

Investigating the Effect of Reduction Temperature and Ionic Liquid Deposition on Gas Separation Performance of Ionic Liquid/Reduced Graphene Aerogel Composites

by

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To Mi Hermana and Lena

ABSTRACT

With the advancements in oil and chemical industries, efficient methods to mitigate the separation problems became increasingly important. Sorption-based gas separation is one of the promising methods that aims to tackle the separation necessities with cost-efficient synthesis steps and high gas selectivities. Carbon-based materials are one of the most preferred sorbents due to their availability and tunability, and metal-organic frameworks (MOFs) are one of the most heavily researched sorbents due to their easily designable nature and exceptional capability to sorb gases with highly porous structure. To enhance the gas separation capability of existing sorbents, many functionalization techniques are being investigated. The incorporation of ionic liquids (ILs) into porous hosts has proved to be an influential functionalization method to tune the sorption-based gas separation performance of porous materials with many reports illustrating the effect of IL deposition in porous composites in the last decade. Inspired by these studies, this thesis is dedicated to investigating the gas separation performance of IL-loaded reduced graphene aerogels (rGAs) and an IL-coated MOF composite.

In this thesis, two different ILs with differing hydrophilic characters were incorporated into graphene aerogels (GAs) thermally reduced at two different temperatures, 300 °C and 500 °C. A detailed structural analysis was done to illustrate the effect of thermal reduction in rGAs, and interactions between IL molecules and host rGAs upon IL addition. Volumetric gas sorption analysis for CO₂ and CH₄ gases was done, and the gas separation performance of the rGAs and IL/rGA composites was compared based on the interactions outlined in the characterization. Based on the CO₂/CH₄ separation performance of the IL-loaded composites, a correlation was made relating the number of oxygenated groups on rGAs and the hydrophilicity of the loaded IL.

The results presented in this thesis show the promising features of IL-deposited rGA composites in CO₂/CH₄ separation. By adjusting the surface characteristics of porous hosts and choosing suitable ILs based on the interactions between host materials and ILs, the performance of the IL-loaded composites can be markedly improved.

ÖZETÇE

Petrol ve kimya endüstrilerindeki gelişmelerle birlikte gaz ayrıştırma problemleri daha da önem kazandı. Bu gaz ayrıştırma gereksinimlerini gidermek için geliştirilen yöntemler arasından gaz yakalama bazlı gaz ayrıştırma yönteminin sentez aşamasındaki uygun maliyetli yaklaşımı ve yüksek ayırma performansı ile yüksek bir potansiyeli vardır. Karbon-bazlı ve Metal Organik Kafesli (MOF) maddeler erişilebilirlikleri, kimyasal özelliklerinin ayarlanabilir olması ve porlu yapılarından dolayı en çok üzerinde çalışılan gaz emici maddelerdendir. Var olan gaz emici maddelerin gaz ayrıştırma performanslarını iyileştirmek için birçok yöntem denenmektedir. Son yıllarda literatürde raporlanan çalışmalara bağlı olarak İyonik Sıvıların (İS) porlu yapıdaki gaz emici maddelere katılması var olan maddelerin gaz ayrıştırma performanslarını geliştirmek için en etkili yöntemlerden biri olarak ortaya çıkmıştır. Bu tezin içeriği literatürdeki çalışmalardan ilham alınarak İS yüklü karbon-bazlı indirgenmiş grafen aerogeller (rGA) ve İS kaplı MOF kompozitlerinin çeşitli gaz ayrıştırma problemlerindeki performanslarını araştırmaya adanmıştır.

Bu tezin kapsamında, farklı hidrofilik özelliklere sahip İS'lar 300 °C ve 500 °C olmak üzere farklı sıcaklıklarda termal olarak indirgenmiş GA'lara yüklenmiştir. Termal indirgenme yönteminin rGA üstündeki etkisi ve yüklenilen İS moleküllerinin rGA arasındaki etkileşimini ortaya koymak adına kapsamlı bir yapısal analiz yapılmıştır. CO₂ ve CH₄ gazları için hacimsel gaz yakalama deneyleri yürütülmüştür, rGA ve İS yüklü rGA kompozitlerinin gaz ayrıştırma performansları karakterizasyon sonuçlarına bağlı olarak karşılaştırılmıştır. İS yüklü kompozitlerin CO₂/CH₄ ayrıştırma performansı, rGA yapısındaki oksijen içeren yüzey fonksiyonel gruplarının miktarı ve yüklenilen İS'lerin hidrofilik karakteri arasında bir korelasyon olduğunu ortaya koymuştur.

Bu tezde sunulan sonuçlar, İS-yüklü rGA kompozitlerinin CO₂/CH₄ ayrıştırma prosesindeki potansiyelini ortaya koymuştur. Porlu yapıdaki maddelerin yüzey özelliklerini ayarlayarak ve uygun İS'lar bu maddelere yüklenmek üzere seçilerek İS-yüklü kompozitlerin gaz ayrıştırma performansları önemli ölçüde iyileştirilebilir.

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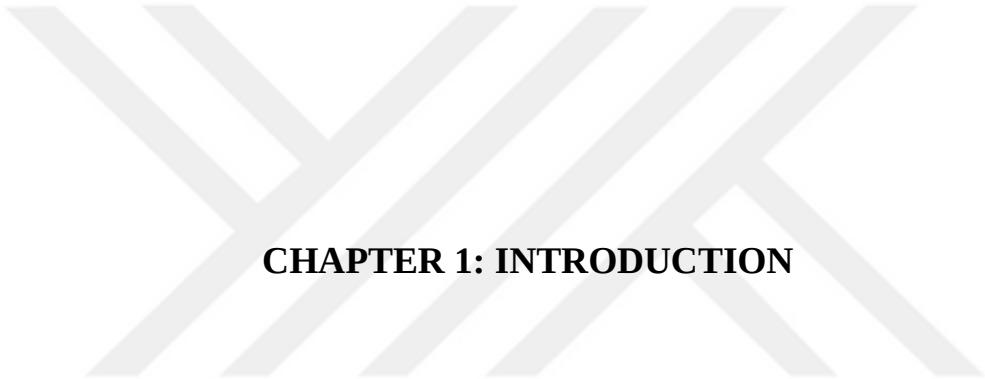
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ABBREVIATIONS

AC	Activated Carbon
BET	Braunuer-Emmett-Teller
COF	Covalent Organic Framework
COSMO	Conductor-like Screening Model
DFT	Density Functional Theory
EDS	Energy Dispersive Spectroscopy
FTIR	Fourier Transform Infrared
GA	Graphene Aerogel
GCMC	Grand Canonical Monte Carlo
GO	Graphene Oxide
IAST	Ideal Adsorbed Solution Theory
MD	Molecular Dynamics
MOF	Metal-Organic Framework
rGO	Reduced Graphene Oxide
SEM	Scanning Electron Microscopy
TGA	Thermogravimetric Analysis
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction



CHAPTER 1: INTRODUCTION

The need to produce pure, efficient chemicals has become one of the most crucial goals in industries with the widespread industrialization and emergence of many chemical processes. The usage of fossil fuels has led the world to a dramatic increase in the concentration of air pollutants such as CO_2 , CO , CH_4 , NO_x , N_2O , and SO_2 all of which are extremely dangerous to human and environmental health.¹ To mitigate the hazardous effects of these pollutants, several processes have been employed in industries to separate toxic gases. The emission of harmful pollutants is exponentially increasing with time and the advancements in technology, which fuels the fatal threat to humanity with fire that is the climate crisis. The main factor upsetting the equilibrium of the climate, hence the life on earth, is the continuous emission of aforementioned gases, predominantly CO_2 among them. Due to an increasing trend in the earth's temperature, the water resources and the plant ecosystem are under imminent threat if necessary actions will not be taken. The climate crisis forces us to seek out efficient methods to capture and separate such toxic and harmful gases without releasing them into the atmosphere untreated. Condensation, physical and chemical absorption, distillation, catalytic oxidation and hydrogenation, separation by membranes, and adsorption can be considered examples of these methods. These processes have their strengths and shortcomings based on the desired outcome.

The absorption methods are widely used in existing industrial plants, but they have several weaknesses that must be addressed to achieve economically and environmentally feasible separation. The cost of using and regenerating solvents that are the main components of absorption processes is too high; additionally, there is the need to dispose of these solvents which can cause damage to the environment, especially in the case of amine-based solvents such as monoethanolamine (MEA) and diethanolamine (DEA). Condensation is another method that utilizes a condenser to liquefy the gases based on their varying physicochemical properties. But since it requires an immense amount of energy to achieve condensation, this method brings the question of economic feasibility. Similarly, distillation is one of the most preferred methods to separate gases, but it also requires a huge capital investment and operating cost to maintain continuous and efficient operation. The reactive separation of gases with catalytic oxidation and hydrogenation is another possibility that has been investigated in the literature and employed by many chemical manufacturers. But catalytic reactions are complex to analyze and handle due to mass-transfer and thermodynamic limitations of reactions. Also, producing the bulk amount of high-performing catalysts is expensive, and operation at a larger scale has the chance to yield low conversions despite high-energy inputs. Gas separation with membranes offers a similar challenge, although the construction of membranes is relatively easier than the catalysts.

The biggest problem with the utilization of membranes is that there is a trade-off for the performance of membranes. If a membrane is highly selective for a gas separation application, it tends to allow gas permeation at a lower rate than other candidates or vice versa. Also, most of the membranes do not react well when encountered with different gases, such as acidic gases which cause plasticization, a deterioration in the polymer-based matrices of membranes.² The plasticization causes an abrupt decrease in separation performance and the lifetime of the membranes. Among the previously discussed methods, adsorption-based gas separation offers energy and cost-efficient solutions for various gas separation applications. The flexible design of adsorption-based processes and adsorbent materials also contribute to the highly attractive benefits of this method. Adsorbents are one of the most important driving components for such processes, their design and characterization are one of the most studied subjects in literature.³ An ideal adsorbent must have the following qualities for high-performance separations: High selectivity for targeted gas mixtures, thermal and mechanical stability, high gas uptakes, low manufacturing cost, and lastly, regenerability or reusability.

Many materials such as silica- and carbon-based materials, and metal-organic frameworks (MOF) derived from different origins are being investigated as promising adsorbents. Silica-based adsorbents have been recognized to display efficient separation for acidic gases such as CO₂ or sulfur-containing gases because of their relatively higher affinity to form covalent bonds with acidic gases.⁴ But their low gas uptakes and high energy needs for regeneration render their usage less preferred compared to other adsorbents. Carbon-based adsorbents present such a vast category that includes carbon nanotubes (CNT), activated carbon, biochar, and graphene oxide (GO); they can be considered the most widely utilized materials among all adsorbents. The surface functionalities of carbonaceous material are usually modified according to separation specifications and are the driving forces facilitating van der Waals and chemical interactions between gases and the adsorbents.⁵ Through functionalization, carbon-based adsorbents have been reported to demonstrate high gas uptakes and separation selectivity values.⁶ Furtherly, MOFs are popular three-dimensional porous adsorbents due to their high surface areas and easily tunable nature consisting of metal nodes and organic linkers. Besides displaying high gas separation performance, the gas uptake capacity of MOFs is higher than that of most adsorbents, and their simple and changeable synthesis routes lead researchers to employ rich, unique ways to obtain these materials. The literature is saturated with reports of CO₂ adsorption and separation performance of both carbonaceous materials and MOFs. Especially for MOFs, CO₂ capture and separation criteria and future expectations have been

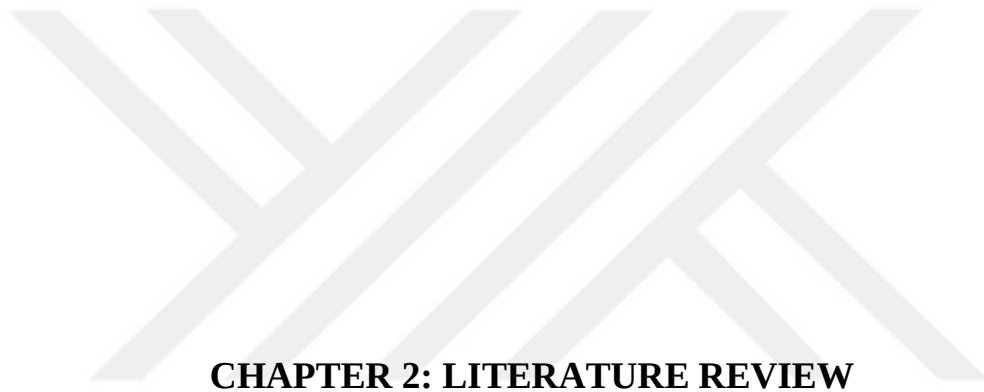
identified with several detailed studies.^{7,8} These materials are also being heavily investigated for other gas separation and capture problems such as acetylene purification (C_2H_2/C_2H_4 , C_2H_2/CH_4 , and C_2H_2/CO_2), oxygen purification (O_2/N_2), light hydrocarbon separation and capture, volatile organic compound (VOC) removal, the capture of highly toxic gases (NO_2 , H_2S , SO_2), and separation of noble gases.^{9–11}

As stated earlier, MOFs and carbonaceous materials have a highly tunable nature through functionalization, and among the plethora of options, ionic liquids (IL) can be considered as one of the promising, emerging tools to functionalize these materials. ILs are essentially molten salts that consist of a cation and an anion part. They have easy synthesis paths which can be tailored according to the aimed application area. The number of cation and anion combinations cannot be strictly quantified since there exists a limitless number of theoretical IL molecules. Despite this limitlessness, only thousands of ILs have been synthesized and investigated in the literature. The library of ILs is an ever-expanding one due to exponentially increasing interest in these interesting materials. ILs, because of their nonvolatile, nonflammable, and water-resistant nature, are considered “green solvents” by researchers and utilized in many areas ranging from electrochemistry to gas and liquid separation. They are used as catalysts, solvents, and reagents for various chemical reactions in their bulk state,¹² however, their incorporation into porous media has proven to result in a considerably different set of physicochemical properties than their bulk states due to interaction with their hosts. ILs are known to demonstrate low gas uptakes and high absorption enthalpies, which were influential for the motivation of the studies featuring their confinement or usage in porous materials. Although the reports of MOF functionalization with ILs have started more than a decade ago,¹³ the investigation of IL/MOF composites for gas separation applications started to appear in the literature later.¹⁴ Similarly, IL mobilization on carbonaceous materials for gas adsorption and separation was reported around the same time as the reports of IL/MOF composites.¹⁵ By incorporating ILs into various porous hosts, the studies demonstrated a prominent boost in the gas separation performance of the IL-loaded composites compared to pristine hosts through the enhanced interactions between adsorbate and adsorbent.

In the scope of this thesis, a detailed literature review on properties and applications of GAs, gas sorption, and separation performance of MOFs, ILs, IL/MOF, and IL/carbon-based composites is featured in Chapter 2. The experimental and computational methods used throughout the study are thoroughly explained in Chapter 3 which encapsulates the synthesis of IL-loaded composites, structural and morphological characterization techniques, sorption

experiments, and computational details. Chapter 4 presents the gas adsorption and separation performance of IL-incorporated reduced graphene aerogels (rGAs). As one of the novel carbonaceous materials, GAs are attracting porous adsorbents with their high surface area, thermal stability, and easily tunable nature.¹⁶ By treating GAs thermally at two different temperatures, 300 °C and 500 °C under a constant flow of a nonreactive gas, the surface oxygen functional groups of GAs were found to be decreasing with an increase in reduction temperature. Also, two different ILs having the same cation with different anions offering opposite hydrophilic/hydrophobic characters, 1-*n*-butyl-1-methylpyrrolidinium dicyanamide ([BMPyr][DCA]) and 1-*n*-butyl-1-methylpyrrolidinium hexafluorophosphate ([BMPyr][PF₆]), were incorporated onto rGAs. Due to variation in the thermal reduction process, rGA300 and rGA500 were found to be displaying different CO₂/CH₄ separation performances and IL incorporation significantly affected the CO₂/CH₄ separation performances of the rGAs. The detailed structure, morphology, and performance-based characterization results were used to explain the effect of sorbate-sorbent interactions on gas separation performance.

Moreover, as a side project in the scope of this thesis, C₂H₂ separation performance of a core-shell type IL/MOF was presented in Appendix B through the structural characterization and volumetric sorption results. A commercially available and frequently researched MOF, ZIF-67 was chosen as the porous host for the synthesis of core-shell type IL/MOF composite. A hydrophilic IL, [HEMIM][DCA], was used to coat the exterior surface of the pristine MOF. The ideal gas selectivities were calculated for C₂H₂/CH₄, C₂H₂/C₂H₄, and C₂H₂/H₂ from the volumetric sorption results obtained at three different temperatures.



CHAPTER 2: LITERATURE REVIEW

To provide a background on the featured materials in this thesis, a comprehensive literature review was done. In this chapter, first, the origin, application areas, and specifically gas adsorption and separation performances of graphene aerogels are outlined. In the second part, the characteristics of MOFs and their usage in gas capture and separation applications are explained through reported data in the literature. The next part covers the physicochemical properties and application areas of ILs. In the final part of this chapter, gas adsorption-based separation performances of IL/GA and IL/MOF composites are reviewed extensively.

2.1 Properties and applications of graphene aerogels (GAs)

Graphene-based materials are getting increasing attention ever since the pioneering work of Geim and Novoselov on graphene was rewarded with a Nobel prize in 2004.¹⁷ Graphene has a 2D structure with an orderly hexagonal lattice and carbon atoms present in the hexagonal skeleton are sp^2 bonded. Due to its attractive qualities such as high electron mobility, thermal stability, surface area, tensile strength, and tunability, graphene, and graphene-based materials are being investigated in physics, chemistry, and materials science.¹⁸ Graphene and its main derivatives, graphene oxide (GO) and reduced graphene oxide (rGO) have a wide range of synthesis steps, but the general synthesis route starts with the oxidation of graphite.¹⁹ The surface functionalities such as carboxyl ($-COOH$), epoxy ($C-O-C$), hydroxyl ($C-OH$), and carbonyl ($-C=O$) are introduced upon the chemical oxidation of carbon-based skeleton during GO synthesis. The synthesis steps are crucial in terms of adjusting the quantity of these functional groups, hence the surface characteristics of GO. First, synthesis methods can be classified into two subgroups: top-down and bottom-up methods. Liquid-phase exfoliation, solid exfoliation, oxidative exfoliation, electrochemical reduction, and arc-discharge methods are some examples of the top-down approach, whereas bottom-up encompasses methods such as thermal pyrolysis, chemical vapor deposition, epitaxial growth, and direct organic synthesis. Compared to bottom-up approaches, top-down methods are easier to utilize and economically feasible, which justifies their widespread usage. Oxidative exfoliation is one of the most used methods in research labs to synthesize GO, and GO-based materials, and it has four main routes proposed by renowned scientists: Brodie, Staudenmaier, Hofmann, and Hummers.²⁰ Although each route has its advantages and disadvantages, the modified Hummers method is very popular since it has a high product yield, utilizes low temperatures during synthesis, and results with less or non-toxic gases, hence it promotes an environmental and safer path to produce GO.²¹

As briefly stated, the oxidation of graphite adds oxygenated functionalities to the graphitic structure which progresses through the intercalation of graphite layers, weakening the van der Waals forces between carbon atoms. GO is known to retain certain functional groups, but a definite chemical composition of this material is yet to be explored due to its complex and varied synthesis route. Despite the ambiguity about GO's structure, there are several representative models such as Hofmann, Ruess, Nakajima-Matsuo, Lerf - Klinowski, Scholz, Boehm, Dekany, and Szabo et al. who have proposed different locations for the oxygenated groups in GO structure.²² GO can be considered one of the first derivatives of graphene, and its electronic, optical, and chemical properties and applications in many areas have been thoroughly investigated. The further functionalization of GO has brought a new class of materials, starting from rGO to graphene aerogels (GA). Through the chemical, thermal, microwave-assisted, and solvothermal reduction of GO, one can obtain rGO,²³ and with hydrothermal reduction,²⁴ crosslinking,²⁵ chemical reduction,²⁶ template-assisted synthesis,²⁷ and 3D printing²⁸ graphene aerogels can be produced from GO. GAs, as one of the subclasses of GO-based materials, come forward since they offer ultra-low density, high surface area, tunable porosity, and high thermal-electrical conductivity.²⁹

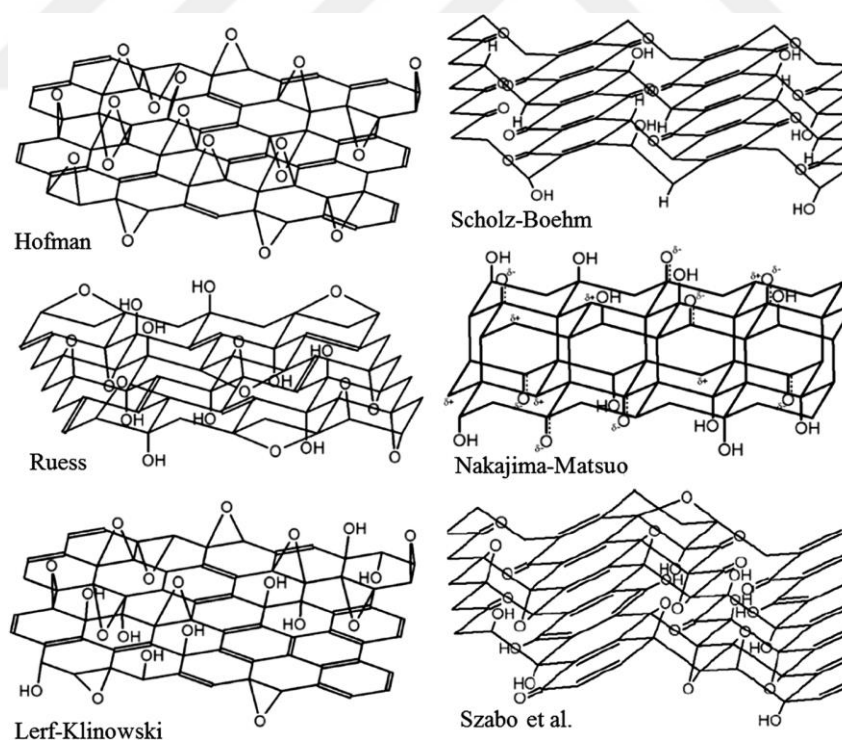


Figure 2.1. Several proposed chemical structure models of GO.³⁰

Different than graphene and GO's 2D structure, a typical GA structure is in 3D form due to the formation of a highly porous network after the specialized treatment of commonly used

GO solution.³¹ Different than other 2D graphene-based materials that are prone to agglomerate when incorporated into polymers, GAs can perform better dispersions through specialized synthesis methods.³² Highly porous GA can be utilized in many applications, such as catalysis,²⁴ adsorption,³³ gas sensing,³⁴ energy storage, and conversion,³⁵ and supercapacitors.³⁶ The literature is rich with the reports on adsorption of oil, dye, and chemical reagents by GAs,^{16,37,38} but only a few studies are reporting their gas adsorption and separation performances.³⁹ After functionalization and applying special treatments to GA, dramatic enhancements in the gas uptakes and separation performances were observed in several studies. To provide examples, Li and coworkers reported ultrahigh separation performance for the benzene/toluene system of tetraethyl orthosilicate (TEOS) functionalized GA.⁴⁰ By adding TEOS to the graphitic structure, the benzene adsorption capacity of GA increased from 201.71 mg/g to 809.51 mg/g at 0.9 P₀. In another approach, a common MOF, Cu-BTC was incorporated into GA to increase the H₂ storage capacity. Despite Cu-BTC's ability to adsorb more H₂ gas than GA, when combined, Cu-BTC/GA composite increased from 1.5 wt.% H₂ uptake capacity of Cu-BTC to 2.2 wt.% at 100 bar due to increased surface area and pore volume.⁴⁰ Similar to this approach, the same group incorporated an IL, [BMIM][BF₄] to Cu-BTC/GA composite and investigated the CO₂ adsorption performance of Cu-BTC, GA, Cu-BTC/GA, and Cu-BTC/GA-IL. At 1 bar, GA and Cu-BTC yielded CO₂ uptakes of 0.3 and 3 mmol/g, respectively, whereas Cu-BTC/GA and Cu-BTC/GA-IL demonstrated CO₂ uptakes of 3.2 and 3.7 mmol/g due to high pore volume and IL addition.⁴¹ GA structure is easily tunable with the addition of chemical functionalities, and chemical and thermal treatments. Since the functional groups retained on GA and its porous network are the driving forces behind differing performances in electrochemical reactions, catalysis, and liquid and gas adsorption, more methods to manipulate surface and pore characteristics of GAs can be explored to tune the gas separation efficiency of these promising materials.

2.2 Metal-Organic Frameworks (MOFs) for adsorption-based gas separation

The existence of many gas separation problems especially in the oil and petrochemical industries was mentioned in Chapter 1. The purification of natural gas (CO₂/CH₄ and CH₄/N₂), and syngas (CO₂/N₂), air purification (O₂/N₂), hydrogen purification (CO₂/H₂ and CH₄/H₂); for the petrochemical industry, acetylene purification (C₂H₂/CH₄, C₂H₂/C₂H₄, and C₂H₂/H₂) can be given as examples to these separation applications. To mitigate the need for separation of these gas mixtures, traditional or newly-emerging methods such as liquefaction and gas hydrate-

based methods,⁴² novel 2D organic compounds,⁴² distillation,⁴³ absorption with solvents,⁴⁴ and adsorption-based porous materials are being investigated.⁴⁵ Among these methods, adsorption-based separation can be obtained through several paths specified clearly in the literature: Size exclusion which is related to the pore size of the porous adsorbent and the size of adsorbate, quantum sieving which is utilized for isotope separation, differences in the diffusing rates in pore channels (kinetic separation), and finally, differing adsorbent-adsorbate interactions. Depending on the adsorbent and the nature of separation, the gas sorption mechanism or combination of several mechanisms can differ, hence the selection of porous adsorbent materials is critical for achieving an effective separation. To give some examples of these porous sorbents, inorganic materials such as zeolites and silicas, carbon-based compounds (graphene, carbon), covalent organic frameworks (COFs), polymer or inorganic-based membranes, and metal-organic frameworks (MOFs) can be specified. MOFs are increasingly getting attention over their highly tunable pore sizes, and surface characteristics for gas separation applications.⁴⁵ They are formed with two main constituents: metal nodes and organic ligands. Since there are infinite combinations of existing metal ions and organic ligands, theoretically, limitless number of MOFs with varying properties can be constructed.

MOFs are reported to display remarkable gas capture and separation performances due to their high surface area and tunable pore sizes.⁴⁶ The structures of MOFs can be accurately tailored depending on the desired gas separation application, and also can be functionalized through pre- and post-synthesis modifications. These modifications are often done to increase the gas storage capacity or the separation performance/selectivity of the materials. Besides these excellent properties, MOFs are known for high thermal, chemical, and water stability, they can be recycled and regenerated for continuous utilization. For the gas adsorption and separation performance evaluation of MOFs, generally, single-component adsorption experiments are conducted with gravimetric and volumetric gas adsorption equipment which provide insight into the static equilibrium of adsorption; through breakthrough experiments, one can observe dynamic equilibrium data of MOFs. As each method has its advantages and disadvantages, it is important to combine several adsorption measurement methods and determine the adsorptive performance of MOFs. Although it is still in the development stage, computational methods based on molecular simulations such as grand canonical Monte Carlo (GCMS), molecular dynamics (MD), and density functional theory (DFT) are being used to predict the adsorption mechanisms and performances of MOFs, and other porous materials by constructing the chemical structure of these materials with high precision. The most prominent significance of

these computational tools can be the construction of MOF structures with high accuracy and logical selection of MOFs for appropriate gas separation applications.

2.3 Ionic Liquids (ILs) for gas capture and separation

ILs are known as molten salts since their melting points are mostly below 100 °C. They possess unique properties such as negligible vapor pressure, non-flammable, and water-stable nature.¹² The researchers also call ILs task-specific designer solvents due to their highly tunable nature for various application areas. Similar to MOFs, theoretically, there is a limitless combination of different anion-cation pairs hence a vast library of ILs is present today, and this library expands exponentially with the introduction of novel ILs. The most known ILs include imidazolium, pyridinium-, pyrrolidinium-, piperidinium-, ammonium-, sulfonium-, phosphonium-based organic cations, and organic anions such as acetate (OAc or Ac), methanesulfonate (MeSO₃) or inorganic anions such as bromide (Br), chloride (Cl), iodide (I), bis(trifluoromethylsulfonyl)imide (NTf₂), tetrafluoroborate (BF₄), hexafluorophosphate (PF₆), dicyanamide (N(CN)₂ or DCA), and trifluoromethylsulfate (TfO). Based on the combination of anion-cation pairs, hence the different interionic interactions, the viscosity, density, thermal stability, and gas solubility of ILs vary uniquely. Several relationships unlocking the effect of cations and anions separately or as a team on these physicochemical properties have been established over the years. Shorter alkyl chains on cations are found to be yielding higher melting points or longer alkyl chain causes a decrease in the solubility in water.⁴⁷ Other studies have investigated conductivity, phase behavior, and physicochemical properties of ILs upon a change in either cation or anion.⁴⁸ Despite the thorough examination and comparison among ILs, there still exists a practically unattainable number of screening tests. Furthermore, to make educated guesses to synthesize good performing ILs, apart from experimental techniques, computational tools such as conductor-like screening model for real solvents (COSMO-RS), equations of states (EOS), and quantitative structure-property relationships (QSPR) can be used. These tools are essential to estimate ILs' properties and choose a suitable candidate for a specific separation problem.⁴⁹ Many studies have confirmed the validity of screening of ILs prior to experimental measurements by comparing Henry's law constants calculated with COSMO-RS and obtained results through the experiments.^{50,51}

One of the application areas of ILs is gas separation by absorption. Previously and to date, industries have been utilizing solvent-based absorption to capture and separate toxic gases such as CO₂, and H₂S; but the environmental and economic cost of operating such absorption

processes is deemed inefficient with the recent studies illustrating the capture and separation performance of ionic liquids.⁵² The traditional absorption solvents require intense heating and chemical treatments for regeneration, however, they are sensitive to high-temperature operations whereas ILs are thermally stable at high temperatures (up to 200 °C).⁴⁸ Many ILs have been proven to demonstrate competitive CO₂ sequestration, and efficient CO₂/N₂ or CO₂/CH₄ separation performance compared to traditional solvents, yet, from an economic perspective, for ILs to be utilized in bulk scale, the process cost has to be lowered or ILs displaying more efficient capture performances at high temperatures should be explored.⁵³ In this aspect, utilizing ILs in smaller amounts or combining them with other favorable materials has emerged as a solution to mitigate this dilemma.

2.4 IL/MOF and IL/carbon-based composites for adsorption-based gas separation

Ionic liquid-incorporated composites have been studied and used in many application areas from ionic conductivity to adsorption-based gas separation due to unique properties unlocked by combining two highly tunable and promising materials. Two approaches exist in order to synthesize these materials: in-situ synthesis techniques and post-synthesis modification techniques.⁵⁴ In-situ techniques involve ionothermal synthesis where IL acts both as a template and a solvent,⁵⁵ and sol-gel method where IL is permanently incorporated into porous material during the synthesis.⁵⁶ Other IL-composites were produced via in-situ techniques for varying purposes as well. Qingmin and co-workers incorporated IL during the reduction of GO to adjust the interlayer distance between graphenic layers to increase the performance of aromatic compound sensing.⁵⁷ In another study, an imidazolium-based IL was used as a stabilizing agent during the chemical exfoliation of graphite.⁵⁸ Compared to in-situ preparation of IL/porous composites, post-synthesis functionalization methods offer more flexibility as a more simplistic but effective IL incorporation approach to porous materials. To briefly sum the characteristics of post-synthesis methods: Grafting is a technique where the support material is pre-treated along with IL,⁵⁹ capillary action technique utilizes direct mixing of IL and porous material for incorporation,⁶⁰ ship-in-bottle is a method where IL precursors are separately introduced to porous structure with a solvent containing solution,⁶¹ incipient wetness which is a frequently used method to prepare catalysts is based on adding meticulously quantified IL and solvent solution to the porous materials until the pores of the target material are filled,⁶² and lastly, wet impregnation is the most favorable method among all and it impregnates IL molecules by

dissolving them in excess solvent then the composite is synthesized through physical addition and stirring of IL dissolved solvent solution with the porous material until solvent evaporates.

Choosing and further utilizing an IL incorporation method depends mostly on the target application, and desired characteristics of the composite. Moreover, after the synthesis of IL-impregnated composites, a detailed characterization step is a must to understand the structure of the constructed material. Many techniques are being used as complementary parts of the story that outline the characteristics of these composites. X-ray Fluorescence (XRF) and inductively coupled plasma mass spectrometry (ICP-MS) are being used to determine IL loading, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC) for the thermal stability investigation, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are being used for the visual observance of the composites. Additionally, for the investigation of the interactions between IL molecules and hosts, Fourier transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy can provide valuable insights while Brunauer-Emmett-Teller (BET) analysis gives information about the pore size distribution and surface area, X-ray diffraction (XRD) the crystal structure, and elemental dispersive spectroscopy (EDS or EDX) the elemental mapping of composites.⁵⁴ Apart from the experimental characterization tools, computational tools such as COSMO-RS, GCMS, and DFT can be beneficial in order to compare the simulated results with obtained experimental ones. Gas solubility is one of the most crucial parameters affecting the selection of IL for IL-composite synthesis, and with COSMO-RS, quick and tough estimations can be made for gas solubilities in ILs. However, the accuracy of these results is expected to be low for IL-loaded porous composites due to additional phenomena occurring during the sorption of gases such as chemisorption and other sorption mechanisms. GCMS can deliver data about the expected sorption trend of IL-composites by building the structure of IL molecules and porous sorbent with DFT-based optimizations, and these gas uptake data can be compared with the experimental data.⁶³ Such computational and experimental techniques are pivotal for understanding the effects of IL incorporation and structure-performance relationships of these composites.

As one of the primary studies on IL incorporation or usage in composites, graphene was covered with an IL layer for gas sensing applications,⁵⁷ and an imidazolium-based IL was incorporated into carbon nanotubes for the hydrogenation of 1-hexene.⁶⁴ For gas adsorption and separation, one of the earlier studies featuring an IL/graphene-based composite showed that the CO₂ adsorption capacity of graphene was improved by adding polymerized IL (PIL).⁶⁵ Also,

the utilization of ILs in IL/MOF composites for gas separation purposes was featured in many works. [BMIM][PF₄] was incorporated into a commercially available MOF, Cu-BTC, with varying loadings, and a decrease was observed in gas uptake capacity as the IL loading increased due to the filling of pores of the parent MOF by IL molecules.⁶⁶ After IL incorporation, CH₄/N₂ and CH₄/H₂ selectivity values of 30 wt.% IL-loaded composites improved pristine MOF's selectivity by 1.5 times at 0.1 bar. Kinik and co-workers reported an IL/MOF composite prepared with [BMIM][PF₆] and ZIF-8 (30 wt.% IL loading) and investigated the CO₂ separation performance by experimental and computational methods, GCMS and DFT. For CH₄ and N₂, decreases in gas adsorption capacity were observed for the composite compared to pristine MOF after IL impregnation, however, up to 0.4 bar, the CO₂ capacity of the composite was higher than that of pristine.⁶⁷ This caused a more selective separation performance toward CO₂ over CH₄ for composite as the selectivities of the composite were doubling pristine ZIF-8's selectivity values up to 1 bar. The isosteric heat of enthalpy values of the composite were pointing out to the interactions between IL and the host, and gas uptakes calculated with GCMS were found to be in agreement with experimental data. Another group also reported improved CO₂ uptakes after the introduction of [BMIM][Ac] to ZIF-8.⁶⁸ They attributed enhanced uptakes to the chemisorption of CO₂ by the IL and confirmed their claim by measuring the heat of adsorption. Not only did they report an increase in CO₂ uptakes by 7 times at 30 °C and 0.1 bar for [BMIM][Ac]@ZIF-30, but they also recorded an 18-times improved CO₂/N₂ selectivity for [EMIM][Ac]@ZIF-30. To further categorize and investigate the effect of incorporating ILs on MOFs on gas adsorption and separation, ten different imidazolium-based ILs were incorporated to ZIF-8.⁶⁹ The results illustrated that IL incorporation improved CO₂/CH₄ separation performance of the pristine ZIF-8 at low pressures. Nozari and coworkers investigated the influence of the interionic energy of ILs on the thermal stability and adsorption performance of IL/MOF composites.⁷⁰ They used Cu-BTC and [BMIM]-based ILs having different cations. The interionic strength of IL/MOF composites was probed by quantifying the FTIR shifts in $\nu(\text{C2H})$ band position and results demonstrated that CO₂ uptakes of composites decreased as the interionic interaction energy in ILs increased.

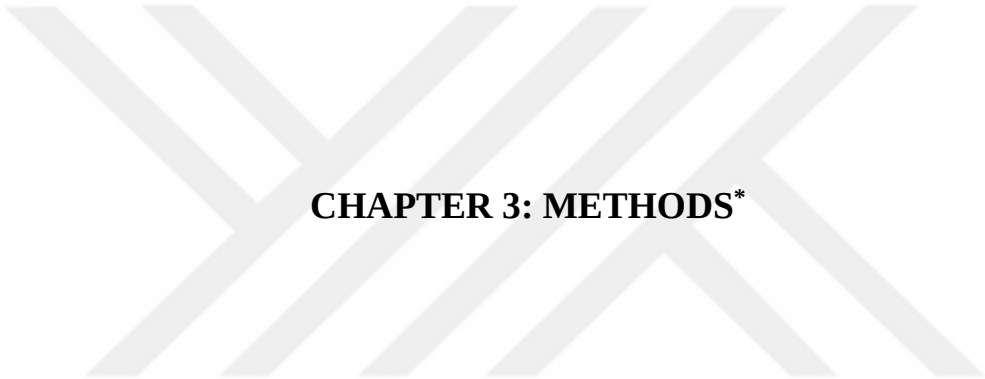
Most of the IL/MOF composites suffer from low gas uptakes due to significantly lowered pore volume and surface area after IL incorporation despite their high separation performance. But as one of the novel composites, core-shell IL/MOF composites were introduced by Zeeshan and coworkers.⁷¹ When a hydrophilic IL, [HEMIM][DCA] was impregnated onto a hydrophobic MOF, ZIF-8, IL was found to be encapsulating the MOF surface rather than going

inside the pores. This composite was displaying higher CO₂ uptakes than the pristine MOF at the low-pressure range, and a very high CO₂/CH₄ selectivity of 110 at 1 mbar, 25 °C. In a very recent study, infinite ideal selectivities (>100 000) for CO₂/N₂ and CH₄/N₂ separations were reported for a composite prepared with [BMPyr][DCA] and UiO-66 at 15, 25, and 35 °C and low pressures.⁷² The affinity of the composite to CO₂ was substantiated with GCMC and DFT results, and CO₂/N₂ performance in this study was illustrated as the top performing IL/MOF composite for this gas separation application up to date. Despite the valuable studies in the literature reporting remarkable gas separation performances, considerably lower gas uptakes remain a challenge for IL/MOF composites, especially at a higher operating pressure range.

Apart from IL/MOF composites, gas adsorption, and separation literature is rich with reports of IL/carbon-based composites. IL/carbon-based composites were reported to demonstrate effective separation for gas separation applications such as mercury capture from flue gas,⁷³ and SO₂ capture from air,⁷⁴ but these materials are being heavily investigated for gas mixtures containing CO₂. Erto and coworkers reported the CO₂ separation from flue gas by utilizing two different ILs and commercial activated carbons (ACs).⁷⁵ They found out that incorporation of [HMIM][BF₄] was causing pore blocking that resulted in worsened CO₂ uptakes whereas [EMIM][Gly] addition to activated carbon improved the CO₂ uptake of pristine material due to IL's affinity toward CO₂. A very recent study reported almost completely CO₂ selective [BMIM][Ac]/AC composite.⁷⁶ The composites with IL loadings varying from 5 to 35 wt.% were synthesized, and a bilayer IL formation was observed for composites prepared with 20, 30, and 35 wt.% loadings of [BMIM][Ac]. Due to the formation of newly formed chemisorption sites and affinity of IL toward CO₂, infinite CO₂/CH₄ selectivity was observed for IL₃₅/AC at 1 mbar, 25 °C; also IL₂₀/AC, IL₃₀/AC, and IL₃₅/AC composites showed infinite CO₂/N₂ selectivities at 1 mbar, 25 °C. Different than IL/MOF composites, most of the reported IL/carbon-based composites up to date are demonstrating higher gas uptakes after IL impregnation.^{65,77} These enhancements in gas sorption capability were explained through the strong interactions between sorbate and IL layer that was covering the surface of host materials. Recently, a novel composite was introduced in the literature that was featuring rGA and an IL.⁷⁸ In this study, GA was thermally annealed at 700 °C to obtain a porous material having a higher surface area and pore volume than the GA, and [BMIM][PF₆] was incorporated into rGA via incipient wetness technique with varying loadings. As the IL loading increased, both CO₂ and CH₄ uptakes decreased but the ideal CO₂/CH₄ selectivity of the composite increased considerably. For 50 wt.% IL-loaded rGA, a selectivity value of 120 was recorded at 1 mbar,

25 °C. Although the reports on effective IL-loaded porous sorbents are promising, to meet the urgent energy and green environment demands, the need of producing materials with high separation performance is incessant. Driven by this need, IL-containing sorbents were designed and constructed for different gas separation applications in this thesis. In chapter 4, two ILs having different hydrophilicities were incorporated into rGAs reduced at two different temperatures, and the resulting composites were tested for CO₂/CH₄ separation. The interactions between IL molecules and host rGAs were explained in detail through various characterization methods. Additionally, in Appendix B, the surface of a commercially available hydrophobic MOF, ZIF-67, was coated with a hydrophilic IL to show the potential of this core-shell type IL/MOF composite for C₂H₂ purification (C₂H₂/CH₄, C₂H₂/C₂H₄, and C₂H₂/H₂ separation).





CHAPTER 3: METHODS*

* Experimental and characterization methods of this chapter were published in the article with following reference under the sections of experimental methods and material characterization: Caglayan, H. P.; Unal, U.; Keskin, S.; Uzun, A. Effect of Surface Characteristics of Graphene Aerogels and Hydrophilicity of Ionic Liquids on the CO₂/CH₄ Separation Performance of Ionic Liquid/Reduced Graphene Aerogel Composites. *ACS Appl. Nano Mater.* **2022**, 6 (3), 2203–2217.

Experimental and computational methods used in this study are covered in this chapter. In the first part, a thorough explanation of experimental methods with materials, synthesis, material characterization, and gas adsorption analysis parts are given; and in the second part, computational methods including IAST, COSMO-RS, and isosteric heat of adsorption calculation are explained.

3.1 Experimental Methods

This section covers the synthesis and characterization methods of utilized materials during the study.

3.1.1 Materials and synthesis of IL-loaded composites

3.1.1.1 Preparation of rGAs and IL/rGAs

In this study, two pristine rGAs and four new IL/rGA composites that have not been featured in the literature were synthesized. Materials used were graphite (powder, 99.9995%, Alfa Aesar), KMnO_4 (99%, ISOLAB), NaNO_3 (99.5%, Merck), H_2SO_4 (95-98%, ISOLAB), 30% H_2O_2 (30%, Sigma Aldrich), Teflon lined autoclave, supercritical CO_2 dryer (Speed SFE 15,000, Applied Separations, Inc), Argon-filled glovebox (Protector, Labconco), acetone (Merck, 99.5%) for the synthesis of GA.

Following the modified Hummers' method,⁷⁹ graphite was oxidized with KMnO_4 in a solution, where NaNO_3 was previously dissolved in ice-cold H_2SO_4 , the details are given elsewhere.²⁴ Briefly, 3.0 g of NaNO_3 was dissolved in H_2SO_4 and after dissolution, graphite was added to the solution. To oxidize the graphite, 18.0 g of KMnO_4 was added very slowly to keep the temperature of the solution stable at approximately 4 °C, under continuous stirring in a water bath. After the addition of KMnO_4 , ice-cold distilled water was added to the solution, and the temperature was kept below 40 °C during the addition. The solution was stirred and heated up to 75 °C till the oxidation was complete, then again, the oxidation reaction was terminated with the rapid addition of 300 mL of ice-cold water. Upon water addition, the color of the solution was observed as dark brown, but after the addition of 30% H_2O_2 , it changed into a light yellow along with the vigorous effervescence observed. The obtained solution was naturally cooled down to room temperature and then washed first with 5 wt.% HCl solution and then distilled water, three times each with centrifugation at 3,000 RPM for 10 min. After the washing was finished, the powder was dispersed in distilled water and stored in beakers, overnight. The next

day, the solution was sonicated for 4 h for exfoliating graphite oxide to graphene oxide nanosheets. The solution was centrifuged at 10,000 RPM for 30 min and the supernatant as the colloidal GO exfoliation solution was collected.

The concentration of the GO colloidal solution was determined through vacuum filtration and was adjusted to 3 g/L with the addition of DI water (18.2 M Ω .cm) if required. Monolithic graphene hydrogels were made via the hydrothermal treatment of 3 g/L GO solution in Teflon-lined steel bombs at 180 °C for 3 h. The monolithic graphene hydrogels were immersed in an acetone bath for solvent exchange three times, to replace the water in the hydrogel pores with acetone. Upon the completion of the solvent exchange, to obtain GAs, hydrogels were dried with supercritical CO₂ at 120 bar, 60 °C for 2 h. GA was further crushed with a pestle and mortar to make the GA in the form of fine powder. This powder was put into a split tube furnace to thermally anneal it at given temperatures with a ramp of 20 °C/min, under a continuous Argon flow (100 mL/min). After the thermal treatment, materials were labeled according to their reduction temperatures as rGA300 and rGA500, corresponding to the materials prepared at 300 and 500 °C, respectively.

To deposit the ILs onto the surface of the as-synthesized rGA materials, the rGAs were first activated in a vacuum oven at 105 °C overnight to evacuate the pores of the material. The ILs were kept in an Argon-filled glovebox, and additionally, prior to synthesis, both ILs were kept at 60 °C overnight in a vacuum oven to get rid of the moisture. [BMPyr][PF₆] has a high melting temperature of 87 °C and it is solid at room temperature, thus excessive heating was avoided not to interfere with the chemistry of IL.⁸⁰ The following day, the stoichiometric amount (50 wt.%) of IL ([BMPyr][DCA] and [BMPyr][PF₆]) was mixed in 2 mL acetone for 1 h to ensure that IL molecules dissolved completely, which was later added to crushed and thermally annealed pristine rGA dropwise. Acetone was specifically chosen as the solvent since it can effectively dissolve both ILs.⁸¹ The IL loading of the IL/rGA composites was fixed at 50 wt.% since such high IL loading resulted in the most prominent increase in selectivity of a similar IL/rGA composite, as demonstrated before.⁷⁸ The resulting material was labeled as the IL/rGA_x, where x stands for the reduction temperature in °C (either 300 or 500 °C), and prepared composites were further dried in a vacuum oven at 125 °C overnight to get rid of the excess solvent and the impurities.

3.1.1.2 Preparation of the IL/ZIF-67 Composite

Materials used to prepare IL/ZIF-67 were ZIF-67 (MOF Technologies) and [HEMIM][DCA] (Sigma Aldrich) that were kept in an Argon-filled glovebox (MBraun, Labstar) prior to usage. Analysis gases used in adsorption experiments were C₂H₂ (Linde, dissolved in acetone, 99.8%), CH₄ (Air Liquide, 99.95%), C₂H₄ (Air Liquide, 99.95%), H₂ (Air Liquide, >99.9%), and Argon (Air Liquide, >99.9%). Acetone ($\geq 99.5\%$) and dimethylformamide (DMF, $\geq 99.0\%$) were purchased from ISOLAB and used in the synthesis and washing experiments.

The pristine MOF was put into the vacuum oven at 150 °C overnight to remove the impurities and to activate the sample for the adsorption experiments and composite synthesis. The wet impregnation method was used for the composite synthesis. After the drying of [HEMIM][DCA] at 80 °C for 2 h, 400 mg of [HEMIM][DCA] was dissolved in 20 mL acetone and stirred for 2 h at room conditions. The activated pristine ZIF-67 with a weight of 600 mg was added to the acetone solution and continuously stirred at 30 °C until acetone was completely evaporated from the mixture. The obtained composite with an IL loading of 40 wt.% was put into the vacuum oven at 125 °C to get rid of contaminants and excess solvent.

3.1.2 Characterization methods

3.1.2.1 Powder X-ray Diffraction (PXRD)

Powder XRD is used to identify and characterize the crystallographic properties of crystal materials. A generic PXRD equipment consists of five parts; X-ray source, sample stage, detector, monochromator, and software used for the analysis of the obtained results. By sending a directed beam of X-rays to the samples, electrons within the sample absorb a part of the sent X-rays and the energy level of their innermost electron increases.⁸² As the excited electrons return to their ground state, they emit X-rays which interfere with each other and create diffraction patterns. The diffraction patterns for pristine materials and composites were obtained by two types of XRD equipment, a Bruker D8 Advance X-ray diffractometer with a Cu K α 1 ($\lambda = 1.5418 \text{ \AA}$) radiation source (1.6 kW tube power) and a Bruker D2 Phaser instrument equipped with a generator supplying 30 kV of voltage and 10 mA of current and a Cu K α 1 ($\lambda = 1.5418 \text{ \AA}$) radiation source. The diffraction data were recorded from $2\theta = 5^\circ$ to 90° with a 0.0189° step size.

3.1.2.2 Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS)

To observe the topological and morphological pictures of the materials, the SEM technique is used. An SEM equipment consists of four main components; electron source (generally tungsten filament or field emission gun), electromagnetic lenses, sample stage, and detector.⁸³ A high-energy electron beam is sent to the surface of the sample which results in the emission of backscattered, secondary, and auger electrons or X-rays. Depending on the type of detector used in SEM analysis, surface topography, morphology, or composition of the samples can be monitored. Secondary electrons give information about surface topography, backscattered electrons can be used to observe the atomic number and density of the samples, and emitted X-rays are used for EDS analysis that provides information about the chemical composition of the sample. SEM analysis was done with a Zeiss Ultra Plus Field Emission Scanning Electron Microscope (FESEM) instrument with an operating voltage of 3 kV and a 4.0 to 5.0 mm working distance. The images were taken with two different magnifications (10 k and 100 k $\times$) under vacuum. Also, EDX was employed with a Bruker XFlash 5010 EDX detector to qualitatively determine elements in the scanned area with an acceleration voltage of 10 kV and a working distance of 5.1 to 5.5 mm.

3.1.2.3 Fourier Transform Infrared (FTIR) Spectroscopy

FTIR is a widely adopted method to identify the functional groups of solids, liquids and organic and inorganic materials.⁸⁴ Its working principle stems from the changes in vibrational energies of molecules upon the introduction of IR radiation. Depending on the nature of bonds within a molecule, the vibrations manifest themselves with unique intensity and location on the spectra. Quantifying the band shifts of the materials provides insight into the interactions between components of the composite materials. There are a few techniques utilizing KBr pellets and Attenuated Total Reflection (ATR) cells to obtain the FTIR spectrum of a sample based on the equipment and the sensitivity of the samples. Throughout this study, ATR-FTIR was employed which has a simple sample preparation method. A Bruker Vertex 80V spectrometer was used for FTIR with an ATR cell in absorbance mode. Measurements were taken in a range of 4000 to 400 cm^{-1} with a resolution of 2 cm^{-1} . 128 scans for background and 256 scans for sample measurements were obtained. The spectra were deconvoluted using the Voigt function with Fityk software.⁸⁵

3.1.2.4 Brunauer-Emmett-Teller (BET) Surface Area and Pore Size Analysis

BET is used for the surface area and porosity measurements through the physical volumetric N₂ adsorption of materials at a very low temperature, generally at -196 °C. The adsorption mechanisms can be determined from the plot of adsorption-desorption isotherms that are classified by IUPAC, and the following equation corresponds to the BET model:⁸⁶

$$\frac{p/p_0}{n(1-p/p_0)} = \frac{c-1(p/p_0)}{n_m c} + \frac{1}{n_m c} \quad \text{Equation 1}$$

where P is the pressure, P_0 is the saturation pressure, n is the amount of adsorbed gas, C is a constant and n_m is the monolayer capacity of the adsorbed gas.

BET analysis was done for pristine rGAs, ZIF-67, and IL-loaded composites with a Micromeritics ASAP 2020 physisorption analyzer. Approximately 120 mg of sample was used for each measurement. Before the analysis, pristine samples were degassed at 105 °C, and composites were degassed at 125 °C for 12 hours under vacuum for the activation (pristine ZIF-67 was degassed at 150 °C). For the N₂ adsorption, the cell was cooled down to -196 °C then analyses were done between 10⁻⁶ and 1 bar. Surface areas were estimated by plotting relative pressure (p/p_0) from 0.05 to 0.3 and fitting the respective data to the BET equation. Pore size distributions (PSD) of pristine rGAs and composites were calculated via Barrett-Joyner-Halenda (BJH) method with Faas correction and plotted for pore volume versus pore width.

3.1.2.5 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis is used to investigate the thermal stability and decomposition mechanism of materials in the presence of inert gases (Ar, N₂) or other interfering gases (such as CO₂ and dry air). The analyses were conducted using the Q500 TA instrument, using a platinum pan, and approximately 15 mg for each sample. First, a ramp of 2 °C/min to 120 °C was employed, then samples were isothermally treated under nitrogen for 8 hours to get rid of any contaminants, and lastly, a ramp of 5 °C/min up to 700 °C/min was employed to test the thermal stability of samples. For all the analyses, the flow was set as 40 mL of N₂ with 60 mL of balance gases. The platinum pan was cleaned under air with a quick ramp to 1000 °C/min

after each analysis. Both thermogravimetry (TG) and derivative thermogravimetry (DTG) curves were illustrated simultaneously. Thermal decomposition temperature for each sample was determined by finding the T'_{onset} of DTG curves since T_{onset} is reportedly overestimating the decomposition temperature as a function of measurement parameters.⁸⁷

3.1.2.6 X-ray Photoelectron Spectroscopy (XPS)

XPS is a powerful tool to determine the surface characteristics of samples as it reports the changes in the electronic states of atoms on the surface of materials.⁸⁸ A typical XPS equipment consists of five main parts; an X-ray source, sample chamber, electron analyzer, detector, and data recording and analysis software. The surface of the sample is excited with a beam of X-ray which causes the emission of photoelectrons. These emitted photoelectrons are captured by detectors and provide information about the chemical environment about the surface level they were ejected from (generally surface sampling depth is 5-10 nm). The recorded data is plotted intensity of the emitted photoelectron with respect to the kinetic energy of the sent X-rays. A Thermo Scientific K-Alpha spectrometer with an aluminum anode (Al K α = 1463.8 eV) was used to obtain XPS spectra. Samples were left in ultra-high vacuum (UHV) conditions for a couple of hours to get rid of the contaminants before the analyses. Data were collected with a resolution of 1.0 eV for survey spectra, core-level spectra were procured with 0.1 eV spectral resolution. For data analysis, Avantage 5.9 software was utilized. The deconvolution was made by fitting the spectra with a function that was a mixture of Gaussian and Lorentzian functions. The correction in the binding energies was done by assigning the C1s signal at 284.5 eV.

3.1.2.7 Raman Spectroscopy

Raman is a technique to determine the chemical composition, phase, and disorder amount in the materials. Its principle is similar to FTIR spectroscopy, but whereas FTIR carries out the functional group identification through transmission or absorbance modes, Raman spectroscopy employs scattering to record the vibrational changes in the molecules.⁸⁴ Its equipment has the following components; a laser source (emitting visible or near-IR light), sample holder, spectrometer, optical filters, microscope, and data acquisition and analysis software. In this study, Raman was used for characterizing the rGAs and IL/rGA composites. RENISHAW inVia microscope equipped with a CCD detector was used to obtain Raman spectra between 800 to

1800 cm^{-1} with a laser excitation wavelength of 532 nm and 50 $\times$ objective. Fityk software was used to deconvolute spectra into five peaks (D, G, D', D'' and D*); two Gaussian (D'' and D*), and three Lorentzian (G, D and D') peaks.

3.1.2.8 Washing Experiments

Washing experiments were used to determine the IL loading and prove that deposited ILs were coating the surface of porous hosts. The washing procedure was as follows: The solvent, acetone which was used to determine the IL loading in IL/rGA and IL/ZIF-67 composites was heated to 50 °C while 100 mg of IL-loaded composites were weighed and put into a filter paper. After keeping it at 50 °C for 30 mins, the solvent was added to IL-loaded composites dropwise. The composites were washed with 3 mL solvent 5 times to extract the IL completely from the porous structure. The washed powder was then put into the oven at 105 °C for 3 h to get rid of the excess solvent and to dry the powder before doing the FTIR analysis. FTIR analysis was crucial to observe the disappearance of the characteristic bands coming from ILs after washing which was the key to proving the core-shell structure of the IL/ZIF-67 composite (washed with DMF). The choice of solvent is important, a solvent with a larger molecular size than the pore size of the pores cannot dissolve the IL molecules within the porous structure, it can only be used to clean the surface of the materials from IL molecules. Whereas for solvents with small molecular sizes, solvent molecules can enter the pores of porous materials and with the quantification of the sample's weight before and after washing, the IL loading can be estimated. IL/rGA composites were washed until all bands belonging to ILs completely disappeared from the spectra. The weights of the samples before and after washing were recorded and used to calculate the approximate IL loading of all composites.

3.1.3 Volumetric Gas Sorption Measurements

Volumetric gas sorption is a method used to determine how much gas is sorbed (sorbate) on the sample material (sorbent). A known amount of gas is introduced to the analysis cell with predetermined intervals, and after waiting for a duration for the sample to reach equilibrium, the final pressure is recorded for each data point. Gas sorption analyses of the pristine materials and composites were performed with a high-pressure volumetric analyzer (HPVA II-200, Micromeritics Particulate Systems) which was used for the analyses of rGAs and IL/rGAs, and a high-pressure gas sorption system (iSorb HP Quantachrome Instruments) was used for ZIF-

67 and [HEMIM][DCA]/ZIF-67 composite. The representative schematic of the volumetric gas sorption equipment is given in Figure 3.1. For all analyses, before adsorption experiments, cells were degassed overnight at 125 °C for rGAs, IL/rGA, and IL/ZIF-67 composites, and 150 °C for pristine ZIF-67 to get rid of any volatile contaminants. The working principle of both equipment is very similar to each other and proceeds as the following: Prior to measurements, an adsorption-desorption profile is set by the user that includes target pressures, equilibrium settings, temperature, and the descriptions of sorbate and sorbent. Before the sample material is loaded into the adsorption cell, it is weighed meticulously, and this weight is recorded as the wet weight of the analysis material. Then, the sample is loaded to the analysis cell and attached to adsorption ports in the presence of a filtered gasket.

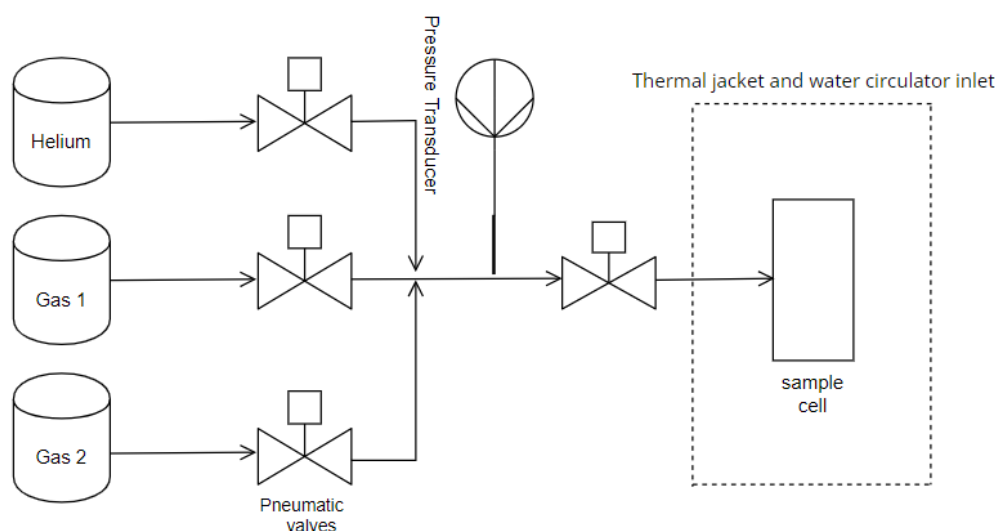


Figure 3.1. Schematic of volumetric gas sorption equipment used in this study.

For the activation of samples, overnight degas were employed for all materials for accurate results. Also, between the analyses with different gases, to get rid of the adsorbed gas molecules and to regenerate the adsorbent, a 2 h degasification at 125 °C was employed for all experiments. Between analyses, a manual purge process was executed for HPVA-II by pressurizing the lines with He multiple times, while the cell was kept under vacuum. The cleaning/purging step between analyses was done automatically for iSorb by flushing helium through the lines. The rGAs and IL/rGAs were analyzed with CO₂ and CH₄, whereas pristine ZIF-67 and IL/ZIF-67 composites were analyzed with C₂H₂, CH₄, C₂H₄, and H₂. The uptakes were collected between the pressure range of 100–1000 mbar for HPVA-II and 10–1000 mbar for iSorb. After recording the gas uptakes of samples for all analysis gases, the sample was

degassed for the final time and the weight of the sample was tared and recorded as dry weight. For the isotherm fitting of gas uptakes, dry weight was considered for all samples.

The uptakes were fitted using Dual-Site Langmuir (DSL), Langmuir-Freundlich (LF), and Dual-Site Langmuir-Freundlich (DSLFL) isotherms models after deciding which model yields the best fit. The equations and parameters of the used isotherms are given in Table 3.1.

Table 3.1. Details of gas adsorption isotherm models used to fit the experimental data.

Isotherm	Equation	Parameters
Dual Site Langmuir	$n(P) = q_1 \frac{k_1 \cdot P}{1 + k_1 \cdot P} + q_2 \frac{k_2 \cdot P}{1 + k_2 \cdot P}$	q_1, q_2 (cc/g), k_1, k_2 (1/mbar)
Langmuir- Freundlich	$n(P) = q \frac{(k \cdot P)^{n^*}}{1 + (k \cdot P)^{n^*}}$	q (cc/g), k (1/mbar), n^* (dimensionless)
Dual Site Langmuir- Freundlich	$n(P) = q_1 \frac{(k_1 \cdot P)^{n_1^*}}{1 + (k_1 \cdot P)^{n_1^*}} + q_2 \frac{(k_2 \cdot P)^{n_2^*}}{1 + (k_2 \cdot P)^{n_2^*}}$	q_1, q_2 (cc/g), k_1, k_2 (1/mbar), n_1^*, n_2^* (dimensionless)

ⁿ Where n is the uptake or amount adsorbed (cc/g), and P is the bulk gas pressure at equilibrium.

3.2 Computational Methods

3.2.1 Conductor-like screening model for realistic solvents (COSMO-RS) calculations

COSMO-RS is a method that was developed to predict the thermophysical properties of gases, liquids, liquid-liquid and gas-liquid systems. Many empirical, semi-empirical thermodynamic models are being used for the quantification of activity coefficients, solubilities, and other thermodynamical properties of materials, but it is not possible to estimate all these properties of countless materials and systems. This induced a necessity that has pushed researchers to develop simulation methods that are based on the results of relevant experiments and other computational tools, and these methods are constructed with the aim of quantifying the target properties with an acceptable error margin. Among these methods, quantum chemistry-based COSMO comes forward with considerably fewer required parameters and

robustness. COSMO handles the simulation by constructing a virtual surface of the materials and acts like this material is submerged in a conductor bath. The interaction energies between materials and many other material properties (activity coefficient, vapor pressures, phase diagrams, density, and viscosity of liquids) can be calculated with this method. With the introduction of statistical thermodynamics, the concept was updated as COSMO-RS by Klamt.⁸⁹ As the name implies, this method employs a more simplistic version of dielectric boundary conditions.⁸⁹ While running the simulations, most of the methods are using vacuum conditions (dielectric constant, $\epsilon = 1$), whereas the COSMO-RS method is assuming that all molecules inputted in the simulation environment are being enveloped by a conductor bath ($\epsilon = \infty$).

IL solubilities in different gases are reported in this study for the two studies. COSMO-RS offers the solubility calculation with respect to temperature and pressure, thus, prior to starting the calculations, anion and cation molecules were selected from the triple-zeta valence polarized basis set (TZVP) library from the COSMOthermX software, version C30_1602. Assuming a 50/50 molecular ratio for the anion/cation molecules, ILs were inputted to the solubility tab, and temperature/pressure values of interest were chosen manually.

3.2.2 Ideal Adsorbed Solution Theory (IAST) Calculations

IAST is a benchmark method of estimating the adsorption equilibria of gas mixtures ever since Prausnitz and Myers published their pioneering article.⁹⁰ By only utilizing the single-component gas uptakes which are easily obtainable, it is possible to predict the mixture gas separation performances of materials with IAST. It applies to ideal mixtures and homogenous and heterogeneous adsorbents (with a margin of error) which makes its usage more appealing. IAST was developed by taking Raoult's law as the basis which defines the partial pressure of components in an ideal mixture. The key assumptions of this theory are: (i) the surface of the adsorbent is equally available to all adsorbate molecules, (ii) the adsorbent does not react with adsorbate molecules, and (iii) the multicomponent gas mixture behaves like an ideal solution. Deviation from these assumptions may decrease the accuracy of the IAST calculations, but the results can be supported with other computational tools such as GCMC and DFT. In the literature, IAST results of several gas mixtures for different MOFs were compared with molecular simulations and found considerably similar.^{91,37} Also, several studies are reporting the IAST calculated gas selectivities of carbon-based materials.^{92,93} In Chapter 4, IAST mixture

selectivity values of CO_2/CH_4 were calculated for rGAs and IL/rGA composites with 50/50 and 5/95 compositions that represent the biogas and natural gas concentrations, respectively.



**CHAPTER 4: EFFECT OF SURFACE CHARACTERISTICS OF
GRAPHENE AEROGELS AND HYDROPHILICITY OF IONIC
LIQUIDS ON THE CO₂/CH₄ SEPARATION PERFORMANCE OF
IONIC LIQUID/REDUCED GRAPHENE AEROGEL COMPOSITES[†]**

[†] The results given in this chapter were published in ACS Applied Nano Materials with the following reference: Caglayan, H. P.; Unal, U.; Keskin, S.; Uzun, A. Effect of Surface Characteristics of Graphene Aerogels and Hydrophilicity of Ionic Liquids on the CO₂/CH₄ Separation Performance of Ionic Liquid/Reduced Graphene Aerogel Composites. *ACS Appl. Nano Mater.* **2022**, 6 (3), 2203–2217. The results and discussion section of this article is formatted for this thesis.

In this chapter, two ILs having the same cation with different anions offering opposite hydrophilic/hydrophobic characters, 1-*n*-butyl-1-methylpyrrolidinium dicyanamide ([BMPyr][DCA]) and 1-*n*-butyl-1-methylpyrrolidinium hexafluorophosphate ([BMPyr][PF₆]), were impregnated onto two different rGAs prepared by the thermal treatment of GA at 300 and 500 °C to investigate the consequences of the changes in the hydrophilic character of ILs and the reduction temperature of the GAs on the corresponding gas sorption and separation performance of the IL/rGAs. The structural analyses of nanoporous rGAs and IL/rGAs pointed to a change in the quantity of oxygenated functional groups upon thermal treatment and a change in the direct interactions between IL molecules and the host rGA surface upon IL deposition. Single-component CO₂ and CH₄ sorption measurements were performed for each rGA and IL/rGA composite and both the ideal and mixture CO₂/CH₄ selectivities were calculated. The samples prepared by reducing GA at 300 and 500 °C yielded ideal CO₂/CH₄ selectivities of 3.6 and 18 at 1 mbar and 25 °C, respectively. Among IL/rGA composites, the one prepared at 300 °C displayed a remarkable CO₂/CH₄ separation performance when combined with the hydrophobic [BMPyr][PF₆] offering an ideal selectivity of 450.9 at 1 mbar and 25 °C, whereas the composite prepared with rGA500 yielded a substantially high CO₂/CH₄ selectivity after the incorporation of the hydrophilic [BMPyr][DCA] of 173.5 at 1 mbar and 25 °C. The ideal CO₂/CH₄ selectivities of [BMPyr][PF₆]/rGA300 and [BMPyr][DCA]/rGA500 surpassed most of the previously reported selectivities of carbon-based materials in the literature. These results demonstrate the broad potential of IL/rGAs in sorption-based gas separations owing to the highly tunable nature of both the structure of IL and the surface characteristics of rGA.

The results illustrated in this chapter were published in ACS Applied Nano Materials by the following authors Hatice Pelin Caglayan, Ugur Unal, Seda Keskin, and Alper Uzun, and the related content of the article was formatted for this thesis.

4.1 Background

Separation of CO₂ from other gases remains one of the most crucial challenges of today, as many industries are heavily reliant on fossil fuels. For instance, to purify natural gas to increase its calorific value, getting rid of the excess CO₂ present in the raw natural gas is crucial. As the demand for natural gas grows steadily, the need to separate CO₂ from CH₄ more efficiently persists. This need urges researchers to find novel ways to separate CO₂ efficiently. Sorption-based gas separation which is a method that includes physisorption, chemisorption, and absorption of gas molecules, is one of the most promising methods to separate CO₂ from other gases as it is less energy-intensive and easier to integrate.⁹⁴ There have been many studies featuring MOFs,⁹⁵ zeolites,⁹⁶ functionalized activated carbons,⁷⁶ covalent organic frameworks (COFs),⁹⁷ silicas,⁹⁸ membranes⁹⁹ for CO₂/CH₄ separation.

Graphene-based materials are getting increasing attention owing to their interesting features, such as high mechanical stability, thermal conductivity, tunability, and applicability to various fields.¹⁰⁰ GAs, as one of the subclasses of graphene-based materials, come forward since they offer ultra-low density, high surface area, and high thermal-electrical conductivity.^{29,101} Different than graphene's 2D structure, where sp² hybridized covalently bonded carbons are packed in a hexagonal skeleton, a typical GA structure is in 3D form because of the formation of a highly porous network following the specialized treatment of commonly used GO solution.³¹ Several methods have been reported to synthesize these 3D structured materials, such as sol-gel polymerization,²⁹ freeze-drying of graphene oxide solution,¹⁰² and one-pot hydrothermal treatment of GO solution without any addition of other chemicals.²⁴ The resulting highly porous GA having a 3D structure can be utilized in many applications, such as catalysis,²⁴ water purification by absorption,³³ gas sensing,³⁴ energy storage, and conversion,³⁵ supercapacitors,³⁶ and gas separation.^{103,78}

GAs can be considered promising candidates for sorption-based gas separation because of their highly nano-sized porous network and easy-to-tune nature. Although some studies reported the superior adsorptive behavior of pristine GAs,^{16,104} in most cases, gas sorption properties of materials were improved with their functionalization. For instance, Sui et al. reported an increase in the amount of adsorbed CO₂ from 6 to 11 wt.% at 1 bar and 0 °C upon steam activation.¹⁰³ Ren et al. showed that H₂ uptake of pristine GA was improved with the incorporation of a MOF material, CuBTC, to GA from 0.3 to 2.1 wt.% at 100 bar and -196 °C.¹⁰⁵ In a different approach, Pruna et al. studied the effect of ethylenediamine (EDA)

functionalization on GO-based aerogels. Pristine aerogel exhibited a CO₂ adsorption capacity of 0.52 mmol/g at 1 bar, 25 °C, whereas under the same conditions, its functionalized counterpart had a CO₂ adsorption capacity of 1.18 mmol/g.¹⁰⁶ Besides these examples, GA structure can be modified with other methods, such as adjusting the thermal activation temperature to tune the pore size,¹⁰⁷ and applying thermal reduction which can control the surface characteristics of GAs by creating defect sites and eliminating some of the functional groups,⁷⁸ and incorporating task-specific chemicals.

Moreover, combining GAs with ILs offers a broad potential. ILs are non-flammable and non-volatile highly viscous salts that are mostly liquid under room conditions.¹² Separating CO₂ from other gases with ILs is promising as many ILs can successfully absorb CO₂, but the operational drawbacks of using ILs arising from their highly viscous and moisture-sensitive nature along with their high costs limit their widespread usage. Incorporating ILs into suitable host materials and tuning the specific interactions between anions-cations of the ILs with the host has been shown to enhance the performances of the host material for different purposes.¹⁰⁸ For instance, Ghosh et al. demonstrated the increase in CO₂ adsorption capacity of graphitic carbon nitride by functionalizing it with an IL, 1-butyl-3-methylimidazolium bis(trifluorosulfonyl)imide, [BMIM][TFSI], and at 15 bar the CO₂ uptake of IL-loaded composite was reported as 19.8 mmol/g, almost two times higher than the uptake of the host material (8.5 mmol/g).¹⁰⁹ Moreover, several recent studies showed that IL incorporation into MOFs, COFs, and other carbonaceous materials offers tremendous potential for enhanced gas separation performance.^{110,54} Our group extended this approach to activated carbon and coated it with an IL, 1-butyl-3-methylimidazolium acetate, [BMIM][Ac], and reported practically complete CO₂ selectivity over CH₄ and N₂.⁷⁶ Moreover, DFT calculations and grand GCMC simulations were used to investigate the impact of IL incorporation to 2D graphene layers, and results showed that choosing 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF₄]) decreased the interlayer spacing between sheets and available pore size, resulting CO₂/CH₄ mixture selectivities as high as ~1000.¹¹¹

The family of imidazolium-based ILs has been widely studied for gas separation applications,^{76,78,112} whereas only a few studies reported the usage of pyrrolidinium-based ILs for the synthesis of highly selective composites.^{113,81} The cations of both IL families are consisting of quaternary ammonium salts, while imidazolium has an aromatic property, the pyrrolidinium ring is nonaromatic. Pyrrolidinium-based ILs are generated to have higher electrochemical and thermal stability, and lower toxicity compared to imidazolium-based

counterparts.⁴⁷ Hence, these ILs can be promising alternatives to imidazolium-based ILs but their contributions to the gas separation performance of composites are yet to be explored.

In this study, to investigate the tunability of the gas separation performance of the IL-deposited rGAs, we prepared two different rGAs by thermally annealing GA at two different temperatures to adjust the surface characteristics of GA. Then, we deposited two different commercially available pyrrolidinium-based ILs having the same cation with different anions offering opposite hydrophobic/hydrophilic characters, [BMPyr][DCA], (hydrophilic) [BMPyr][PF₆] (hydrophobic) onto the surface of rGAs. In-depth characterization of the composites indicated that the reduction temperature of the GAs and the hydrophobic/hydrophilic character of the ILs control the molecular interactions. The volumetric gas sorption measurements performed for CO₂ and CH₄ demonstrated that the CO₂ separation performance of IL/rGA composites depends strongly on these interactions. Accordingly, reduction at a higher temperature increases the gas sorption capacity and selectivity of pristine rGA, and IL deposition improves the CO₂/CH₄ separation performance remarkably when the hydrophilicity of the incorporated IL and the number of oxygen-containing functional groups on the surface were inversely proportional. These results not only demonstrate that the IL-loaded rGAs are promising materials for future gas separation applications, but also provide valuable insights into structural factors controlling the separation performance.

4.2 Results and Discussion

4.2.1 Structural Characterization

Thermal treatments change the structural characteristics of the GAs.¹¹⁴ Thus, we first reduced GA in flowing Ar at 300 and 500 °C to modify its structure. Our BET measurements indicated surface areas of 342 and 363 m²/g for rGA500 and rGA300, respectively. These values are lower than that of the previously reported as-treated and untreated GAs prepared with similar synthesis methods.^{24,115} The decrease in surface areas might be arising from overlapping sheets and the collapse of the porous carbon structure due to thermal reduction and synthesis conditions.⁷⁸ The synthesis steps of IL/rGA composites are given in Figure 4.1 which encapsulates the fabrication of pristine rGAs from GO solution, the representative chemical structure of GA and rGAs, and the preparation of IL-loaded composites using the incipient wetness method. Firstly, morphologies of pristine rGAs and composites were investigated and compared using SEM and BET analyses.

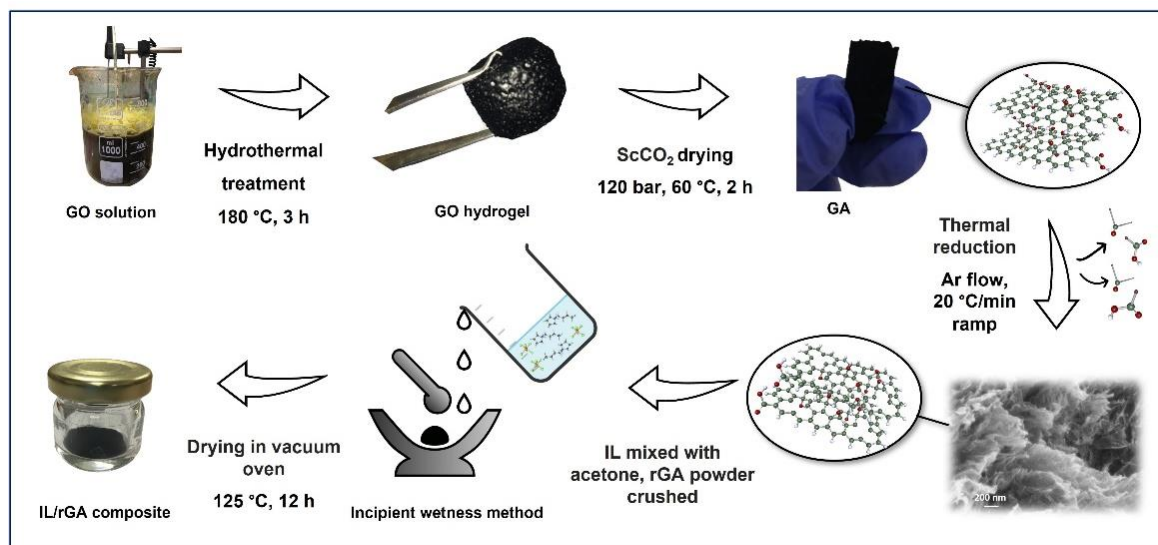


Figure 4.1. Schematic illustration of the synthesis of IL/rGA composites.

Figure 4.2 shows representative SEM images of the pristine rGAs and IL-loaded rGAs. The clear, randomly oriented, wrinkled-sheet structures of pristine rGAs shown in Figure 4.2(a, b) are consistent with the previous reports.^{115, 116} The wrinkled nature of the composites prepared with rGA500 was more prominent compared to rGA300 composites, consistent with its higher surface area and pore volume. With the impregnation of ILs, rGAs became smoother by losing their roughness as can be seen in Figure 4.2(c, d) for [BMPyr][DCA] and Figure 4.2(e, f) for [BMPyr][PF₆]-loaded rGAs. These changes indicate that ILs were successfully deposited onto the surface of the host materials. The results of the EDX analyses of the pristine rGA300 and [BMPyr][DCA]-loaded rGA300 are given in Figure A.1, where the distribution of IL on the rGA structure can be distinguished by uniformly distributed nitrogen atoms. The elemental mapping obtained by EDX spectroscopy showed that nitrogen, fluorine, and phosphorus elements associated with [DCA]⁻ and [PF₆]⁻ containing ILs were present on the surface. This result also proves the successful IL deposition of the ILs on the rGA surface.

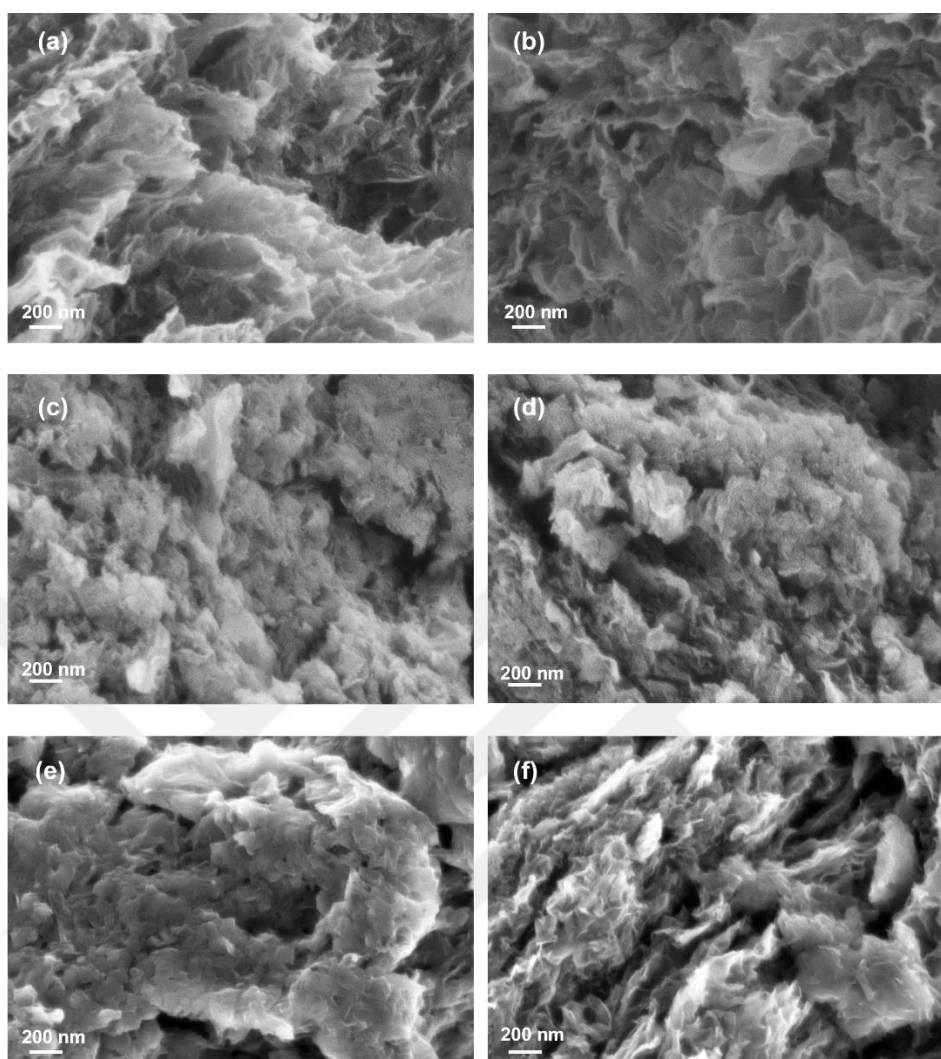


Figure 4.2. SEM images of (a) rGA300, (b) rGA500, (c) [BMPyr][DCA]/rGA300, (d) [BMPyr][DCA]/rGA500, (e) [BMPyr][PF₆]/rGA300 and (f) [BMPyr][PF₆]/rGA500 at 100 K $\times$ magnification.

To quantify the corresponding IL amounts in each IL-deposited IL/rGA composite, the composites were washed with acetone to extract all IL. The IR spectra of the washed samples were checked with FTIR analyses, and the results are shown in Figure A.2. The spectra range where the features coming from ILs are the most prominent illustrated that after acetone washing, the features associated with [DCA]⁻ and [PF₆]⁻ disappeared completely, confirming the complete removal of ILs from composites. Next, the weights of the composite before and after washing (and drying) were considered for IL loading calculation. Accordingly, the IL loading for [BMPyr][DCA]/rGA300 and [BMPyr][DCA]/rGA500 were determined as 44 wt.% and 43 wt.%, respectively, whereas the corresponding values were 40 wt.% and 42 wt.% for

[BMPyr][PF₆]/rGA300 and [BMPyr][PF₆]/rGA500, respectively. The difference between the targeted IL loading, 50 wt.%, and the amounts determined by these washing experiments might be related to the loss of some ILs on the sample flask during the deposition of IL onto the rGA^{110,54} and to the possibility of incomplete removal of ILs from the composites during the washing experiments. However, the results still confirm that each composite has the same IL loading of approximately 42 ± 2 wt.%.

Structures of the composites were further analyzed by XRD to check whether there was a change in the pristine material's crystal structure after IL impregnation. Results are presented in Figure 4.3. Accordingly, the first and the most intense peak in the XRD data of pristine rGA300 was observed at a 2θ of 25° as shown in Figure 4.3(a), which signifies the presence of the (002) plane, as reported previously.^{116,117} For the pristine rGA500, the 2θ peak observed at 25° for pristine rGA300 shifted slightly to a higher angle (Figure 4.3(b)), which might be an indicator of the decrease in the interlayer spacing of the (002) plane due to the removal of oxygen-containing groups,¹¹⁸ which was further supported by TGA and Raman data as presented below. Moreover, the peak observed at $2\theta = 25^\circ$ for pristine rGAs remained at almost the same position for all IL-loaded samples, but the peak width broadening was observed for [BMPyr][DCA]-loaded composites, which indicates an increase in the poor ordering of the graphitic layers due to the IL addition along with the presence of few-layer stacked graphene sheets.¹¹⁷ Shifting to lower angles for all IL-loaded composites corresponds to a slight increase in the interlayer spacing of the (002) plane, which might be arising from the incorporation of ILs to basal planes of the layered structure.

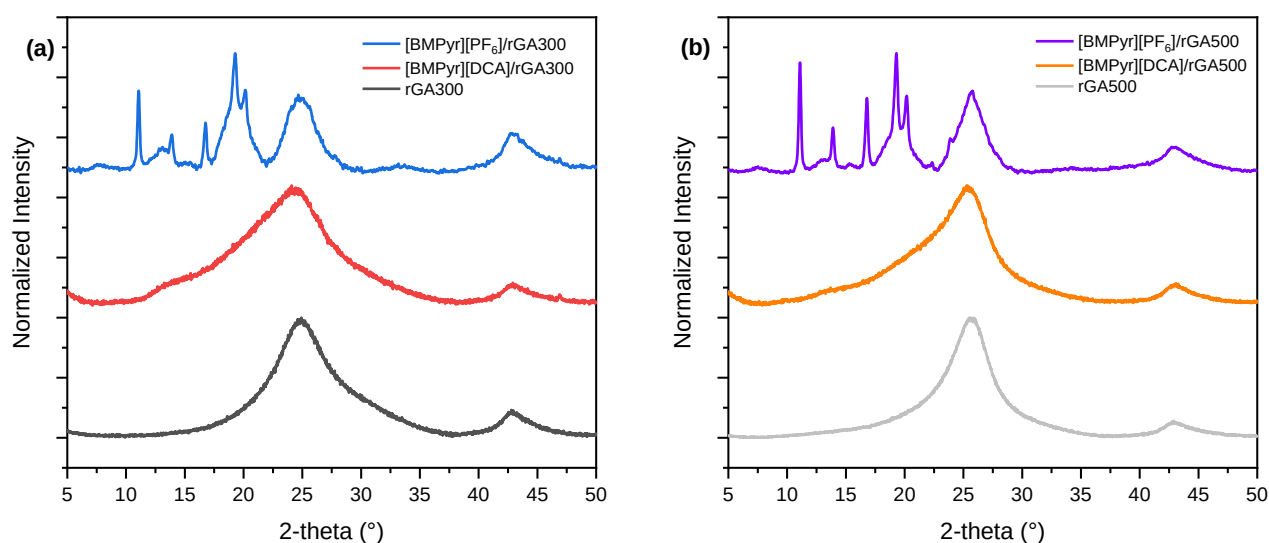


Figure 4.3. XRD spectra of (a) rGA300 and IL-loaded rGA300 composites, (b) rGA500 and IL-loaded rGA500 composites.

The second peak in the XRD data of the pristine rGA materials was located at $2\theta = 43^\circ$, representing the (101) plane of the materials, remained the same for all composites.¹¹⁶ Besides the peak broadening and shifting, for the [BMPyr][PF₆]-loaded composites, additional lower angle peaks were observed along with the peaks of (002) and (101) planes, which were found to be mostly consistent with the bulk IL's diffraction pattern (Figure A.3). Some lower angle peaks belonging to bulk IL disappeared when they were deposited onto the surface of rGAs. During incorporation, bulk IL could be favoring specific crystal orientation according to the confined space within rGAs which could be the reason why these peaks disappeared and slightly shifted.

Figure 4.4 shows the N₂ adsorption and desorption isotherms for pristine rGAs and IL/rGA composites. Pristine rGAs were found to display Type IV isotherms and H2-type hysteresis loops that point out the mesoporous structure of materials.²⁴ Hysteresis loops of pristine materials indicated that mesopores display a nonuniform shape, which is often described as “ink-bottle pores”, and the type of the hysteresis loops suggests that a portion of pores were in the form of micropores as well as mesopores. Despite an increase in surface area, the hysteresis loop for rGA300 was larger than rGA500, hinting that the pore volume of pristine rGA500 decreased compared to that of rGA300, which might be related to a sudden collapse of the pore network during supercritical CO₂ drying or thermal reduction due to a fluctuation in the drying or heating rate.¹¹⁹

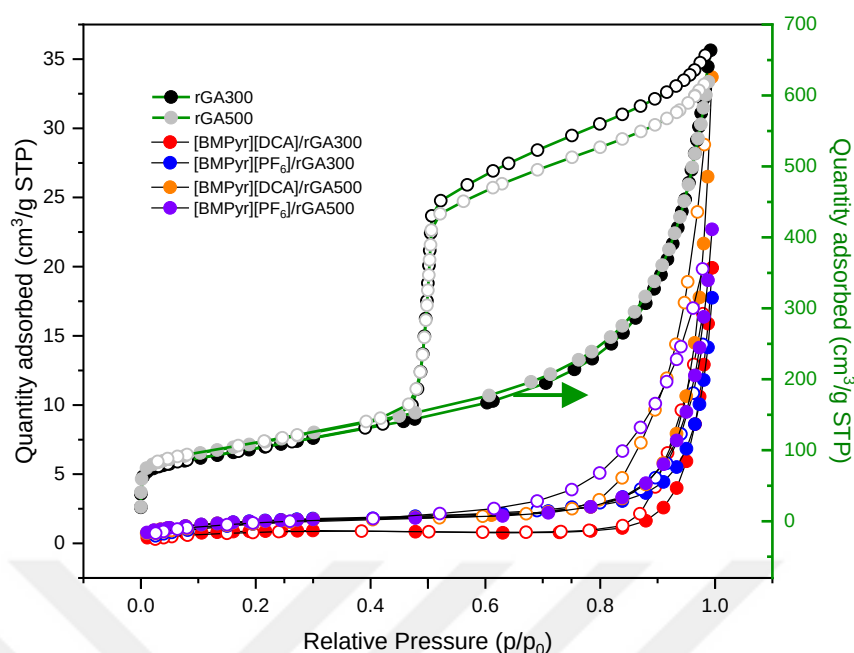


Figure 4.4. N₂ adsorption-desorption results of pristine rGAs and IL/rGA composites. Filled symbols represent the adsorption data and empty symbols represent the desorption data.

Upon IL impregnation, the surface area of the composites decreased dramatically as can be seen in Figure 4.4 with decreased N₂ uptakes. Considerable decreases in the surface areas and pore volumes of the composites upon IL impregnation are reported in Table 4.1. A significant reduction in the available pore volumes for IL-loaded composites indicated that pores were filled with ILs.

Table 4.1. Measured BET surface areas and pore volumes of rGAs and IL-loaded rGAs.

Sample	BET surface area	Total pore volume
	(m ² /g)	(cm ³ /g)
rGA300	341.2	0.966
[BMPyr][DCA]/rGA300	2.9	0.0308
[BMPyr][PF ₆]/rGA300	5.7	0.0259
rGA500	363.6	0.887
[BMPyr][DCA]/rGA500	5.5	0.0515
[BMPyr][PF ₆]/rGA500	5.5	0.0342

Additionally, PSDs of pristine materials and composites were plotted with the BJH method in Figure A.4. The mesopores of pristine rGA500 were found to be in the range of 20-40 nm with the sharpest peak having 27.1 nm pore width, whereas, for pristine rGA300, pores were populated at around 20-50 nm with the sharpest peak having a 33.1 nm width. As shown in Figure A.4 and Table 4.1, available pore volumes of IL-loaded rGA composites decreased significantly compared to pristine materials. But also, densely populated pore widths for IL-loaded composites shifted to values that were exceeding the mesopores of the pristine materials which shows the overestimation of pore sizes by the BJH method.¹²⁰ In addition to the consistent decrease in the surface area and total pore volume upon IL impregnation, it is important to note that the N₂ solubility of ILs might be very poor at the liquid nitrogen temperature, which directly affects the uptakes, hence the accuracy of the BET measurements.¹²¹

Figure 4.5 presents the results of the TG and DTG analyses. The decrease in the weight of the composites up to 100 °C was associated with the moisture captured by the composites prior to measurements. Even though ILs were kept in an oven before usage, the weight loss before 100 °C was more severe for [DCA]⁻ containing IL and its composites as illustrated in Figure 4.5(a). This moisture sensitivity was related to the hydrophilic character of this IL. On the contrary, for the bulk [BMPyr][PF₆] and its composites, no such weight losses were observed up to 100 °C due to the hydrophobicity of the IL (Figure 4.5(b)). The bulk [BMPyr][DCA] started to decompose at 250 °C, while the decomposition temperature of [BMPyr][PF₆] was approximately 340 °C as determined by the T'_{onset} . The change in the IL's anion resulted in a significant difference in the decomposition temperature of bulk ILs, which might be arising from the respective interionic interaction between the cation and hydrophilic or hydrophobic anions.¹²¹ Furthermore, pristine rGA300 lost 20% of its initial weight at 700 °C, whereas rGA500 only lost 12% of its weight at the same temperature as shown in Figure 4.5. The decrease in interlayer distance due to the removal of oxygen-containing functional groups was demonstrated with the shifts in XRD spectra of rGAs before, and higher weight loss for rGA300 shown here further proves the elimination of functional groups in rGA500.⁸⁷ When TG and DTG curves of pristine rGAs were compared, the thermal stability of rGA500 was found to be higher than rGA300 with T'_{onset} values of 495 and 350 °C, respectively (Figure 4.5(c)). To investigate the effect of IL incorporation, the TG and DTG curves of bulk ILs and IL/rGA composites were compared.

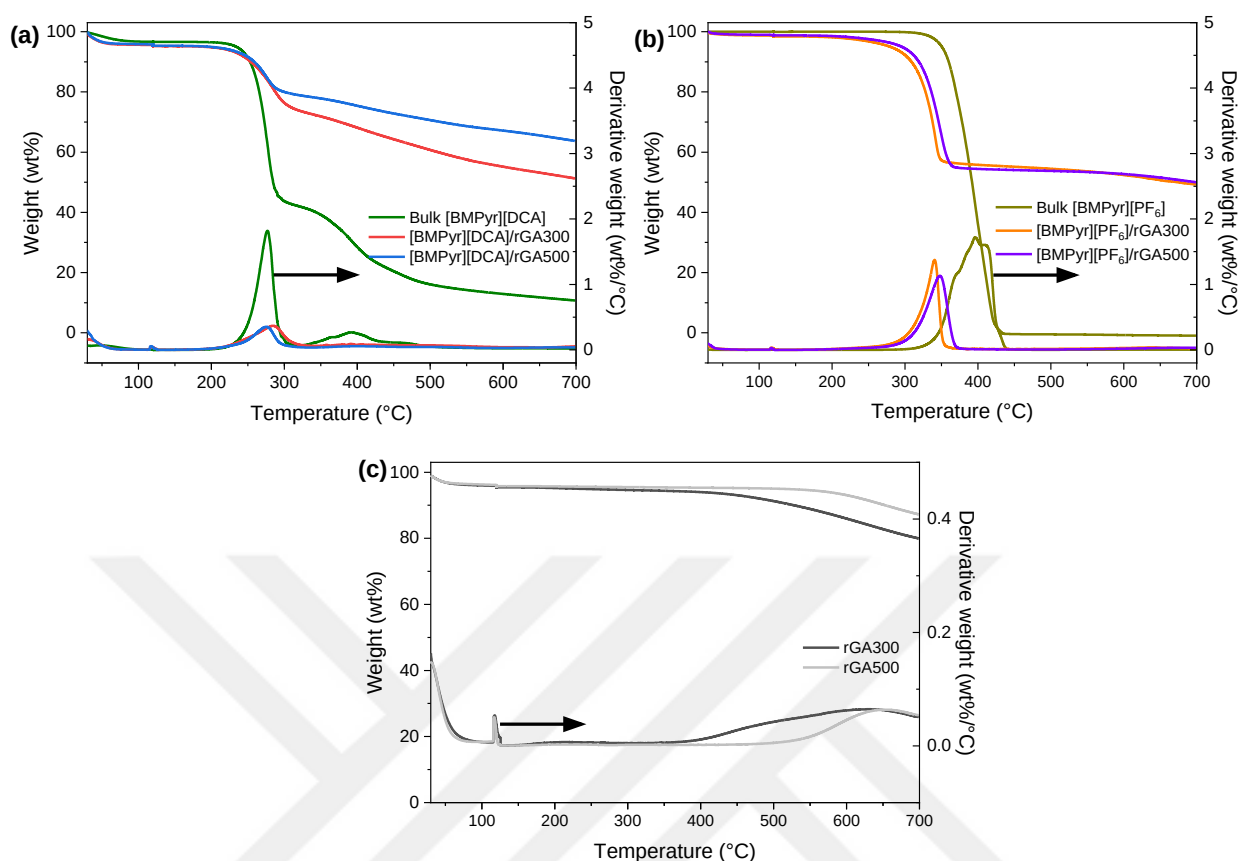


Figure 4.5. TG and DTG curves of (a) [BMPyr][DCA] and its composites with the rGAs, (b) [BMPyr][PF₆] and its composites with the rGAs, and (c) pristine rGAs.

The [BMPyr][PF₆]-incorporated rGAs followed a similar thermal decomposition trend as the bulk IL, one-step decomposition mechanism, while the decomposition of [BMPyr][DCA]-loaded composites deviated from the bulk IL's two-step decomposition and demonstrated a one-step decomposition mechanism upon introduction to the rGA. As illustrated in Figure 4.5(a), the T'_{onset} of bulk [BMPyr][DCA] was recorded as 250 °C, it decreased to 240 and 230 °C, when this IL was deposited onto rGA300 and rGA500, respectively. As for [BMPyr][PF₆]-loaded composites, bulk IL's T'_{onset} of 340 °C decreased to 310 and 305 °C on rGA300 and rGA500, respectively, as can be seen in Figure 4.5(b). These decreases in the thermal stability of the IL-loaded composites indicate the presence of molecular interactions between the rGA surface and the IL molecules, which play a role in the decomposition mechanisms.^{121,122}

By comparing the impregnation of two ILs having the same cation with different-sized anions on the same host and the impregnation of the same ILs on hosts prepared at different reduction temperatures, the interactions between rGAs and ILs were examined. The composites

consisting of bulky, fluorinated anion showed higher thermal stability compared to composites having [DCA]⁻ anion due to higher thermal stability of [BMPyr][PF₆]. Even though pristine rGA300 displayed lower thermal stability compared to pristine rGA500, IL-composites prepared with rGA300 were found to be slightly more thermally stable than IL/rGA500 composites. Hence, we can deduce that IL incorporation to rGAs decreased the thermal stability of bulk ILs but in varying degrees depending on the differences in the interactions between the IL molecules and the rGA surfaces.

To explore the molecular interactions between ILs and rGAs, FTIR spectroscopy was used. Comparative IR spectra are presented in Figure 4.6 and detailed band assignments are provided in Table A.1. The features present in the region between 2800-3200 cm⁻¹ were attributed to the cation of both ILs (Figure 4.6(a, c)). The deconvoluted peaks of bulk [BMPyr][DCA] were located at 2967, 2953, and 2876 cm⁻¹ as shown in Figure 4.6(a), and assigned to the stretching of CH₂ and CH₃ groups of the cation.¹²³ The peaks at 2967 and 2953 cm⁻¹ red-shifted when the IL was deposited onto rGAs by 3, 7 cm⁻¹ for rGA300 and 9, 10 cm⁻¹ for rGA500, respectively. But for the peak located at 2876 cm⁻¹, a red-shift was observed for IL/rGA300 (by 5 cm⁻¹), whereas a blue-shift was observed when the same IL was deposited onto rGA500 (by 13 cm⁻¹). The strength of the bonds in butyl/methyl groups attached to the pyrrolidinium ring was found to be weakening upon [BMPyr][DCA] deposition onto rGAs. [BMPyr][DCA]/rGA500 presented more severe red-shifts regarding the strength of alkyl groups attached to the pyrrolidinium ring, but also, the major blue-shift was observed at the butyl chain of cation indicating the difference in the interactions between rGA500 and the bulk IL compared to those in IL/rGA300. As for the dicyanamide anion of the IL, the spectra between 2300 and 2000 cm⁻¹ were deconvoluted into four peaks, and the bands were assigned to asymmetric stretching of C–N and C≡N bonds as illustrated in Table S1 and Figure 4.6(b).¹²⁴ All peaks presented red-shifts, but the most significant red-shift was observed in the asymmetric stretching of C≡N bonds for [BMPyr][DCA]/rGA500 (Figure 4.6(b)). These red-shifts indicate decreases in the strength of dicyanamide bonds upon IL deposition to rGAs, which might be arising from the interaction of deprotonated nitrogen atoms of the anion and the electrophilic carbon atoms on the rGA surface, hence the weakened bonds within the anion.¹²⁵

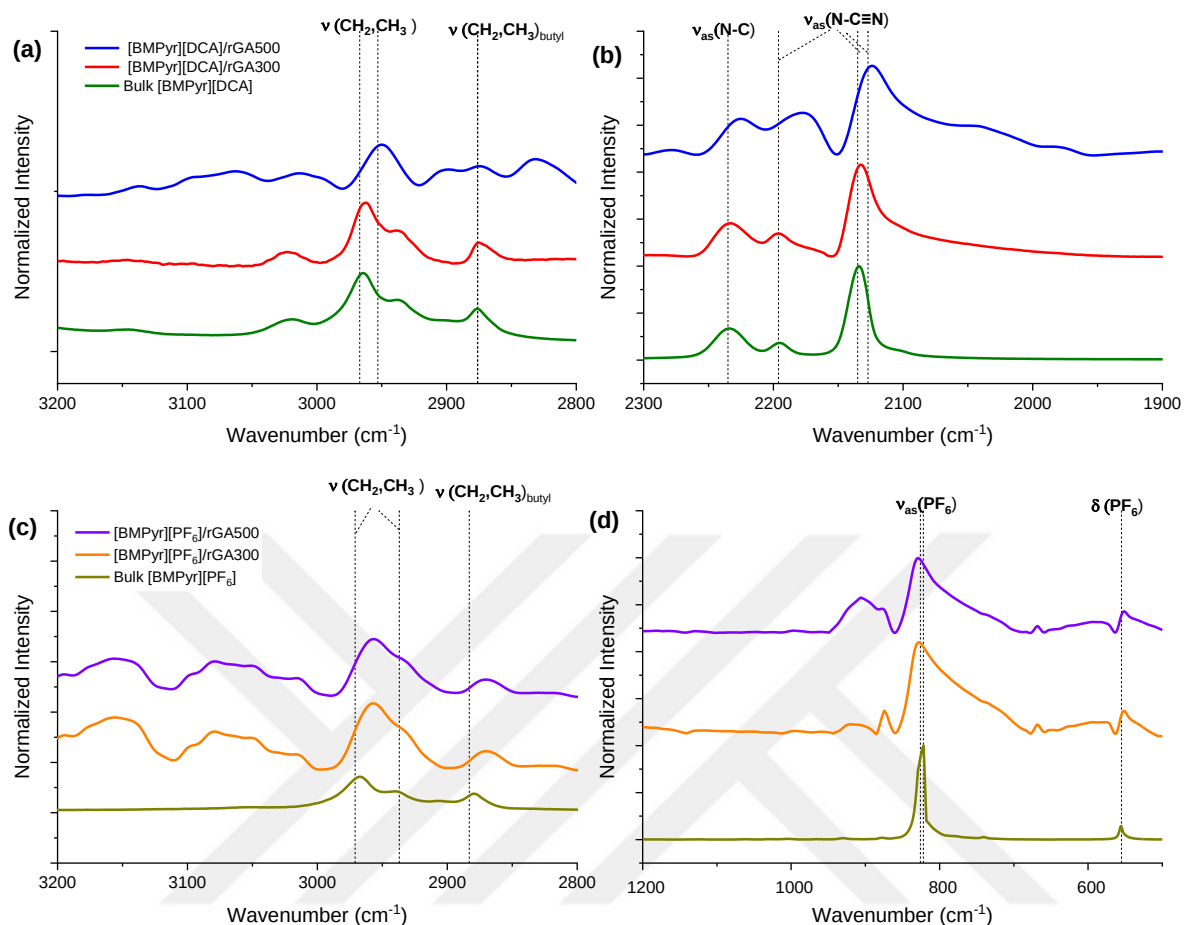


Figure 4.6. FTIR spectra of bulk IL and 50 wt.% IL-loaded composites between (a) 3200-2800 cm⁻¹, (b) 2300-1900 cm⁻¹ for [BMPyr][DCA]; (c) 3200-2800 cm⁻¹ and (d) 1200-500 cm⁻¹ for [BMPyr][PF₆].

For the cation of [BMPyr][PF₆], on the other hand, the bands at 2971 and 2883 cm⁻¹ showed similar red-shifts after deposition onto rGAs (by 9, 11 cm⁻¹ for rGA300 and 9, 10 cm⁻¹ for rGA500). In addition to these red-shifts, weak blue-shifts (which might be even below the spectral resolution of the measurements) were observed for bulk IL's peak at 2937 cm⁻¹ by 3 and 1 cm⁻¹ for IL/rGA300 and IL/rGA500, respectively. In the lower frequency region, the peaks between 900-400 cm⁻¹ were attributed to the anion of [BMPyr][PF₆], as shown in Figure 4.6(d). The most intense peak for asymmetric PF₆ stretching was located at 826 cm⁻¹ and it displayed blue-shifts of 4 and 5 cm⁻¹ for [BMPyr][PF₆]/rGA300 and [BMPyr][PF₆]/rGA500, respectively. The remaining peaks at 822 and 555 cm⁻¹ exhibited red-shifts of 9 and 8 cm⁻¹ for [BMPyr][PF₆]/rGA300 and 11 and 7 cm⁻¹ for [BMPyr][PF₆]/rGA500, respectively.

Based on these results, we infer that the interactions between [BMPyr][PF₆] and rGAs are different than those between [BMPyr][DCA] and rGAs since the most characteristic bands of the anions interacted with rGAs in opposite directions; bonds within dicyanamide weakened upon deposition of this IL onto rGAs, whereas the vibrations in P–F bonds became stronger. Both the anion and cation of two ILs were found to be interacting with their hosts to varying extents. When IL-loaded rGA300 composites were considered, for both ILs, the electrostatic interaction between rGA300 and the cation part was more prominent. However, for IL-loaded rGA500 composites, the rGA surface was strongly interacting with respective anions of ILs which resulted in major shifts for these bonds. The higher frequency region (above 3200 cm⁻¹) was not deconvoluted since this region is generally assigned to water absorption bands coming from the moisture in samples.¹²³ Also, vibrational bands coming from the rGAs were not illustrated in this work. These bands are hard to detect and deconvolute due to the challenges associated with interpreting the spectra as materials that are mostly composed of carbon, such as rGAs, tend to absorb IR radiation.¹²⁶

The shifts in the characteristic IR features of ILs indicated that changing rGA structure and anion of IL are important to tune the characteristics of interactions between IL molecules and rGAs. These interactions are further analyzed by XPS. The related spectra are provided in Figure 4.7. The XPS survey spectra of rGA500 showed a decrease in the intensity of O1s peak compared to that of pristine rGA300's and a change in oxygen amount was observed as the following: 12.9 and 8.7 atomic% for rGA300 and rGA500, respectively. This decrease in the oxygen amount indicates the expected removal of oxygen-containing functional groups as the reduction temperature increases.

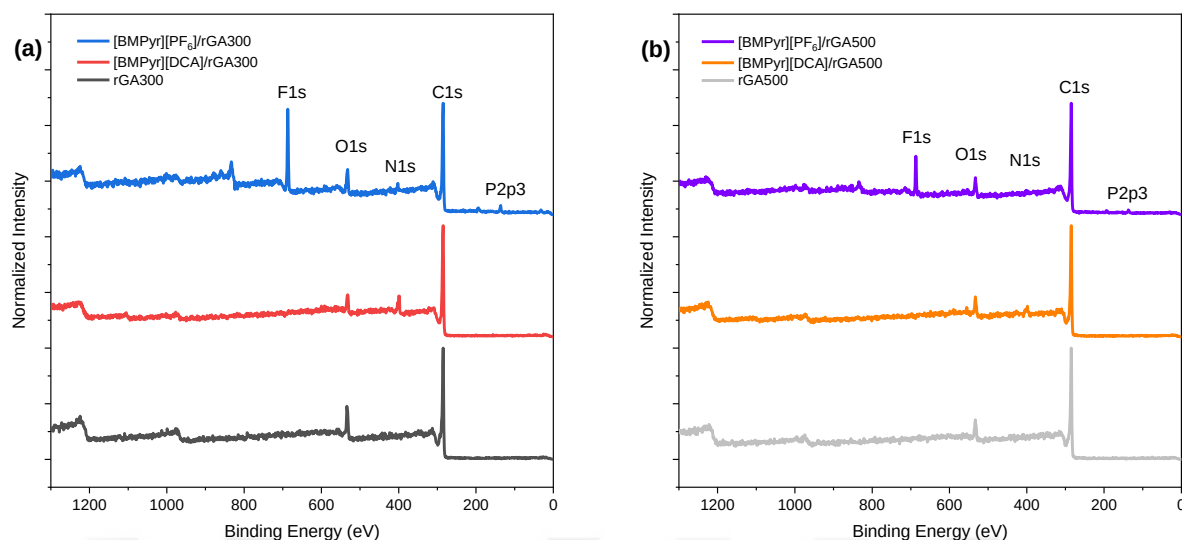


Figure 4.7. Survey spectra of (a) rGA300 and its IL-loaded composites and (b) rGA500 and its IL-loaded composites.

To assess the interactions between IL molecules and rGAs in detail, the shifts in the C1s and O1s were examined. All the obtained peak positions from XP spectra are given in Table A.2. C1s of the pristine materials were deconvoluted into four peaks; the peaks at 284.5, 285.8, 287.5, and 290.4 eV were assigned to C–C/C=C/C–H, C–O in alkoxy and epoxy, C=O in carbonyl and O–C=O bonds in carboxyl, respectively.¹²⁷ Figure A.5 shows that all these C1s peaks shifted to lower binding energies upon the deposition of ILs onto the rGAs. These shifts imply the weakening of carbon bonds on the rGA skeleton upon the introduction of additional elements associated with the anion or cation parts of the ILs. The most severe C1s peak shifts were observed for [BMPyr][PF₆]/rGA300 and [BMPyr][DCA]/rGA500 among all composites, 0.68 eV at C–OH and 1.71 eV at O–C=O peak position, respectively. This could be related to the enhanced interaction between these specific IL-rGA pairs. Moreover, the intensity of C1s peaks corresponding to C–OH and C=O bonds exhibited considerable decreases for the composites prepared with rGA500 compared to those prepared with rGA300 (Figure A.5), which further indicates the decrease in the number of oxygen-containing functional groups with an increase in the reduction temperature.²⁴

The effect of depositing two ILs having different hydrophilicity/hydrophobicity on the electronic structure of the resulting composites was elucidated with O1s shifts. Based on different surface functionalities of rGAs and hydrophilicity/hydrophobicity of the incorporated

ILs, the shifts in the O1s for the IL-loaded composites were found to be alternating with varying degrees as given in Table A.2. The peaks in the increasing binding energy order were assigned to C=O bonds in quinonoid form, C=O (carboxyl, carbonyl) bonds, and C–OH (hydroxyl), C–O–C (epoxy) bonds for pristine rGAs and IL-composites.¹²⁸ When composites prepared using the same IL and different rGAs were compared, major differences were observed. Among [BMPyr][DCA]-loaded rGAs, only IL/rGA300 showed significant red-shifts in quinonoid C=O and carboxyl/carbonyl bonds, whereas shifts for IL/rGA500 were smaller than the spectral resolution (0.1 eV). All [BMPyr][PF₆]-loaded composites displayed blue-shifts at O1s peak positions which indicate that upon IL impregnation, the electron density around oxygen atoms belonging to surface functionalities decreased due to the existence of electrostatic interactions between IL molecules and the rGA surface. In contrast to this result, upon [BMPyr][DCA] deposition, all O1s peaks showed red-shifts, which could be arising from the interactions between rGAs and nucleophilic centers of hydrophilic [BMPyr][DCA]. When the rGA surface contacts with [DCA][−] anion, the electron dislocations between rGA's carbon atoms and electronegative N-atoms of anion might be making oxygen atoms in surface groups more electron-rich, hence giving rise to decreases in binding energies of oxygenated groups.¹²⁹

Additional to these above-mentioned shifts, a substantial reduction in the amount of single- and double-bonded oxygen groups was observed for [BMPyr][PF₆]/rGA300 based on the intensities of peaks located around 532 and 533 eV. These decreases in peak intensities might be implying a higher amount of defect sites for this composite.¹³⁰ Also, in addition to the decrease in the number of oxygenated groups on its surface, O1s peaks shifted to lower binding energies for pristine rGA500 compared to rGA300. The binding energies of [BMPyr][PF₆]-loaded composites were found in accordance with this trend, but among [BMPyr][DCA]-loaded composites, [BMPyr][DCA]/rGA500 exhibited substantially higher binding energies for O1s peaks compared to its IL/rGA300 counterpart. These results proved that the choice of IL was not the only important factor affecting the electronic structure of composites, but also the reduction temperature of GA which determines the quantity of surface functional groups contributed strongly to the molecular interactions. Additional to C1s and O1s peaks, N1s peaks coming from the pyrrolidinium ring of ILs and dicyanamide of hydrophilic IL, F1s, and P2p coming from the anion of hydrophobic IL were deconvoluted, and assigned accordingly.^{18,131} The peak shifts of these elements were slightly higher than the spectral resolution.

To investigate the defects in the pristine materials and composites, Raman spectra in a region between 1800 to 800 cm⁻¹ (Figure 4.8) were deconvoluted into five peaks (*D*, *G*, *D'*, *D''*, and *D**). The corresponding I_D/I_G , $I_{D'}/I_G$, and I_{D^*}/I_G ratios of each material are given in Table A.3. Accordingly, pristine rGA500 presented higher I_D/I_G , $I_{D'}/I_G$, and I_{D^*}/I_G ratios compared to rGA300. These increases in the calculated ratios with increased reduction temperature for GA imply that there were more defect sites for the pristine rGA500 compared to rGA300, which was in compliance with TGA and XRD results.²⁴ Also, the band position of *D''* and intensity of *D** were reported as crucial parameters to predict the number of oxygen groups as follows: a shift to a higher wavenumber for rGA500 and a decrease in the intensity of *D** signify the reduced oxygen-containing functional groups on rGA500.¹³² GA structure retains carbonyl, carboxyl, epoxy, and hydroxyl functional groups attached to hexagonal rings after the hydrothermal treatment of GO and supercritical drying,¹³³ but following the thermal annealing of GA at varying temperatures, some of these groups were removed from the structure creating various defect sites on the carbon skeleton. As I_D/I_G is generally used to measure the amount of structural deformation,¹³⁴ I_{D^*}/I_G for the quantification of disordered graphitic lattice in the structure,¹³² and I_D/I_G is used to determine the presence of pentagon, heptagon, zigzag defects,¹³⁵ we can conclude that parallel to increase in these ratios, higher reduction temperature resulted in more structural defects on GA.

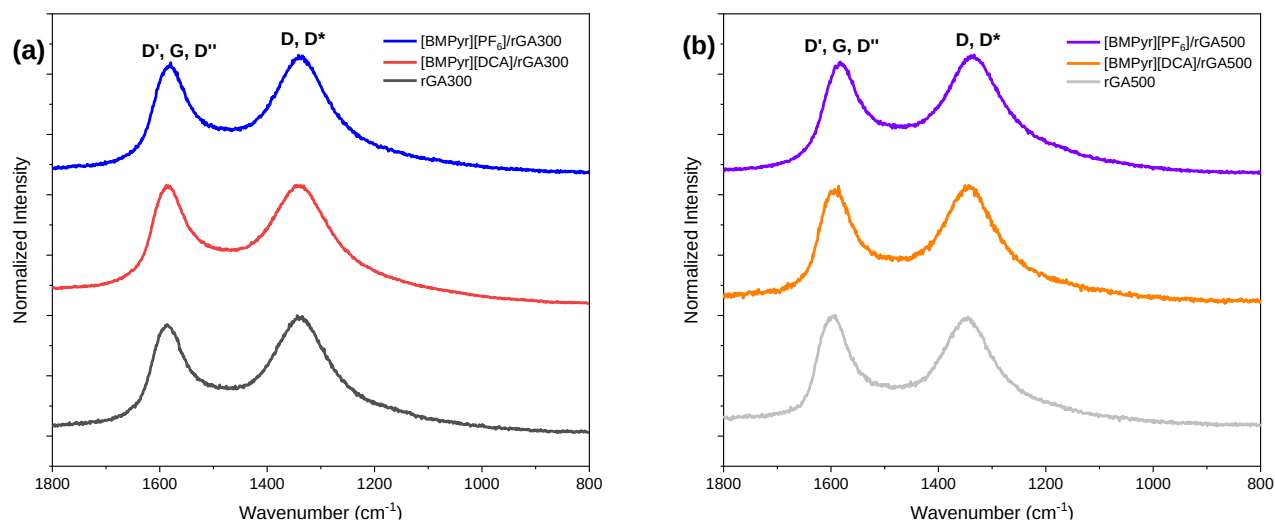


Figure 4.8. Raman spectra of (a) rGA300 and its IL-loaded composites, (b) rGA500 and its IL-loaded composites between 1800-800 cm⁻¹.

In addition to the established direct correlation between the amount of defect and reduction temperature, after IL impregnation the defect amounts were found to be varying as a function of IL structure for the hosts prepared at the same reduction temperatures. The consistent increase in I_D/I_G values after IL impregnation indicated that ILs were capable of enhancing the number of structural defects as reported in the literature.¹³⁶ [BMPyr][PF₆]-loaded rGAs demonstrated the highest I_D/I_G values among the composites. Furthermore, the calculated I_D/I_G value of [BMPyr][PF₆]/rGA300 was surpassing the value of pristine rGA300, and similarly, I_D^*/I_G ratio of [BMPyr][PF₆]/rGA500 was higher than that of rGA500. These results might be associated with the enhanced [BMPyr][PF₆] interaction with rGAs, resulting in a decrease in the size of sp² domains of rGA, hence higher I_D/I_G , I_D^*/I_G , and I_D^*/I_G ratio values for [BMPyr][PF₆]-loaded composites.¹³⁷

4.2.2 Gas Sorption and Separation Performances

4.2.2.1 Pristine rGAs

Volumetric gas sorption measurements were performed at a pressure range from 1 to 1000 mbar, at 25 °C, for single-component CO₂ and CH₄ gases. The selectivity of each material was calculated by dividing the gas uptake of the more strongly sorbed gas to that of the less strongly sorbed one at the same pressure. The CO₂ and CH₄ uptakes for pristine rGAs are given in Figure 4.9(a, b) and Figure 4.9(c, d), respectively. Gas uptakes of rGA500 were higher than that of rGA300, but the most significant difference was observed in the low-pressure region for CO₂ as shown in Figure 4.9(a, b), where rGA500 was outperforming rGA300 by up to six-fold higher uptakes at 1 mbar. CH₄ uptakes of rGA500 were slightly higher than rGA300, as presented in Figure 4.9(c, d).

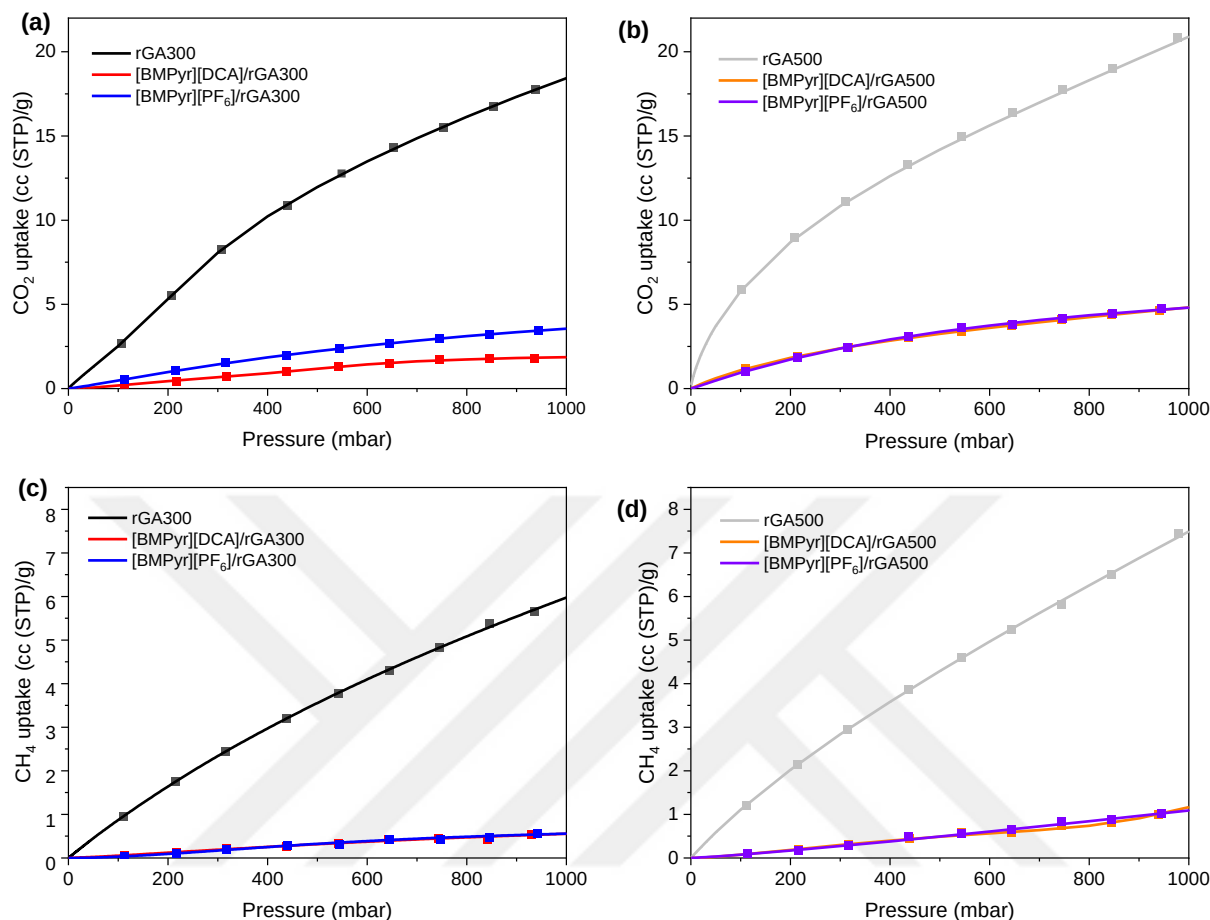


Figure 4.9. CO₂ uptakes of (a) rGA300 and its IL-composites, (b) rGA500 and its IL-composites, and CH₄ uptakes of (c) rGA300 and its IL-composites, (d) rGA500 and its IL-composites between 0-1000 mbar at 25 °C, points correspond to experimental data whereas lines are for the fitted data.

Moreover, Figure 4.10(a) shows the calculated ideal selectivities of pristine rGAs. By only changing the reduction temperature of the GA, the CO₂/CH₄ selectivity of rGA500 was found to be surpassing that of rGA300 by two-times at 100 mbar and six-times at 1 mbar. This improvement in the CO₂/CH₄ separation performance of rGA500 might be related to enhanced CO₂ sorption of the material at low-pressure range. Reduction of GA at a higher temperature was found to be yielding lower amount of oxygen-containing functional groups as illustrated with XRD, TGA, and XPS analyses. Also, Raman results presented a higher amount of defect sites for rGA500 which arose from the elimination of oxygen functionalities. These findings

are in parallel to the literature, where a recent study reported the positive impact of oxygen defects in GO structure on CO₂ adsorption.¹³⁸

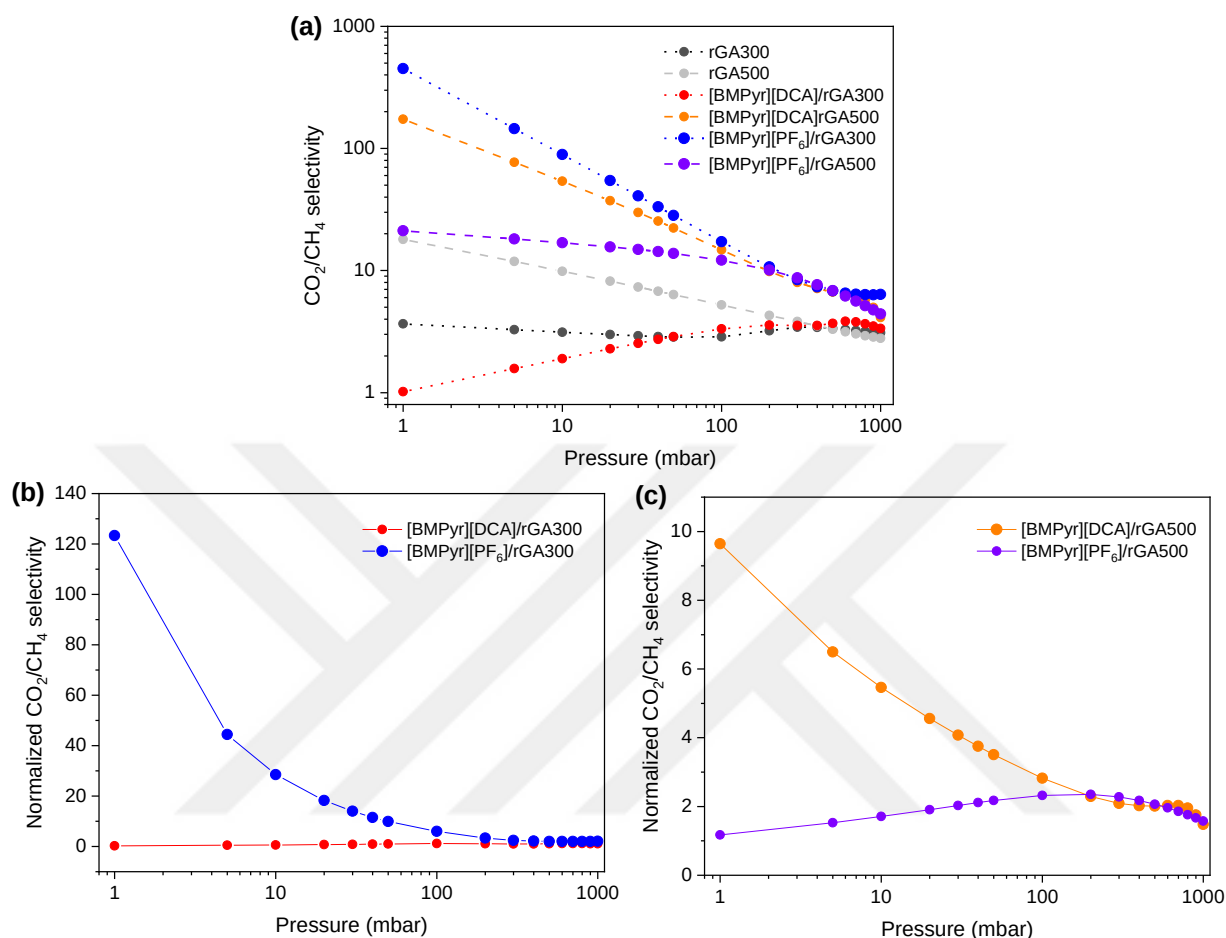


Figure 4.10. (a) Ideal CO₂/CH₄ selectivity values calculated for pristine rGAs and all composites, normalized CO₂/CH₄ selectivity values of (b) IL/rGA300 and (c) IL/rGA500 composites with respect to pristine rGAs.

4.2.2.2 IL/rGA composites

Compared to the pristine rGAs, all IL-loaded rGA composites demonstrated major decreases in both CO₂ and CH₄ uptakes as shown in Figure 4.9. These decreases were associated with the reduction in available pore volumes upon IL incorporation, which was evidenced by the BET results. According to Figure 4.9(a), [BMPyr][PF₆]/rGA300 exhibited the lowest decrease in CO₂ uptake within the low-pressure region compared to all other IL-loaded composites, whereas its CH₄ uptakes decreased more severely at the same pressure region. These differences in the uptakes indicate the composite's relatively high affinity to CO₂ than CH₄ at the low-pressure region (1 to 100 mbar). When the same hydrophobic IL, [BMPyr][PF₆],

was loaded onto rGA500, the composite demonstrated the least decreased CH₄ uptakes among composites at the low-pressure region which was the complete opposite trend observed for [BMPyr][PF₆]/rGA300. A similar observation was made for the CO₂ uptakes of [BMPyr][DCA]-loaded composites. While [BMPyr][DCA]/rGA500 yielded high uptakes in the low-pressure region compared to other composites, the composite prepared with rGA300 displayed the lowest CO₂ uptakes among all composites in this region. These differences in gas uptakes eventually resulted in differing CO₂/CH₄ selectivities of composites as a function of varying interactions between rGAs and ILs.

Among all materials, the highest CO₂/CH₄ selectivity values within the low-pressure region were of [BMPyr][PF₆]/rGA300. Data showed that the deposition of [BMPyr][PF₆] boosted the CO₂/CH₄ selectivity of rGA300 from 2.9 to 17.2 at 100 mbar and 3.7 to 450.9 at 1 mbar (Figure 4.8(a, b)). The high CO₂ capacity of [BMPyr][PF₆]/rGA300 among the composites and its severely decreased CH₄ uptakes generated high separation performance at this low-pressure region. Computational studies reported that the defect sites on graphitic structures might lead to enhanced electron transport and higher affinity to promote CO₂ adsorption.¹³⁹ XPS and Raman results displayed a higher amount of defect sites for [BMPyr][PF₆]/rGA300, which could be affecting the CO₂ uptake capacity of this composite. Moreover, COSMO-RS calculations demonstrated that bulk [BMPyr][PF₆] offers a very poor affinity for CH₄ as shown in Figure A.6. Such low affinity might be the reason for particularly low CH₄ uptakes in the low-pressure region. The deposition of the same IL, [BMPyr][PF₆], onto rGA500 improved the pristine rGA's CO₂/CH₄ separation performance slightly as shown in Figure 4.8(c), and at 1000 mbar, the composite was still doubling the CO₂/CH₄ selectivity of rGA500.

Furthermore, when the effect of depositing a highly hydrophilic IL, [BMPyr][DCA], to rGA structures was investigated, no improvement was observed in the low-pressure region for [BMPyr][DCA]-loaded rGA300 since pristine material had a higher selectivity as illustrated in Figure 4.10(a, b). The CO₂/CH₄ selectivity of this composite was calculated as 3.6 at 1000 mbar, which was almost equal to rGA300's selectivity of 3.1 at 1000 mbar. However, [BMPyr][DCA]/rGA500 exhibited significantly high CO₂/CH₄ selectivity values of 4.1 at 1000 mbar, 14.8 at 100 mbar, and 173.5 at 1 mbar surpassing the performance of [BMPyr][DCA]-loaded rGA300 and [BMPyr][PF₆]-loaded rGA500. This improvement was interpreted as the outcome of this composite's selectively decreased gas uptakes, which were originating from the enhanced interactions demonstrated by the shifts in spectroscopic features (observed on both IR and XP spectra) upon IL impregnation. IR spectroscopy analysis of this composite showed

major red-shifts on the band positions of triple and single-bonded nitrogen atoms indicating direct interactions between rGA surface and the IL's anion, and in addition to that, XPS results further supported the presence of these interactions with substantial redshifts on C=O and O–C=O bonds of deconvoluted C1s peaks. The interplay between IL's anion and carbon atoms on rGA might be producing a higher affinity toward CO₂ and lower affinity toward CH₄ for this composite than that for [BMPyr][DCA]-loaded rGA300.

Since the gas uptakes were measured up to 1000 mbar and selectivity values were calculated accordingly, the predominant factor affecting the separation performances of IL/rGA composites was the IL-host interactions. Our results illustrated high CO₂/CH₄ separation performance for [BMPyr][PF₆]/rGA300 and [BMPyr][DCA]/rGA500 composites, especially at the low-pressure region where these IL-host interactions led to CO₂ affinity of the sorbents. The structural changes in rGA500 were explained and evidenced as a function of thermal treatment since rGA500 offered higher thermal stability, more defect sites, and a fewer number of functional groups compared to rGA300. In addition to these reported structural changes, the charge distribution on the surface of rGAs might play a significant role in controlling the separation performance. Molecular dynamics simulations demonstrated that by negatively charging the surface of nanoporous graphene, the permeation of CO₂ was considerably improved which increased the CO₂/CH₄ separation performance of graphene-based membranes. This improvement was shown to be arising from the interactions between negative charges and linear CO₂ molecules that affected adsorption layers around the membrane.¹⁴⁰ The change in the number of surface functional groups and defect sites on the carbon skeleton through thermal reduction might lead to a change in charge distribution of rGA surfaces which would interfere with the separation performance of the composites. Due to differences in surface characteristics between rGAs, as we illustrated above when impregnated with the same ILs, selective gas separation performances of composites changed significantly. Upon the incorporation of [BMPyr][PF₆] which consists of a relatively bulky, neutral, and highly hydrophobic anion, IL/rGA300 composite showed the best CO₂/CH₄ separation performance due to higher amount of defect sites and bulk IL's poor affinity for CH₄ as shown in Figure A.6. Whereas the incorporation of [BMPyr][DCA], which has a relatively small, Lewis basic, and hydrophilic anion to rGA500 amplified the gas separation performance of pristine rGA remarkably as the interactions were illustrated with major shifts in XPS and IR spectra.

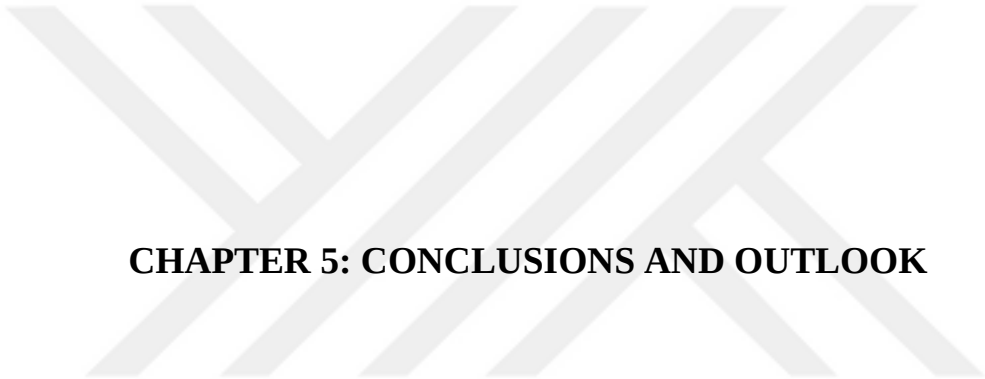
4.2.3 Mixture Selectivities of rGAs and Their Composites with ILs

So far we presented the ideal selectivities but in industrial sorption-based separations, gases are present as mixtures, and thus, reporting mixture selectivities is crucial. Hence, the Ideal Adsorbed Solution Theory (IAST) was used to compute the uptakes of CO₂/CH₄:50/50 and CO₂/CH₄:5/95 mixtures representing the approximate compositions of biogas and natural gas, respectively.⁹⁰ Calculated mixture selectivities for all composites are given in Figure A.7 and compared with the literature in Table A.5. The CO₂/CH₄ mixture selectivities of pristine rGAs at 1000 mbar were calculated as 4.4 and 3.7 for rGA300, 6.2 and 8.6 for rGA500 at 50/50, 5/95 concentrations, respectively. As it was discussed before for ideal CO₂/CH₄ selectivities, when a hydrophilic IL, [BMPyr][DCA], was loaded onto rGA300, the mixture and ideal selectivities decreased with respect to the pristine material but the incorporation of a hydrophobic IL containing the same cation to rGA300 increased the CO₂/CH₄ selectivity, especially at the low-pressure region (Figure A.7(a, c)). For composites prepared on rGA500, a completely different scenario was observed, IL impregnation was found to be improving the ideal and mixture selectivities as shown in Figure A.7(b, d). Besides displaying high ideal CO₂/CH₄ selectivities, the mixture selectivities of composites for CO₂/CH₄:50/50 were also competitive compared to literature values (Table A.5). For example, the selectivity values of 19.8 and 12.6 were determined for [BMPyr][PF₆]/rGA300 and [BMPyr][DCA]/rGA500, respectively, at 1000 mbar whereas, at the same pressure the selectivity values of 3.8 and 14 were reported for the 50/50 concentration of CO₂/CH₄ gas mixture previously for N-doped porous carbon and the GO incorporated CU-BTC, respectively.^{141,142}

Changing both the host material and the impregnated IL while keeping the loaded IL amount constant dramatically changed the materials' performances. For example, [BMPyr][DCA]-loaded rGA500 demonstrated 170-times enhanced CO₂/CH₄ selectivity compared to rGA300 composite prepared with the same IL at 1 mbar, and for the [BMPyr][PF₆]-loaded composites, IL/rGA300 surpassed the selectivity of IL/rGA500 by 20-times at 1 mbar. The effect of using ILs with the same cation and different anions on gas separation performance has been reported before. It was suggested that changing the interionic interaction energy of ILs was altering the electronic environment on host MOF material, hence directly influencing the thermal stability and gas storage capability of the composite material.¹²¹

A similar observation was made with this study, but here, we demonstrated the impact of changing not only the anion of the incorporated IL but also tuning the surface characteristics of the host material as well. The results demonstrated that the surface properties of pristine materials are influential in tuning the gas separation performance of rGA composites and apart from thermal reduction, there are many possibilities to modify the structure of GAs or rGAs, such as elemental doping, chemical crosslinking, and introducing organic solvent. We infer that the ease of tunability of the surface characteristics of GAs combined with the presence of an almost limitless number of ILs offer a broad potential for the design of IL/rGA composite for any target gas separation application.

In conclusion, the results of this study illustrated that the reduction temperature of host GAs and the hydrophilic/hydrophobic character of the impregnated ILs have a significant effect on the selective gas separation performance of the resulting IL/rGA composites. Especially in the low-pressure region, IL-based composites exhibited immensely increased CO₂/CH₄ selectivities due to unique interactions between nanoporous rGAs and the ILs. These interactions were explained through high defect amounts, significant shifts in the peak positions of the spectroscopic features, and varying thermal stabilities for the best-performing IL/rGA composites. [BMPyr][PF₆]/rGA300 increased the selectivity of pristine rGA300 from 2.9 to 17.2 at 100 mbar and 3.6 to 450.9 at 1 mbar, while [BMPyr][DCA]/rGA300 demonstrated lower selectivities than pristine rGA up to 100 mbar. Also, both IL-loaded rGA500 composites improved the selectivity of pristine rGA500, but major enhancement was recorded for [BMPyr][DCA]/rGA500. This composite boosted the CO₂/CH₄ selectivity of rGA500 from 5.2 to 14.8 at 100 mbar and 18 to 173.5 at 1 mbar, whereas [BMPyr][PF₆]-loaded rGA500 resulted in selectivity values of 12.2 and 21.1 at 100 and 1 mbar, respectively. These values prove that modifying IL/rGA composites offers remarkable CO₂/CH₄ separation performances among graphene-based materials for low pressures. Our findings point out the tunability and high performance of these materials hence their remarkable potential in sorption-based gas separation applications. IL/rGA composites can be further tested for other gas separations and computer-based simulations can be beneficial for the rational design of these composites.



CHAPTER 5: CONCLUSIONS AND OUTLOOK

The promising features of ILs have been demonstrated in the literature for various areas such as catalysis, electrochemistry, gas sensing, and separation-based applications. It has been demonstrated by many studies that the incorporation of ILs into porous materials improved the performance of porous hosts due to interactions between IL molecules and hosts. In this thesis, the improving effect of IL addition to porous hosts on different adsorption-based gas separation applications was illustrated.

In Chapter 4, two different ILs ([BMPyr][DCA] and [BMPyr][PF₆]) with hydrophilic and hydrophobic characters were loaded to rGAs that were reduced at two different temperatures (rGA300 was reduced at 300 °C and rGA500 was reduced at 500 °C) and the CO₂/CH₄ separation performance of resulting composites was investigated with the volumetric sorption method. The thorough and systematic structural characterization results of the rGAs evidenced the importance of GA's reduction temperature in terms of adjusting the quantity of oxygenated surface functional groups, and also the investigation of IL/rGA composites with characterization techniques displayed the interactions between ILs and host rGAs that influenced the gas separation of the composites. Gas uptakes illustrated that rGA500's higher gas capacity compared to rGA300 was arising from the increased surface area and pore volume, and upon IL addition, gas uptakes of pristine rGAs considerably decreased since pore volumes of rGAs were filled with IL molecules. Depending on the interactions between oxygenated groups in rGAs and anions of ILs which were demonstrated with TGA, FTIR, XPS, and Raman, the composite prepared with rGA300 and a hydrophobic IL, [BMPyr][PF₆] displayed high CO₂/CH₄ ideal selectivities at low-pressure range whereas the promising CO₂/CH₄ separation performance was observed for the composite prepared with rGA500 and hydrophilic IL, [BMPyr][DCA], at low-pressure range. The ideal CO₂/CH₄ selectivity results were further supported with the IAST-calculated mixture selectivities for the concentrations of 50/50 and 5/95. Especially in the low-pressure region, the CO₂/CH₄ separation performance of [BMPyr][DCA]/rGA500 and [BMPyr][PF₆]/rGA300 composites were surpassing most of the carbon-based materials whose CO₂/CH₄ separation capability has been reported in the literature.

The C₂H₂ separation performance of a core-shell type IL/MOF composite was featured in Appendix B. The surface of a hydrophobic MOF, ZIF-67 was coated with a hydrophilic IL, [HEMIM][DCA] by wet impregnation method for the experimental investigation of volumetric C₂H₂, C₂H₄, CH₄, and H₂ sorption at three different temperatures. The core-shell type structure of the IL/ZIF-67 composite was verified with washing experiment, TGA, SEM, and XRD techniques. The addition of IL immensely boosted the ideal C₂H₂/CH₄, C₂H₂/C₂H₄, and C₂H₂/H₂

selectivities of the pristine ZIF-67. The IL-loaded ZIF-67 composite was almost completely C_2H_2 selective up to 45 mbar for C_2H_2/CH_4 separation since no CH_4 uptake was observed up to 45 mbar for the composite. Similarly, due to no H_2 sorption up to 50, 80, and 200 mbar at 10 °C, 25 °C, and 40 °C, respectively, infinite ideal selectivities were calculated for the IL-loaded ZIF-67.

IL/rGA and IL/ZIF-67 composites reported in this study have promising results for CO_2/CH_4 , C_2H_2/CH_4 , C_2H_2/C_2H_4 , and C_2H_2/H_2 separations due to interactions between hosts-IL molecules and composites-sorbates. To take the improvements in the gas separation performance of IL-composites reported in this thesis further, several points can be addressed in future works as they are briefly explained through the following headlines:

Functionalization of GA before IL/GA (or IL/rGA) synthesis: Particularly, IL/rGA composites showed the importance of tuning the characteristics of host porous materials before the synthesis of IL-composites. The thermal reduction at different temperatures yielded a distinct change in rGAs properties due to varying defect sites and functional groups, and there exist many other methods to functionalize GAs such as chemical reduction which has been proved to result in a higher amount of defect sites compared to thermal reduction.¹⁴³ Additional to chemical reduction, deposition of metal nanoparticles,¹⁴⁴ and biological functionalization through bacteria,¹⁴⁵ and elemental doping¹⁴⁶ are among the possible functionalization methods. Thus, GAs and rGAs can be functionalized, their surface and bulk characteristics can be adjusted with these promising methods prior to IL addition, and resulting composites can be tested for CO_2/CH_4 separation or other gas separation applications.

Using computational tools to select the IL before the synthesis of IL/porous composite: The choice of IL has proved to be very crucial according to the results illustrated in this thesis. In Chapter 4, two different ILs featured in the composite synthesis were sharing the same cation but different anions. Related to the differing interionic interactions between anion and cation, they were exhibiting different hydrophobicities.¹²¹ When these ILs were incorporated into the same rGAs, depending on the interactions between anions of ILs and rGA, the gas separation performance of the IL/rGA composites was found completely different. Several studies in the literature illustrated the importance of locating low and high-adsorption energy sites on GA structures prior to functionalization.¹⁴⁷ Motivated by this, before deciding on the ILs, both possible sorption sites on rGAs can be investigated with DFT calculations and a thorough screening on the acidity, and hydrophilicity of ILs can be done so that the IL with the most compatible properties with GAs or rGAs can be chosen. In Appendix B, an IL/MOF composite

was prepared by depositing the IL on the MOF surface. For such core-shell type IL/MOF composites, since absorption is as important as the adsorption in the sorption mechanism of the gases, a detailed and more realistic screening can be made by looking at the gas solubilities of potential ILs for the target separation. These are crucial points for selecting the most suitable ILs before IL-loaded composite synthesis since with the most compatible combination of IL and porous host, it is possible to produce the best-performing composites for various gas separation applications.

Adjusting the location and homogeneity of IL molecules in IL-loaded MOF composites:

As shown in Appendix B, the location of the IL molecules is also another important parameter to tune the interaction between sorbent and sorbate. With the general approach of IL incorporation to MOF structures, the pores of the MOFs are being filled IL molecules hence the adsorption capacity of the composite dramatically decreases.^{103,121} For core-shell type IL/MOF composites, such decreases in gas uptakes can be avoided and even gas sorption can be improved compared to the host material. Although [HEMIM][DCA]/ZIF-67 composite in this study did not show increased gas uptakes compared to pristine ZIF-67, which was attributed to the moisture absorbed by IL, the low solubility of sorbates in bulk IL and possible inhomogeneity of the IL shell, it is possible to construct composites that can demonstrate higher gas uptakes than that of pristine hosts through taking advantage of the solubility of the sorbates in ILs as it was reported in the literature.^{148,149} To prepare core-shell type IL/MOF composites with a homogenous IL layer, the physical mixing duration can be increased during the synthesis, and ultrasound or centrifugation treatments can be applied to obtain a better dispersion of IL molecules on the MOF surface. These techniques resulted in increased gas uptakes and homogenous IL layer on host MOF according to the reports of some groups in the literature recently.^{149,150}

Reporting the thermal and chemical stability of IL/rGA and IL/MOF composites: While choosing an IL for IL-loaded composite synthesis, it is crucial to investigate the thermal stability of ILs and porous hosts beforehand since thermal activation of IL/porous composite is strictly dependent on decomposition temperatures of the components. However, it is also important to note that TGA results provided in Chapter 4 and Appendix B account for the short-term thermal stability of the IL/rGA and IL/MOF composites. In real-life applications, due to continuous operation and repeated regeneration steps, composites might be subjected to thermal treatment for a prolonged duration. To show the thermal stability and applicability of the IL-based composites in realistic cases, long-term thermal stability tests such as cycling tests that are

repeated sorption experiments for different batches might be useful. The chemical stability of IL-based composites encapsulates the resistance of the composites toward moisture, solvents, and aqueous solutions. Rigid, dense structured MOFs with surface hydrophobicity have been proven to demonstrate high chemical stability.¹⁵¹ Some MOF structures are reportedly prone to structure collapsing when they come in contact with water and some ILs are very hydrophilic. Thus, choosing moisture-resistant MOFs and ILs, or tuning the hydrophilicity of rGAs can be effective to get rid of the gas separation performance loss that might be encountered in humid operating conditions. To prove the applicability of an IL-loaded composite, running sorption tests in the presence of moisture, subjecting composites to aqueous conditions, and then repeating the structural characterization methods can be critical.

Testing the gas separation performance of IL/rGA and IL/MOF composites for multicomponent gas mixtures: Most of the studies investigating gas sorption and separation performance report the single-component volumetric gas sorption results. The results shown in this thesis are also mostly featuring single-component gas uptakes for sorbates. The calculation of ideal gas selectivities is directly related to the isotherms obtained from these single-component experimental data. IAST-calculated selectivities provide a glimpse into the practical usability of IL-loaded composites, but isotherms derived from volumetric sorption experiments are also being inputted into the IAST equation which decreases the credibility of this method. To further support ideal gas selectivity and IAST gas mixture selectivity calculations, dynamic sorption experiments might be carried out for gas mixture concentrations that are relevant to real-life gas separation applications. Considering C₂H₂ purification processes, in a realistic case, a gas stream emerging from a petrochemical process contains not only C₂H₂ and CH₄ or C₂H₂ and C₂H₄, but it contains C₂H₂, C₂H₄, CH₄, H₂, and possibly other C₂-based hydrocarbons. To investigate the gas separation potential of IL-based porous composites, running breakthrough experiments with multicomponent gas mixtures as well as with different mixture compositions can provide invaluable information.

The content of this thesis portrays the high potential of IL/rGAs and IL/ZIF-67 composites on gas separation applications clearly and thoroughly. The reported sorption performances of the IL-loaded composites are among the best reported in the literature so far, and the characterization and performance results illustrated here will be useful to design composites with higher sorption and separation capacities. Furthermore, utilizing the abovementioned points in future studies will elevate the performance of these composites and make their widespread usage in various industries competitive compared to existing solutions.

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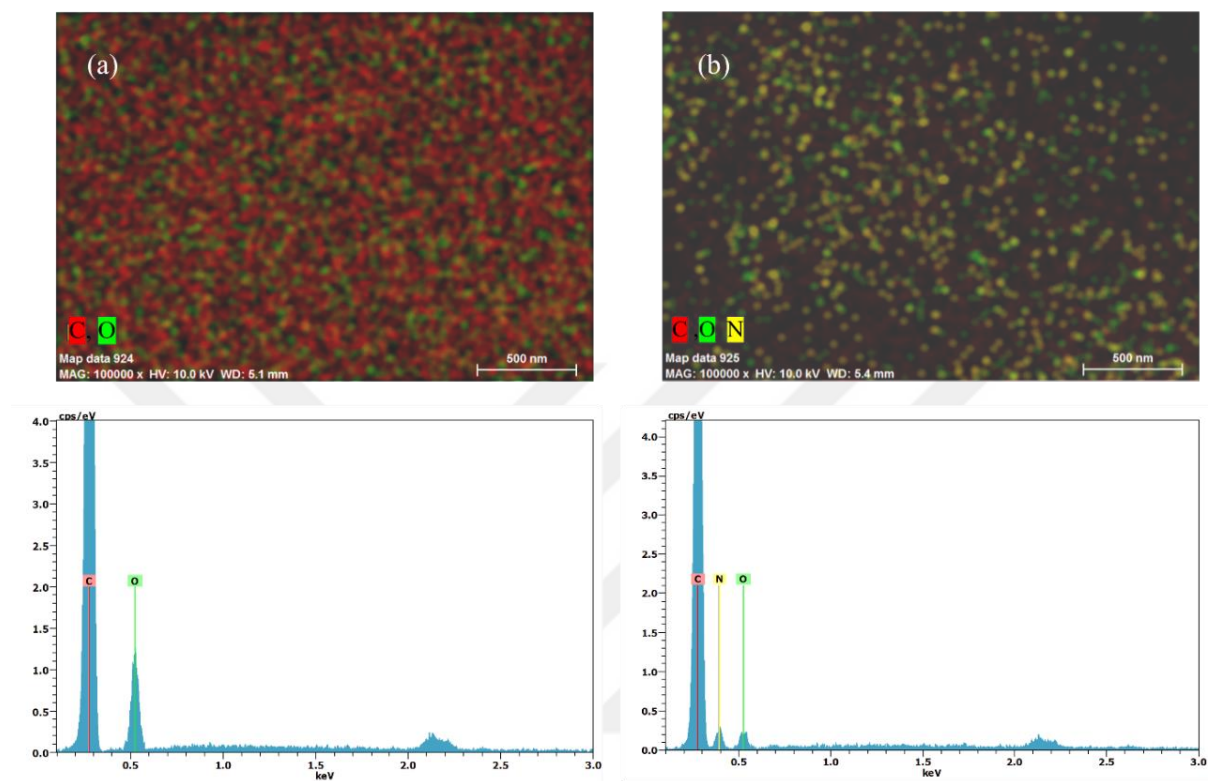
APPENDIX A: SUPPLEMENTARY INFORMATION FOR CHAPTER 4

Figure A.1. EDX results of (a) rGA300 and (b) [BMPyr][DCA]/rGA300.

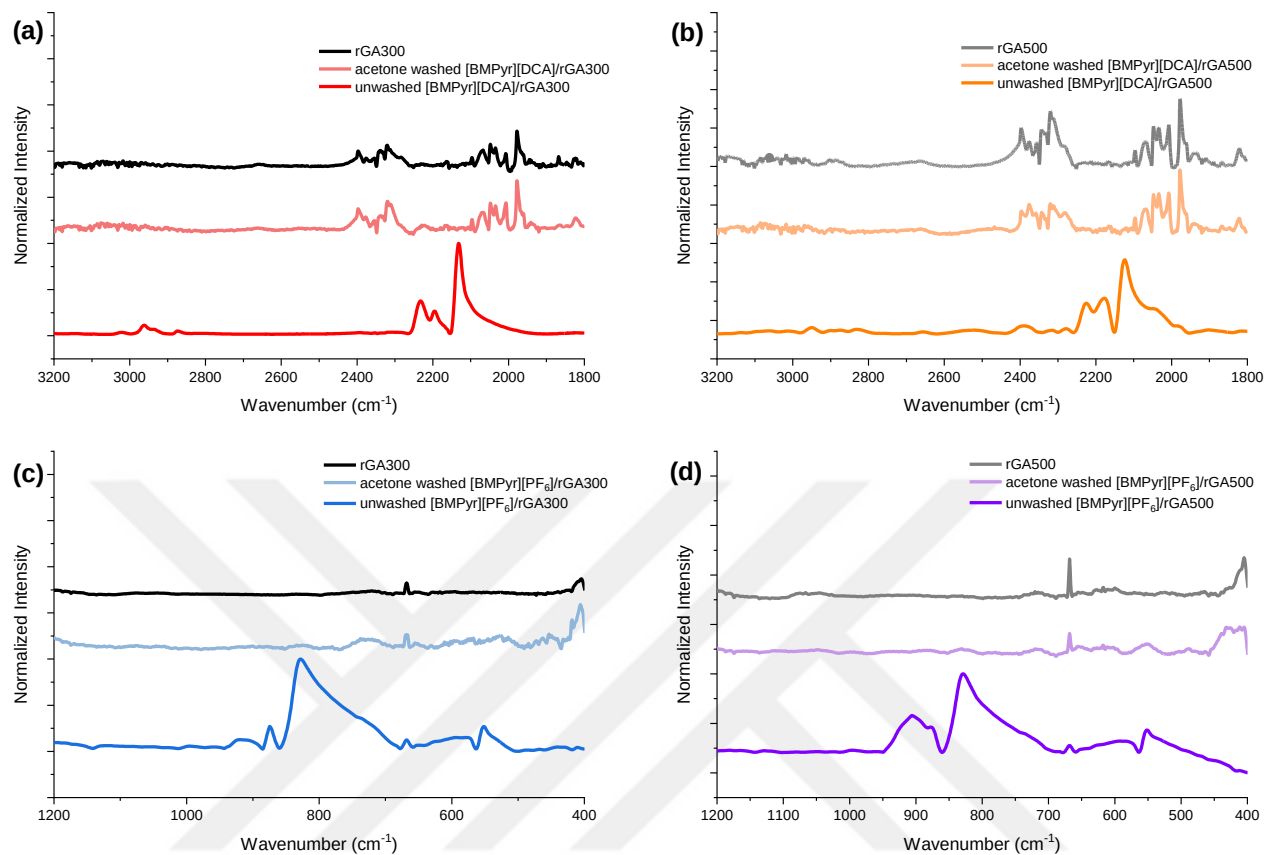


Figure A.2. FTIR spectra of rGAs, unwashed IL/rGAs, and acetone-washed IL/rGA composites: between 3200–1800 cm^{-1} for (a) [BMPyr][DCA]/rGA300, (b) [BMPyr][DCA]/rGA500; between 1200–400 cm^{-1} for (c) [BMPyr][PF₆]/rGA300, (d) [BMPyr][PF₆]/rGA500.

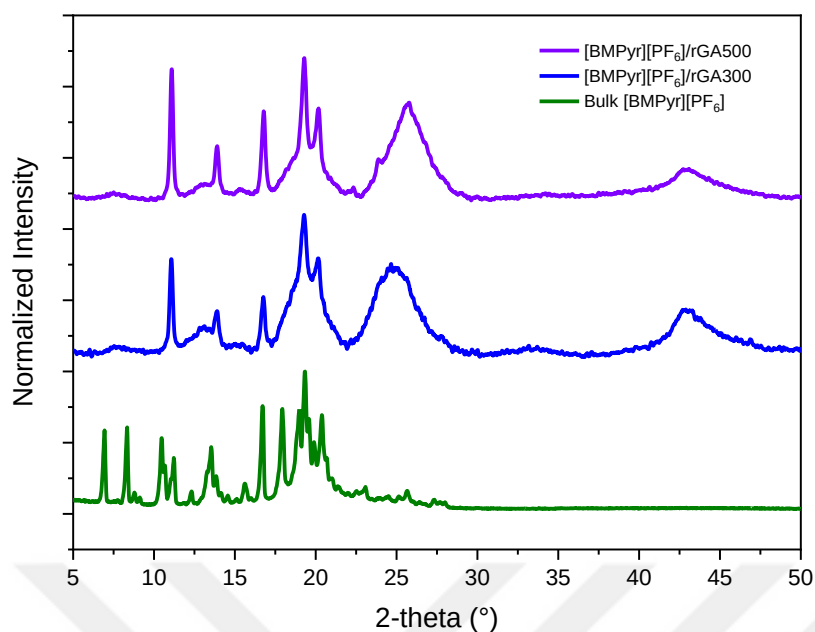


Figure A.3. XRD spectra of bulk [BMPyr][PF₆] and its composites.

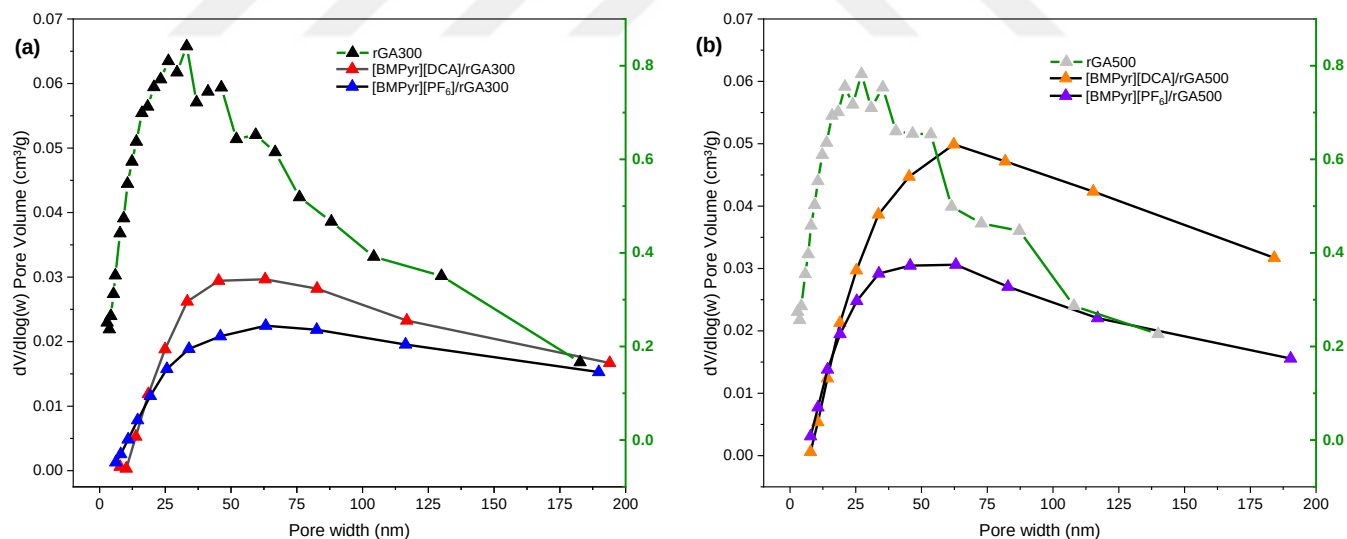


Figure A.4. PSDs of (a) pristine rGA300 and its IL-loaded composites and (b) pristine rGA500 and its IL-loaded composites calculated by using Barrett-Joyner-Halenda (BJH) method.

Table A.1. FTIR band assignments of bulk ILs and composites.

Assignment	Bulk [BMPyr][DCA]	[BMPyr][DCA]/ rGA300	[BMPyr][DCA]/ rGA500	Ref.
$\nu_{\text{as}}(\text{C-N})$	2235	2234	2230	152,124
$\nu_{\text{as}}(\text{N-C}\equiv\text{N})$	2196	2193	2172	152,153
$\nu_{\text{as}}(\text{N-C}\equiv\text{N})$	2135	2133	2129	153,124
$\nu_{\text{as}}(\text{N-C}\equiv\text{N})$	2127	2116	2109	154,124
$\nu(\text{CH}_2)$, $\nu(\text{CH}_3)$ in alkyl chain	2967	2964	2958	155,156
$\nu(\text{CH}_2)$, $\nu(\text{CH}_3)$ in alkyl chain	2953	2946	2943	155,156
$\nu(\text{CH}_2)$, $\nu(\text{CH}_3)$ in butyl chain	2876	2871	2889	155,156
	Bulk [BMPyr][PF ₆]	[BMPyr][PF ₆]/rGA300	[BMPyr][PF ₆]/rGA500	
$\nu_{\text{as}}(\text{PF}_6)$	826	830	831	157, 67
$\nu_{\text{as}}(\text{PF}_6)$	822	813	811	157, 67
$\delta(\text{PF}_6)$	555	547	548	5,157
$\nu(\text{CH}_2)$, $\nu(\text{CH}_3)$ in alkyl chain	2971	2962	2962	155,156
$\nu(\text{CH}_2)$, $\nu(\text{CH}_3)$ in alkyl chain	2937	2940	2938	155,156
$\nu(\text{CH}_2)$, $\nu(\text{CH}_3)$ in butyl chain	2883	2872	2873	155,156

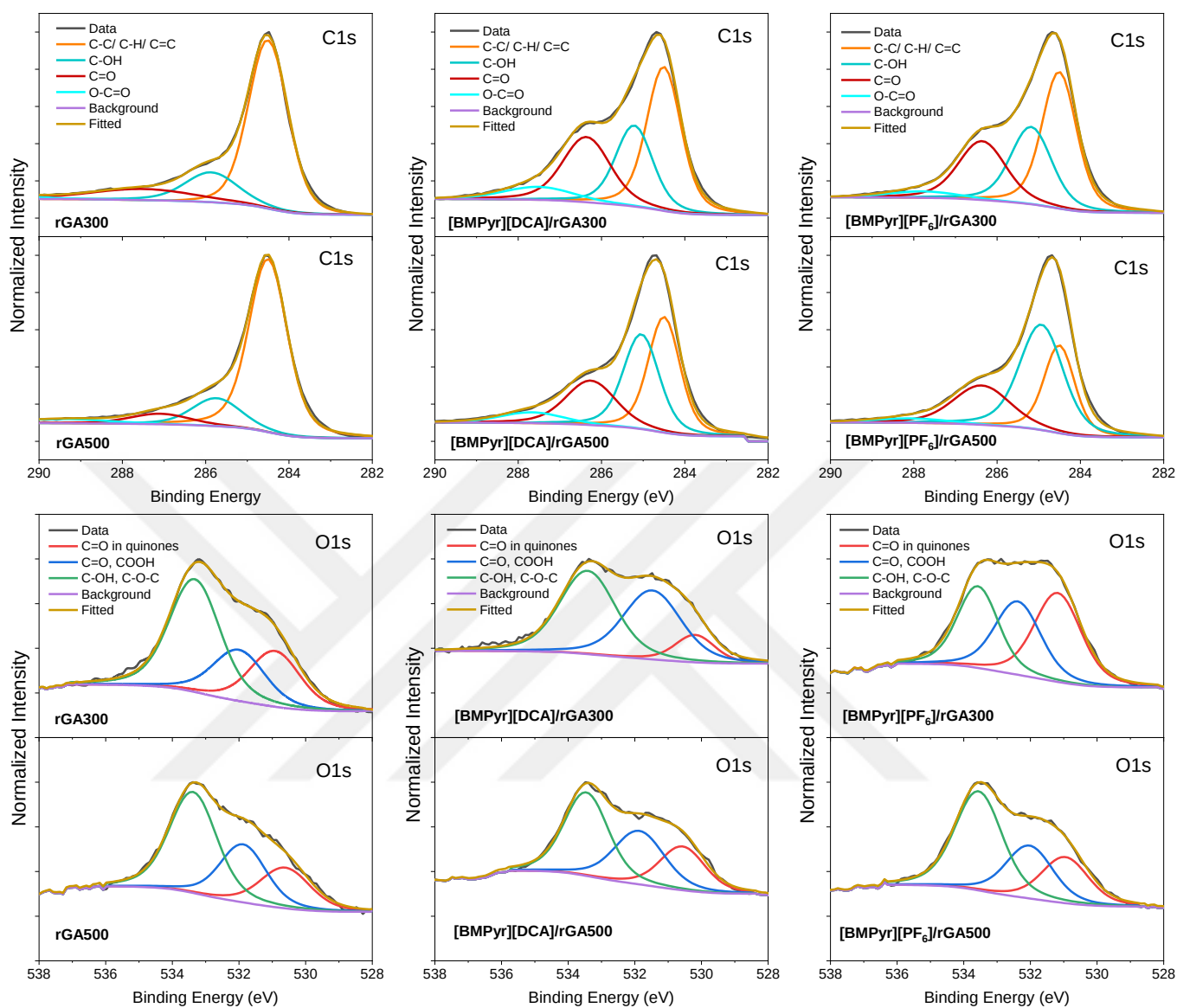


Figure A.5. Deconvoluted C1s and O1s peaks of all samples.

Table A.2. Positions of deconvoluted peaks of C1s and O1s scans for all materials.

Samples/ Assignments	Deconvoluted C1s scans				Deconvoluted O1s scans		
	C-H, C-C, C=C	C-OH	C=O	O-C=O	C=O bonds in quinonoid form	C=O (carboxyl, carbonyl)	C-OH (hydroxyl) C-O-C (epoxy)
rGA300	284.5	285.86	287.51	290.38	530.92	532.01	533.33
[BMPyr][DCA]/rGA300	284.5	285.21	286.36	287.51	530.29	531.48	533.42
[BMPyr][PF ₆]/rGA300	284.5	285.18	286.36	287.77	531.18	532.38	533.58
rGA500	284.5	285.74	287.09	289.38	530.61	531.88	533.38
[BMPyr][DCA]/rGA500	284.5	285.04	286.26	287.67	530.57	531.87	533.46
[BMPyr][PF ₆]/rGA500	284.5	284.93	286.36	288.08	530.95	532.03	533.55

Table A.3. I_D/I_G , $I_{D'}/I_G$, and I_{D^*}/I_G ratios of rGAs and their composites.

Sample	I_D/I_G ratio	$I_{D'}/I_G$ ratio	I_{D^*}/I_G ratio	D'' band position (cm ⁻¹)
rGA300	1.31	0.35	0.076	1504.9
[BMPyr][DCA]/rGA300	1.41	0.19	0.038	1538.7
[BMPyr][PF ₆]/rGA300	1.77	0.57	0.052	1545.9
rGA500	1.50	0.76	0.087	1548.1
[BMPyr][DCA]/rGA500	1.58	0.59	0.048	1544.7
[BMPyr][PF ₆]/rGA500	1.79	0.59	0.096	1541.1

Table A.4. Parameters of sorption isotherms fitted to Dual Site Langmuir, Langmuir-Freundlich and Dual Site Langmuir-Freundlich models.

Sorbent	Gas	Dual Site Langmuir					Langmuir-Freundlich				Dual site Langmuir-Freundlich						
		q_1	k_1	q_2	k_2	R^2	q	k	n	R^2	q_1	k_1	n_1	q_2	k_2	n_2	R^2
rGA300	CO ₂	-	-	-	-	-	-	-	-	-	58.65	$3.39 \cdot 10^{-4}$	0.93	2.76	$4.05 \cdot 10^{-3}$	3.45	0.99
	CH ₄	5.50	$1.12 \cdot 10^{-3}$	44.57	$7.40 \cdot 10^{-5}$	0.99	-	-	-	-	-	-	-	-	-	-	-
[BMPyr][DCA]/ rGA300	CO ₂	-	-	-	-	-	-	-	-	-	1.76	$2.4 \cdot 10^{-3}$	1.53	0.48	$1.8 \cdot 10^{-3}$	6.83	0.99
	CH ₄	-	-	-	-	-	-	-	-	-	1.21	$8.8 \cdot 10^{-4}$	1.26	$4.4 \cdot 10^{-9}$	88.25	0.27	0.99
[BMPyr][PF₆]/ rGA300	CO ₂	-	-	-	-	-	-	-	-	-	$4.1 \cdot 10^{-15}$	$2.58 \cdot 10^{-6}$	0.07	7.14	$9.9 \cdot 10^{-4}$	1.14	0.99
	CH ₄	-	-	-	-	-	-	-	-	-	0.77	$1.7 \cdot 10^{-3}$	1.84	$6.0 \cdot 10^{-16}$	4.43	1.75	0.99
rGA500	CO ₂	-	-	-	-	-	-	-	-	-	81.12	$2.32 \cdot 10^{-4}$	$8.8 \cdot 10^{-7}$	24.31	$1.48 \cdot 10^{-3}$	0.75	0.99
	CH ₄	2.44	$2.76 \cdot 10^{-3}$	330.26	$1.76 \cdot 10^{-5}$	0.99	-	-	-	-	-	-	-	-	-	-	-
[BMPyr][DCA]/ rGA500	CO ₂	3.28	$3.56 \cdot 10^{-3}$	77.88	$2.98 \cdot 10^{-5}$	0.99	-	-	-	-	-	-	-	-	-	-	-
	CH ₄	-	-	-	-	-	-	-	-	-	1.08	$1.8 \cdot 10^{-3}$	1.50	1.11	$9.5 \cdot 10^{-4}$	10.01	0.99
[BMPyr][PF₆]/ rGA500	CO ₂	-	-	-	-	-	-	-	-	-	7.91	$1.5 \cdot 10^{-3}$	1.06	0.31	$2.6 \cdot 10^{-20}$	0.62	0.99
	CH ₄	-	-	-	-	-	159.47	$1.33 \cdot 10^{-5}$	1.15	0.99	-	-	-	-	-	-	-

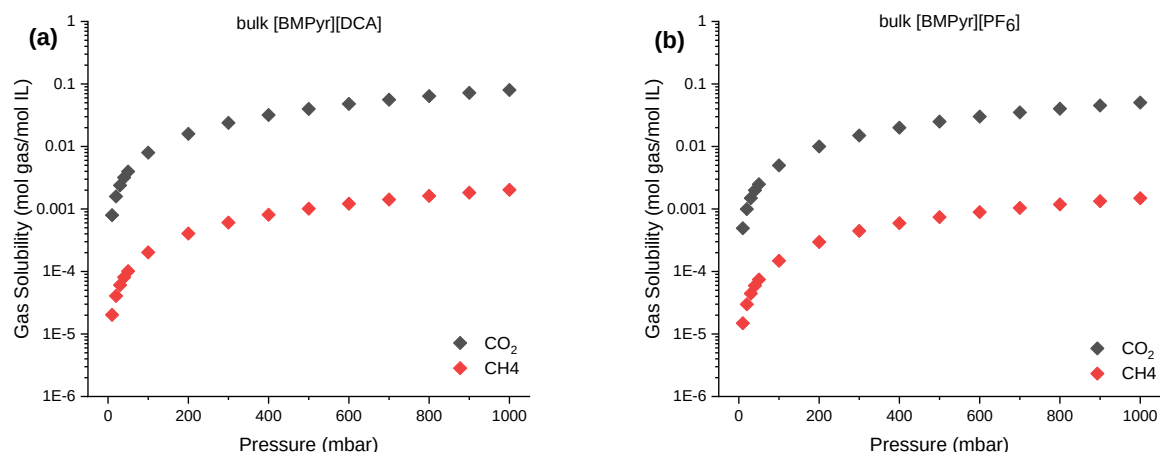


Figure A.6. COSMO-RS calculated CO₂ and CH₄ solubilities in bulk (a) [BMPyr][DCA] and [BMPyr][PF₆].

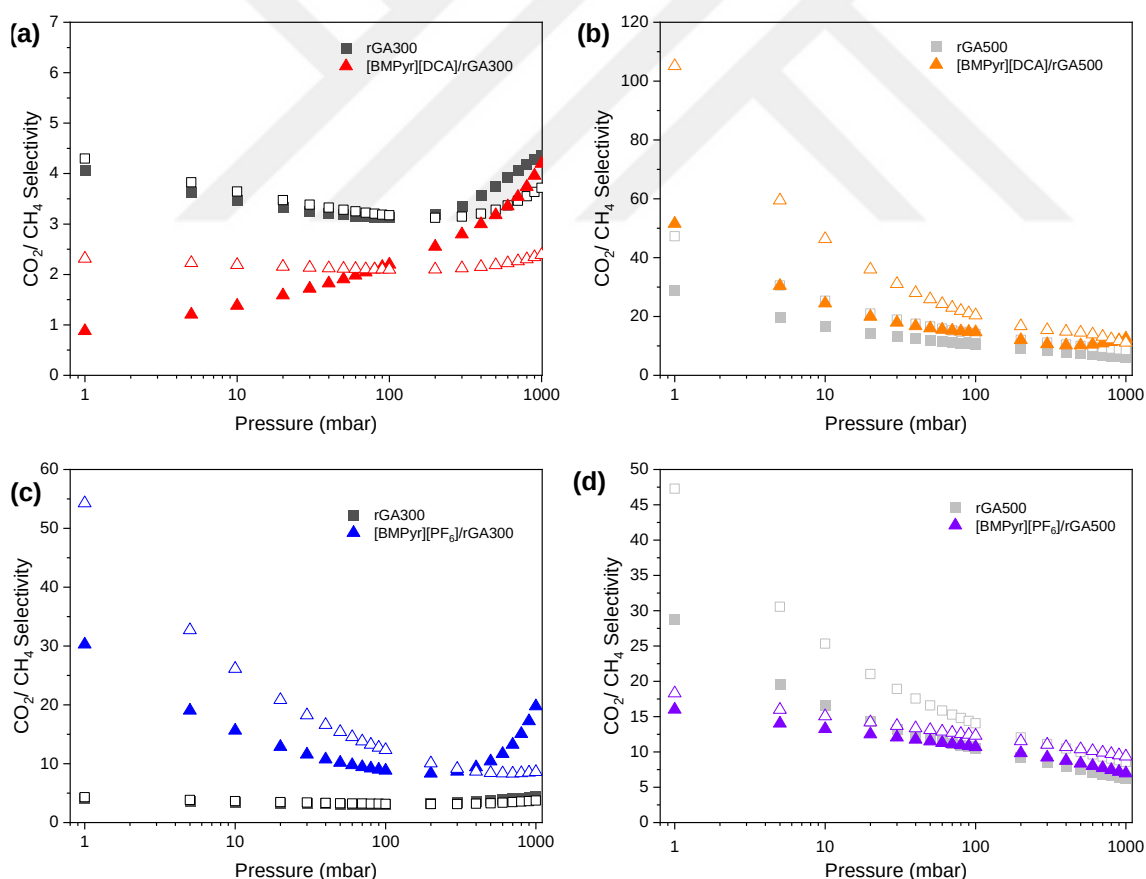


Figure A.7. IAST-calculated mixture selectivities of (a) [BMPyr][DCA]/rGA300, (b) [BMPyr][DCA]/rGA500, (c) [BMPyr][PF₆]/rGA300 and (d) [BMPyr][PF₆]/rGA500 in comparison with pristine rGAs. Filled symbols representing 50/50 and empty symbols 5/95 CO₂/CH₄ concentrations.

Table A.5. Comparison of ideal and IAST-calculated mixture CO₂/CH₄ selectivities for [BMPyr][PF₆]/rGA300 and [BMPyr][DCA]/rGA500 with literature values.

Adsorbent	Temperature (°C)	Pressure (mbar)	Ideal CO ₂ /CH ₄ selectivity	CO ₂ /CH ₄ IAST selectivity		REFs
				(50/50)	(5/95)	
10GrO@MIL-53(Cr)	25	1000		8*		158
N-doped porous carbon	25	1000		3.2	8.7	159
MOF-200/GO	25	1000	18.4			160
Nanographene	25	1000	8.6			161
N-Doped Graphene Aerogel	0	1000	4**			39
MOF-505 @ 5GO	25	1000		8.6		162
1GrO@Cu-BTC	0	1000		14		142
aPPy/GO10	25	1000	2.5			163
Cu-BTC/GO10	25	1000	5.8			163
Ordered Mesoporous Carbon	25	1000		3*		164
3D-Printed Carbon Monolith	25	1000	2.5*			94
DES-glycerol/C-PKS	25	1000	4.5			165
N-Doped Carbon, NPC-1	25	1000		3.8		141
Zeolite, Fe-PKU-2	25	1000		15*		166
3D carbonaceous architectures containing BCNO nanocrystals	25	966	15			167
		266	86			
C125-220	25	1200	10.8			168
CPC-550	25	1000	12			169
50CPDA@A-C	25	1000		5.1		170
NbO-type MOF	23	1000		6.2*	6*	171
[BMIM][PF ₆]/ZIF-8	25	1000	5	8.8		67
[HEMIM][DCA]/ZIF-8	25	1000	11	30	70	71
	25	1	110			
[BMIM][PF ₆]/MIL-53(Al)	25	1000	8.6			172
[BMIM][PF ₆]-50/ rGA700	25	1	121			78
		1000	3.1			
[BMPyr][DCA]/rGA500	25	1	173.5			THIS WORK
		1000	4.1	12.6	11.2	THIS WORK
[BMPyr][PF ₆]/rGA300		1	450.9			THIS WORK
		1000	6.4	19.8	8.6	THIS WORK

*Data read from the given plot for the respective reference.

**Data calculated from the given isotherms for the respective reference.

APPENDIX B: C₂H₂ SEPARATION PERFORMANCE OF EXTERNALLY [HEMIM][DCA] COATED ZIF-67 COMPOSITE

B.1 Structural Characterization

To prove the existence of externally located IL molecules on the ZIF-67 surface, washing experiment was conducted with DMF and FTIR spectra are given in Figure B.1.1. The disappearance of bulk IL's [DCA]⁻ peaks (around 2300-2000 cm⁻¹) was observed with FTIR for the DMF washed IL/MOF composite. The morphology of the pristine ZIF-67 and composite was inspected with FESEM and obtained pictures are presented in Figure B.1.2. From this figure it can be seen that the characteristic dodecahedral shape of the pristine MOF was maintained in the composite,¹⁷³ but the sharp outline of the crystal structure was smoothened due to apparent ionic layer deposition on the exterior (Figure B.1.2(b)). Also, EDX mapping of the [HEMIM][DCA]-loaded ZIF-67 showed a uniform distribution of IL molecules based on the elemental mapping of oxygen which comes solely from the IL (Figure B.1.2(e)).

XRD was employed to check the crystal structure of the samples, and the diffractogram is given in Figure B.1.3. The characteristic peaks of the ZIF-67 were assigned according to literature reports,¹⁷⁴ and the noisy diffractogram of IL/MOF composite was attributed to the existence of IL layer on MOF surface. The thermal stability of bulk IL, ZIF-67, and IL/MOF was investigated with TGA/DTG analysis, and the thermogram is provided in Figure B.1.4. The composite illustrated a similar thermal decomposition mechanism with bulk IL until the T'_{onset} of the bulk IL, 175 °C, which might be due to the outer IL layer of the IL-loaded composite.

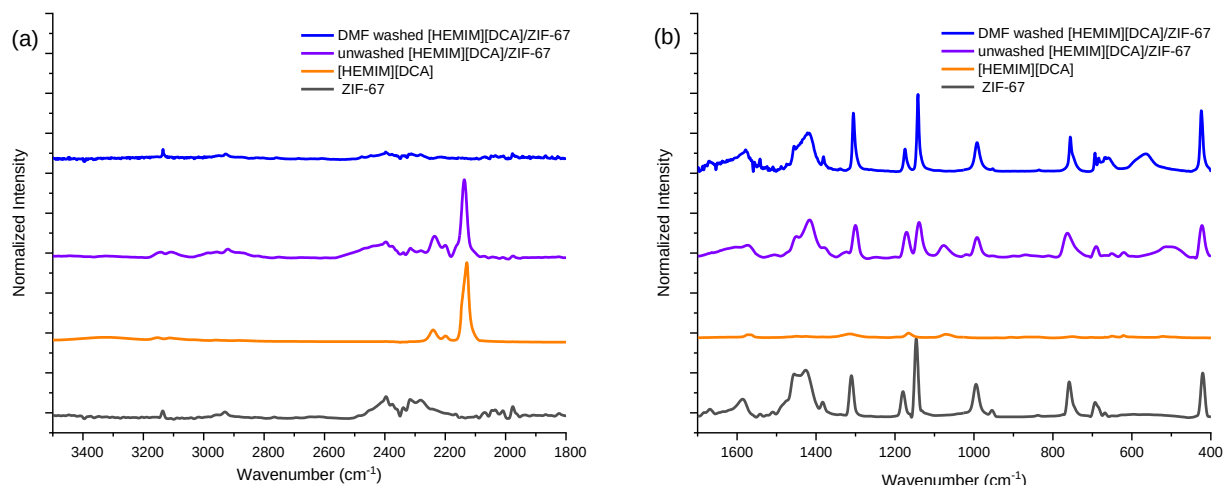


Figure B.1.1. FTIR spectra of ZIF-67, bulk [HEMIM][DCA], and DMF washed [HEMIM][DCA]/ZIF-67 between (a) 3500-1800 cm⁻¹.

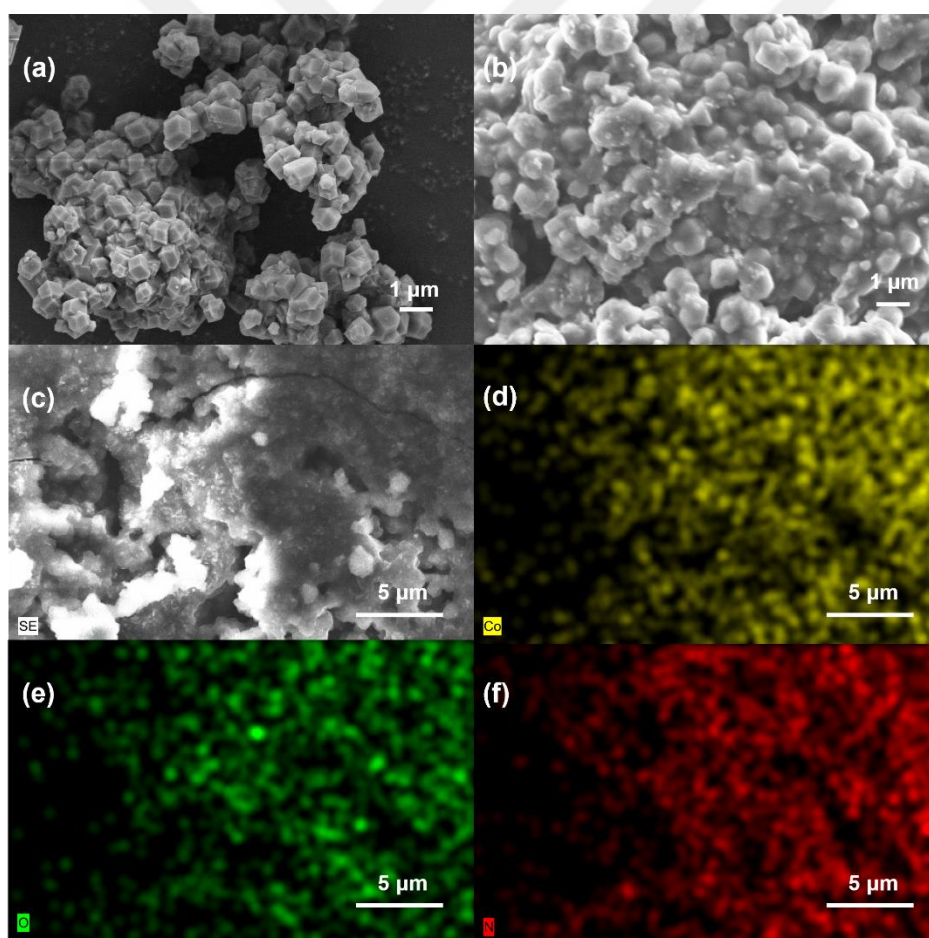


Figure B.1.2. SEM images of the (a) pristine ZIF-67 and (b) [HEMIM][DCA]/ZIF-67, and EDX elemental mapping results of [HEMIM][DCA]/ZIF-67 illustrating (c) the composite, (d) Co, (e) O, and (f) N distribution.

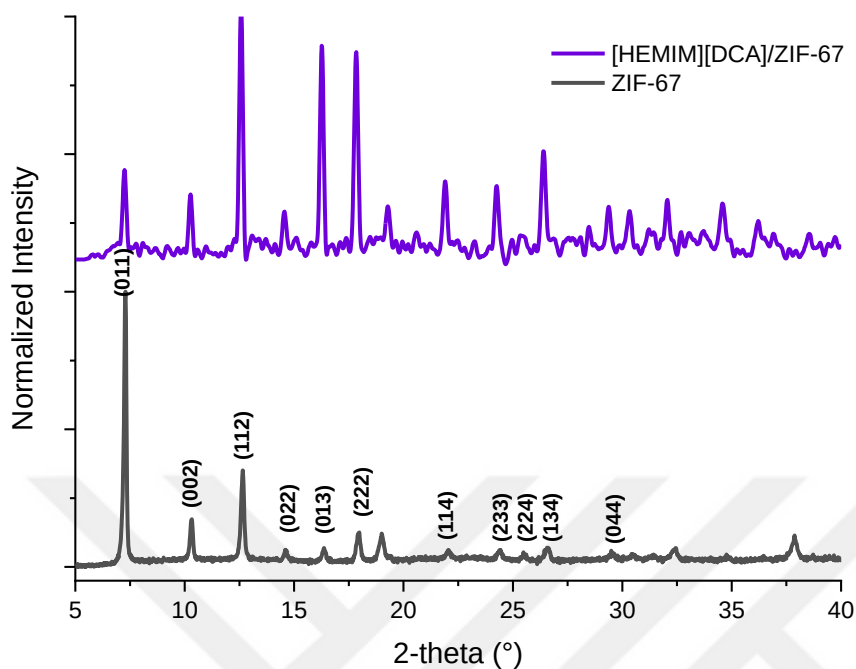


Figure B.1.3. XRD diffractogram of ZIF-67 and [HEMIM][DCA]/ZIF-67 between 5-40°.

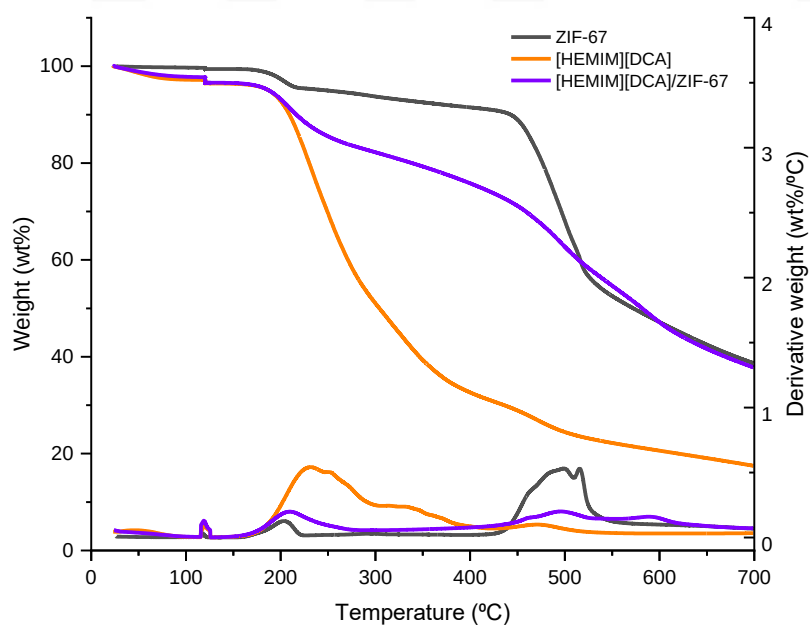


Figure B.1.4. TGA and DTG curves of ZIF-67 and [HEMIM][DCA]/ZIF-67.

B.2 Volumetric Gas Sorption and Ideal Gas Selectivity Results

Equilibrium-based volumetric gas sorption experiments were conducted for C₂H₂, CH₄, C₂H₄, and H₂ between 0-1000 mbar and at three different temperatures, 10 °C, 25 °C, and 40 °C. The experimental data points and fitted isotherms are illustrated in Figure B.2.1. The fitting parameters of the experimental sorption results are given in Table B.2.1. With IL addition to ZIF-67, significant decreases in gas uptakes were observed for all gases at three temperatures. For the low-pressure region, up to 45 mbar, the composite showed no CH₄ sorption at 10 °C and 25 °C. Additionally, IL/ZIF-67 composite displayed zero H₂ sorption up to 48, 78, and 150 mbar at 10 °C, 25 °C, and 40 °C, respectively. The ideal gas selectivities were calculated by dividing the gas uptakes corresponding to the same pressure points for the gases in the target separation mixture. The ideal C₂H₂/CH₄, C₂H₂/C₂H₄, and C₂H₂/H₂ selectivity values of ZIF-67 and IL/ZIF-67 composite are provided in Figure B.2.2. Due to recorded zero CH₄ uptakes for IL/ZIF-67 composite at 25 °C, and 40 °C up to 45 mbar, ideal C₂H₂/CH₄ selectivity values were assumed infinite up to 45 mbar. Similarly, infinite ideal C₂H₂/H₂ selectivity values were obtained up to 50, 80, and 200 mbar due to zero H₂ capacities recorded up to these pressure points for IL-loaded ZIF-67 composite.

The cycling experiments for the IL/ZIF-67 were done with the three times repeated sorption experiments for all sorbates, and results are given in Figure B.2.3. Based on the obtained uptakes, it can be commented that the composite displays good reproducibility of the sorption experiments. The calculated ideal gas selectivities for [HEMIM][DCA] /ZIF-67 were compared with literature values in section B.3, Table B.3.1.

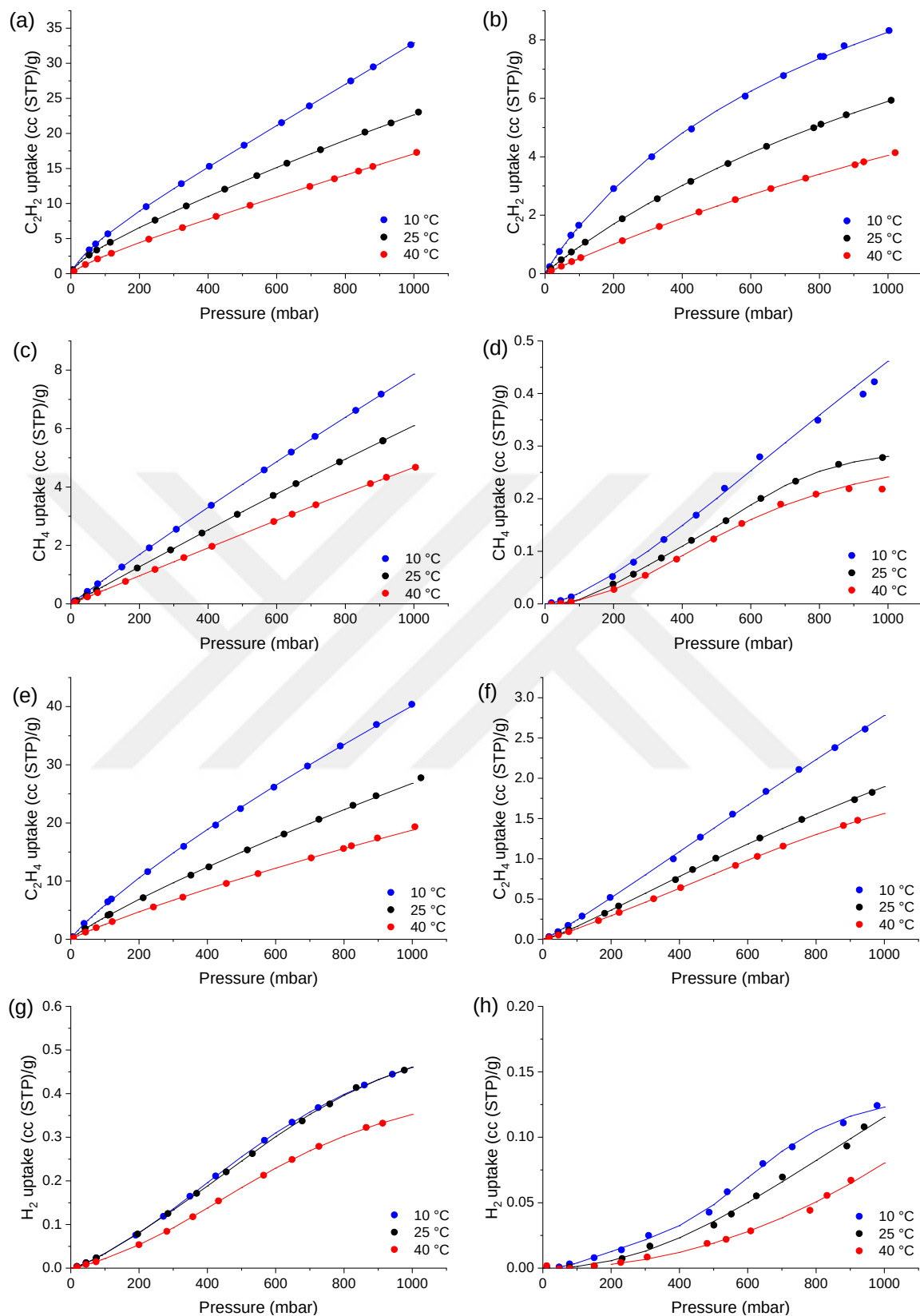


Figure B.2.1. Single component (a), (b) C₂H₂ sorption isotherms; (c), (d) CH₄ sorption isotherms; (e), (f) C₂H₄ sorption isotherms, and (g), (h) H₂ sorption isotherms for ZIF-67 and [HEMIM][DCA]/ZIF-67, respectively at 10 °C, 25 °C, and 40 °C between 0-1000 mbar.

Table B.2.1. Parameters of sorption isotherms of ZIF-67 and [HEMIM][DCA]/ZIF-67 fitted to Langmuir- Freundlich and Dual Site Langmuir-Freundlich models.

Sorbent	Gas	Temperature (°C)	Langmuir-Freundlich				Dual site Langmuir-Freundlich						
			q	k	n	R^2	q_1	k_1	n_1	q_2	k_2	n_2	R^2
ZIF-67	C ₂ H ₂	10	-	-	-	-	17.50	2.38×10^{-3}	0.78	293.05	1.50×10^{-4}	1.34	0.99
		25	-	-	-	-	7.30	6.04×10^{-3}	0.77	71.29	4.02×10^{-4}	1.29	0.99
		40	-	-	-	-	4.36	4.78×10^{-3}	0.84	160.30	1.29×10^{-4}	1.16	0.99
	CH ₄	10	-	-	-	-	128.36	6.33×10^{-5}	0.99	1.95×10^{-2}	6.81×10^{-26}	1.08×10^{-2}	0.99
		25	-	-	-	-	51.66	1.46×10^{-4}	1.05	5.06×10^{-2}	1.26×10^{-2}	0.71	0.99
		40	-	-	-	-	26.47	2.51×10^{-4}	1.19	0.49	4.37×10^{-3}	0.88	0.99
	C ₂ H ₄	10	718.25	3.68×10^{-5}	0.85	0.99	-	-	-	-	-	-	-
		25	-	-	-	-	3.01×10^{-4}	1.39×10^{-3}	8.47×10^{-5}	604.03	2.89×10^{-5}	0.87	0.99
		40	-	-	-	-	4.04×10^{-9}	1.32	8.22×10^{-7}	221.27	7.08×10^{-5}	0.90	0.99
	H ₂	10	-	-	-	-	0.53	1.51×10^{-3}	2.19	0.088	5.00×10^{-3}	1.31	0.99
		25	-	-	-	-	0.24	1.43×10^{-3}	3.25	0.39	1.83	1.39	0.99
		40	-	-	-	-	0.37	1.49×10^{-3}	2.53	9.70×10^{-2}	3.49×10^{-3}	1.34	0.99
	C ₂ H ₂	10	-	-	-	-	2.40×10^{-16}	1.95×10^{-5}	3.0×10^{-10}	17.33	9.07×10^{-4}	0.94	0.99
		25	-	-	-	-	2.99×10^{-3}	0.12	147.85	19.16	4.24×10^{-4}	0.94	0.99
		40	-	-	-	-	16.44	3.27×10^{-4}	1.00	6.87×10^{-16}	1.67×10^{-5}	5.32×10^{-4}	0.99
[HEMIM] [DCA]/ ZIF-67	CH ₄	10	1.70	5.12×10^{-4}	1.48	0.99	-	-	-	-	-	-	-
		25	-	-	-	-	0.12	1.53×10^{-3}	5.59	0.18	2.77×10^{-3}	2.36	0.99
		40	-	-	-	-	0.30	1.70×10^{-3}	2.41	6.36×10^{-3}	9.83×10^{-3}	4.56	0.99
	C ₂ H ₄	10	-	-	-	-	20.84	1.88×10^{-4}	1.12	5.83×10^{-25}	4.95×10^{-7}	9.82×10^{-10}	0.99
		25	-	-	-	-	7.59	2.87×10^{-4}	1.16	0.84	1.14×10^{-3}	1.38	0.99
		40	-	-	-	-	1.39	1.11×10^{-3}	2.48	1.12	1.92×10^{-3}	1.25	0.99
	H ₂	10	-	-	-	-	0.10	1.52×10^{-3}	4.86	3.38×10^{-2}	3.83×10^{-3}	2.11	0.99
		25	0.35	7.18×10^{-4}	2.11	0.99	-	-	-	-	-	-	-
		40	180.37	2.42×10^{-5}	2.07	-	-	-	-	-	-	-	-

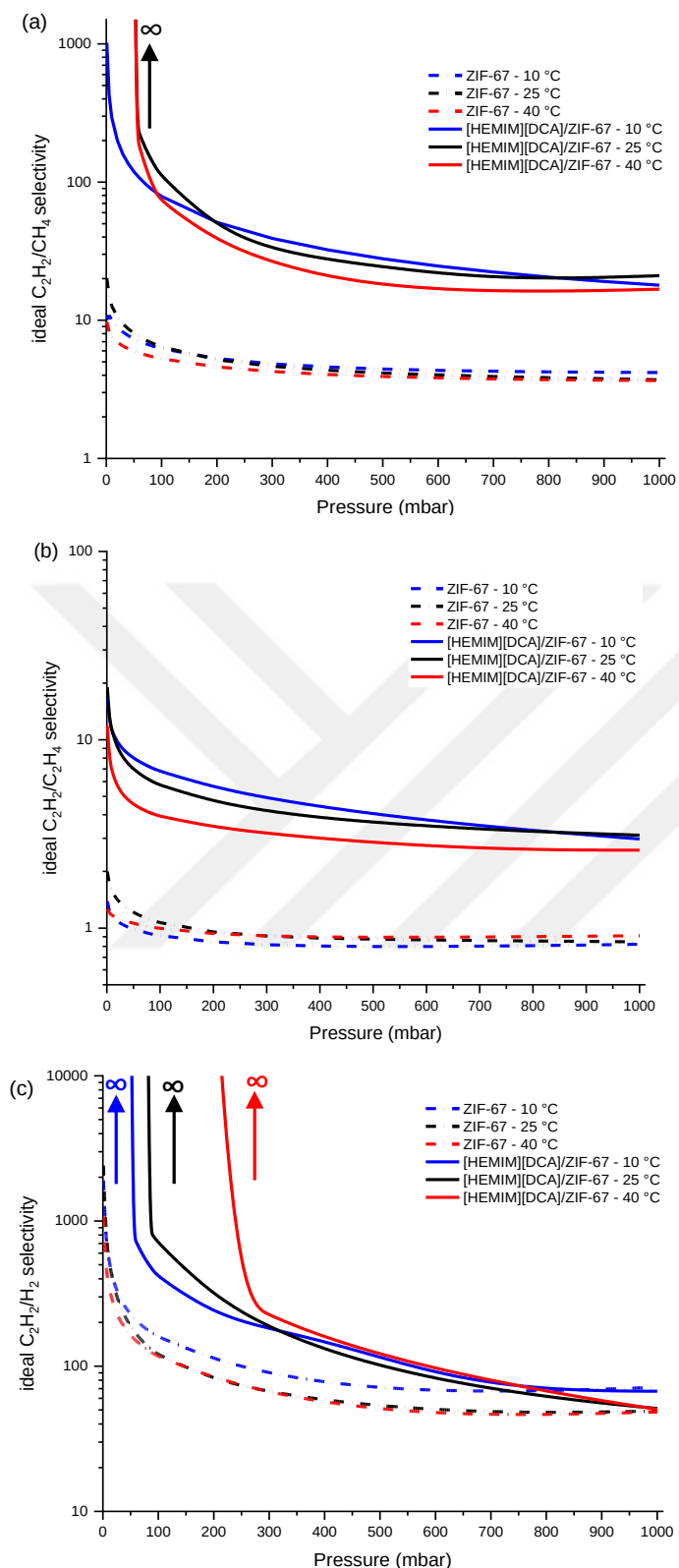


Figure B.2.2. Ideal (a) C₂H₂/CH₄, (b) C₂H₂/C₂H₄, and (c) C₂H₂/H₂ sorption selectivities calculated from Langmuir-Freundlich and Dual Site Langmuir-Freundlich isotherms for ZIF-67 and [HEMIM][DCA]/ZIF-67 at 10 °C, 25 °C, and 40 °C between 1-1000 mbar.

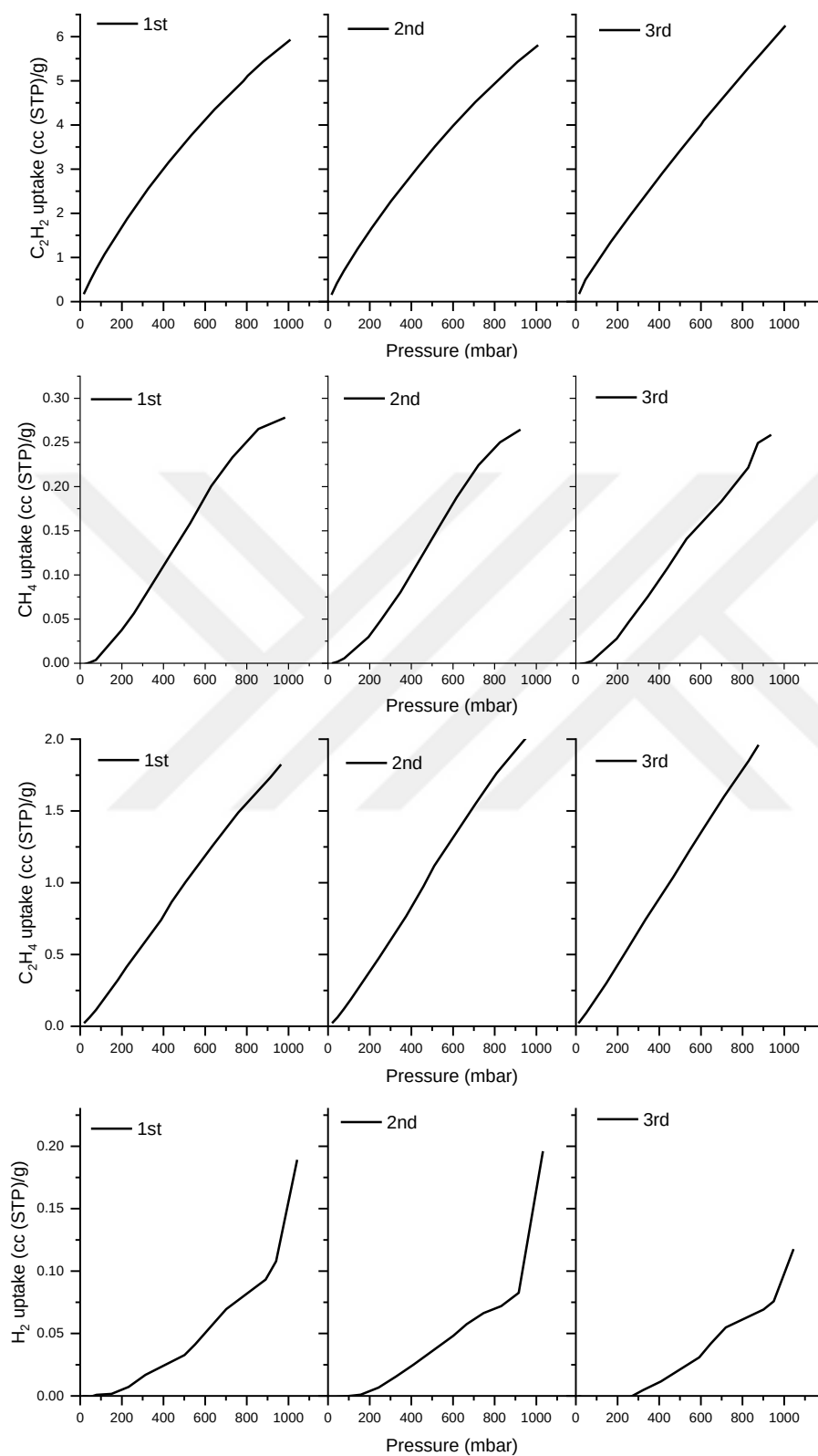


Figure B.2.3. Cyclic performance results of [HEMIM][DCA]/ZIF-67 for volumetric sorption of C₂H₂, CH₄, C₂H₄, and H₂ recorded at 25 °C.

B.3 Literature Overview

Table B.3.1. Comparison of ideal and IAST-calculated C₂H₂/CH₄ and C₂H₂/C₂H₄ selectivity and Q_{st} values with literature values.

Adsorbent	Temperature (°C)	Pressure (mbar)	Ideal C ₂ H ₂ /CH ₄ selectivity	Ideal C ₂ H ₂ /C ₂ H ₄ selectivity	IAST selectivity			REF
					C ₂ H ₂ /CH ₄ (50/50)	C ₂ H ₂ /C ₂ H ₄ (50/50)	C ₂ H ₂ /C ₂ H ₄ (1/99)	
CuDTTA	25	1000	3.6*	1.8*	166	-	8.3	175
UTSA-50	25	1000	5*					176
NUM-15	25	1000		3.2*			2.5	177
NbU-9-NH ₂	0	1000	3.7*	1.7*	70 (at 1 mbar)			178
Cu-OMS MOF	25	1000	2.6*		131 (at 1 mbar)			179
PCN-250	22	500		3.3*				180
BSF-3	25	1000		1.4*		13	8.1	181
BSF-3-Co	25	1000		1.5*		10.2	8.5	181
BSF-9	25	1000		2.2*		41.4	19.7	182
Ni-MOF	25	1000		1.6*, 6* (at 1 mbar)		130 (at 1 mbar)	168 (at 1 mbar)	183
Tb-N MOF	25	1000	6.7*		25*			184
MOF-1	25	1000	3.8*	1.6*				185
MOF-2	25	1000	21.7*	2.1*	332	3.9		185
Co-MOF	25	1000	5.6*		23.7			186
ZJU-74a	23	1000	3.4*	1.1*	1313		24.2	187
Ni-MOF (1a)	25	1000	6.7*	1.6*	15			188
In-MOF	25	1000	4.5*		137			189
NbFFIVE-1-Ni	25	1000		3*		30		190
ZU-32	25	1000		1.8*			70	191
ZU-33	25	1000		7.7*			1000	191
APPT Cd-MOF	25	1000		3.8			14	192
Cu-MOF	25	1000	5.2*		100			193
NbO-Cu-MOF	25	1000	9.5*	1.3*	32			194
UPC-80	25	1000		1.5*		4.78		195
Zn-MOF	25	1000	7.3*	1.3*	12			196
Fe/Ni bimetallic MOF-HS	25	1000	3.76*		198.9			197
JLU-66	25	1000	6.5*		90			198
JLU-67	25	1000	4.8*		20			198
Zr-MOF	25	1000		2*		4.4	3.7	199
SNNU-333-Ni	25	1000		1.9*		6.6		200
SNNU-333-Co	25	1000		2*		6.7		200
ZIF-67	25	1	20.1	2				THIS WORK
		100	6.4	1.1				
		1000	3.7	0.8				
[HEMIM][DCA]/ZIF-67	25	1	infinite	19				THIS WORK
		100	109.3	5.7				
		1000	21	3.1				

*Data read from the given plot for the respective reference.

APPENDIX C: FULL NAMES OF IONIC LIQUIDS MENTIONED

[EMIM][DCA]	1-ethyl-3-methyl-imidazolium-dicyanamide
[BMIM][DCA]	1-butyl-3-methyl-3-imidazolium dicyanamide
[BMIM][PF ₄]	1-butyl-3-methylimidazolium tetrafluorophosphate
[BMIM][TFSI]	1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
[BMIM][Ac]	1-butyl-3-methylimidazolium acetate
[BMPyr][DCA]	1-butyl-1-methylpyrrolidinium dicyanamide
[BMPyr][PF ₆]	1-butyl-1-methylpyrrolidinium hexafluorophosphate
[BzMIM][DCA]	1-benzyl-3-methylimidazolium dicyanamide
[EMIM][Ac]	1-ethyl-3-methylimidazolium acetate
[EMIM][Gly]	1-ethyl-3-methylimidazolium glycine
[HEMIM][DCA]	1-(2-hydroxyethyl)-3-methylimidazolium dicyanamide
[HMIM][BF ₄]	1-hexyl-3-methyl-imidazolium tetrafluoroborate
[MPPyr][DCA]	1-methyl-1-propyl pyrrolidinium dicyanamide
[THTD][DCA]	trihexyltetradecylphosphonium dicyanamide