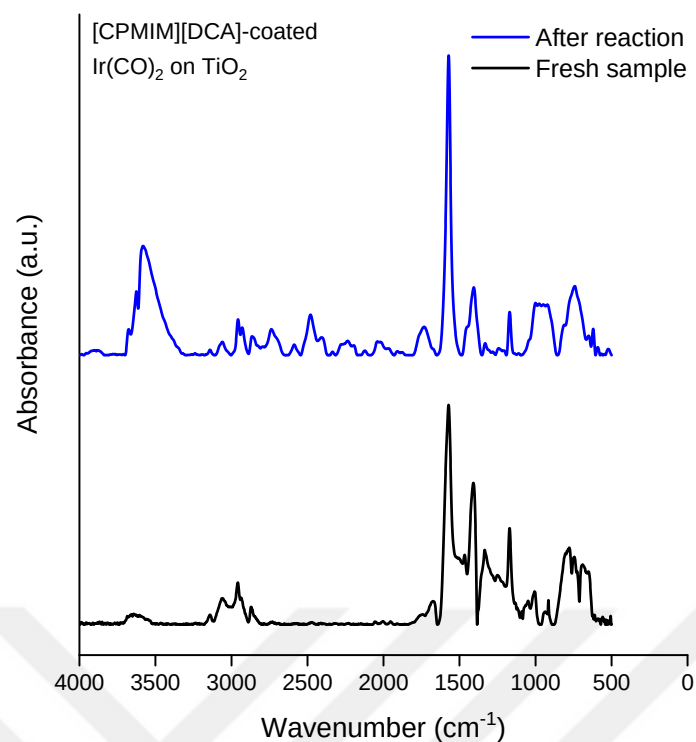


Figure A6-74. IR spectra of [CPMIM][DCA]-coated Ir(CO)₂ complexes on TiO₂ before (black) and after (blue) ethylene exposure.

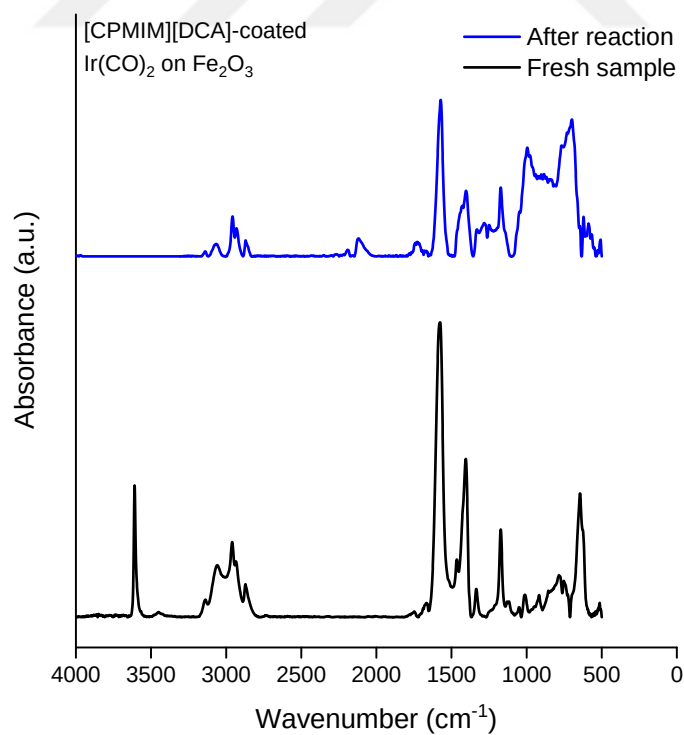


Figure A6-75. IR spectra of [CPMIM][DCA]-coated Ir(CO)₂ complexes on Fe₂O₃ before (black) and after (blue) ethylene exposure.

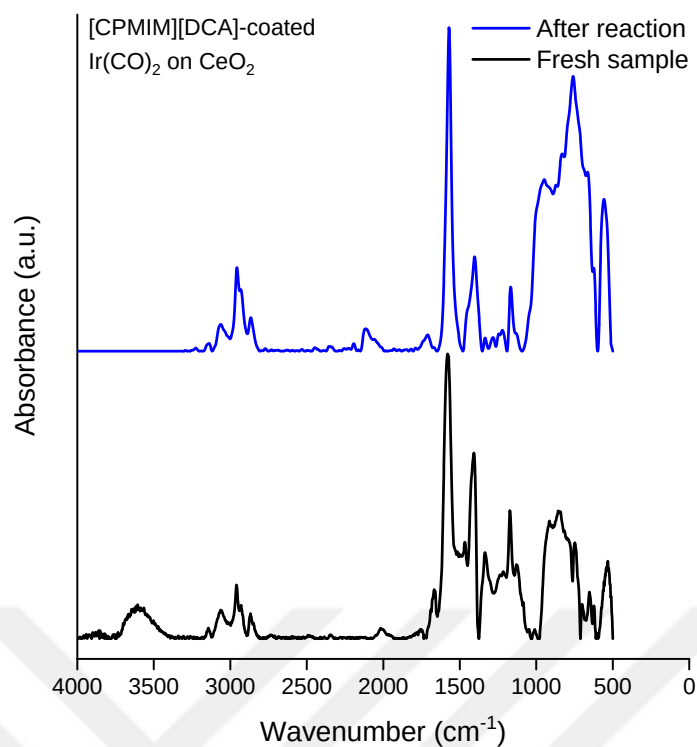


Figure A6-76. IR spectra of [CPMIM][DCA]-coated $\text{Ir}(\text{CO})_2$ complexes on CeO_2 before (black) and after (blue) ethylene exposure.

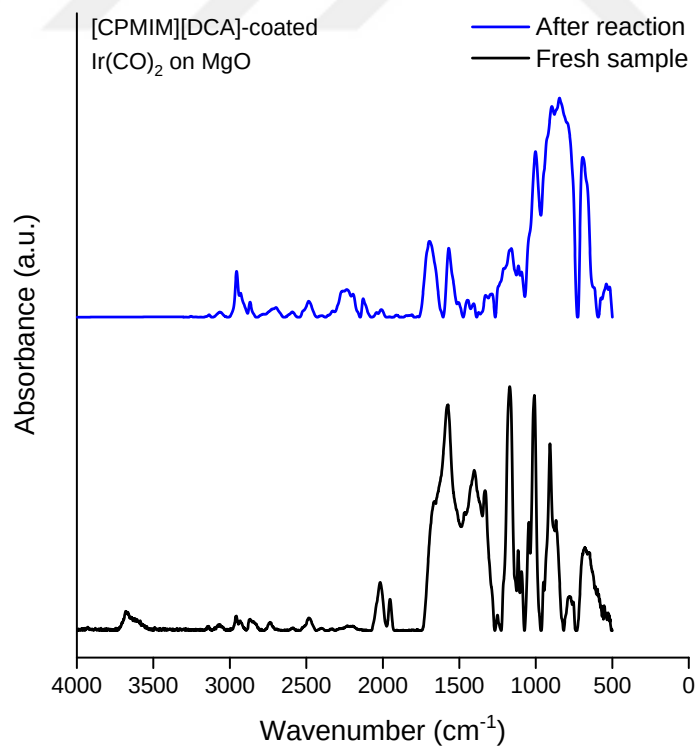


Figure A6-77. IR spectra of [CPMIM][DCA]-coated $\text{Ir}(\text{CO})_2$ complexes on MgO before (black) and after (blue) ethylene exposure.

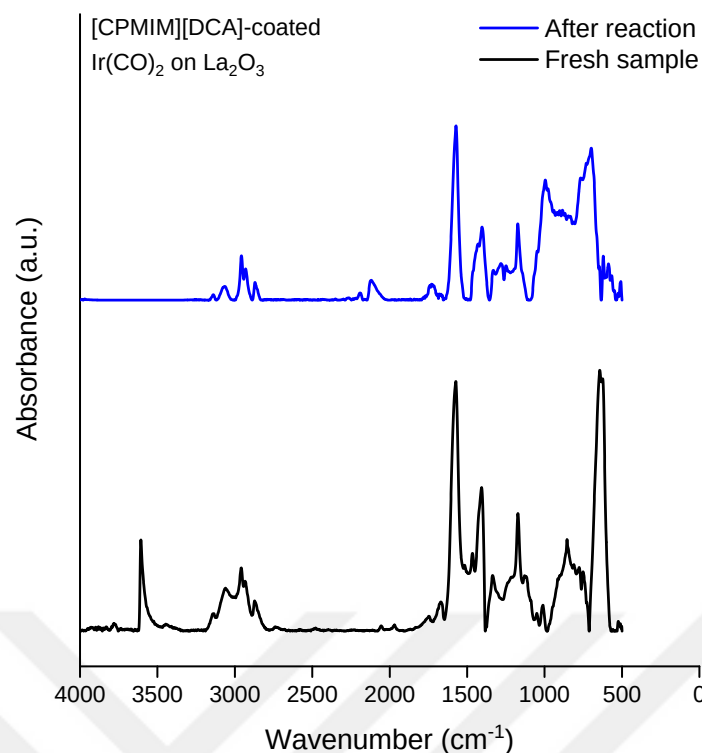


Figure A6-78. IR spectra of [CPMIM][DCA]-coated Ir(CO)₂ complexes on La₂O₃ before (black) and after (blue) ethylene exposure.

Following the activation of each supported iridium complex by reaction with ethylene, it was cooled to 333 K in flowing helium before the start of the catalytic reaction by introduction of a stream of H₂:1,3-butadiene in a molar ratio of 2:1 at a space velocity ensuring operation under differential conversion conditions (conversions <2%). Figure A6-79 illustrates that 1,3-butadiene conversion in the presence of [BMIM][BF₄]-coated Ir(CO)₂/γ-MgO remains almost constant during the reaction in the flow reactor for 3 h on stream.

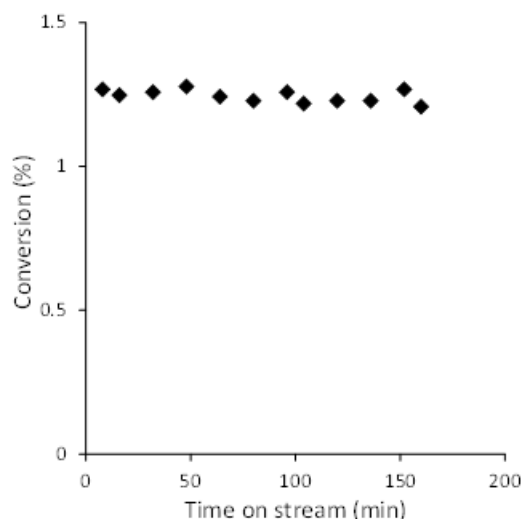


Figure A6-79. Change in 1,3-butadiene conversion with time on stream on a representative sample, [BMIM][BF₄]-coated Ir(CO)₂/SiO₂ at an H₂:BD ratio of 2:1 at 333 K and 1 atm.

A6-8. References

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Appendix A7

Supplementary Materials for

Elucidating the Relative Strengths of Individual Structural Factors Controlling the Partial Hydrogenation Performance of Supported Iridium Catalysts: A Comparison of the Effects of Metal Nuclearity, and the Electron Donor Character of Supports and Ionic Liquid Coatings

A7-1. Extended X-Ray Absorption Fine Structure (EXAFS) Results

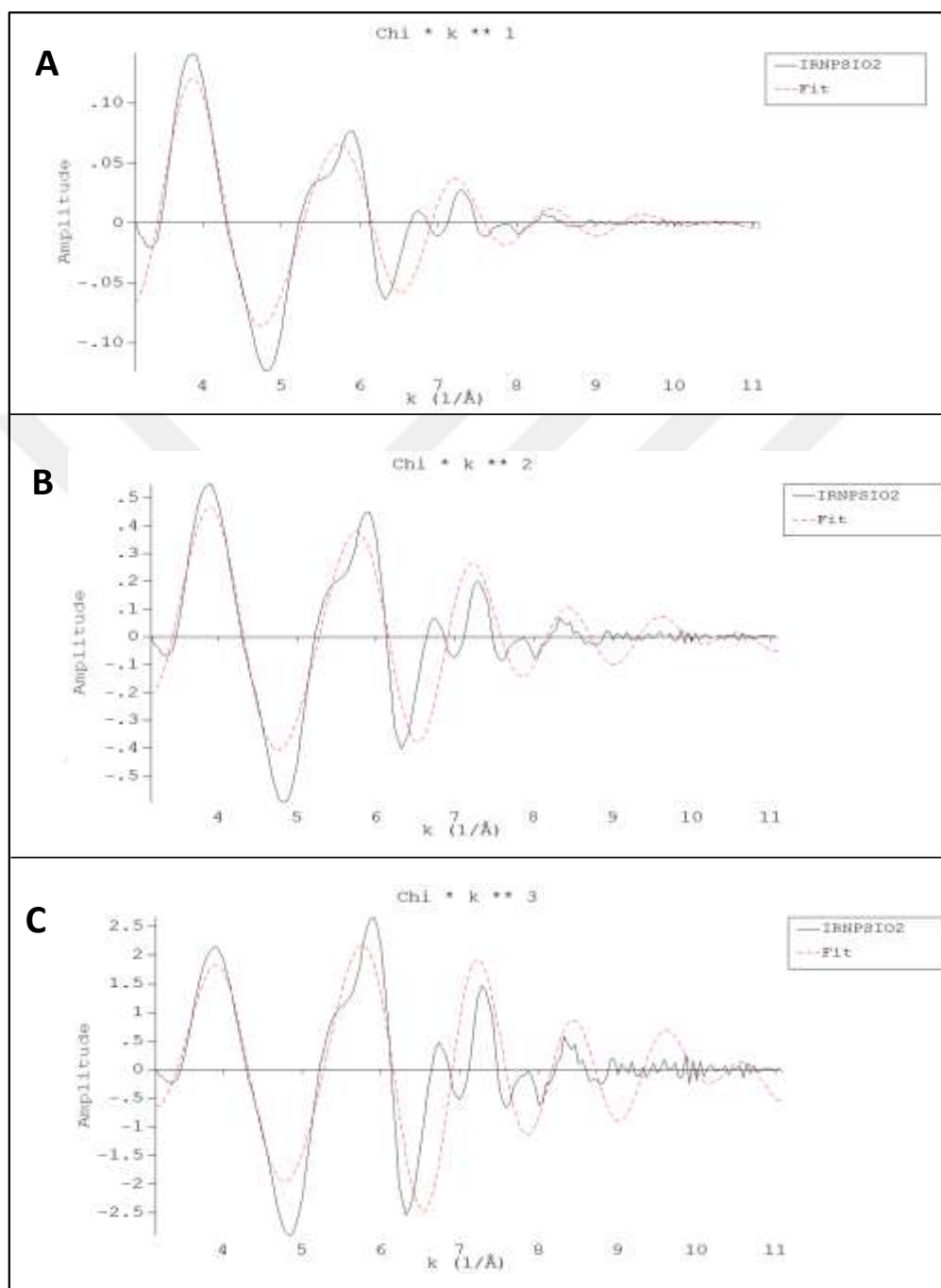


Figure A7-9. Results of EXAFS analysis characterizing the supported nanoclusters formed by treatment of atomically dispersed Ir(CO)₂/SiO₂ in flowing H₂ at 673 K. EXAFS function, χ (solid line), and calculated contribution (dotted line) (A, k^1 -weighted; B, k^2 -weighted; and C, k^3 -weighted).

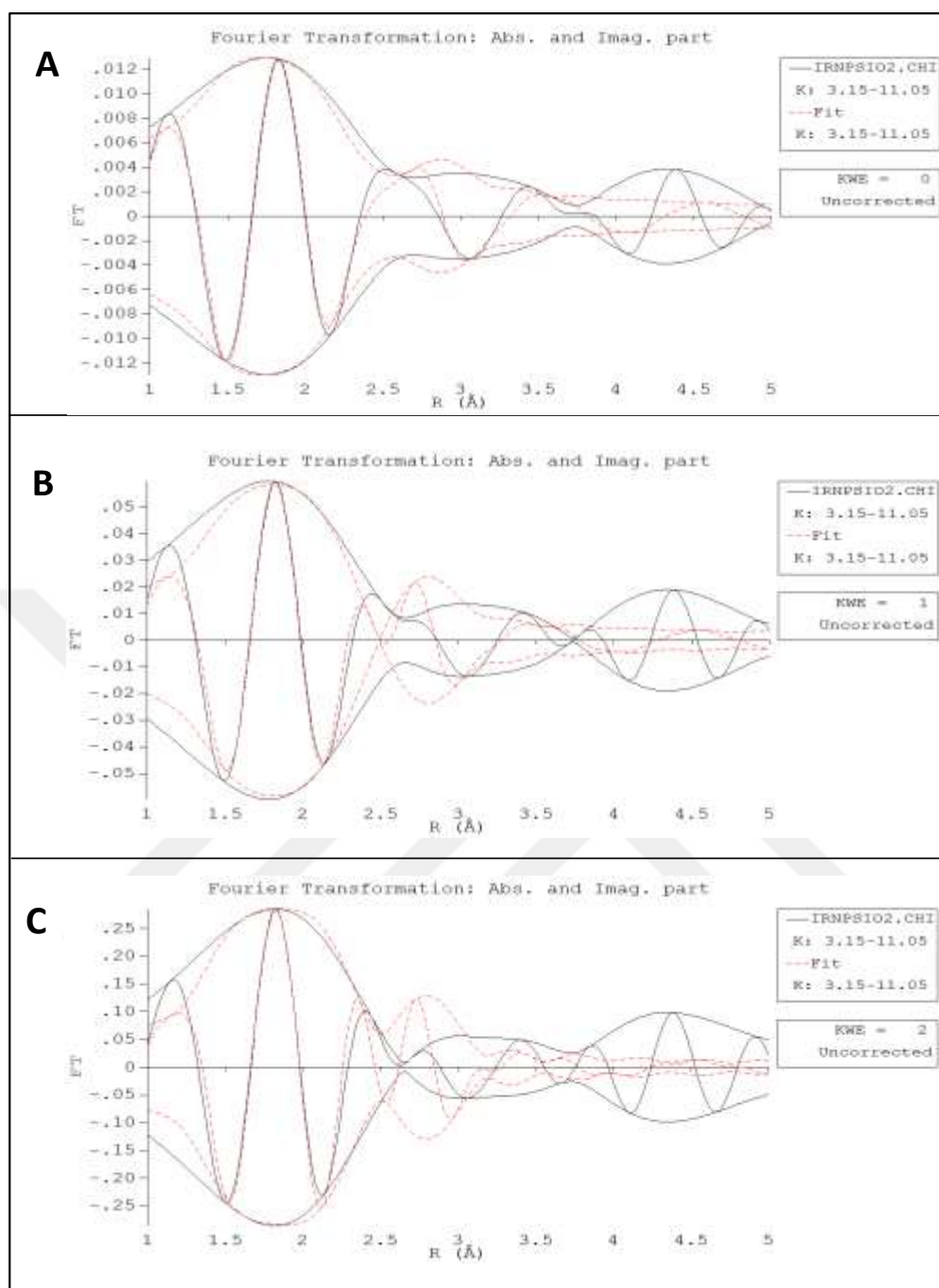
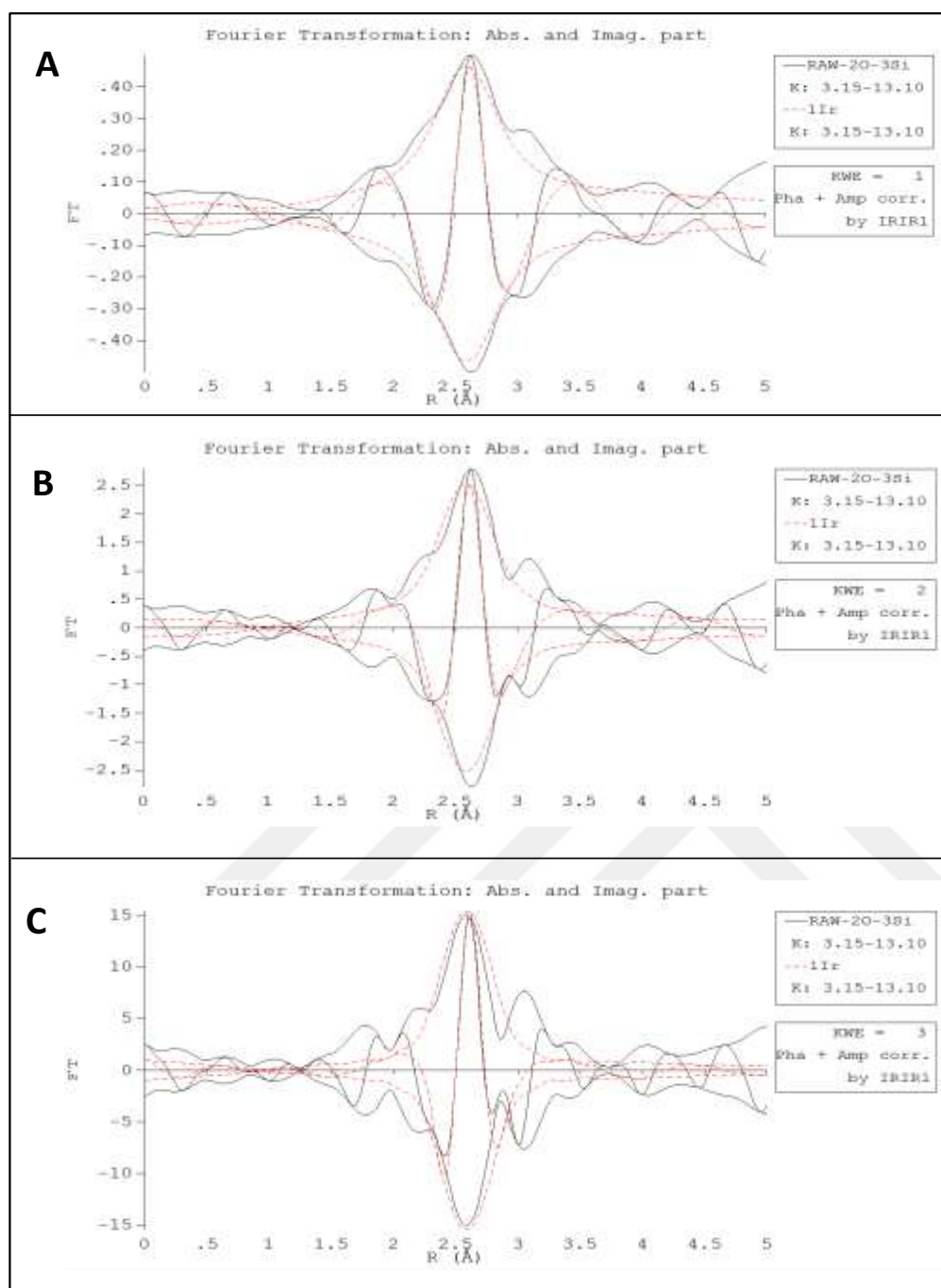


Figure A7-10. Results of EXAFS analysis characterizing the supported nanoclusters formed by treatment of atomically dispersed $\text{Ir}(\text{CO})_2/\text{SiO}_2$ in flowing H_2 at 673 K. Imaginary part and magnitude of the Fourier transform of data (solid line), and calculated contribution (dotted line) (A, k^1 -weighted; B, k^2 -weighted; and C, k^3 -weighted).

**Figure A7-3.**

Imaginary part and magnitude of phase- and amplitude-corrected Fourier transform (A, k^1 -weighted; B, k^2 -weighted; and C, k^3 -weighted) of raw data minus calculated Ir-O_s and Ir-Si contribution (solid line) and calculated Ir-Ir_{1st} contribution (dotted line) characterizing the supported nanoclusters formed by treatment of atomically dispersed Ir(CO)₂/SiO₂ in flowing H₂ at 673 K.

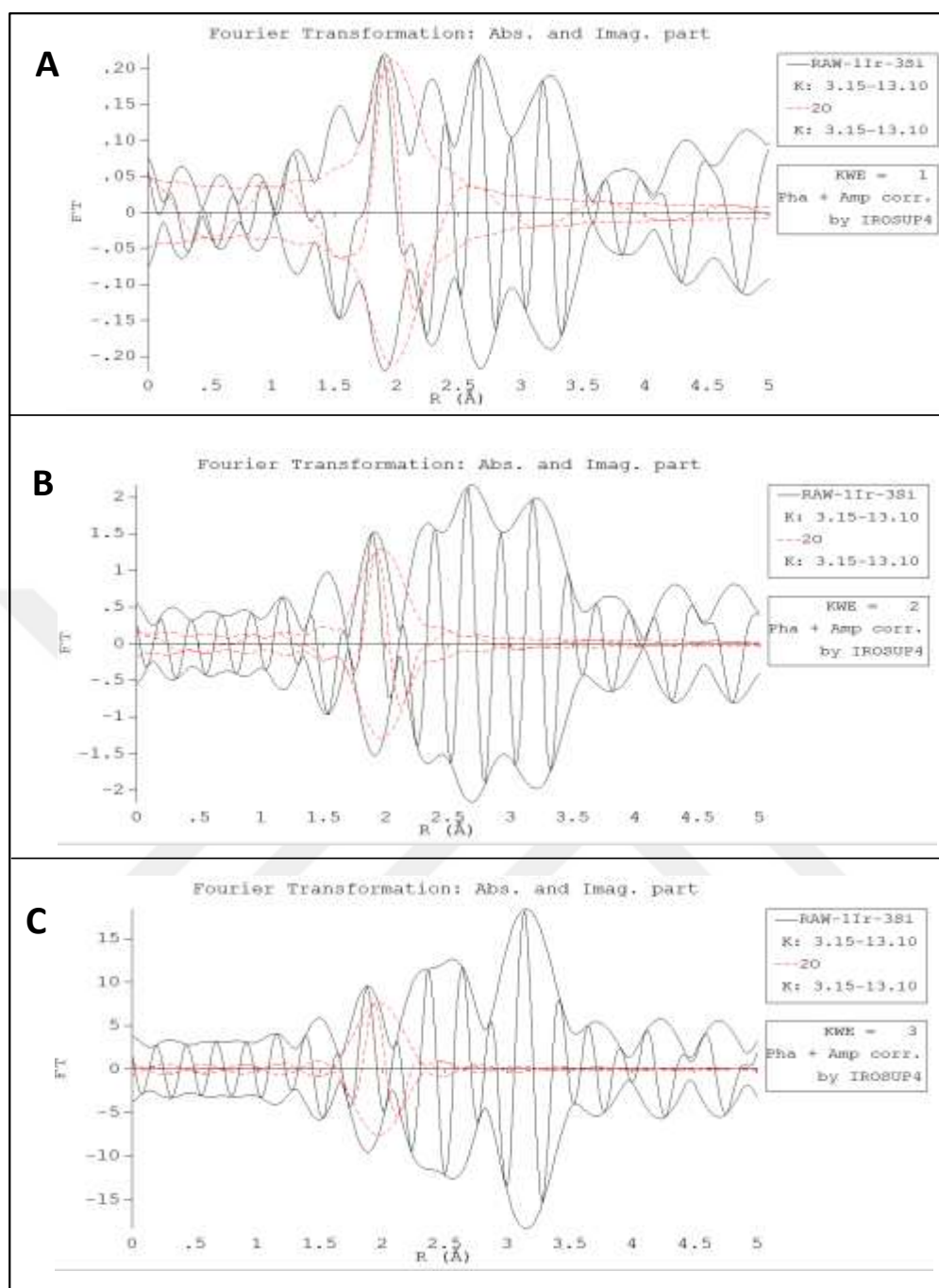


Figure A7-4. Imaginary part and magnitude of phase- and amplitude-corrected Fourier transform (A, k^1 -weighted; B, k^2 -weighted; and C, k^3 -weighted) of raw data minus calculated Ir-Ir_{1st} and Ir-Si contribution (solid line) and calculated Ir-O_s contribution (dotted line) characterizing the supported nanoclusters formed by treatment of atomically dispersed Ir(CO)₂/SiO₂ in flowing H₂ at 673 K.

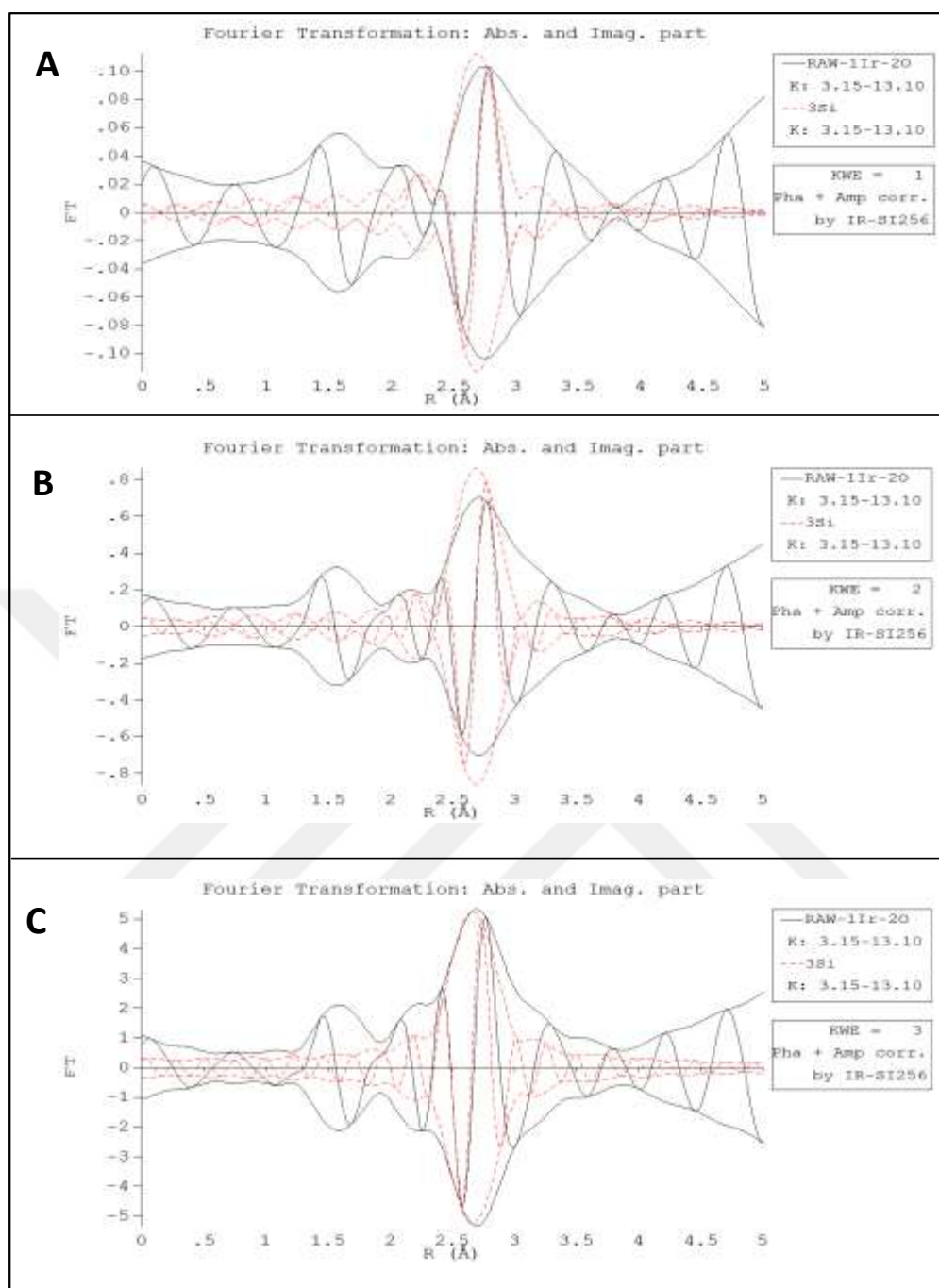


Figure A7-5. Imaginary part and magnitude of phase- and amplitude-corrected Fourier transform (A, k^1 -weighted; B, k^2 -weighted; and C, k^3 -weighted) of raw data minus calculated Ir–Ir and Ir–O_s contribution (solid line) and calculated Ir–Si contribution (dotted line) characterizing the supported nanoclusters formed by treatment of atomically dispersed Ir(CO)₂/SiO₂ in flowing H₂ at 673 K.

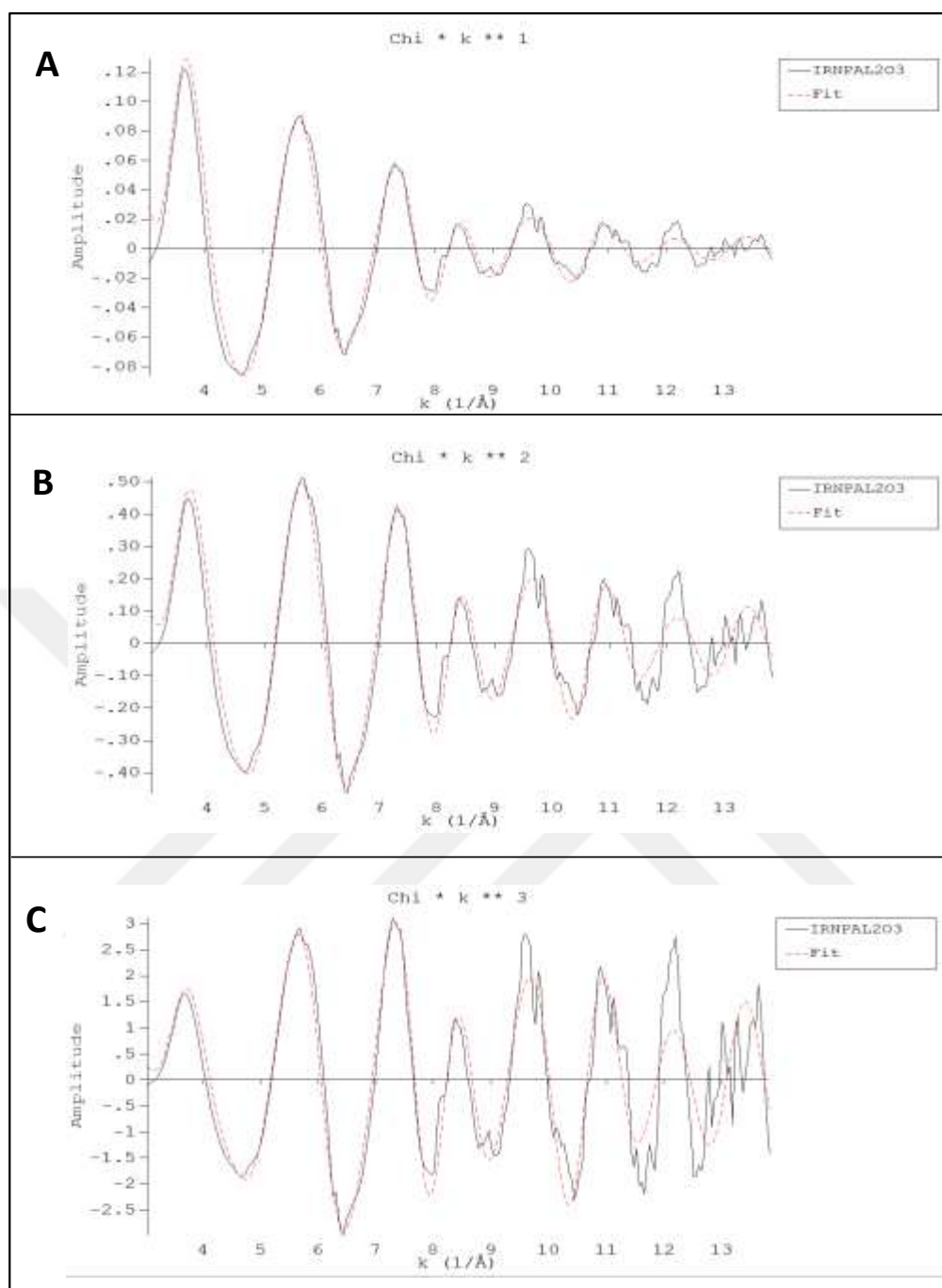


Figure A7-7. Results of EXAFS analysis characterizing the supported nanoclusters formed by treatment of atomically dispersed $\text{Ir}(\text{CO})_2/\gamma\text{-Al}_2\text{O}_3$ in flowing H_2 at 673 K. EXAFS function, χ (solid line), and calculated contribution (dotted line) (A, k^1 -weighted; B, k^2 -weighted; and C, k^3 -weighted).

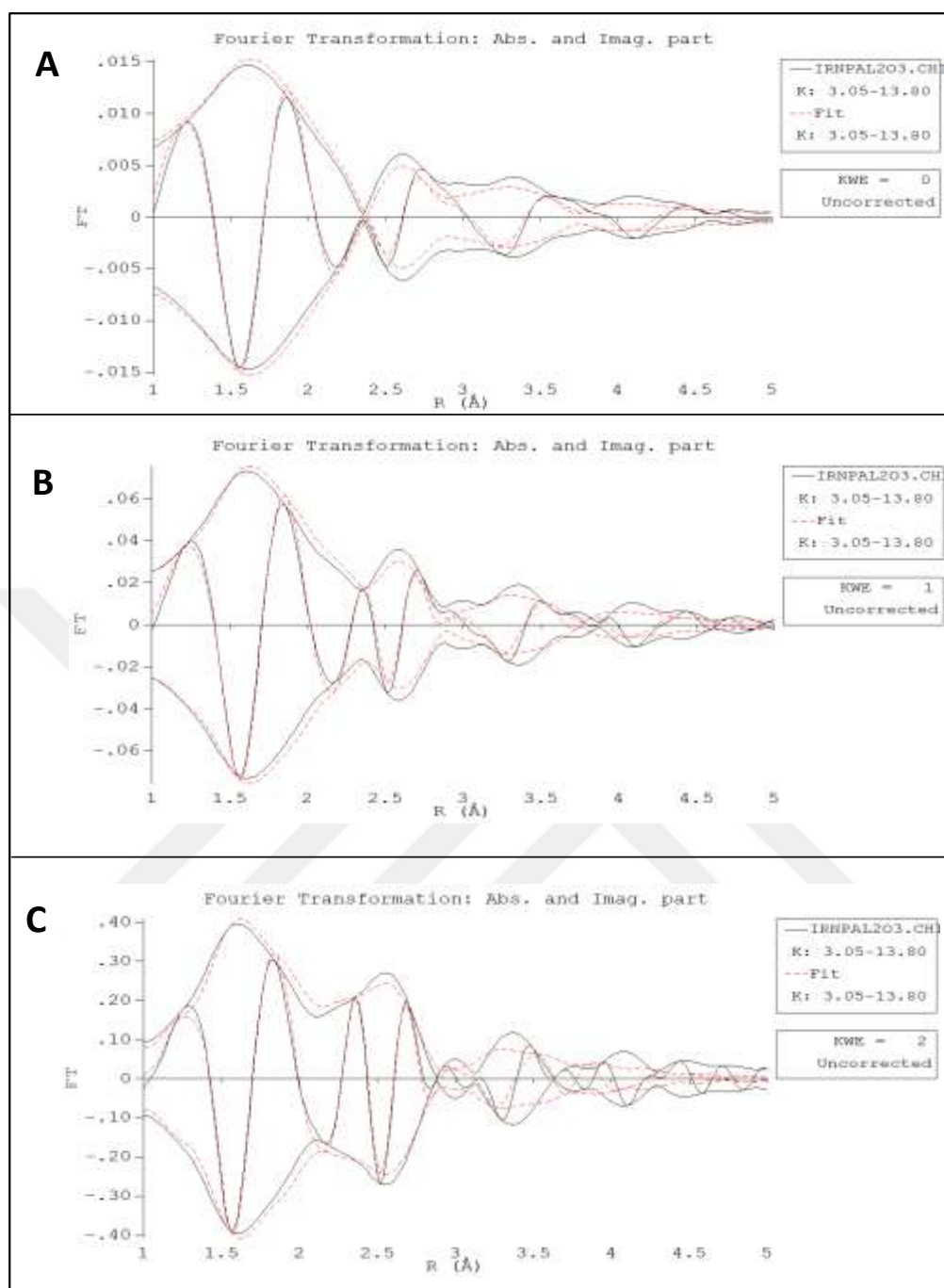


Figure A7-8. Results of EXAFS analysis characterizing the supported nanoclusters formed by treatment of atomically dispersed $\text{Ir}(\text{CO})_2/\gamma\text{-Al}_2\text{O}_3$ in flowing H_2 at 673 K. Imaginary part and magnitude of the Fourier transform of data (solid line), and calculated contribution (dotted line) (A, k^1 -weighted; B, k^2 -weighted; and C, k^3 -weighted).

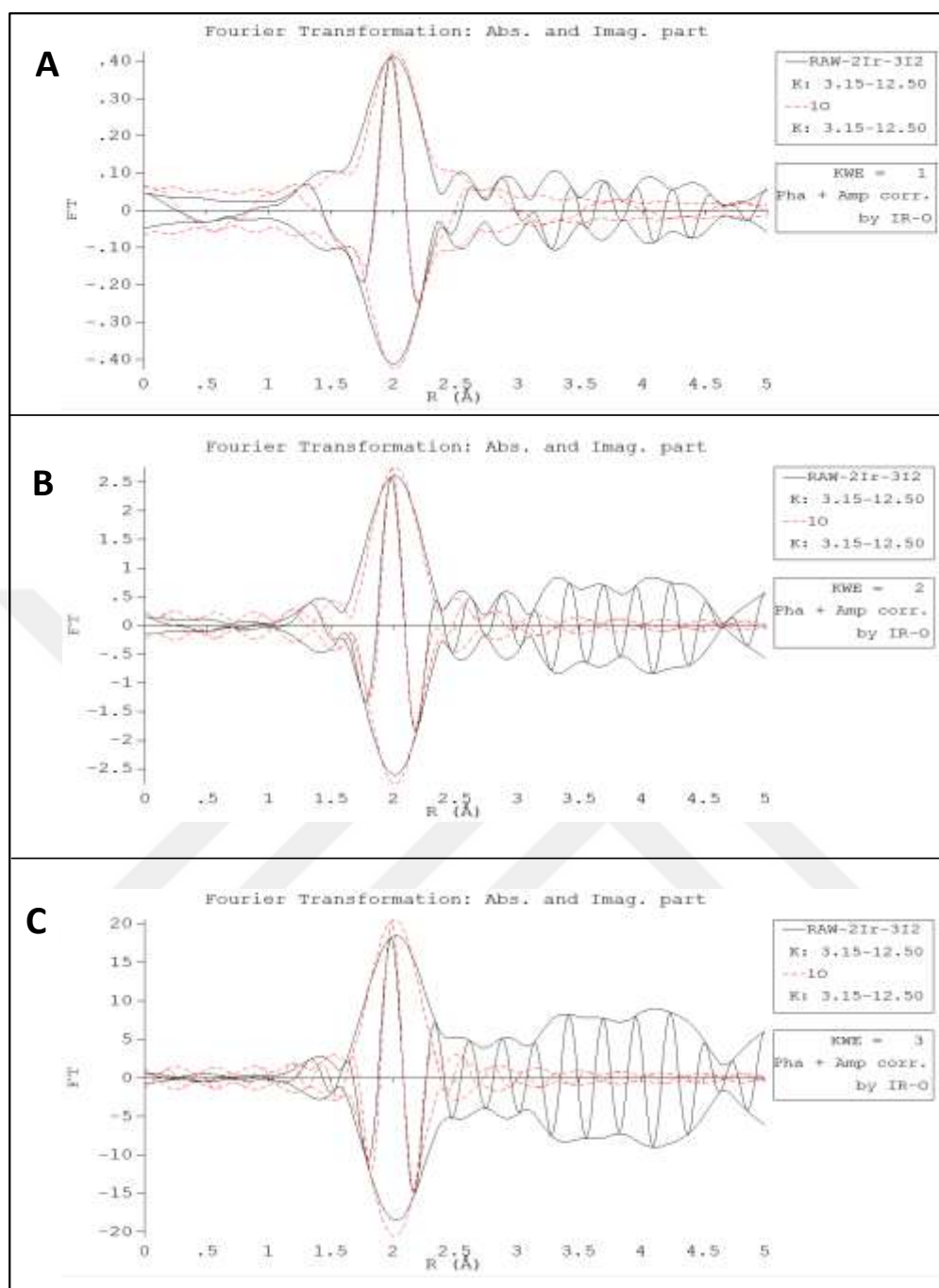


Figure A7-9. Imaginary part and magnitude of phase- and amplitude-corrected Fourier transform (A, k^1 -weighted; B, k^2 -weighted; and C, k^3 -weighted) of raw data minus calculated Ir–Ir_{1st} and Ir–Ir_{2nd} contribution (solid line) and calculated Ir–O_s contribution (dotted line) characterizing the supported nanoclusters formed by treatment of atomically dispersed Ir(CO)₂/γ-Al₂O₃ in flowing H₂ at 673 K.

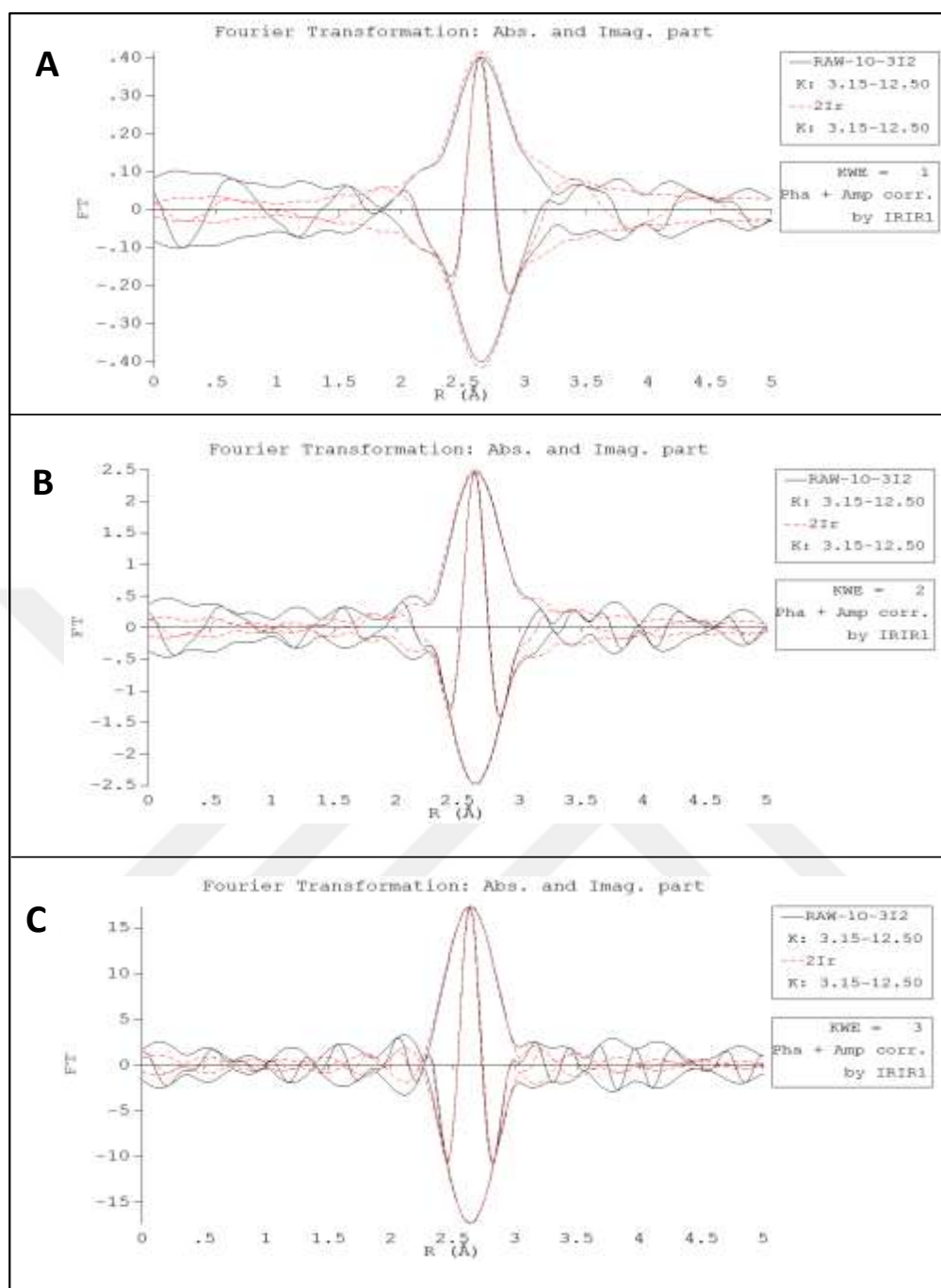


Figure A7-10. Imaginary part and magnitude of phase- and amplitude-corrected Fourier transform (A, k^1 -weighted; B, k^2 -weighted; and C, k^3 -weighted) of raw data minus calculated Ir–Ir_{2nd} and Ir–O_s contribution (solid line) and calculated Ir–Ir_{1st} contribution (dotted line) characterizing the supported nanoclusters formed by treatment of atomically dispersed Ir(CO)₂/γ-Al₂O₃ in flowing H₂ at 673 K.

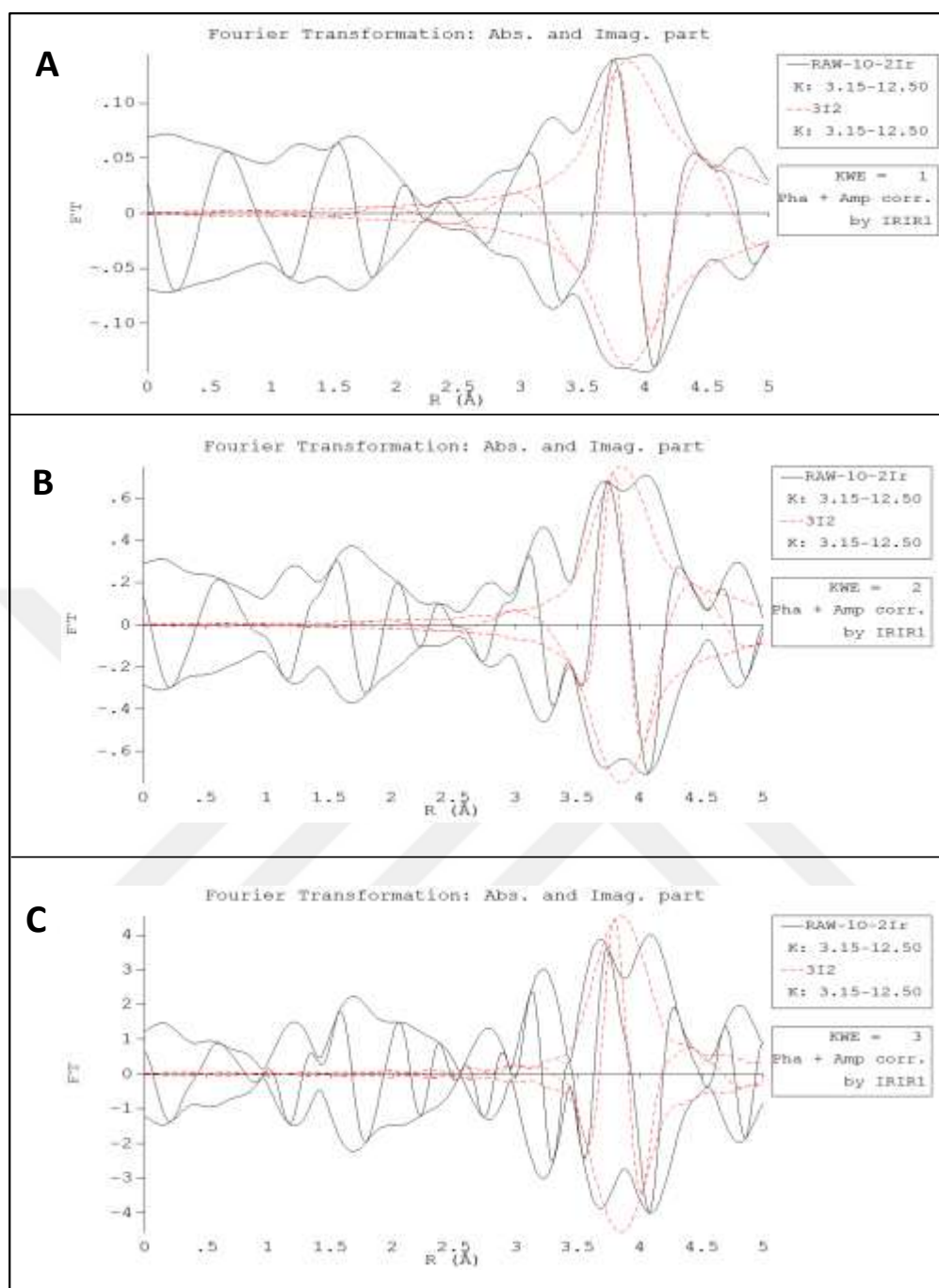


Figure A7-11. Imaginary part and magnitude of phase- and amplitude-corrected Fourier transform (A, k^1 -weighted; B, k^2 -weighted; and C, k^3 -weighted) of raw data minus calculated Ir–O_s and Ir–Ir_{1st} contribution (solid line) and calculated Ir–Ir_{2nd} contribution (dotted line) characterizing the supported nanoclusters formed by treatment of atomically dispersed Ir(CO)₂/γ-Al₂O₃ in flowing H₂ at 673 K.

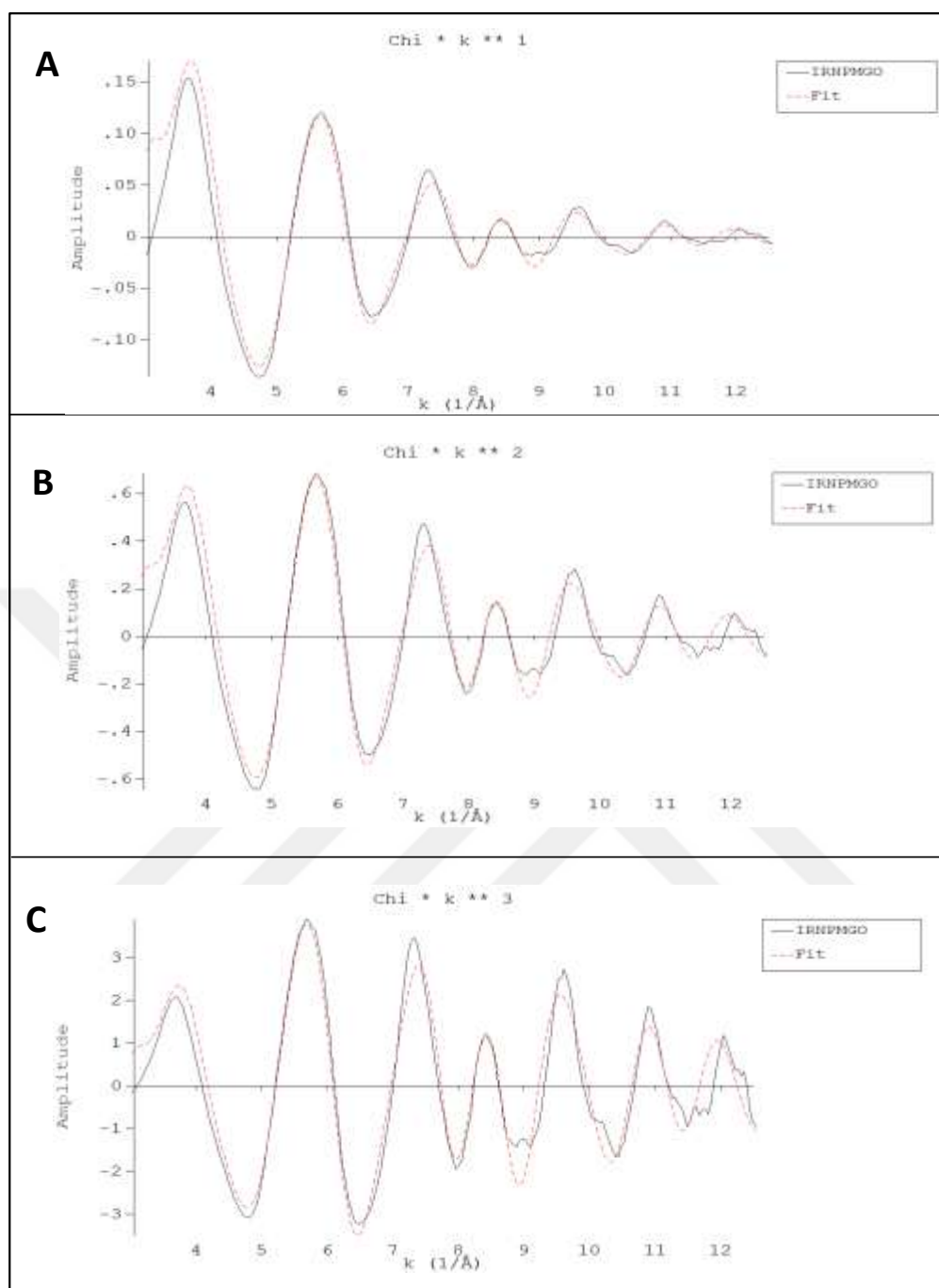


Figure A7-13. Results of EXAFS analysis characterizing the supported nanoclusters formed by treatment of atomically dispersed Ir(CO)₂/MgO in flowing H₂ at 673 K. EXAFS function, χ (solid line), and calculated contribution (dotted line) (A, k^1 -weighted; B, k^2 -weighted; and C, k^3 -weighted).

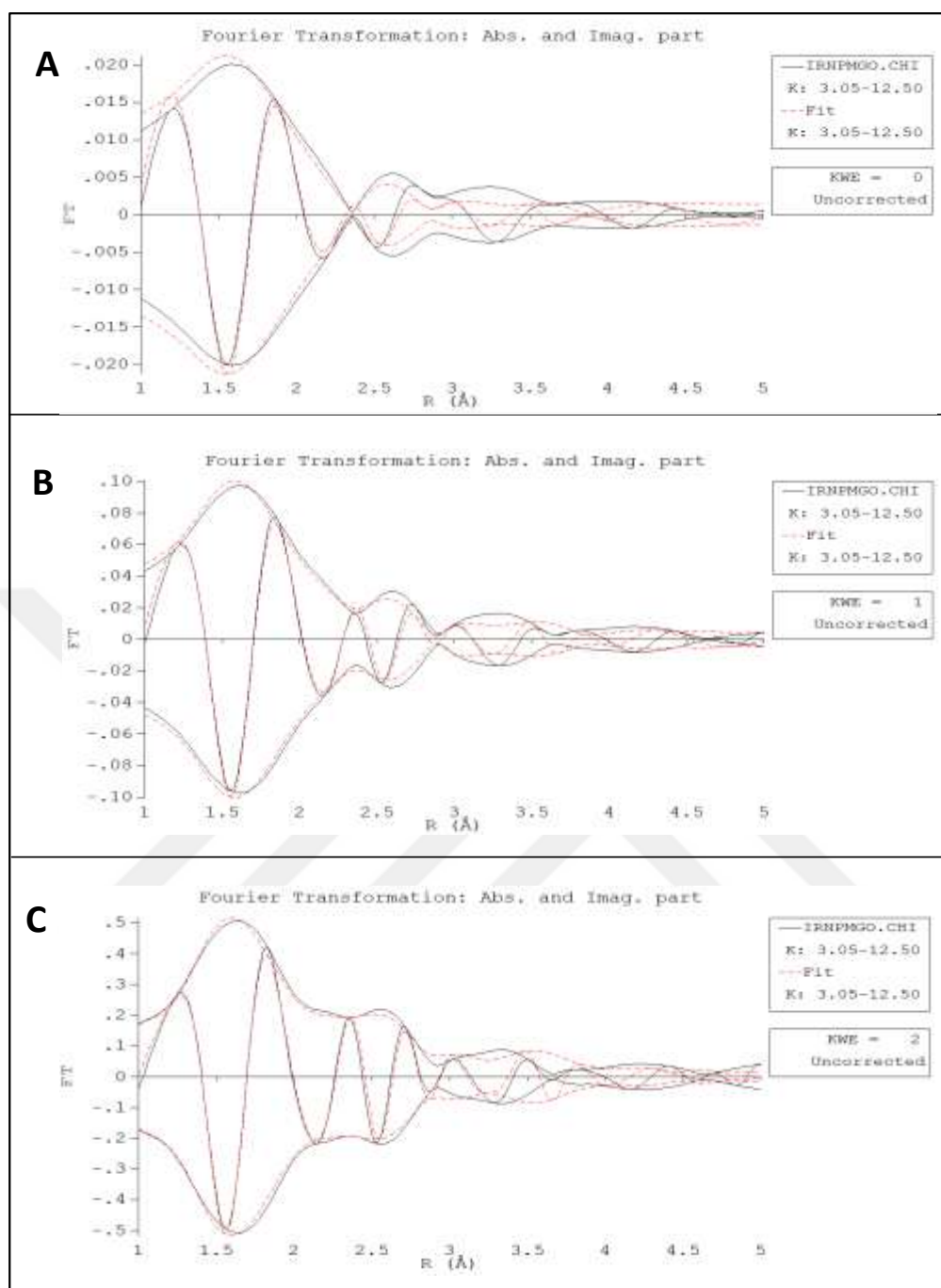


Figure A7-14. Results of EXAFS analysis characterizing the supported nanoclusters formed by treatment of atomically dispersed Ir(CO)₂/MgO in flowing H₂ at 673 K. EXAFS function, χ (solid line), and calculated contribution (dotted line) (A, k^1 -weighted; B, k^2 -weighted; and C, k^3 -weighted).

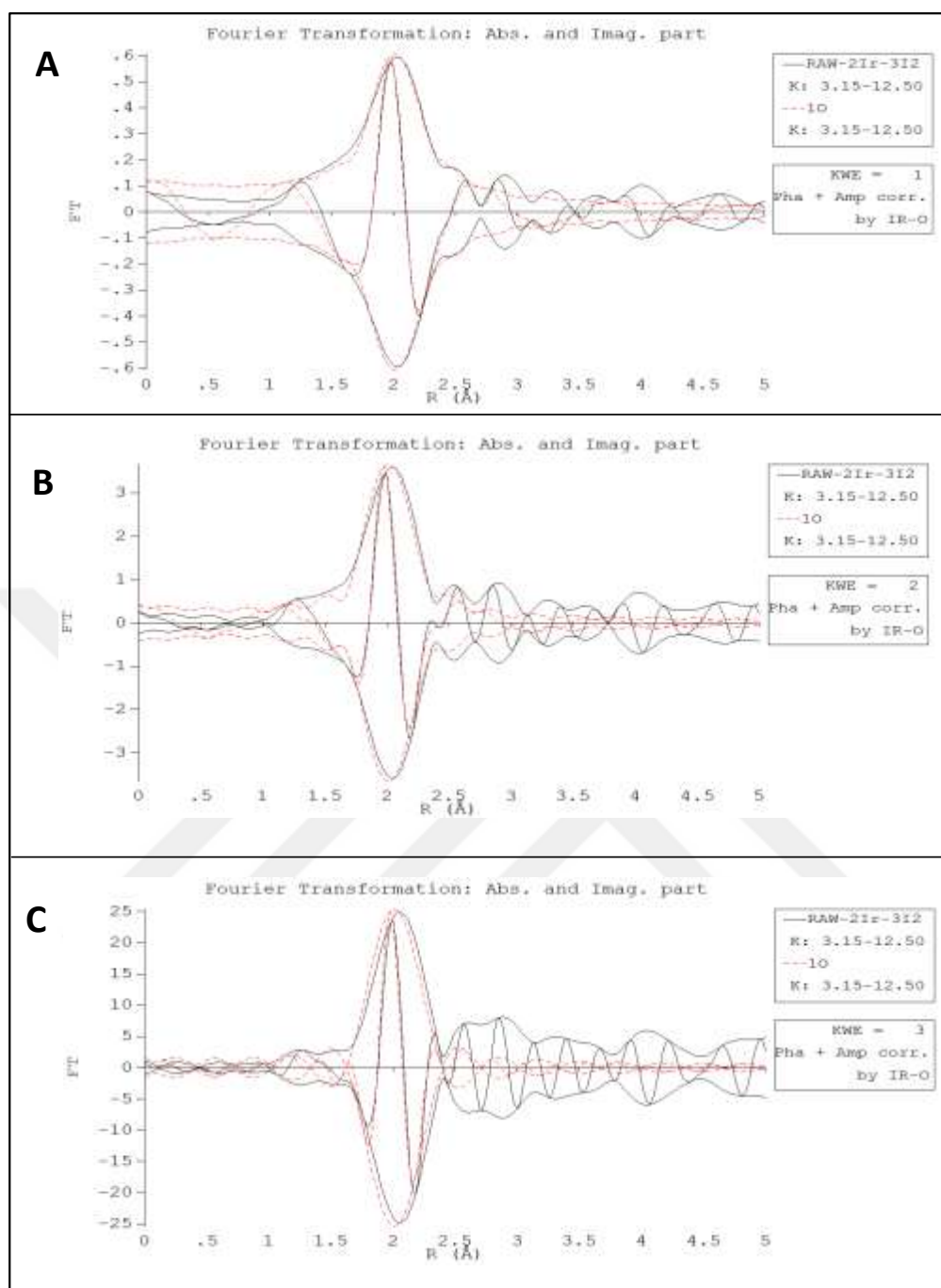


Figure A7-15. Imaginary part and magnitude of phase- and amplitude-corrected Fourier transform (A, k^1 -weighted; B, k^2 -weighted; and C, k^3 -weighted) of raw data minus calculated Ir-Ir_{1st} and Ir-Ir_{2nd} contribution (solid line) and calculated Ir-O_s contribution (dotted line) characterizing the supported nanoclusters formed by treatment of atomically dispersed Ir(CO)₂/MgO in flowing H₂ at 673 K.

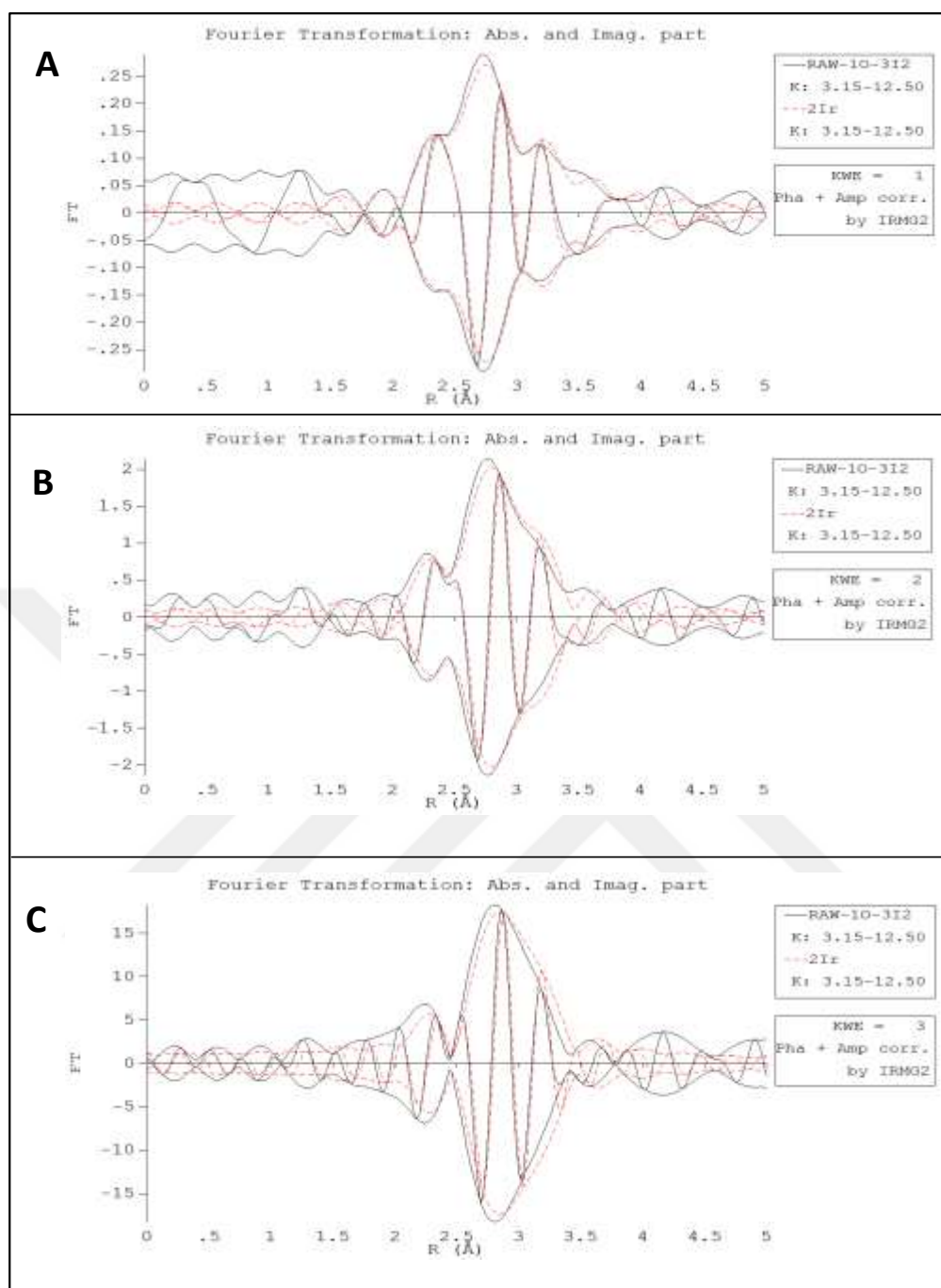


Figure A7-16. Imaginary part and magnitude of phase- and amplitude-corrected Fourier transform (A, k^1 -weighted; B, k^2 -weighted; and C, k^3 -weighted) of raw data minus calculated Ir-Ir_{2nd} and Ir-O_s contribution (solid line) and calculated Ir-Ir_{1st} contribution (dotted line) characterizing the supported nanoclusters formed by treatment of atomically dispersed Ir(CO)₂/MgO in flowing H₂ at 673 K.

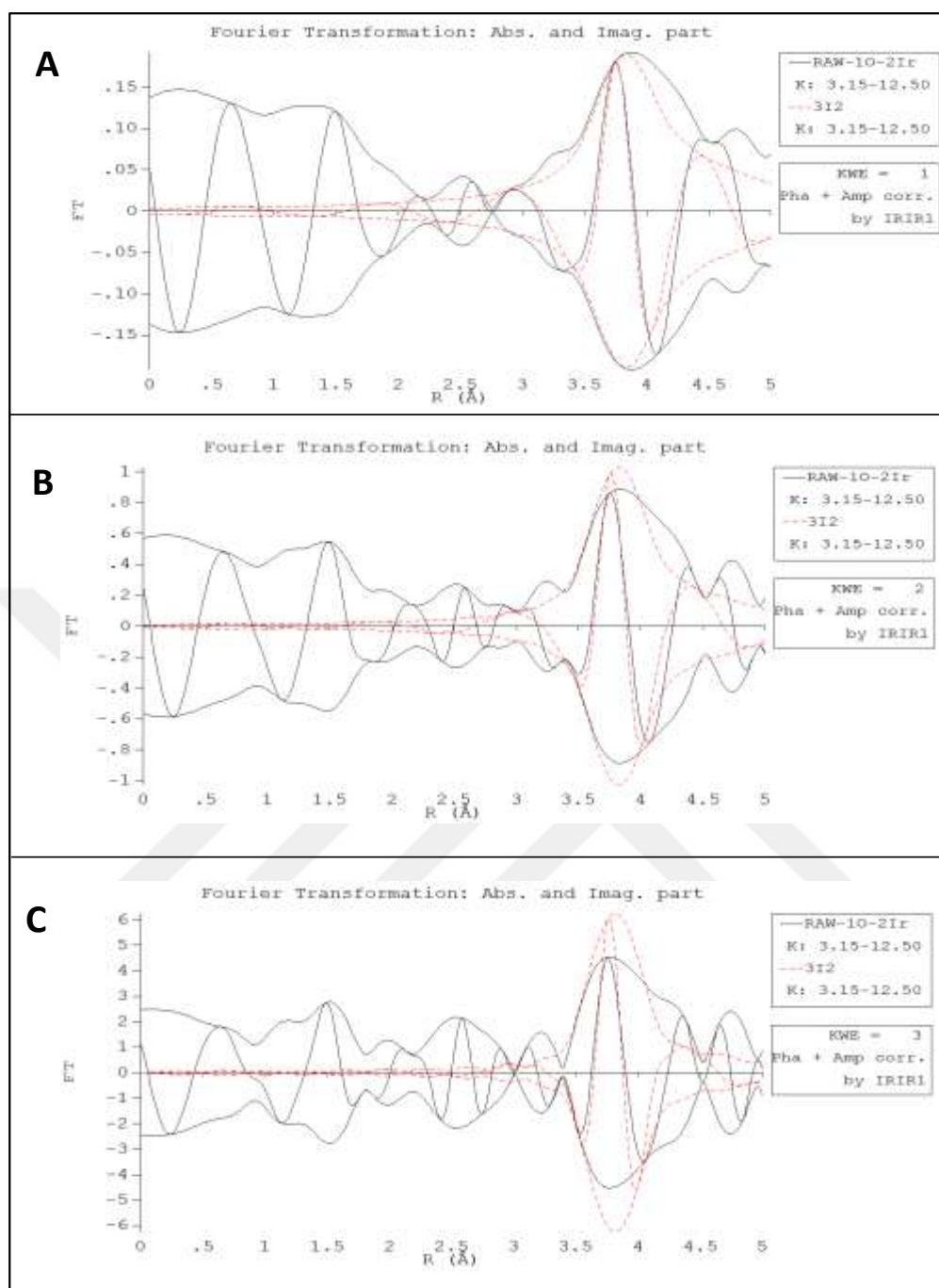


Figure A7-17. Imaginary part and magnitude of phase- and amplitude-corrected Fourier transform (A, k^1 -weighted; B, k^2 -weighted; and C, k^3 -weighted) of raw data minus calculated Ir-Ir_{1st} and Ir-O_s contribution (solid line) and calculated Ir-Ir_{2nd} contribution (dotted line) characterizing the supported nanoclusters formed by treatment of atomically dispersed Ir(CO)₂/MgO in flowing H₂ at 673 K.

A7-2. CO chemisorption for particle size analysis

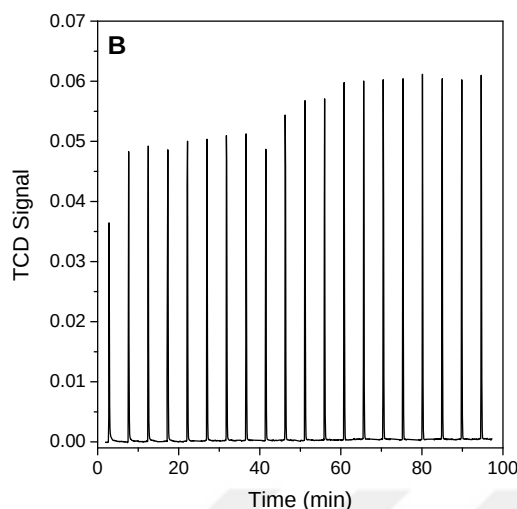


Figure A7-18. CO pulse chemisorption results of iridium nanoclusters supported on A) SiO_2 , B) $\gamma\text{-Al}_2\text{O}_3$, and C) MgO after activating the samples at 373 K in flowing H_2 .

A7-3. Powder X-ray diffraction (XRD)

For particle size measurements of the supported nanoclusters, XRD was performed. XRD measurements of the iridium nanoclusters supported on SiO_2 , $\gamma\text{-Al}_2\text{O}_3$, and MgO were performed by a Bruker D8 discover X-Ray Diffraction System with a $\text{Cu K}\alpha_1$ radiation source employing 1.5418 wavelength to detect phases. AVantec-1 detector was used with a slit of 1 mm. The set powerrating of the X-ray generator was 30 kV and 40 mA. The 2 θ range of the patterns varied between 5 and 90° with a step size of 0.01215°. Approximately 8 mg of sample was fixed to the glass slide with a double-side tape and the glass slide was attached to the holder by gum.

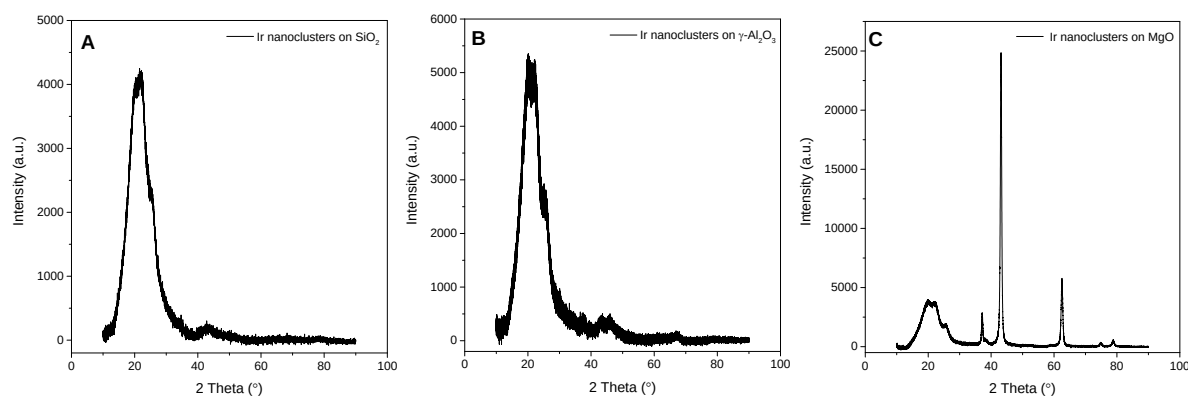


Figure A7-19. XRD pattern of Ir nanoclusters on SiO_2 , $\gamma\text{-Al}_2\text{O}_3$, and MgO .

A7-4. XANES data of uncoated supported Ir nanoclusters

The XANES show that Ir L_{III} edge energies of nanoclusters supported on SiO_2 , $\gamma\text{-Al}_2\text{O}_3$ and MgO are 11216.3, 11216.0 and 11215.6 eV, respectively. The decrease in the edge energy is attributed to the changing surface electronic structure of the metal oxides.¹

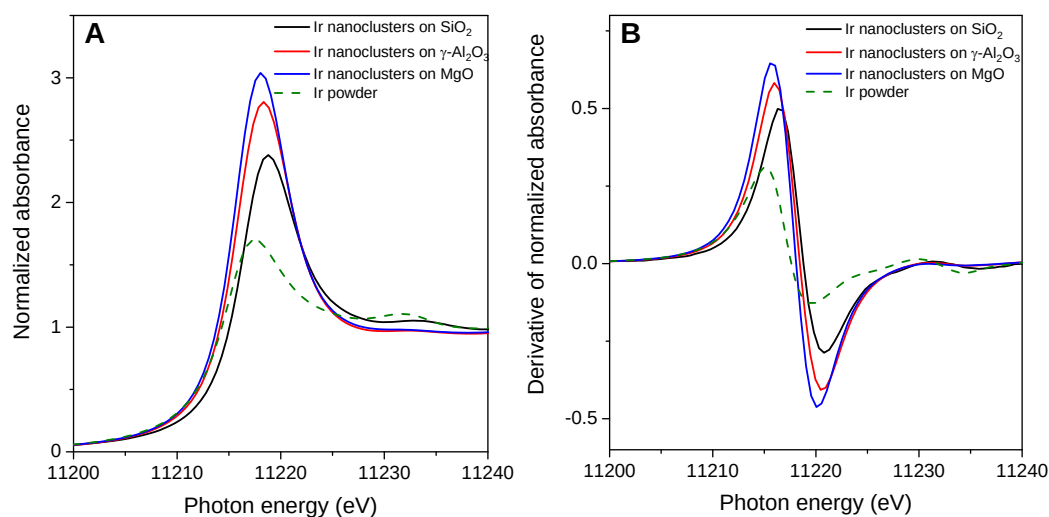
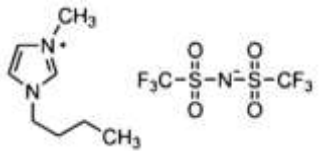
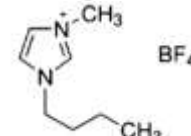
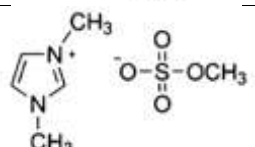
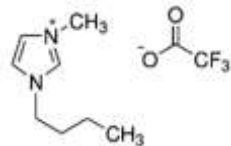
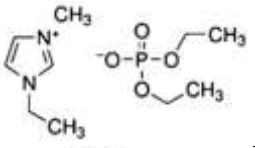
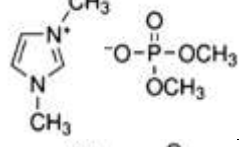
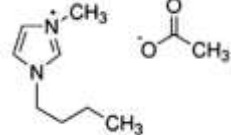


Figure A7-20. A) Normalized B) Derivative of normalized XANES spectra at the Ir L_{III} edge characterizing the samples: Ir nanocluster supported on SiO_2 (solid black line), Ir nanocluster on $\gamma\text{-Al}_2\text{O}_3$ (solid red line) and Ir nanocluster on MgO (solid blue line) For comparison, the spectrum of iridium foil (measured in transmission mode) is also shown (dashed green line).

A7-5. IL-coating of the samples

Table A7-1. Names, abbreviations and structures of the ILs. The ILs were chosen from 1,3-dialkylimidazolium family.

Name of the IL	Abbreviation	Structure
1-Butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide	[BMIM][NTf ₂]	
1-Butyl-3-methylimidazolium tetrafluoroborate	[BMIM][BF ₄]	
1,3-Dimethylimidazolium methyl sulfate	[DMIM][MSO ₄]	
1-Butyl-3-methylimidazolium trifluoroacetate	[BMIM][TFA]	
1-Ethyl-3-methylimidazolium diethyl phosphate	[EMIM][DEP]	
1,3-Dimethylimidazolium dimethyl phosphate	[DMIM][DMP]	
1-Butyl-3-methylimidazolium acetate	[BMIM][Ac]	

A7-6. Scanning Electron Microscopy Coupled with Energy-Dispersive X-ray Spectroscopy (SEM/EDX) Analysis

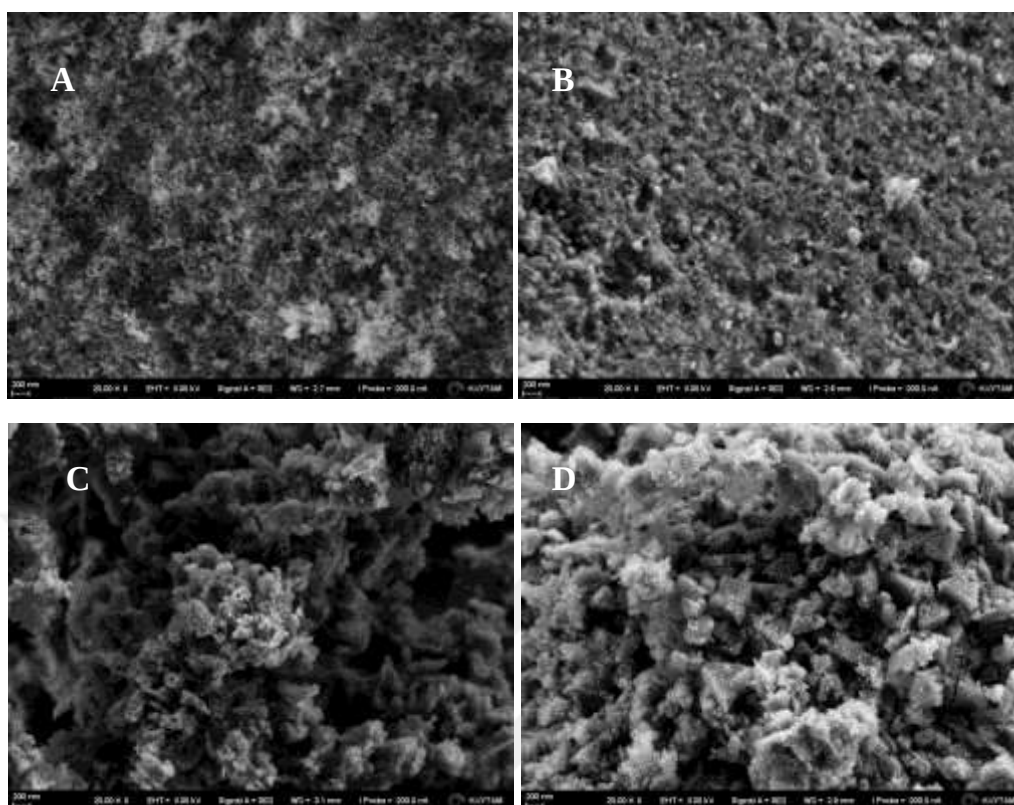


Figure A7-21. SEM images characterizing [BMIM][TFA]-coated Ir nanoclusters supported on A) SiO₂, B) γ -Al₂O₃, and C) MgO. For comparison, SEM image of uncoated MgO-supported Ir nanoclusters is also given in D.

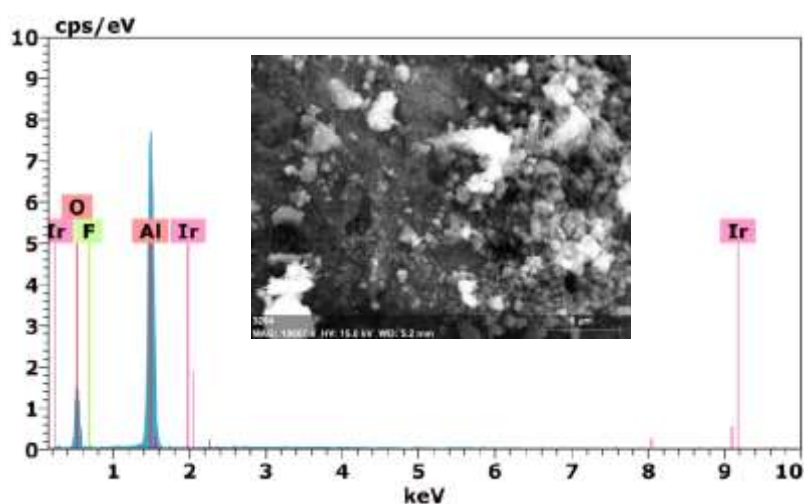


Figure A7-22. EDX spectra of [BMIM][TFA]-coated Ir nanoclusters on γ -Al₂O₃.

A7-7. Brunauer–Emmett–Teller (BET) Pore Volume and Surface Area Analysis

A7-7-1. Ir nanoclusters on SiO₂

Summary Report

Surface Area

Single point surface area at $p/p^* = 0,275621297$: 185,3116 m²/g

BET Surface Area: 191,3056 m²/g

Langmuir Surface Area: 305,6701 m²/g

t-Plot Micropore Area: 6,4369 m²/g

t-Plot External Surface Area: 184,8687 m²/g

BJH Adsorption cumulative surface area of pores
between 17,000 Å and 3.000,000 Å width: 176,202 m²/g

BJH Desorption cumulative surface area of pores
between 17,000 Å and 3.000,000 Å width: 212,3192 m²/g

D-H Adsorption cumulative surface area of pores
between 17,000 Å and 3.000,000 Å width: 168,080 m²/g

D-H Desorption cumulative surface area of pores

Surface Area

between 17,000 Å and 3.000,000 Å width: 169,2204 m²/g

Pore Volume

t-Plot micropore volume: 0,001522 cm³/g

BJH Adsorption cumulative volume of pores
between 17,000 Å and 3.000,000 Å width: 0,274127 cm³/g

BJH Desorption cumulative volume of pores
between 17,000 Å and 3.000,000 Å width: 0,361059 cm³/g

Pore Size

BJH Adsorption average pore width (4V/A): 62,230 Å

BJH Desorption average pore width (4V/A): 68,022 Å

D-H Adsorption average pore width (4V/A): 66,770 Å

D-H Desorption average pore width (4V/A): 79,222 Å

A7-7-2. [BMIM][BF₄]-coated Ir nanoclusters on SiO₂

Summary Report

Surface Area

Single point surface area at $p/p^* = 0,299888377$: 81,8076 m²/g

BET Surface Area: 89,2869 m²/g

Langmuir Surface Area: 156,7544 m²/g

t-Plot External Surface Area: 119,1810 m²/g

BJH Adsorption cumulative surface area of pores
between 17,000 Å and 3.000,000 Å width: 94,207 m²/g

BJH Desorption cumulative surface area of pores
between 17,000 Å and 3.000,000 Å width: 106,2802 m²/g

D-H Adsorption cumulative surface area of pores
between 17,000 Å and 3.000,000 Å width: 107,458 m²/g

D-H Desorption cumulative surface area of pores
between 17,000 Å and 3.000,000 Å width: 110,2433 m²/g

Pore Volume

Single point adsorption total pore volume of pores
less than 3.873,040 Å width at $p/p^* = 0,995000000$: 0,946165 cm³/g

t-Plot micropore volume: -0,017988 cm³/g

BJH Adsorption cumulative volume of pores
between 17,000 Å and 3.000,000 Å width: 0,156380 cm³/g

BJH Desorption cumulative volume of pores
between 17,000 Å and 3.000,000 Å width: 0,185716 cm³/g

Pore Size

Adsorption average pore diameter (4V/A by BET): 423,8764 Å

BJH Adsorption average pore width (4V/A): 66,398 Å

BJH Desorption average pore width (4V/A): 69,897 Å

D-H Adsorption average pore width (4V/A): 66,442 Å

D-H Desorption average pore width (4V/A): 73,525 Å

A7-7-3. Ir nanoclusters on γ -Al₂O₃

Summary Report

Surface Area

Single point surface area at $p/p^\circ = 0,299615163$: 102,5166 m²/g

BET Surface Area: 105,8223 m²/g

Langmuir Surface Area: 175,6212 m²/g

t-Plot External Surface Area: 114,8722 m²/g

BJH Adsorption cumulative surface area of pores
between 17,000 Å and 3.000,000 Å width: 139,937 m²/g

BJH Desorption cumulative surface area of pores
between 17,000 Å and 3.000,000 Å width: 165,4992 m²/g

D-H Adsorption cumulative surface area of pores
between 17,000 Å and 3.000,000 Å width: 130,479 m²/g

D-H Desorption cumulative surface area of pores
between 17,000 Å and 3.000,000 Å width: 158,2986 m²/g

Pore Volume

Single point adsorption total pore volume of pores
less than 3.873,040 Å width at $p/p^\circ = 0,995000000$: 0,257973 cm³/g

t-Plot micropore volume: -0,005993 cm³/g

BJH Adsorption cumulative volume of pores
between 17,000 Å and 3.000,000 Å width: 0,190424 cm³/g

BJH Desorption cumulative volume of pores
between 17,000 Å and 3.000,000 Å width: 0,216841 cm³/g

Pore Size

Adsorption average pore diameter (4V/A by BET): 97,5116 Å

BJH Adsorption average pore width (4V/A): 54,431 Å

BJH Desorption average pore width (4V/A): 52,409 Å

D-H Adsorption average pore width (4V/A): 59,932 Å

D-H Desorption average pore width (4V/A): 58,760 Å

A7-7-4. [BMIM][BF₄]-coated Ir nanoclusters on γ -Al₂O₃

Summary Report

Surface Area

Single point surface area at $p/p^\circ = 0,299516399$: 52,9286 m²/gBET Surface Area: 57,2387 m²/gLangmuir Surface Area: 95,3470 m²/gt-Plot External Surface Area: 75,7547 m²/gBJH Adsorption cumulative surface area of pores
between 17,000 Å and 3.000,000 Å width: 84,800 m²/gBJH Desorption cumulative surface area of pores
between 17,000 Å and 3.000,000 Å width: 112,2801 m²/gD-H Adsorption cumulative surface area of pores
between 17,000 Å and 3.000,000 Å width: 84,677 m²/gD-H Desorption cumulative surface area of pores
between 17,000 Å and 3.000,000 Å width: 114,8181 m²/g

Pore Volume

Single point adsorption total pore volume of pores
less than 3.873,040 Å width at $p/p^\circ = 0,995000000$: 0,162744 cm³/gt-Plot micropore volume: -0,011180 cm³/gBJH Adsorption cumulative volume of pores
between 17,000 Å and 3.000,000 Å width: 0,112485 cm³/gBJH Desorption cumulative volume of pores
between 17,000 Å and 3.000,000 Å width: 0,139933 cm³/g

Pore Size

Adsorption average pore diameter (4V/A by BET): 113,7301 Å

BJH Adsorption average pore width (4V/A): 53,059 Å

BJH Desorption average pore width (4V/A): 49,851 Å

D-H Adsorption average pore width (4V/A): 59,616 Å

D-H Desorption average pore width (4V/A): 56,907 Å

A7-7-5. Ir nanoclusters on MgO

Summary Report

Surface Area

Single point surface area at $p/p^0 = 0,299589876$: 31,1940 m²/g

BET Surface Area: 31,6905 m²/g

Langmuir Surface Area: 55,3777 m²/g

t-Plot External Surface Area: 36,2521 m²/g

BJH Adsorption cumulative surface area of pores
between 17,000 Å and 3.000,000 Å width: 55,390 m²/g

BJH Desorption cumulative surface area of pores
between 17,000 Å and 3.000,000 Å width: 61,7442 m²/g

D-H Adsorption cumulative surface area of pores
between 17,000 Å and 3.000,000 Å width: 55,480 m²/g

D-H Desorption cumulative surface area of pores
between 17,000 Å and 3.000,000 Å width: 67,8686 m²/g

Pore Volume

Single point adsorption total pore volume of pores
less than 3.873,040 Å width at $p/p^0 = 0,995000000$: 0,264607 cm³/g

t-Plot micropore volume: -0,003036 cm³/g

BJH Adsorption cumulative volume of pores
between 17,000 Å and 3.000,000 Å width: 0,081449 cm³/g

BJH Desorption cumulative volume of pores
between 17,000 Å and 3.000,000 Å width: 0,105855 cm³/g

Pore Size

Adsorption average pore diameter (4V/A by BET): 333,9888 Å

BJH Adsorption average pore width (4V/A): 58,819 Å

BJH Desorption average pore width (4V/A): 68,577 Å

D-H Adsorption average pore width (4V/A): 66,001 Å

D-H Desorption average pore width (4V/A): 74,726 Å

A7-7-6. [BMIM][BF₄]-coated Ir nanoclusters on MgO**Summary Report****Surface Area**

Single point surface area at $p/p^* = 0,274762435$: 9,4912 m²/g

BET Surface Area: 10,1795 m²/g

Langmuir Surface Area: 17,3875 m²/g

t-Plot External Surface Area: 15,2984 m²/g

BJH Adsorption cumulative surface area of pores
between 17,000 Å and 3.000,000 Å width: 28,208 m²/g

BJH Desorption cumulative surface area of pores
between 17,000 Å and 3.000,000 Å width: 29,0364 m²/g

D-H Adsorption cumulative surface area of pores
between 17,000 Å and 3.000,000 Å width: 29,622 m²/g

D-H Desorption cumulative surface area of pores
between 17,000 Å and 3.000,000 Å width: 33,6177 m²/g

Pore Volume

Single point adsorption total pore volume of pores
less than 3.873,040 Å width at $p/p^* = 0,995000000$: 0,178608 cm³/g

t-Plot micropore volume: -0,002912 cm³/g

BJH Adsorption cumulative volume of pores
between 17,000 Å and 3.000,000 Å width: 0,038477 cm³/g

BJH Desorption cumulative volume of pores
between 17,000 Å and 3.000,000 Å width: 0,044702 cm³/g

Pore Size

Adsorption average pore diameter (4V/A by BET): 701,8335 Å

BJH Adsorption average pore width (4V/A): 54,562 Å

BJH Desorption average pore width (4V/A): 61,581 Å

D-H Adsorption average pore width (4V/A): 62,315 Å

D-H Desorption average pore width (4V/A): 72,021 Å

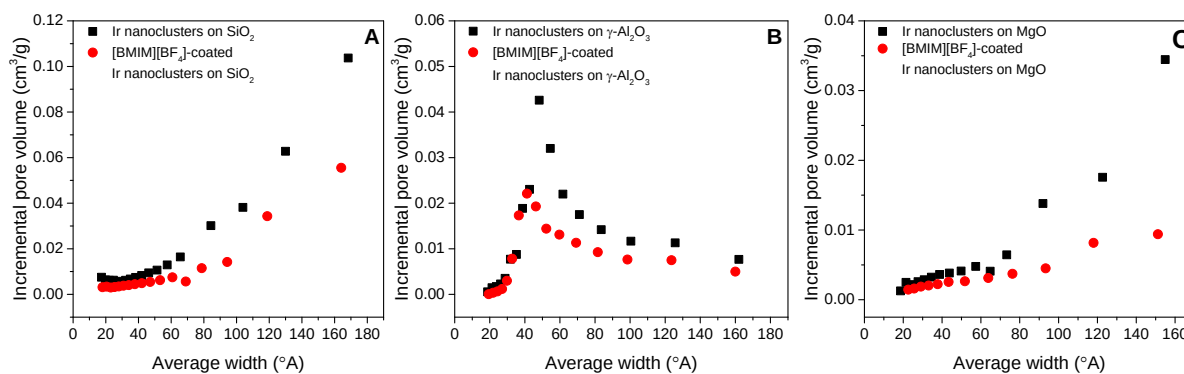


Figure A7-23. Desorption pore size distribution of uncoated and [BMIM][BF₄]-coated catalysts: A) Ir nanoclusters on SiO₂, B) Ir nanoclusters on γ -Al₂O₃, and C) Ir nanoclusters on MgO.

A7-7-6. IL thickness calculation from BJH pore volume and BET surface area

IL thickness of the samples were calculated based on the difference of BJH pore volumes of the [BMIM][BF₄]-coated and uncoated Ir nanoclusters; divided by the BET surface area of the uncoated samples. The calculated thicknesses are 4.9 nm, 0.9 nm, and 2.7 nm for Ir nanoclusters supported on SiO₂, γ -Al₂O₃, and MgO, respectively.

A7-8. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for IL loading calculations

Table A7-2. ICP-MS results and calculated IL loading of the [BMIM][BF₄]-coated iridium nanoclusters supported on γ -Al₂O₃ and MgO. The concentration the IL was measured based on the concentration of boron atom inside the IL.

Samples	11 B [He]		Calculated [BMIM][BF ₄] loading (%)
	Conc. (ppm)	Conc. Relative standard deviation (%)	
Washing	<0.000000	N/A	N/A
IL-coated Ir nanoclusters on γ -Al ₂ O ₃	13.69584374	3.201446939	18.57
IL-coated Ir nanoclusters on MgO	18.2533698	2.503769908	20.62

A7-9. FTIR Characterization Before and After Activation of the Samples at 373 K in Flowing H₂

Figure A7-24 demonstrates the IR bands of bulk [BMIM][TFA], supported iridium nanoclusters, [BMIM][TFA]-coated supported iridium nanoclusters, and [BMIM][TFA]-coated supported iridium nanoclusters after activating the samples at 373 K in flowing H₂, followed by cooling down to room temperature in flowing He. The spectra indicate no change in the IR band positions of the bulk IL upon activation, indicating that our activation conditions do not cause the decomposition of the IL.

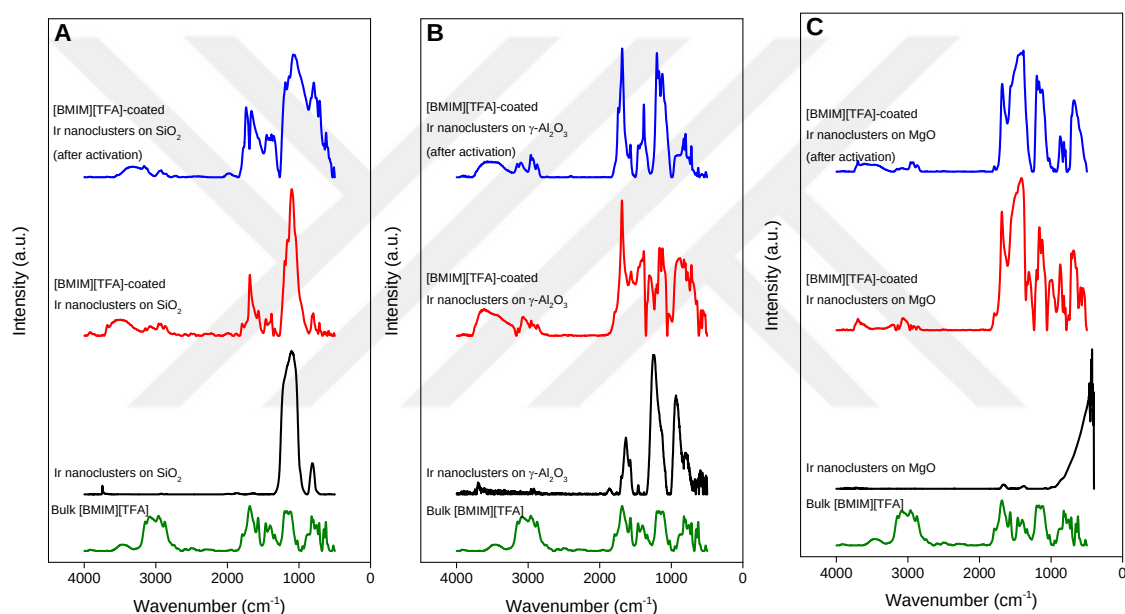


Figure A7-24. IR spectra of bulk [BMIM][TFA] (green), as-is uncoated supported Ir nanocluster (black), [BMIM][TFA]-coated supported Ir nanoclusters (red), and [BMIM][TFA]-coated supported Ir nanoclusters after activating the sample at 373 K in flowing H₂ for 1 h. The catalysts are supported on A) SiO₂, B) γ -Al₂O₃, and C) MgO.

A7-10. Catalyst Performance Measurements

Table A7-3. Individual butenes selectivity values measured at steady-state and differential conversions (below 2%) characterizing partial hydrogenation of 1,3-butadiene (BD) at an H₂/BD feed molar ratio of 2:1 at 373 K and 1 atm catalyzed by uncoated and IL-coated Ir nanoclusters supported on metal oxides with various electron-donor characteristics.

Catalysts		Individual selectivity of the products for partial hydrogenation of 1,3-butadiene at 333 K (%)			
		butane	<i>trans</i> -2-butene	1-butene	<i>cis</i> -2-butene
SiO ₂ -supported samples	Uncoated supported single-site iridium	58	11	21	10
	[BMIM][NTf ₂]-coated supported single-site iridium	43	11	27	20
	[BMIM][BF ₄]-coated supported single-site iridium	27	17	41	13
	[DMIM][MSO ₄]-coated supported single-site iridium	33	20	28	20
	[BMIM][TFA]-coated supported single-site iridium	25	14	51	11
	[EMIM][DEP]-coated supported single-site iridium	20	22	36	22
	[DMIM][DMP]-coated supported single-site iridium	18	25	37	19
	[BMIM][Ac]-coated supported single-site iridium	7	45	18	31
	Uncoated supported Ir nanoclusters	76	4	15	5
	[BMIM][NTf ₂]-coated supported Ir nanoclusters	74	5	15	6
	[BMIM][BF ₄]-coated supported Ir nanoclusters	74	5	15	6
	[DMIM][MSO ₄]-coated supported Ir nanoclusters	68	8	16	7
	[BMIM][TFA]-coated supported Ir nanoclusters	52	9	27	11
	[EMIM][DEP]-coated supported Ir nanoclusters	43	17	22	18
	[DMIM][DMP]-coated supported Ir nanoclusters	41	13	30	17
	[BMIM][Ac]-coated supported Ir nanoclusters	32	24	16	25
γ -Al ₂ O ₃ -supported samples	Uncoated supported single-site iridium	49	15	24	13
	[BMIM][NTf ₂]-coated supported single-site iridium	39	18	32	11
	[BMIM][BF ₄]-coated supported single-site iridium	38	17	31	14
	[DMIM][MSO ₄]-coated supported single-site iridium	35	20	29	16
	[BMIM][TFA]-coated supported single-site iridium	36	20	28	17
	[EMIM][DEP]-coated supported single-site iridium	34	20	34	13
	[DMIM][DMP]-coated supported single-site iridium	27	19	44	10
	[BMIM][Ac]-coated supported single-site iridium	22	22	42	14
	Uncoated supported Ir nanoclusters	68	7	19	7
	[BMIM][NTf ₂]-coated supported Ir nanoclusters	64	7	19	10
	[BMIM][BF ₄]-coated supported Ir nanoclusters	61	7	24	8
	[DMIM][MSO ₄]-coated supported Ir nanoclusters	53	9	28	10
	[BMIM][TFA]-coated supported Ir nanoclusters	47	11	30	12
	[EMIM][DEP]-coated supported Ir nanoclusters	54	18	26	22
	[DMIM][DMP]-coated supported Ir nanoclusters	33	14	38	15
	[BMIM][Ac]-coated supported Ir nanoclusters	23	23	32	22

MgO-supported samples	Uncoated supported single-site iridium	28	24	33	16
	[BMIM][NTf ₂]-coated supported single-site iridium	25	23	31	21
	[BMIM][BF ₄]-coated supported single-site iridium	20	26	40	14
	[DMIM][MSO ₄]-coated supported single-site iridium	23	21	33	23
	[BMIM][TFA]-coated supported single-site iridium	21	26	30	23
	[EMIM][DEP]-coated supported single-site iridium	16	24	41	19
	[DMIM][DMP]-coated supported single-site iridium	15	31	29	25
	[BMIM][Ac]-coated supported single-site iridium	16	27	39	18
	Uncoated supported Ir nanoclusters	61	7	24	8
	[BMIM][NTf ₂]-coated supported Ir nanoclusters	47	14	25	15
	[BMIM][BF ₄]-coated supported Ir nanoclusters	46	9	33	11
	[DMIM][MSO ₄]-coated supported Ir nanoclusters	40	14	34	14
	[BMIM][TFA]-coated supported Ir nanoclusters	27	9	44	19
	[EMIM][DEP]-coated supported Ir nanoclusters	18	23	37	22
	[DMIM][DMP]-coated supported Ir nanoclusters	20	13	53	14
	[BMIM][Ac]-coated supported Ir nanoclusters	10	22	43	26

A7-11. References

1. J. Lu, et al., Supported Molecular Iridium Catalysts: Resolving Effects of Metal Nuclearity and Supports as Ligands. *Journal of the American Chemical Society*, **2011**, 133, 16186-16195.

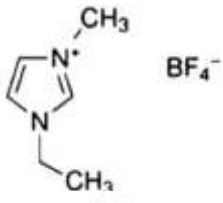
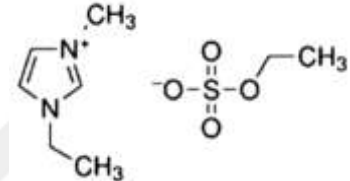
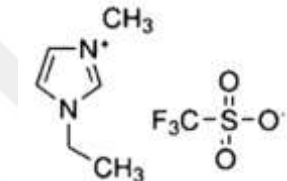
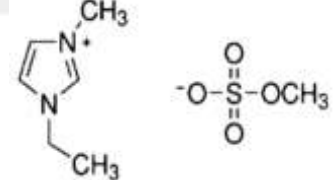
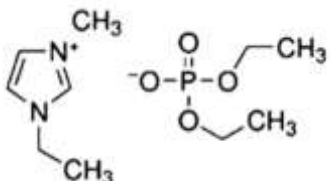
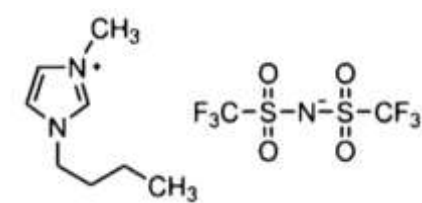
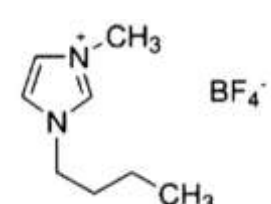
Appendix A8

Supplementary Materials for Tailoring the Performance of Supported Small Metal Nanoparticles by Ligand Modification



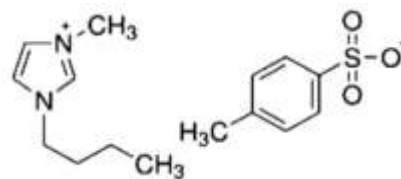
A8-1. Materials

Table A8-1. Names, abbreviations and structures of the ILs.

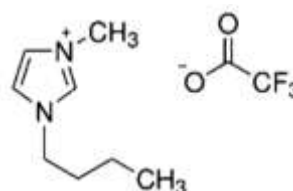
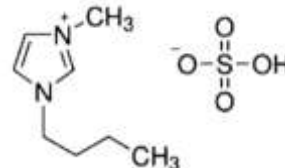
Name of IL	Abbreviation	Structure
1-Ethyl-3-ethylimidazolium tetrafluoroborate	[EMIM][BF ₄]	
1-Ethyl-3-methylimidazolium ethyl sulfate	[EMIM][EtSO ₄]	
1-Ethyl-3-methylimidazolium trifluoromethanesulfonate	[EMIM][TfO]	
1-Ethyl-3-methylimidazolium methyl sulfate-95%	[EMIM][MSO ₄]	
1-Ethyl-3-methylimidazolium diethyl phosphate	[EMIM][DEP]	
1-Butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide	[BMIM][NTf ₂]	
1-Butyl-3-methylimidazolium tetrafluoroborate	[BMIM][BF ₄]	

1-Butyl-3-methylimidazolium
tosylate

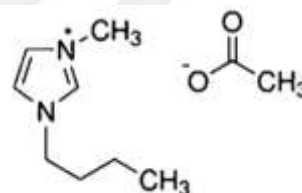
[BMIM][TOS]

1-Butyl-3-methylimidazolium
trifluoroacetate

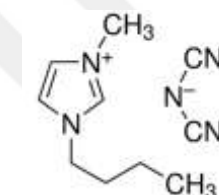
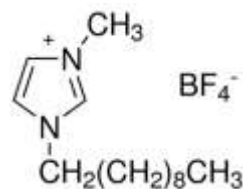
[BMIM][TFA]

1-Butyl-3-methylimidazolium
hydrogen sulfate[BMIM][HSO₄]1-Butyl-3-methylimidazolium
acetate

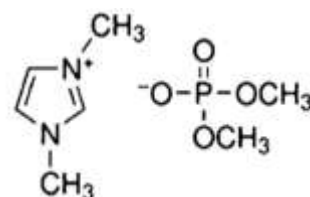
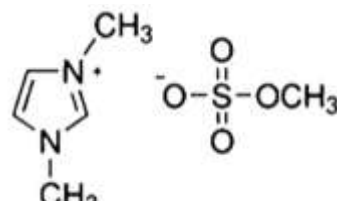
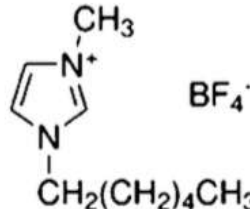
[BMIM][Ac]

1-Butyl-3-methylimidazolium
dicyanamide

[BMIM][DCA]

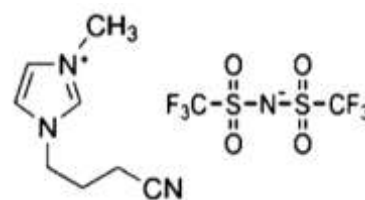
1-Decyl-3-methylimidazolium
tetrafluoroborate[C₁₀MIM][BF₄]1,3-Dimethylimidazolium
dimethyl phosphate

[DMIM][DMP]

1,3-Dimethylimidazolium
methyl sulfate[DMIM][MSO₄]1-Hexyl-3-methylimidazolium
tetrafluoroborate[HMIM][BF₄]

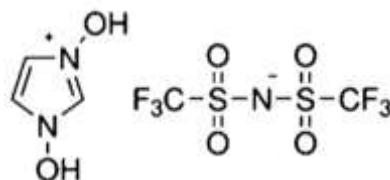
1-(3-Cyanopropyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide

[CPMIM][NTf₂]



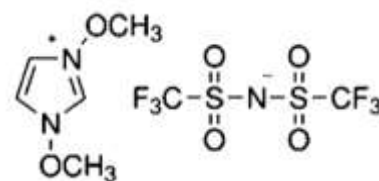
1,3-Dihydroxyimidazolium bis(trifluoromethylsulfonyl)imide

[DHIM][NTf₂]



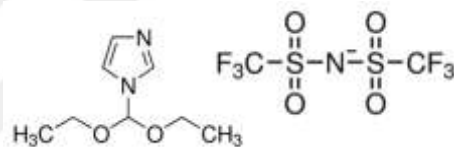
1,3-Dimethoxyimidazolium bis(trifluoromethylsulfonyl)imide

[DMOIM][NTf₂]



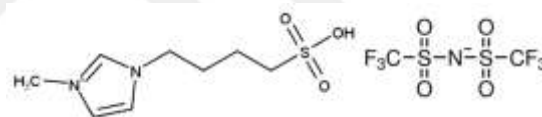
1-(Diethoxymethyl)imidazole bis(trifluoromethylsulfonyl)imide

[DEOIM][NTf₂]



1-(4-Sulfobutyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide

[SUMIM][NTf₂]



Conclusions and Outlook

This present thesis is a guide for synthesizing ionic liquid (IL) coated supported metal catalysts, their characterization with various techniques, and their catalytic performance tests which provides structure-performance relationship at fundamental level.

The catalysts were chosen to have simplest structures; thus, they were synthesized in the form of atomically dispersed catalysts supported on metal oxides. The three design variables considered in this research that have impacts on the electronic structure and the performance of the catalysts are metal nuclearity (changing from single-site to small nano-size), the electron donating properties of the supports, and IL structures. The main conclusions are:

A) The electron donating abilities of the metal oxide supports significantly influence the local electronic environment of the active sites and consequent selectivity and activity performance of the catalysts.

B) Ionic liquids act as ligands and donate/withdraw electron density to/from active sites. This electron transfer between ILs and active sites alters the performance of the catalysts. Performance of the catalysts can be controlled by systematically changing the IL structure.

C) Supports and ILs have synergistic ligand effects on supported catalysts: the influence of the ILs on the performance of the supported catalyst is less significant when the active sites are supported with highly electron donating supports.

D) The influence of the metal nuclearity was investigated by converting single-site supported metals into small nanoparticles. As the size of the active sites increases, the influence of the support on performance becomes less significant while IL's effect is the dominant factor. On the other hand, when the catalysts were in the form of atomically dispersed species, the support is more influential.

The results demonstrate that the structure-performance relationship in IL-coated supported metal catalysts was obtained. The findings of this research can be used to fine-tune the performance of the IL-assisted catalysts.

As an outlook to this research, there are several other studies that can be conducted.

A) Elucidation of the influence of metal nanoparticle size on the electronic environment and catalytic performance of the IL-coated supported metals is important since size of the catalysts is one of the dominant factors controlling the performance. In the present thesis, the single-site catalysts and small nanoparticles were studied, however, more detailed and systematic changes in the metal nanoparticle size can be investigated. Metals in single-site form, Ir₄ clusters, Ir₆ clusters, small iridium nanoparticles and iridium nanoparticles (nanoparticle size > 1 nm) can be compared in terms of the electronic environment of the active sites and catalytic performance.

B) Cluster formation of the single-site supported catalysts during reaction is one of the important limitations of this type of catalysts. Single-site catalysts tend to agglomerate at high temperatures and/or different reactive gas environment such as H₂. The presence of IL layer on the catalysts may delay the cluster formation based on their structures and interactions with the active sites. Thus, in order to understand the IL effect on cluster formation chemistry, uncoated and IL-coated catalysts can be treated at different reactive environments.

C) Although there are findings indicating the ligand effect of the ILs, there are still unclear points about the binding of the IL layers to the active sites. Thus, the interactions between ILs and active sites can be understood by the help of DFT calculations and the binding of ILs to the active sites can be clarified.

D) The high electron density on the ILs may influence the uniform distribution of the single-site catalysts on supports. Therefore, by the help of IR and imaging techniques, the effect of IL layer on the uniformity can be elucidated.

E) The present thesis consists of many reaction data, however, the influence of the IL layer on the reaction kinetics is still not known. The presence of an IL layer may change the reaction orders as well as activation energy for the reaction. Therefore, the reaction pathways for 1,3-butadiene hydrogenation in the absence and presence of the IL layer can be investigated. The binding mode and energy of the reactants and intermediates to the IL-coated catalysts can be elucidated.

(F) Zeolites, metal organic frameworks, carbon-based materials and other promising high-surface-area materials can be utilized to support the catalysts. The interactions of each support with active sites and consequent influence on the performance can be investigated.

(G) The metal oxide supports used in this research can be doped by some other atoms such as boron and phosphonyl to elucidate the variations in the electronic properties of the supports on the active sites.

(H) IL have almost infinite number of combinations. This study can be expanded by using ILs other than imidazolium-type.

(I) Bifunctional ILs can be used as coating layers to reach many other reactions.