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BOLU ABANT İZZET BAYSAL UNIVERSITY
INSTITUTE OF GRADUATE STUDIES
DEPARTMENT OF CHEMISTRY

RUTHENIUM (0) NANOPARTICLES SUPPORTED ON TITANIUM DIOXIDE:A HIGHLY ACTIVE AND LONG-LIVED CATALYST IN DEHYDROGENATION OF DIMETHYLAMINE BORANE

MASTER OF SCIENCE

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APPROVAL OF THE THESIS

RUTHENIUM (0) NANOPARTICLES SUPPORTED ON TITANIUM DIOXIDE : A HIGHLY ACTIVE AND LONG-LIVED CATALYST IN DEHYDROGENATION OF DIMETHYLAMINE BORANE submitted by **AHMED AL-AREEDHEE** and defended before **the Examining Committe Members listed below in partial fulfillment of the requirements** for the degree of Master of Science in **Department of Chemistry, Director of Institute of Graduate Studies of Bolu Abant Izzet Baysal University in 20.07.2022 by**

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AHMED HAMMOODI YOUSIF AL-AREEDHEE

ABSTRACT

RUTHENIUM (0) NANOPARTICLES SUPPORTED ON TITANIUM DIOXIDE:A HIGHLY ACTIVE AND LONG-LIVED CATALYST IN DEHYDROGENATION OF DIMETHYLAMINE BORANE

MSC THESIS
AHMED HAMMOODI YOUSIF AL-AREEDHEE
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In recent years, global warming becomes life-threatening due to the increase in carbon dioxide levels in the atmosphere. Global warming has several effects that greatly harm the globe, the environment, and the climate and living organisms. Therefore, scientists have resorted to search alternative energy resources such as clean energy. In this regard, hydrogen is an energy carrier could be used as an alternative of other fuels. However, the safety storage of hydrogen is still key point. B-N compounds have high hydrogen capacity can be store hydrogen and release it under proper ambient conditions. One of the boron compounds is dimethylamine borane could be release hydrogen by suitable catalyst and reaction conditions. The main of the catalysts used in these types of reactions is agglomeration problems of them during the reaction course. Metal oxides are used as stabilizers in the production of transition-metal nanoparticles, which gives them benefits in terms of shelf life, reusability, and thermal stability. The ex-situ production, characterization, and catalytic performance of TiO_2-supported ruthenium (0) nanoparticles in the dehydrogenation of DMAB at a temperature of 60.0 ± 0.5 °C are demonstrated in this thesis. Transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and optical emission spectrometry were used to analyze transition metal nanoparticles (0) supported by metal oxides. Experiments with various catalyst concentrations and temperatures were performed to evaluate the reaction kinetics.

KEYWORDS: Dehydrogenation, Dimethylamine borane, Heterogeneous catalyst, Ruthenium (0) nanoparticles, Titanium (IV) oxide.

ÖZET

RU(0)/TIO$_2$ NANOKUMLERI ESLIGINDE DIMETILAMIN BORANIN DEHIDROJENLENMESI

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Son yıllarda atmosferdeki karbondioksit seviyesinin artması nedeniyle küresel ısınma hayatı tehdit edici hale gelmektedir. Küresel ısınmanın dünyaya, çevreye, iklime ve canlı organizmalara büyük zarar veren çeşitli etkileri bulunmaktadır. Bu nedenle bilim adamları, temiz enerji gibi alternatif olabilecek enerji kaynakları aramaya başlamıştır. Bu bağlamda hidrojen, diğer yakıtlara alternatif olarak kullanılabilecek bir enerji taşıyıcısıdır. Bununla birlikte, hidrojenin güvenli bir şekilde depolanması hala önemli bir noktadır. Yüksek hidrojen kapasitesine sahip B-N bileşikleri, hidrojeni depolayabilir ve uygun ortam koşullarında serbest bırakabilir. Bor bileşiklerinden biri olan dimetilamin boran (DMAB), uygun katalizör ve tepkime koşullarında yapısındaki hidrojeni salabilir. Bu tip reaksiyonlarda kullanılan katalizörlerin temel sorunu, tepkimenin seyri sırasında aglomerasyon problemleridir. Metal oksitlerin geçiş metali nanoparçacıklarının sentezinde kararlılaştırıcı olarak kullanılması, katalizörler için uzun ömür, termal kararlılık ve tekrar kullanılabilirlik açısından avantaj sağlamaktadır. Tezde, Titanium (IV) oxide, TiO_2, destekli rutenyum (0) nanoparçacıklarının ex-situ hazırlaması, karakterizasyonu ve DMAB tan 60.0 ± 0.5 ^{o}C de hidrojen eldesindeki katalitik performansı araştırılmıştır. Metal oksit destekli geçiş metali (0) nanoparçacıklarının karakterizasyonu, iletim elektron mikroskobu (TEM), X-ışını fotoelektron spektroskopisi (XPS), X-ışını kırınımı (XRD) ve indüktif eşleşmiş plazma optik emisyon spektrometrisi (ICP-OES) ile gerçekleştirilmiştir. Reaksiyon kinetiği, farklı katalizör derişimlerinde ve farklı tepkime sıcaklıklarında deneyler yapılarak belirlenmiştir.

ANAHTAR KELİMELER: Dehidrojenlenme, Dimetilamin boran, Heterojen Katalizor, Rutenyum(0) Nanoparcaciklar, Titanyum(IV) Oksit

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NPs :	Nanoparticles
DMAB :	Dimethylamine borane
TOF :	Turnover frequency
TON :	Turnover number
$\Delta H\neq$:	Activation enthalpy
$\Delta S\neq$:	Activation entropy
nm :	Nanometer

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1. INTRODUCTION

1.1. Concerns About Hydrogen

Hydrogen is a viable replacement to oil if the technique to collect it from a source is developed, as it is expected that hydrogen will power anything in the future, and it is a colorless, odorless gas that is abundant across the world. Hydrogen has been utilized in spacecraft since the 1960s and has been recognized as a fuel for a long time. (1), The Apollo ship's issues stemmed from hydrogen escaping from the craft's fuel cells. To create power and propel automobiles, hydrogen is used in place of gasoline in automobile engines or mixed with oxygen in energy cells. (1) . Although these two types of technology are now available, the second type has received more interest than the first.

Given the importance of hydrogen in the process of modern and clean energy, because there are difficulties and obstacles that limit the use of hydrogen gas, and this difficulty is related to the process of storing hydrogen gas because it is a highly flammable gas that can explode when combined with oxygen at a certain temperature. Therefore, scientists resorted to inventing new compounds that carry the hydrogen atom (2). Hydrogen is collected from oil and gas, which is the most popular and least expensive way, but it contradicts one of the key purposes of hydrogen use, which is to reduce dependency on oil and gas (3).

At the present time, some compounds containing hydrogen gas have been adopted, which are safe and stable and at the same time easy to use in the process of extracting hydrogen gas from them. Among these compounds are ammonia borane and its derivatives (4). Compounds containing the element hydrogen represented in the ammonia borane compound and its derivatives such as DMAB are solid, stable and can be used at any time to produce one equivalent of hydrogen gas (5).

In the process of extracting hydrogen gas from compounds that contain it, catalysts must be used in this process, and some metals were used in previous studies, recently many transition metal catalysts which includes noble (6) and non-noble metal nanoparticles were appoint dehydrogenation from the hydrolysis of ammonia borane.in this study ruthenium will used and supported on nanotitania to give good results in the hydrogen extraction process from DMAB.

$$2MeNH.BH_3 \xrightarrow{\qquad\qquad} (Me_2N.BH_2) + 2H_2$$

The element ruthenium was fortified in the titanium dioxide combination that was used in multiple tests because it is a solid and stable element, and since earlier studies and research have established the stability of this element. It proved its approval of the user because it contains a wide surface area that allows the element ruthenium to bind with it and form a catalyst capable of extracting hydrogen gas from the dimethylamine-borane compound (7).

Also, four different ruthenium loadings (0.5, 0.8, 1.2, and 2.1) percent were employed, and the best loading was discovered to be (0.5 % $Ru@TiO_2$) because of its high TOF value of (1683 h-1). To minimize issues caused by the diffusion of porous materials, a large surface area of non-porous titanium dioxide (10-300m2/g) can be utilized as a basis. (8) Because of the high chemical stability, it's interesting to look into. (9)

1.2. Hydrogen Energy's Advantages and Disadvantages

In terms of environmentally friendly and sustainable, hydrogen energy plays a critical role in the effective utilization of renewable and non-toxic energy sources. In this sense, it can be stated that 9.5 kg of hydrogen and 25 kg of gasoline have roughly the same energy. For example, hydrogen based on mass (energy/mass). has a great deal of specific energy. In addition, hydrogen has been found in many industrial processes including natural gas evaporation, coal gasification, direct and indirect thermochemical decomposition, and water electrolysis, Petrochemical industry, food processing and chemical synthesis, and manufacturing metallurgy. Hydrogen needs to be stored for a relatively long time, and there are some difficulties in storing hydrogen in liquid form because liquefied hydrogen requires very low temperatures. Produces non-toxic exhaust gas emissions. In addition to a certain proportion of equivalent high flame temperature will produce a large amount of NOx in the exhaust gas, for safety reasons, hydrogen can be burned at a lower concentration when in contact with air (10).

1.3. Hydrogen's Economic Impact

The idea of long-term viability solves the challenges that require long-term persistence. Given that fossil fuels will not last forever, one of the most crucial elements in achieving sustainability is the use of energy. A sustainable development path is becoming a priority, aiming at the emergence of a "hydrogen economy", which is essentially a proposed system that uses hydrogen to generate energy. Hydrogen-based energy systems are considered to be suitable and has many advantages of high quality, wide application, high efficiency, safety, purity, and relatively long storage time.

However, there are several challenges. due to the extremely high temperature needed for hydrogen liquefaction when stored in liquid form. Another disadvantage of using Although hydrogen generates non-toxic pollutants, it may be used as an energy carrier. when burned, except for a few equivalents with high flame temperature that will produce a large amount of NOx in the exhaust gas, hydrogen can be burned and exposed to a higher concentration. Low. Use air for safety reasons (11), (10).

The important of hydrogen can be summarized simply, Hydrogen is one among the best and most overabundant components on earth. (1) Can be stored and used to transmit useful energy. (2) It is a chemical element that carries energy, not its source. (3) Can store a lot of energy. (4) It may be employed in fuel cells to come up with electricity or generate electricity and warmth. Fuel cells only produce water, electricity and heat. But hydrogen not only exists in nature, but also must be produced from the compounds that contain it.

In fact, atomic number 1 is gift in several organic compounds, particularly hydrocarbons corresponding to gasoline, natural gas, fuel and propane.

At present, most of the hydrogen is made from natural gas, the hydrogen market will be strengthened and its foundation will grow. In the long run, this opens up more opportunities for renewable energy systems. For example, many renewable energy technologies, resembling temporary alternative energy or electrical phenomenon systems, can improve electrolysis to supply element for fuel cells. H_2 is used in fuel-cells to generate energy through chemical energy conversion to make up for the high energy demand and support the energy transition (10).

As a result, when hydrogen needs to replace fossil fuels, it can solve both energy and environmental problems; however, because molecular hydrogen is not readily available on Earth, it must be synthesized from H_2-rich compounds using energy, which is why hydrogen energy is regarded as an carrying energy rather than an alternative fuel (12), (13).

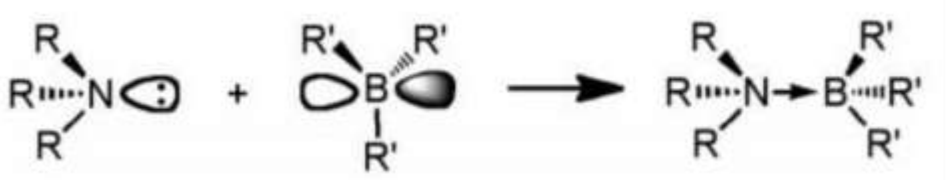

Figure 1.1 Bonding in amine-boranes

One of the key issues with the hydrogen economy is this. Due to the high hydrogen content, the chemical storage of hydrogen is very important. It is now possible to produce hydrogen from renewable energy in a variety of environmentally friendly ways, but in many cases, it is not efficient: for example, solar, wind, hydropower, Electrolysis, photolysis, water separation, gasification and fermentation of biomass can be used to produce hydrogen (14), (15), (16).

1.4. Amine Boranes and Its Compounds as a Source of Hydrogen Materials

The Covalent bonds between nitrogen and boron are coordinated in amine borane molecules and have received more and more often noticed lately. Due to their high hydrogen capacity, they can be used as hydrogen storage materials. It is considered to provide a lone pair of electrons for the B particle that does not have enough electrons and picks up a double electron in the free p orbital. At present, people's interest in hydrogen storage for the dehydrogenation of ammonia borane and adducts is becoming more and more important. DMAB is one of the most significant BN compounds with a low molecular weight (58.9 g/mol) and a high H_2 capacity (16.9%). Because this boron-based compound shows promise, it is very interesting for hydrogen storage (17), (18), (19).

It is particularly important that DMAB dehydrogenation and a suitable catalyst can release hydrogen under mild conditions.

For the dehydrogenation of dimethylamine borane, a range of transition metal catalysts, such as ruthenium, as well as another metal, have been utilized thus far. As a homogeneous system for DMAB dehydrogenation, the titanium precursor complex [(5C5H31,3 (SiMe3) 2) 2Ti] 2 (2, 1, 1, N2) was investigated. (20).

Recent publications indicate that the use of titanium dioxide nano powders as a carrier is effective for Ru.

Hydrolysis of ammonia borane produces hydrogen nanoparticles. In this work we try to dehydrogenation of DMAB by using Ru nanoparticle supported on TiO_2.

1.5. Typical Nanocluster Chemistry Methods

Characterizing nanoclusters is mostly used to assess particle size and content. In addition, it is more important to check the surface composition. The figure below provides an overview of the most common methods for characterizing nanoclusters (21).

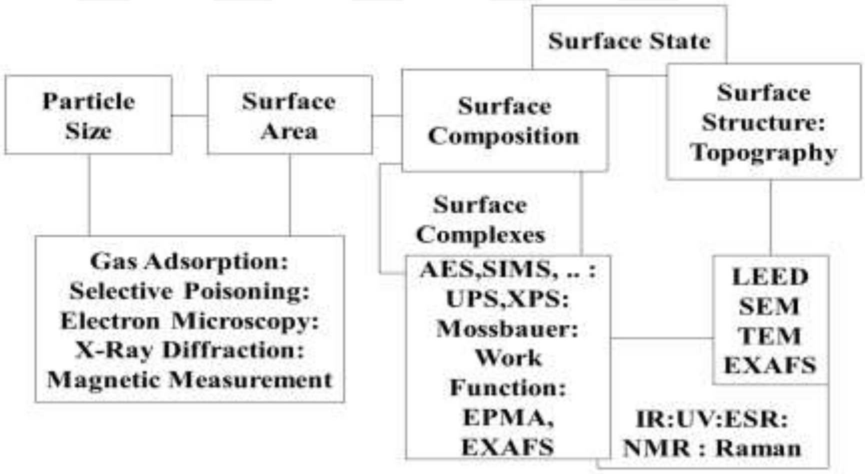

Figure 1.2 Techniques for analyzing nanoclusters that are often used (8).

Transmission electron microscopy (TEM). Since nanoclusters generally do not crystallize, When the determination of the state of the combined colloid is obvious, it can be seen that this is a state that cannot be crystallized (8). More molecule collisions supply the energy necessary to reach the transition state, allowing the catalyst to stimulate processes that might otherwise be stopped or retarded by kinetic impediments. If catalyst activity can be expressed by speed (TOF), then catalytic efficiency can be determined by speed (or TON).

1.6. Catalysis

Catalysis Principles in General

A catalyst is a chemical compound that may speed up a process without changing the standard Gibbs free energy or causing it to reach a pure state. The catalytic process will not diverge if each catalyst molecule runs in numerous repeating cycles.

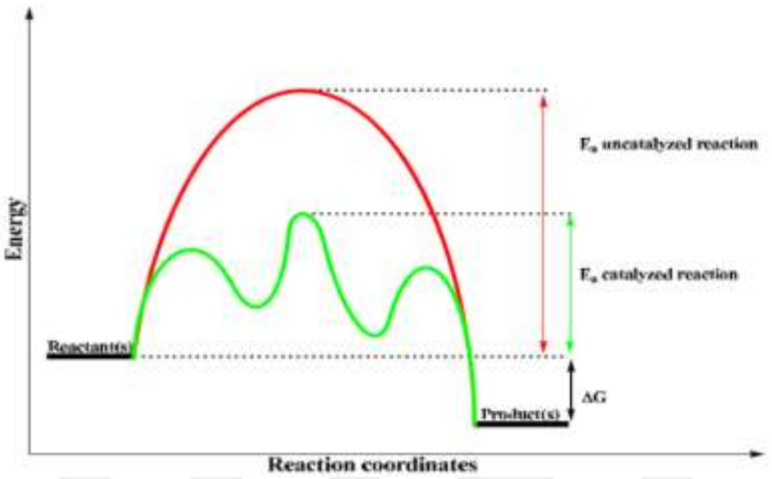

Figure 1.3. The difference in activation energy and the reaction curve between catalyzed and non-catalytic processes are depicted in this potential energy diagram.

The catalyst alters the reaction's chemical route and lowers the activation energy, resulting in several transition states during the reaction. The activation energy of the reaction is defined as the least energy required for the reaction to occur. As the energy barrier reduces, the collision with the energy necessary to enter the transition state happens.

The catalyst ensures that the reactants interact molecularly and lowers the activation energy. In other words, the catalyst lowers the transition state's energy, which does not affect the equilibrium state (8).

Since the catalyst isn't consumed stoichiometrically, every catalyst molecule may be recycled multiple times; therefore, solely a tiny low quantity of catalyst is required relative to the substrate (22).

There are many varieties of catalysts, as well as protons and plenty of differing kinds of compounds, Examples include organometallic complexes, Lewis’s acids, enzymes, and organic or inorganic polymers., and so forth merely put, we are able to say that there are primarily 3 kinds of contact action; (i) heterogeneous catalysis, (ii) homogenous catalysis and (iii) biocatalysts. The concept of the use of catalysts to growth the response price is primarily based totally at the transition nation theory, and is the reason the response price of fundamental chemical reactions. Catalysis affords an opportunity mechanism, such as decrease activation strength and one-of-a-kind transition states. Since the transition nation stays at the floor of the catalyst, ensuing with inside the lack of translational freedom, the activation entropy of catalytic reactions is commonly decrease than that of non-catalytic chemical reactions.

The activation heat content ought to be reduced accordingly. To compensate for this decrease, the activation energy of the chemical process reaction should be lower than the activation energy of the analogous non-catalytic reaction, according to theory.

Finally, extra molecule collisions supply the energy required to succeed in the transition state, allowing the catalyst to drive processes that would otherwise be stopped or slowed by kinetic impediments. If catalyst activity can be expressed by speed (TOF), then catalytic efficiency can be determined by speed (or TON).

$$\mathbf{TON} = \mathit{mole\ of\ product} \,/\, \mathit{mole\ of\ catalyst}$$

$$\mathbf{TOF} = \mathit{mole\ of\ product} \,/\, \mathit{mole\ of\ catalyst\ x\ time}$$

1.7. Catalytic Activity in Heterogeneous Catalysis Via Way of Means of Decreasing the Particle Size

The nearby length of the catalyst debris impacts their performance (i.e... the expanded hobby of the heterogeneous catalyst because of the lower in particle length is an instance of those adjustments because of the hobby and floor place of the heterogeneous catalyst (23). In particular, metal nanoclusters offer a replacement perspective on surface chemistry because they need uncommon surface morphology and additional reactive surfaces, and since of their giant surface area, they have Brobdingnagian chemical change potential. Several atoms present on surfaces are thought to yield sensible atom savings in reactions on surface liquids, gases, or perhaps solid surfaces. (24).

1.8. Nano-Catalysis

With the advancement of nanoscience since the late 1990s, nano-catalysts has clearly bridged the gap between heterogeneous and homogeneous catalysis. A substance possessing catalytic characteristics in at least one dimension at the nanoscale is defined as nano-catalysis. Because of their tiny size, they have a high surface-to-volume ratio, allowing them to operate as attractive catalysts. The field of using nanomaterials as catalysts in various reactions is growing rapidly (25) (22). The main goal is to improve a well-defined catalyst consisting of metal nanoparticles and nanomaterials as support materials. Nano-catalysts combine the best features of heterogeneous and homogeneous catalysts, allowing for facile reuse and recycling, as well as excellent efficiency, selectivity, and stability. Despite the usage of the word nano until recently, researchers have always concentrated on very tiny particles of the active catalytic agent in order to achieve the maximum level of reaction efficiency. Due to the unusual features and uses of the in many domains like as electronics, optics, and magnetism, it has attracted a lot of attention. chemistry and energy (26), (27), (28), (29), (30), (31).

The fact that nanoparticles have more perfect catalytic capabilities than bulk metals add to the fascination. Due to their small size, nanoparticles will have a higher atomic-to-surface ratio, leading to increased catalytic activity. In 1980, Haruta reported the catalytic conversion of oxygen to carbon monoxide at low temperatures (32).

1.9. Transition Metal Nanoparticles As Catalysts

Nanoclusters are defined as nearly monodisperse particles with a diameter of less than 10 nm (100 Å) (33). Over time, they have received a lot of attention. The main reason is that the characteristics of these particles are between the characteristics of bulk particles and, most importantly, the characteristics of individual particles (34), (35). This supports the belief in the unique properties of nanoclusters in the future. The use of nanoclusters includes the use of photochemical patterns, such as flat panel displays (36), quantum dots for cell separation and LEDs, or industrial lithography "ferrofluid" chemical sensors for computers and quantum devices, can all serve as examples of potential uses. In addition, these "strange substances" (37), (36), (38), (39), (40), (41), (42), (43). they have great potential to increase new types of activity and selectivity. To illustrate this point, the important work of Schmid laboratories provides a glimpse into unexpected catalytic selectivity, such as the expected properties of nanoclusters (44).

Chemists believe that the potential of nanoclusters as catalysts is greater than it is now. The key causes are as follows: For starters, a major portion of the atoms in metal nanoclusters are on the surface, and the atoms on the surface are not the same as the atoms in the body. Additionally, space constrains electrons in nanoclusters, restricting their journey to just a few atoms across energy levels, resulting in quantum size effects (45). Finally, nanoclusters may manage the size of surface ligands and nanoclusters in a changeable, quantifiable, and variable way for heterogeneous supported catalysts (46).

The use of nanoparticles was limited to the production of high-quality glass, ceramics and bricks until the 18th century. In the 1850s, Michael Faraday began to discover the stability of nanoparticles. In the late 19th century, Mee investigated the color properties of nanoparticles. Following the findings of this study, Richard Sigmondi received the Nobel Prize in Chemistry for his work entitled "Colloidal Suspension of Gold Nanoparticles Using Supermicroscopic Techniques" in 1925. Metal nanoparticles that do not include copper are regarded suitable catalyst options since they have a large surface area per unit volume or weight when compared to bulk metals. They usually operate on metal surfaces. Metal nanoparticles that may be employed as catalysts are gaining popularity due to their catalytic and electrochemical capabilities in a number of applications. Plastics, pockets, surfactant, and water-soluble polymers are just a few examples. The size of metal nanoparticles is the main force behind their catalytic activity since MNPs are essentially determined by their size. The square of the nanoparticle diameter is inversely proportional to it.

1.10. Stabilization of Metal Nanoparticles

The catalytic activity of metal nanoparticles is set by an interaction between their size and activity, which leads to catalytic stability. Despite the fact that metal nanoparticles are catalytically active, they prefer to agglomerate at higher temperatures and under more demanding reaction circumstances. During the catalytic process, the catalyst loses a large amount of catalytic activity as a result of this. In order to avoid agglomeration of metal nanoparticles, long-term stability of the nanoparticles can be achieved. The choice of stabilizer is very important in the synthesis of transition metal nanoparticles. The chemical structure of the stabilizer used determines the shape and size of metal nanoparticles. Many articles on the types of stability of nanoparticles can be found in the top-down and bottom-up charts. Method Most studies are discussed in the literature (47). According to the type of protective equipment used, five different types of stabilization can be distinguished.

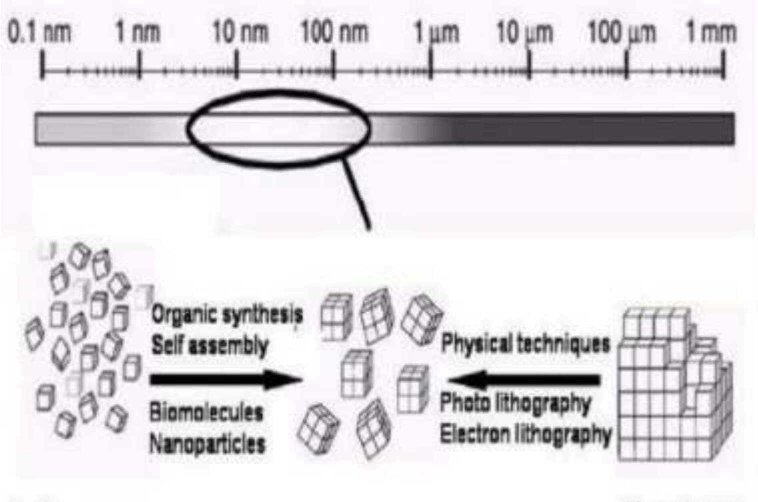

Figure 1.4. Schematic presentation of bottom up and top-down approach

1.11. Methods of Synthesizing of Metal Nanoparticles

The synthesis of nanoparticles of transition metals is aimed at obtaining simultaneously a clean surface, finer particles and a well-defined composition in different areas of application. Two methods can be used to obtain metallic woofers. The first method is the top-down method, which is the first. Mechanical crushing was used to break up the bulk material into tiny fragments (48).

In the second approach, the down-top method was used to collect fractions, consisting of chemical and physical treatments. Transition and ligand are two words that come to mind when thinking of a ligation Metalloid movement, metal vapor synthesis, and metal salt recovery.

2. AIM AND SCOPE OF THE STUDY

This dissertation's purpose is to build and represent Ru (0) NPs based on titania nanocrystals for DMAB dehydrogenation. While ruthenium (0) NPs set on titania nanocrystals, dubbed Ru (0)/nanoTiO_2, were created by subtracting ruthenium (III) chloride trihydrate, which was employed as a precursor in the dehydrogenation of DMAB at 60.0 ± 0.5 C. After the catalytic dehydrogenation response of DMAB was tested by XRD, XPS, SEM, EDX, and TEM, Ru (0)/TiO_2 has an amazing catalytic interest with a turnover frequency of 1683 h-1 in liberating 1 equal of natural H2 fuel line in accordance with mole of $(CH_3)_2NHBH_3$ at 60.0 ± 0.5 °C. The outcomes of the reusability assessments and catalytic lifestyles time experiments suggest that Ru (0)/TiO_2 is a good catalyst in dehydrogenation of DMAB. That is the highest TOF rate for dehydrogenation of DMAB using a homogeneous or heterogeneous catalyst ever measured. Ru (0)/nanoTiO_2 is likewise pretty reusable catalyst maintaining 57% of the preliminary catalytic interest even after the third run of dehydrogenation response liberating 1 equal of natural H_2 fuel line in keeping with mole of $(CH_3)_2NHBH_3$ at 60.0 ± 0.5 °C. Kinetic analysis of the catalytic dehydrogenation of $(CH_3)_2NHBH_3$ in relation to temperature and catalyst concentration turned into additionally blanketed on this dissertation.

3. EXPERIMENTAL

3.1 . Materials and Characterization

Ruthenium tri-chloride trihydrate ($RuCl_3$ $3H_2O$), titanium di-oxide (anatase.) and dimethylammonium borane. The deionized water was distilled through a water purification system and all glassware and magnetically Teflon-coated. The stirring bars were cleaned with distilled water, after that washing it with ethanol and drying in an oven at 150 ° C. for 24 h.

3.2. Synthesis of Ruthenium (III) Ions loaded on TiO2 (Ru0 /TiO2).

$RuCl_3 \cdot 3H_2O$ (13 mg) in 50 ml of H_2O in a 100 ml beaker, and add TiO_2 (1000 mg) to the solution, and the mixture was stirred at room temperature for 24 hours. Add $NaBH_4$ (15 mg) in 10 ml H_2O and drop it into the solution and the cause of adding the $NaBH_4$ solution to ensure that all Ru ions are reduced from (+3 to 0), and then centrifuge the Ru_3/TiO_2 sample, wash it with 100ml distilled water and dry it in a vacuum system at room temperature for 48 hours.

3.3. Formation of Ruthenium (0) Nanoparticles (Ru (0) / TiO_2) on The TiO_2 Support, Accompanied by The Catalytic Dehydrogenation of DMAB.

Ruthenium (0) nanoparticles on TiO_2(Ru(0)/TiO_2), put a jacketed reaction flask (20ml) with a PTFE-coated stirrer on a magnetic stirrer and keep the temperature to 60.0±0.1° C, the water comes from the constant temperature bath through the jacket circulation. After that, a graded glass tube (60 cm tall, 3.0 cm in diameter) is filled with water. To measure the volume of hydrogen produced by the reaction, water was connected to the reaction flask. Then 7 milliliters of toluene and 100 milligrams of Ru(0)/TiO_2 powder (0.5 wt% Ru) were added to the reactor, and DMAB dissolved in 3 milliliters of toluene was added to the solution in the reactor. The reaction medium is stirred at a speed of 1000 rpm. After adding DMAB, ruthenium (0) nanoparticles are formed, and the catalytic dehydrogenation of DMAB starts immediately. The amount of hydrogen released is calculated by monitoring the change in water level every 30 seconds under a constant air pressure of 693 kPa. Support. The reaction is terminated when no more hydrogen is evolved. Observable.

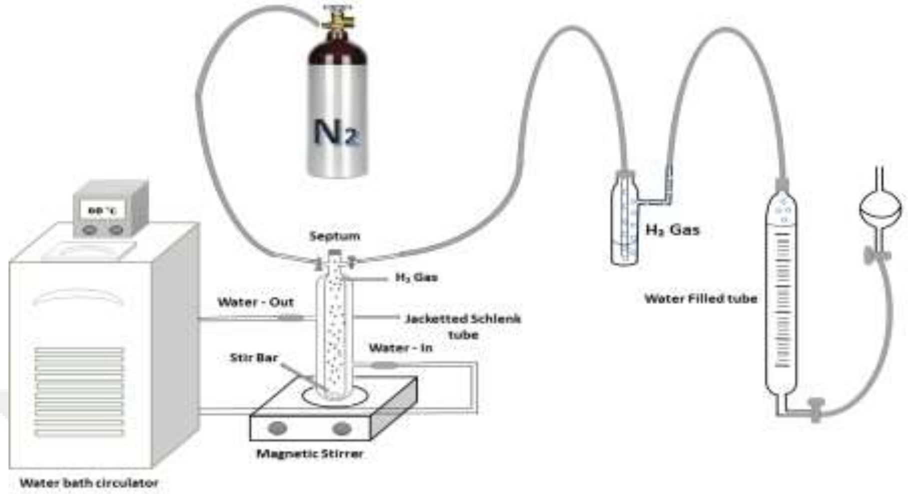

Figure 3.1. The reaction setup for dehydrogenating DMAB

3.4. In The Hydrogen Production of $(CH_3)_2NHBH_3$, a Leaching Test and Kinetic Competence of Ru(0)/TiO_2

The catalyst was expected to settle after the catalytic dehydrogenation of DMAB for the first time from 10 mL of 100 mM DMAB (60.12 mg (CH_3) 2NH.BH_3) and 0.0005 mM Ru (III) impregnated on 100 mg TiO_2 at 60.0 ± 0.5 °C, so the reaction solution was filtered into another reaction flask under an inert gas atmosphere. By adding an amount of DMAB to the separated solid and filtered solution, its catalytic activity was evaluated under the identical reaction conditions (100 mM). In addition, the filtrate was tested with the use of ICPOES to demonstrate that the free Ruthenium is leached into solution from the surface of the nano TiO_2 during the dehydrogenation of DMAB.

3.5. The Recyclability of TiO_2 Supported Ruthenium (0) Nanoparticles.

Without removing anything from the reaction medium, a second batch of DMAB (60.12 mg) was added to the solution for two times (after finishing the second run, add the third batch). The rate of hydrogen production was used to evaluate catalytic activity.

3.6. Ru (0)/TiO_2 Catalytic Lifetime in The Dehydrogenation of $(CH_3)_2NHBH_3$

The total number of rotations was used to evaluate the catalytic lifetime of Ru (0) / TiO_2 in the dehydrogenation of DMAB (TTO). 0.0005 mM Ru (0) / TiO_2 and 150 mg DMAB in a 10 mL toluene solution were employed in a lifetime experiment. More DMAB was added to the reaction flask once 100% conversion was accomplished by purging with N_2.

3.7. Characterization of Titania Supported Ru (0) NPs

The Ru (0) generated in situ was characterized after the catalytic reaction of dimethylamine borane with X-ray photoelectron spectra (XPS), X-ray diffraction (XRD) and transmission electron microscopy (TEM).

3.8. Analysis of TEM

A 0.2 ml aliquot of the reaction medium was removed for TEM analysis after the dehydration reaction and transferred to a glass vial diluted with 2 ml of methanol. To deposit the nanoparticles, a carbon-coated copper grid was submerged in the colloidal solution for 5 seconds. The copper grid's volatiles were then evaporated in an inert environment. The samples were analyzed using a TEM JEM2010F instrument (JEOL) operated at 200 kV.

3.9. Analysis of (ICP-OES) Spectroscopy

The ruthenium concentration of the filtrate was analyzed by ICP-OES and found no leaching of ruthenium in the solution. The filtered solution has no catalytic activity in the dehydrogenation of DMAB. This observation supports the conclusion that ruthenium does not leak from solution during dehydrogenation and suggests that ruthenium (0) nanoparticles supported on TiO_2 are heterogeneous and kinetically competent catalysts in the dehydrogenation of DMAB.

3.10. Analysis of (XRD)

The X-ray diffraction pattern of the materials was determined using a Rigaku MiniFlex X-ray powder diffractometer (XRD) equipped with a Cu-K line radiation source (= 154056) and a scanning speed of 5 degrees per minute in a range of 3 degrees from 10 to 90 degrees. The TiO_2 crystals, on the other hand, do not alter either before or after the addition of Ru +3 nanoparticles.

3.11. Analysis of (XPS):

X-ray photoelectron spectra of Ru (0) NPs carried by Titania were recorded with the Physical 15 Electronics 5800 spectrometer. Tube operating at 15 kV, 350 W.

4. RESULTS & DISCUSSIONS

4.1. Ex-situ ruthenium (0) Nanoparticle Synthesis Supported By TiO_2 (Ru (0) @TiO_2) And Concurrent Catalytic Dehydrogenation of DMAB

The reduction of Ru^{+3}/TiO_2 by sodium borohydride in distilled water before the catalytic dehydrogenation of DMAB, resulted in the Ruthenium (0) nanoparticles coating on nano TiO_2 ($Ru(0)/TiO_2$) production A jacketed flask (20 mL) with a teflon lined stir bar turned into located on a magnetic stirrer (Heidolph MR301) and thermostated at 60 ± 0.5 °C with the aid of using offering water thru its jacket from a consistent temperature tubtub earlier than beginning catalyst synthesis and catalytic dehydrogenation. The amount of hydrogen gas produced by the reaction was then measured using a graduated glass tube filled with water (60 cm high with a diameter of 3 cm) connected to the reaction flask. Then there's a 100 mg granule of Ru^0/TiO_2 (0.5 wt.% Ru) In a reaction flask with a thermostat set at 60 ± 0.5 °C, was distributed in 10 mL toluene. The flask was then filled with 60 mg DMAB (1.0 mmol H3N.BH3) and the reaction liquid was stirred at 1000 revolutions per minute.

Ru^0/TiO_2 NPs with different Ru loadings (0.5, 0.8, 1.2 and 2.1) were obtained from ex-situ reduction of Ru^{3+} ions using $NaBH_4$ as a shorthand agent in water. Ru contest in the sample was identified by ICP-OES analysis (Supporting Material). So, The ICP analysis and leaching test findings show that Ru (0) is retained on the surface of nanoTiO_2 during the catalytic process (table 1). As a result, we may infer that nanotitania supported ruthenium (0) nanoparticles are a capable dehydrogenation catalyst.

Concentration of catalyst	ICP-OES result
0.5	0.48 ± 0.02
0.8	0.73 ± 0.03
1.2	1.20 ± 0.02
2.1	1.94 ± 0.02

Table 4.1. ICP-OES analysis

The crystallinity of $Ru0/TiO_2$ NPs was scanned by X ray diffraction. (Figure 4.1) shows the p-XRD pattern of bare TiO_2, Ru^0/TiO_2 NPs before and after catalytic reaction of DMAB. The comparison of XRD pattern of three samples indicates that there are no significant changes in crystallinity of titania after reduction of ruthenium by sodium borohydride on the surface of titania and after catalytic dehydrogenation. The diffractogram of all samples indicates Bragg's reflection at about 25.2°, 36.9°, 37.8°, 38.5°,48.4°, 53.8°, 55.0°, 62.1°, 62.6°, 68.7°, 70.3°, 75.0°, 76.0° and 83.1° assigned to the (101), (103), (004), (112), (200), (105), (211), (213), (204), (116), (220), (215), (301) and (312) reflections of anatase TiO_2, respectively (PDF Card 21-1272). It can be concluded that ruthenium loading does not affect the crystallinity of the supporting material (8), (49).

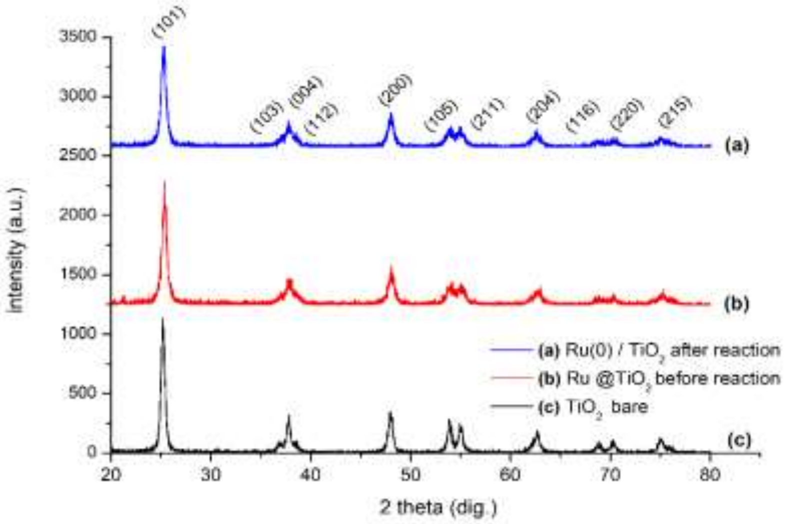

Figure 4.1. p- XRD patterns of (a) Ru (0)/TiO_2 after reaction (b) Ru (0)/TiO_2 before reaction (c) bare TiO_2

4.2. XPS Was Used to Determine The Oxidation State of Ruthenium in The Catalyst Sample.

The survey scan and high-resolution spectrum of the catalyst sample could be seen in (Figure 4.2). The survey scan of the catalyst sample shows the ruthenium metal with the framework of TiO_2 (Ti, O) (50). High resolution of ruthenium 3d XPS spectrum exhibits two peaks 279.3 and 283.4 eV (51) which are assigned to $3d_{5/2}$ and $3d_{3/2}$, respectively. Carbon 1s peak at 283.1 eV overlaps with Ru^0 $3d_{3/2}$ peak that makes difficult to observe Ru 3d. However, the peak at 462.4 (52) eV confirms the existence of Ru $3p_{3/2}$ with Ru $3p_{3/2}$ satellite at 471.5 eV.

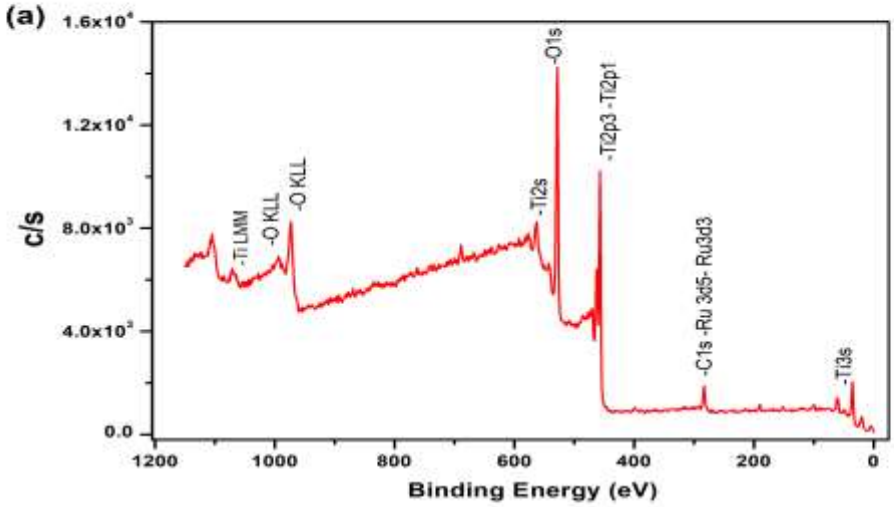

Figure 4.2. XPS spectrum of Ru0/TiO_2 NPs : Survey scans

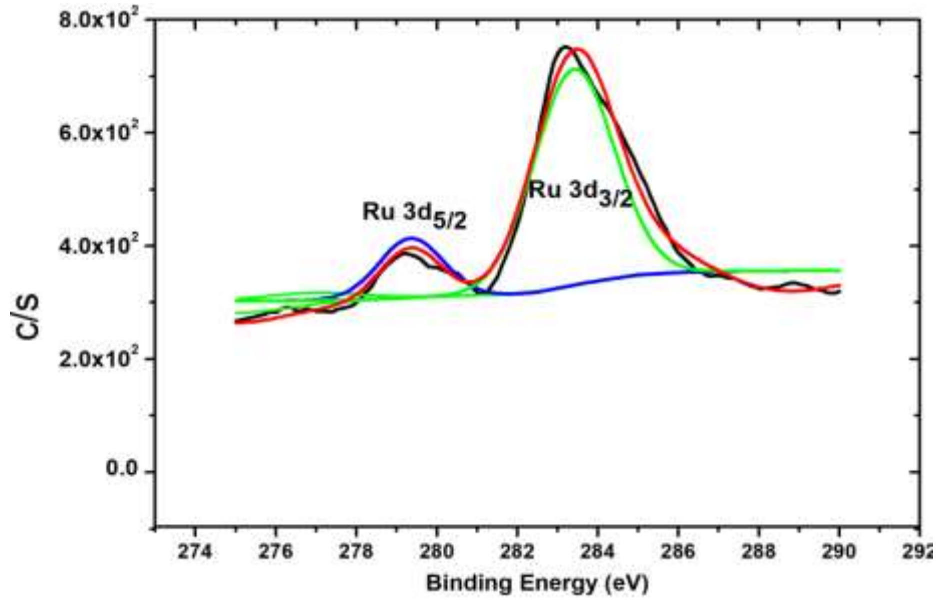

Figure 4.3. XPS spectrum of Ru0/TiO_2 NPs : High resolution

4.3. TEM Analysis

The surface morphology of the catalyst and particle size of Ru^0 NPs was determined from TEM analysis. (Figure 4.4) shows the TEM images of Ru^0/TiO_2 NPs in different magnifications. The TEM images of the sample depict that Ru^0 NPs are well dispersed on the surface of titania. The histogram (Figure 4.4) The presence of ruthenium (0) NPs with an average particle size of 6.71± 1.29 nm on the surface of titania is demonstrated.

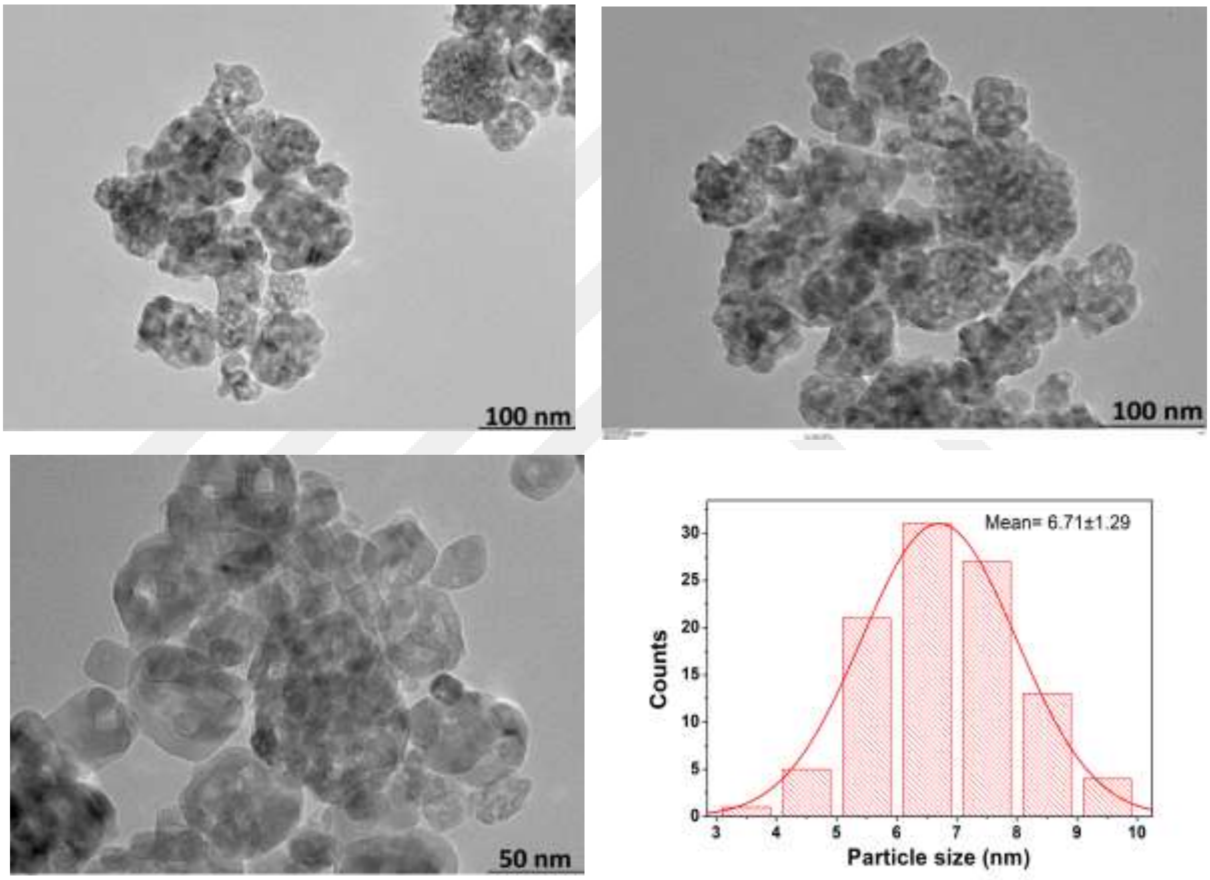

Figure 4.4. analysis of TEM with partical size

4.4. Catalytic Activity of The Ru^0/TiO_2 NPs in Dehydrogenation of DMAB

The catalytic activity of Ru0/TiO_2 NPs in the hydrogen generation from DMAB was investigated at 60.0 ± 0.5 °C. (Figure 4.5) displays the hydrogen evolution from DMAB with different Ru loadings of Ru(0)/TiO_2 NPs. The control experiment, which began at 60.0 0.5 °C with 1.0 mmol $(CH_3)_2NHBH_3$ and fifty mg TiO_2 in 10 mL toluene, showed no hydrogen evolution after 1 hour, suggesting titania inactivity in the hydrogen generation from DMAB under the circumstances where ruthenium catalysts would be evaluated(53). Ru (0)/nanoTiO_2 samples, on the other hand, were shown to be a super active catalyst in the hydrogen evolution from DMAB. (Figure 4.5) illustrates the graphs of equivalent H_2 generated per mole of DMAB over time during the catalytic dehydrogenation process at 60.0 ± 0.5 °C, commencing with 100 mM $(CH_3)_2NHBH_3$ and Ru (0)/nanoTiO_2 with varying Ru loading, resulting in various ruthenium concentration. The hydrogen production average was calculated from the linear section of each graphic and mapped against the starting ruthenium concentration.

In (Figure 4.6), Both axes are scaled in logarithms. The slope of the straight line was determined to be 0.98, suggesting that in terms of Ru concentration, the hydrogen releasing from DMAB catalyzed by Ru (0)/nanoTiO_2 is first order. Experimenting with four different concentrations and loads (0.5, 0.8, 1.2, and 2.1 mM) with Ru (0)/nanoTiO_2, it was discovered that the 0.5 mM concentration yielded the highest value for (TOF 1683 h-1) in hydrogen production from DMAB at 60.0 ± 0.5 °C. The TOF value will drop as the ruthenium storing in the Ru (0)/TiO_2 catalyst build of TOF, as has been shown in the literature for several catalytic processes (54), (55), (56) We further show that when the particle size of the nanoparticles grows with the increases loading of Ru, the catalytic activity of Ru (0) @TiO_2 in H_2 production from DMAB reduces. begin with 100 mM $(CH_3)_2NHBH_3$ and 100 mg Ru (0) @ nanoTiO_2 catalyst with (0.5 mM Ru), DMAB was catalytically dehydrogenated at temperatures ranging from 45 to 60 °C.up, reducing to 494 h^{-1} for the Ru (0)/nanoTiO_2 nanoTiO_2 catalyst with (0.5 mM Ru), DMAB was catalytically dehydrogenated at temperatures ranging from 45 to 60 °C.up, reducing to 494 h^{-1} for the Ru (0)/nanoTiO_2

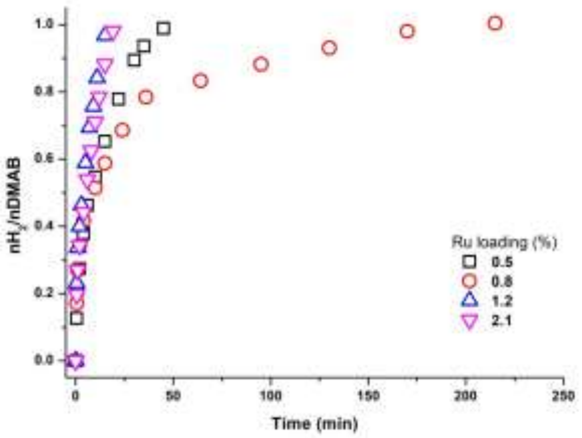

Figure 4.5. The emission of hydrogen from the dehydrogenation of DMAB in the presence of various Ru loadings is shown.

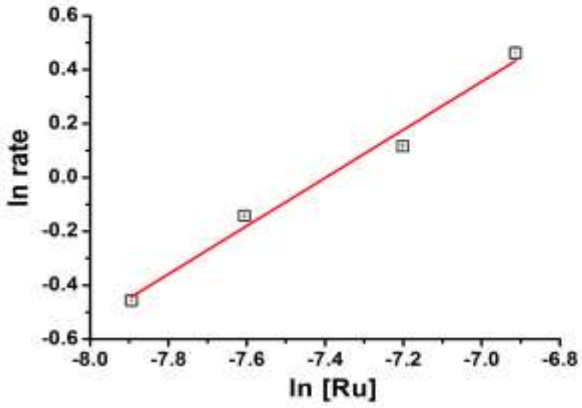

Figure 4.6. The graph shows the relationship between ln (rate) and ln (Ru)

NO.	catalyst	% conv.	temp	TOF h^{-1}	Particle size(nm)	Activation Energy (kJ/mol)	References
1	Ru0 /CeO2	100	60	812	1.80	62 ± 3	(57)
2	Ru@GO-PVP	100	25	896.0	2.09	11.45 ± 2	(58)
5	Ru@Graphite	100	25	281.50	3.75	45 ± 2	(59)
6	CuRu@GO	100	25	256.70	3.86	16.68 ± 2	(60)
7	PdRu@PVP	100	25	808	3.82	60.49 ± 2	(61)
8	RuCo@G-MWCNT	100	25	775.30	3.72	13.72 ± 2	(62)
9	PdRuNi@GO	100	25	737.00	3.78	55.47 ± 2	(63)
10	RuPtNi@GO	100	25	727.00	3.40	49.43 ± 2	(64)
11	RuNi@PVP	100	25	458.60	3.51	36.52 ± 3	(65)
12	OAm stabilized Ru0 NPs	100	25	137.00	1.80	29 ± 2	(66)
13	RuNPs/ZIF-8	100	40	59.00	1.90	42.5	(67)
14	Ru@PVP NCs	100	35	56.00	12.9		(59)
15	Ru0/APTS	100	25	55.00	2.36	61.1 ± 3.1	(68)
16	Ru@Al2O3 NCs	100	35	51.00	11.9		12
17	Ru@PS-co-MA NCs	100	35	29.00	24.9		12
18	Ru(acac)3	100	60	1068.0	-	85 ± 2	(69)
19	Ru(acac)3/Oleylamine	100	60	77.80	-	58 ± 2	(70)
20	trans-RuMe2(PMe3)4	100	25	12.40	-		(71)
21	Ru Cl3.3H2O	77	25	2.7	-		(72)
22	[Ru (1,5-cod) Cl2]n	70	25	2.5	-		43
23	[Ru(1,3,5-cot)(1,5-cod)]	40	25	1.6	-		43
24	[RuH(PMe3)(NC2H4PPr2) 2]	100	25	1.5	-		(73)
25	Ru @ TiO_2		60	1683.40	6.71± 1.29	61 ± 2	this study

Table 4.2 In the dehydrogenation of DMAB, catalytic activity (Turnover frequency TOF h-1) and activation energy of several catalysts were compared to other characteristics.

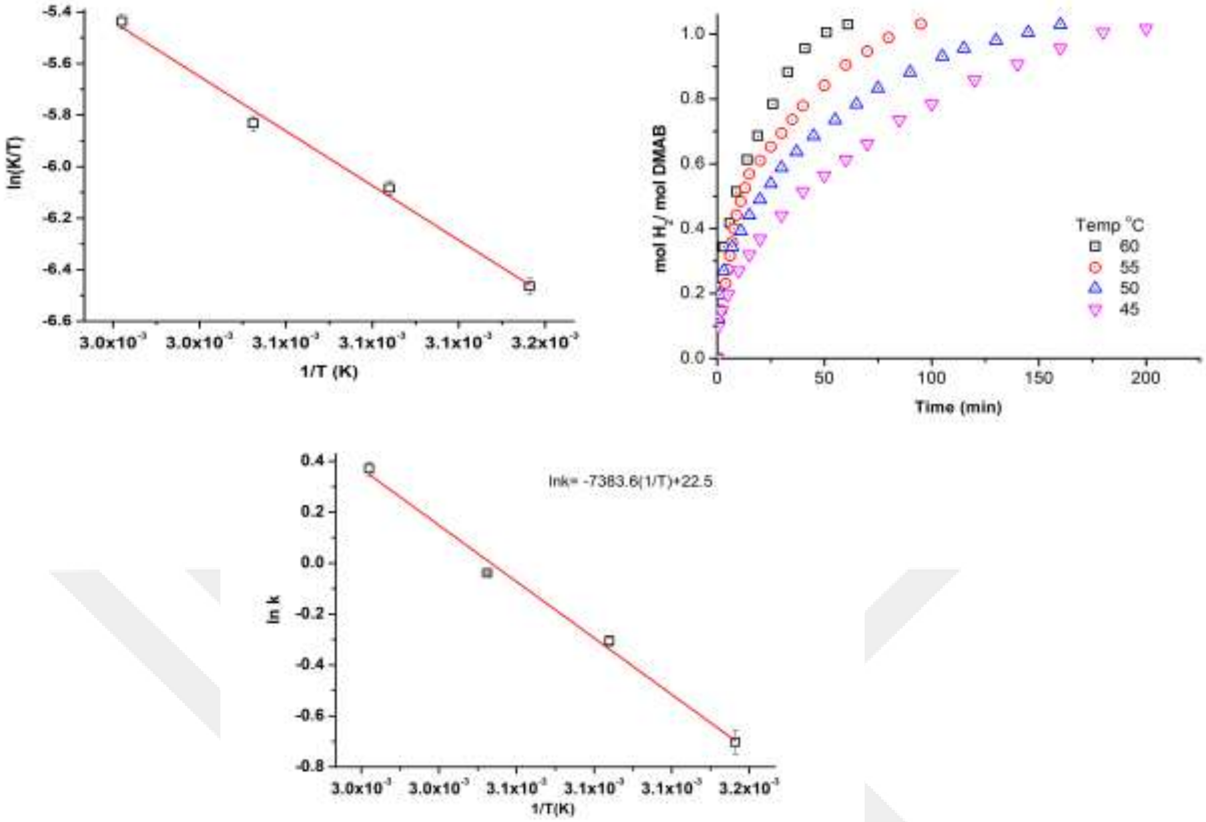

Figure 4.7. mole H_2 generated per mole of DMAB vs time for DMAB catalytic dehydrogenation of at 45-60 °C commencing with 100 mM DMAB and 100 mg Ru0/TiO_2 (0.5 wt. percent Ru, [Ru]= 0.49 mM) in 10 mL solution of toluene.

The apparent TOF value of 1683 h-1 is close to the previous best heterogeneous catalyst (ruthenium catalyst), but it is significantly higher than the other heterogeneous catalysts. The H_2 removed from DMAB activation values in the presence of a Ru (0)/nanoTiO_2 catalyst were estimated using the Arrhenius (74) and Eyring (Eyring, 1935) equations: Ea =61±2 kJ/mol; ΔH =58± 2 kJ/mol; respectively which are comparable to the previously reported in literature (75).

Due to the minimal activation enthalpy and significant negative activation entropy, During the hydrogen evolution from DMAB, it is possible to suppose that the reaction follows an associative mechanism (76).

4.5. Titania Supported Ruthenium (0) Nano-Particles' Recyclability and Catalytic Lifetime in The Hydrogen Evolution of DMAB

In the hydrogen evolution from DMAB at 60.0 ± 0.5 °C, the recyclability ruthenium nanoparticle catalysts based on nanotitania was tested. First, 100 mg ruthenium (0)/TiO_2 with 0.5 percent wt. Ru ([Ru] = 0.0005 mM) with 100 mM $(CH_3)_2NHBH_3$ in 10 mL toluene solution were used to perform a standard dehydrogenation of DMAB. After the whole dehydrogenation yielded 1.0 equivalent, a new equal amount of 100 mM DMAB was adjusted to the reactors and a second run of dehydrogenation was started. Hydrogen evolution per mole of DMAB. At 60.0 ± 0.5 °C, the hydrogen production procedure was performed three times in the same way for both sets of trials.

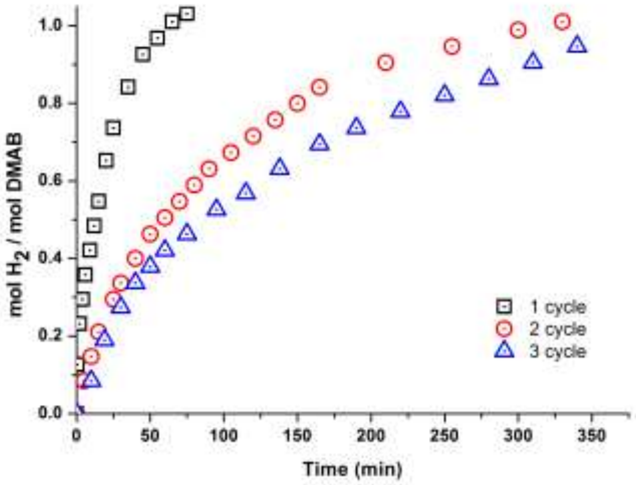

Figure 2.8. The catalytic performance of Ru0/TiO_2 NPs

The overall turnover number in H_2 production from the hydrogen evaluation from DMAB was used to determine the Ru (0)/nanoTiO_2 catalytic lifetime. Lifetime of the catalyst was determined performing an experiment starting with 100mg Ru0/TiO_2 catalyst sample with 150 mM DMAB 60.0 ± 0.5 °C (Figure 4.9). Defined amount of substrate being 150 mM was added to reaction medium for each run of the experiment. The catalytic reaction was followed until until no hydrogen gas was produced. The Ru0/TiO_2 NPs provides 1465 turnovers over 23 h. The decrease in catalytic lifetime may be related with the agglomeration of the Ru0 NPs on the surface of the titania. The other reason for obtaining the low TTO value of the Ru0/TiO_2 catalyst may be due to the side product of dimethylamine borane. The cyclic side product of the substrate could be blocked the active site of the catalyst.

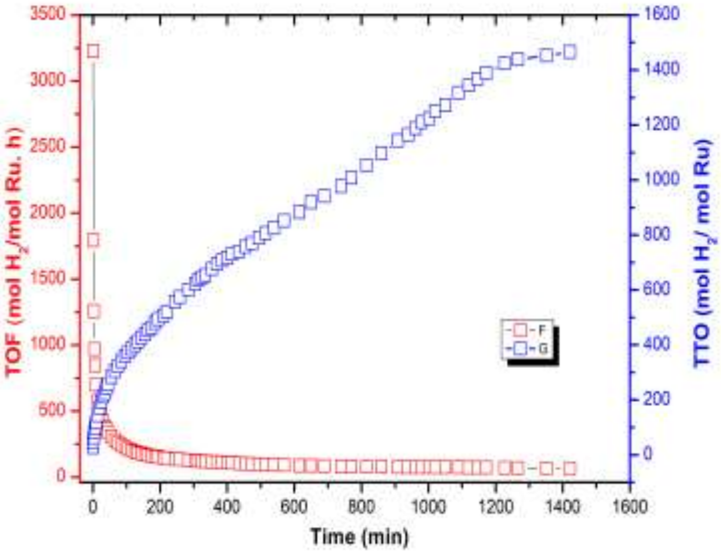

Figure 4.9. Lifetime of Ru0/TiO_2 NPs

4.6. Leaching Test for Ru (0) @ NanoTiO_2

At the end of the catalyzed process, the catalytic activity of the filtrated solution in the hydrogen evolution from $(CH_3)_2NHBH_3$ (100 mM) was examined to check if any ruthenium was released to the liquid component by the solid Ru (0)/nanoTiO_2. Graphs of mol H_2 produced per mole of DMAB vs. time are shown in Figure 4.10. throughout the dehydrogenation of 100 mM DMAB at 60.0 ± 0.5 °C. commencing with (a) 0.0005 mM Ru (0.5 percent wt. Ru, Ru(0)/nanoTiO_2) and progressing to (b) a solid sample filtered following the initial run in (a), and (c) After the initial run in, the filtrate solution was filtered (a). Because of material loss during the separation and redistribution processes, The separated solid Ru (0)/nanoTiO_2 sample's catalytic activity declines. In the hydrogen generation from DMAB Catalytically, the filtrate solution is inactive. The filtrate solution formed by filtering it from the reaction media during the first cycle of dehydrogenation was evaluated using the ICP technique. The filtrated solution had a ruthenium concentration of 0.0005 mM in solution, which was a little in comparison to the first Ru concentration in the solution of the reaction at the mM level. The leaching test and ICP analysis findings show that Ru (0) is retained on the surface of nanoTiO_2 during the catalytic process. As a result, we may infer that nano TiO_2 supported ruthenium (0) nanoparticles are a capable dehydrogenation catalyst.

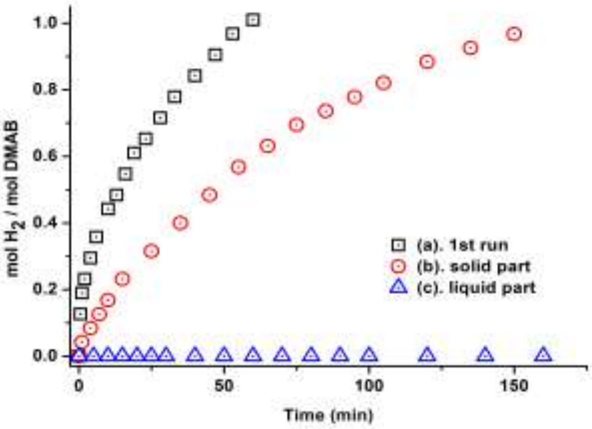

Figure 4.10. The development of equal H_2 per mole of DMAB vs time for the hydrogen generation from 100 mM DMAB at 60.0 ± 0.5 °C beginning with Ru(0)/TiO_2 (a). Following the first run, a solid sample of Ru (0)/nanoTiO_2 was obtained by filtration (b), and a filtrate

5. CONCLUSIONS

The main outcomes of the study can be summarized as;

a) Ru^0/TiO_2 NPs can be used as an active catalyst in H_2 evolution from dimethylamine borane. They can be prepared from the reduction of Ru(III) ions by sodium borohydride on the surface of TiO_2.

b) Four catalyst samples with different amount of Ru contents were tested in H2 evolution from DMAB. Ru0/TiO_2 NPs sample with 0.5% loaded Ru found as highly catalytic activity that provides 1683 h-1 in H_2 (g) production from DMAB. Furthermore, Ru0/TiO_2 NPs are long-lived catalyst being produce 1465 TTO from dehydrogenation of DMAB at 60.0 ± 0.5 °C.

c) The results of TEM analysis disclosed that Ru0 NPs with average particle size 6.71± 1.29 nm were well dispersed on the surface of titania.

d) Recyclability and leaching test of the catalyst were also performed. The results of the tests reveal that Ru0 NPs were compenent catalyst as a kinetically in H_2 generation from DMAB.

e) The nanotitania supported ruthenium (0) NPs are a viable choice for producing extremely effective catalysts in dimethylamine borane dehydrogenation processes because to their simplicity of production, high activity, recyclability, and long lifetime.

6. REFERENCES

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