T.R.
BOLU ABANT İZZET BAYSAL UNIVERSITY
INSTITUTE OF GRADUATE STUDIES
DEPARTMENT OF CHEMISTRY

CATALYTIC DEHYDROGENATION OF DIMETHYLAMINE BORANE IN THE PRESENCE OF CU^0/WO_3 NANOCLUSTERS

MASTER OF SCIENCE

DOAA MAJID HAMEED AL-HAMEEDAWI

ACADEMIC SUPERVISOR
Prof. Dr. İZZET MORKAN
ACADEMIC CO-ADVIZOR
DR. SEDA TANYILDIZI KARABOĞA

BOLU, JULY - 2022

APPROVAL OF THE THESIS

Catalytic dehydrogenation of dimethylamine borane in the presence of Cu^0/WO_3 nanoclusters submitted by **DOAA MAJID AL-HAMEEDAWI** and defended before the Examining Committe Members listed below in partial fulfillment of the requirement for the degree of **Master of Science** in **Department of Chemistry, Institute of Graduate Studies of Bolu Abant Izzet Baysal University in** 20/07/2022 by

Examining Committee Members	**Signature**
Supervisor Prof. Dr. İzzet Morkan Bolu Abant Izzet Baysal University	.....
Member Prof. Dr. Erhan Budak Bolu Abant Izzet Baysal University	.....
Member Prof. Dr. Mecit Aksu Düzce University	.....

Prof. Dr. İbrahim Kürtül

Director of Instıtute of Graduate Studies

ETHICAL DECLARATION

In the thesis dissertation that was properly prepared according to the Thesis Writing Rules of Bolu Abant İzzet Baysal University of the Institute of Graduates Studies, I hereby declare that;

- All data, information, and documents presented in the thesis were obtained in accordance with the academic and ethical rules,
- All data, documents, assessments, and results were presented in accordance with the scientific ethical and moral rules,
- All works that were benefitted in the thesis were appropriately cited,
- No alteration was made in the data used,
- Study presented in this thesis is original,

Otherwise, I declare that I accept the loss of all my rights in case any contradiction that may arise against me.

Based on the plagiarism report that was generated on the date of 23/4/2022 by using predetermined filtrations set by Directorate of the Institute of Graduate Studies of the Turnitin programme, a plagiarism detection software, the rate of plagiarism detected was 20%.

_____

DOAA MAJID AL-HAMEEDAI

ABSTRACT

CATALYTIC DEHYDROGENATION OF DIMETHYLAMINE BORANE IN THE PRESENCE OF CU^0/WO_3 NANOCLUSTERS
MASTER OF SCIENCE
DOAA MAJID HAMEED AL-HAMEEDAWI
BOLU ABANT IZZET BAYSAL UNIVERSITY
INSTITUTE OF GRADUATE STUDIES
DEPARTMENT OF CHEMISTRY
(SUPERVISOR.PROF.DR. İZZET MORKAN)
(CO-ADVISOR: DR. SEDA TANYILDIZI KARABOĞA)
BOLU, JULY 2022
(XII + 31 pages)

In recent years, hydrogen as an energy carrier is accepted as being the fuel of the future that could help end the world's dependence on fossil fuel and aid the transition to carbon-zero emissions. However, the safe and effective storage of H_2 (g) is one of the major issues that must be conquered for stationary and mobile fuel cell applications in the use of hydrogen Economy. Dimethylamine borane is known as a chemical hydrogen storage material that contains a great percentage of H_2 by weight, nontoxicity, and stability in solution, so it is considered a promising candidate as a hydrogen source used in fuel cells. Hydrogen gas could be released from DMAB using suitable catalyst. Transition metals are use as catalysts in the production of H_2 from boron-nitrogen compounds. However, metal nanoparticles have a penchant to agglomerate with the forming of bulk metal, causing a momentous decrease in catalytic activity with growing particle size. At this concern, supporting on the surface of appropriate materials is one way to prevent the agglomeration of NPs. Herein, the research includes the preparation, catalytic usage and characterization of WO_3 supported Cu^0 NPs, Cu^0/WO_3 nanoparticles, as a catalyst for hydrogen obstetrics from dimethylamine borane. WO_3 supported Cu^0 NPs were in-situ generated from the reduction of copper (II) 2-ethylhexanoate by DMAB through its dehydrogenation reaction at 60.0 ± 0.5 °C. Cu^0/WO_3 nanoparticles were detached from the solution and characterized by using some leading analytic techniques such as Transmission electron microscopy (TEM), UV-Visible electronic absorption spectroscopy (UV-Vis), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS).

KEYWORDS: Dimethylamine borane, Dehydrogenation, Heterogeneous catalyst, Copper (0) Nanoparticles, Tungsten (VI) oxide.

ÖZET

CU^0/WO_3 NANOKÜMELER EŞLİĞİNDE DİMETİLAMİN BORANİN KATALİTİK DEHİDROJENLENMESİ
YÜKSEK LİSANS TEZİ
DOAA MAJID HAMEED AL-HAMEEDAWI
BOLU ABANT İZZET BAYSAL ÜNİVERSİTESİ
LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ
KİMYA ANABİLİM DALI
(TEZ DANIŞMANI: PROF DR. İZZET MORKAN)
(İKİNCİDANIŞMAN: DR. SEDA TANYILDIZI KARABOĞA)
BOLU,TEMMUZ – 2022
(Xİİ + 31 sayfa)

Son yıllarda, bir enerji taşıyıcısı olarak hidrojen, dünyanın fosil yakıta bağımlılığını sona erdirecek ve karbon-sıfır emisyonlarına geçişe yardımcı olabilecek geleceğin yakıtı olarak kabul edilmektedir. Ancak, hidrojen ekonomisinde taşınabilir ve sabit yakıt pili uygulamaları için aşılması gereken temel konulardan biri hidrojenin güvenli ve verimli bir şekilde depolanmasıdır. Dimetilamin boran, ağrlıkça yüksek oranda hidrojen barındırması, toksik olmayışı ve kararlı oluşu ile kimyasal hidrojen depolama malzemelerinden biri olarak bilinir ve bu nedenle yakıt hücrelerinde kullanılan hidrojen kaynağı olarak umut verici bir aday olarak kabul edilir. Uygun katalizörler eşiliğinde DMAB tan hidrojen gazı salınabilir. Geçiş metallerinin bor-azot bileşiklerinden H_2 eldesinde katalizör olarak kullanıldığı bilinmektedir. Ancak, metal nanopartiküller, artan parçacık boyutu ile katalitik aktivitede önemli bir azalmaya neden olan külçe metal oluşumu ile aglomerasyon eğilimine sahiptirler. Bu bağlamda, metal nanoparçacıkların aglomerasyonunu önlemenin yollarından biri onları uygun malzemelerin yüzeyinde kararlılaştırmaktır. Bu çalışma, dimetilamin borandan (DMAB) hidrojen üretimi için bir katalizör olarak tungsten (VI) oksit destekli bakır (0) nanoparçacıkların (Cu^0/WO_3 NPs) hazırlanmasını, katalizör olarak kullanılmasını ve tanımlanmasını içermektedir. Tungsten (VI) oksit destekli bakır (0) nanoparçacıklar, bakır (II) 2-etilheksanoatın dimetilamin-boran tarafından 60.0 ± 0.5°C'de tepkime ortamında indirgenmesiyle üretildi. Cu^0/WO_3 nanoparçacıklar çözeltiden izole edildi ve iletim elektron mikroskobu (TEM), UV-Görünür elektronik absorpsiyon spektroskopisi (UV-Vis), X-ışını kırınımı (XRD), X-ışını fotoelektron spektroskopisi (XPS) gibi bazı gelişmiş analitik teknikler kullanılarak karakterize edildi.

ANAHTAR KELİMELER: Dimetilamin boran, Dehidrojenlenme, Heterojen katalizör, Bakır(0) Nanoparçacıklar, Tungsten (VI) oksit

TABLE OF CONTENT

Page

LIST OF FIGURES

Page

LIST OF TABLES

Page

LIST OF ABBREVIATIONS AND SYMBOLS

DMAB : Dimethylamine borane

nm : Nanometer

TOF : Turnover frequency

TON : Turnover number

NPs : Nanoparticles

LMCT : Ligand to Metal Charge Transfer

ΔH≠ : Activation enthalpy

ΔS≠ : Activation entropy

ACKNOWLEDGEMENTS

Sincerest thanks to my supervisor Prof. Dr. İzzet MORKAN head of the department of chemistry sciences for his, patience, guidance, support, friendship, inspiration and encouragement throughout the research.

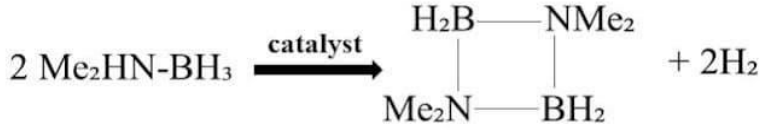
I am thankful to my lovely Co-advisor Dr. Seda TANYILDIZI KARABOĞA for her advice, fruitful suggestions, continuous support and multiple efforts to do the work properly. I learnt many things especially in Metal Nanoparticles. It is my pleasure to work with you and thanks for much knowledge I gain from you.

The dream has come true because of you; I would like to thank my great parents for making a great effort for my sake to be here, brother Abdallah, sisters Rounaa and Dania for supporting me, last not least my cousin Dr.Layth and my Aunt's family to help me in everything.

1. INTRODUCTION

In the next century, global innovation is necessary for sustainable energy due to environmental damage by burning fossil fuels (1,2) The sustainable power supply and safe storage is one of demanding situations of the approaching years. Improvement in hydrogen technology, which includes the manufacturing of hydrogen from an appropriate and renewable substances in addition to its store and diversion to electricity are an important major component. Regrettably, hydrogen is hard to transport and handle, constructing it is a broad utilize in applications problematically. To resolve this issue hydrogen may be saved in chemicals that effortlessly release H_2 (g) whilst needed. Light, Hydrogen-wealthy B-N compounds species have attracted enormous on this regard (3-5). Amine-borane adducts are taken into consideration promising applicants for diverse packages due to the fact they have a excessive H_2 ability. Furthermore, the liberation of H_2 from them as an energy carrier is effortlessly viable with the use of suitable catalysts (6). In addition, they are very soluble in water at the room temperature and simple to therapy (7). Borane ammonia and its derivatives play an important part in numerous areas like a polymer industry (8).

Dimethylamine borane is one of the strong B-N compounds applied as H_2 (g) store substances for removed hydrogen because of the decrease molecular weight (58.9 g mol-1) and highly H_2 gas capacity (16. 9 % wt.) (6,9). DMAB could be providing hydrogen either during solvolysis (10) or dehydrogenation under ambient conditions (11,12).The yields of dehydrogenation of dimethylamine borane up to 3.5% wt. H_2 (precisely 1.0 Equivalent of hydrogen gas per mole of dimethylamine borane which can be obtained by employing appropriate catalysts under mild conditions (Equation (1)) (8,13).



(1)

The present research focused on the advancement of heterogeneous catalysts with highly activism because of the characteristics of heterogeneous regimes, which includes smooth product insulation, catalyst recovery, and reuse. In the H_2 gas evolution reaction, Nano catalysts are paramount importance because they have a smaller size and a high volume to surface area ratio, resulting in better catalytic performance and a large number of active atoms on the surface (14-20).

However, transition-metal nanoparticles tend to aggregate into bulk metals, resulting in decreased catalytic activity (21). The usage of appropriate supports for instance metal oxides, polymers, carbon, and mesostructured materials can also provide particular catalytic functionality, including insulation of the metal NP active site From agglomeration and synergistic results because of strong metal–carbon interactions (SMSI).Various methods of increasing the surface area of catalysts have been tried using different supports to prevent agglomeration. In this context, various candidate materials such as zeolites (22) carbonaceous materials (23) metal-organic-frameworks (24) can be used as an alternative method to inhibit further NP growth. In this report, WO_3 was chosen as a supporting material due to its reducible oxide nature. WO_3 can facilitates transfer of electrons under reaction conditions, and this status causes a negative charge to excess on the surface, which improves the catalytic performance for the catalyst to obtain a strong interaction between metal and the oxide support(25).

1.1. Hydrogen as Energy Carries

Hydrogen is the most abundant and natural substance of the universe (26, 27). It is a colourless, savourless, scentless and element, a clean, safety, and sustainable energy carrier. As opposed to traditional Petroleum-based fuels and natural gas derivatives, it has a completely small and mild molecular structure. The nucleus of

H_2 includes one proton and one electron. Neutron bombardment of hydrogen-involving compounds malead to the forming of hydrogen isotopes, H_2 and H_3 that can be known as deuterium and tritium respectively. H_2 isotopes have a radioactive nature and nuclear gadgets had been constructed and examined employing those materials (28).

Hydrogen has energy per mass substance of 143 MJ kg-1, which is up to three times greater than liquid hydrocarbon-based fuels energy density of some commonly fuels. Furthermore, H_2 has a much down density in the gasiform condition and liquefying such is an energy consumption operation. The indicated later considers as a flaw for this substance while utilized like a fuel. On the other hand, hydrogen is unavailable as a naturally disconnected substance in consumptive scope as additionally it is attached to different substances, especially C and O_2.

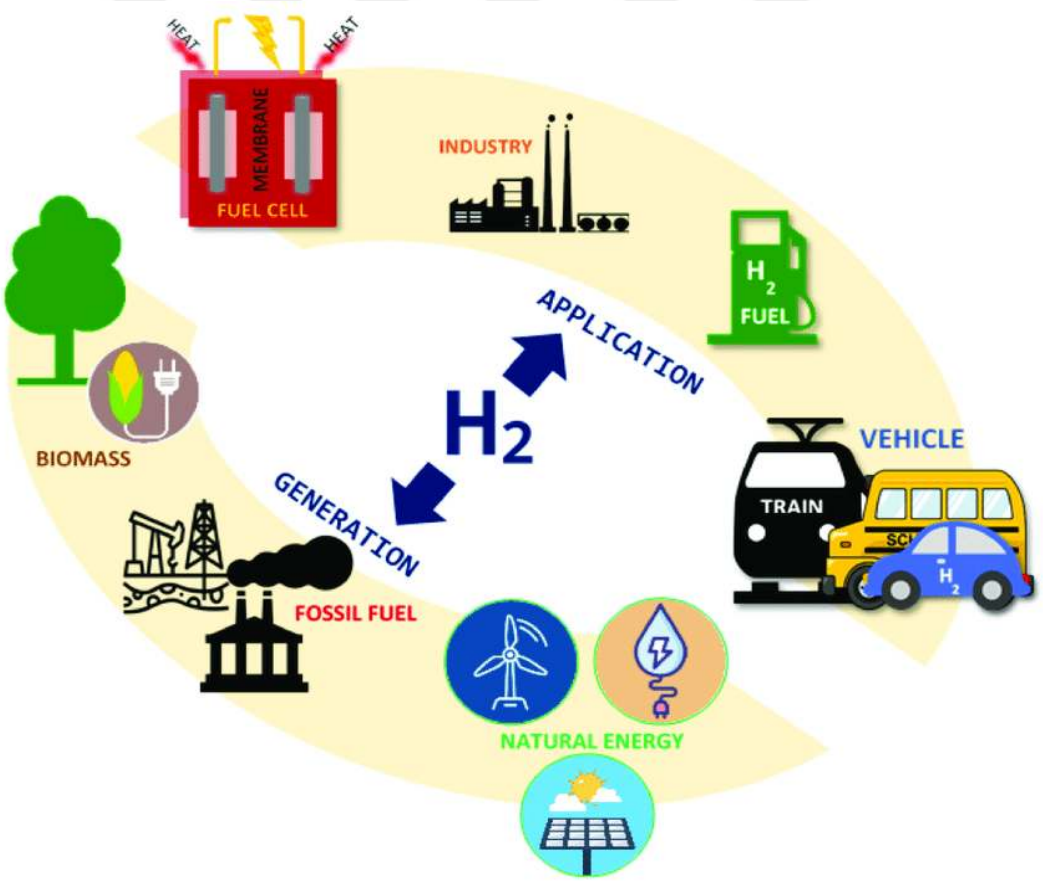


Figure 1.1. The sustainable hydrogen cycle.

1.1.1. Hydrogen Economy

Hydrogen and power have an extended common history – powering the primary inner burning motors over 2 hundred years in the past to turning into a necessary fraction of the present day refinery manufacture. It is power-dense, light, storable and products no immediate emissions of pollution or greenhouse gases. However, for hydrogen to provide a tremendous participation to smooth power transmission, it wishes to be followed in intersectoral where in it is far nearly truant, which includes transportation, homes and energy obstetrics. The Future of Hydrogen gives an intensive and impartial study of H_2 that lays out wherein matters stand now; the methods wherein H_2 gas enable assist to acquire a smooth, steady and low-priced power Future; and the way we will cross approximately realizing its potential.

1.1.2. The Dangers of Hydrogen

As fuel, hydrogen is completely flammable and so hydrogen leaks generate a critical danger of fire. However, hydrogen fires are markedly special from fires related to different fuels. Hydrogen is odorless, colorless and tasteless, so leaks are difficult to stumble on the use of Only human senses. Hydrogen is not toxic; however, in indoor environments like battery garage rooms, hydrogen might also additionally increase and reason asphyxiation with the aid of using displacing oxygen.

1.1.3. Methods of Hydrogen Storage

Considering the difficulty of storing hydrogen gas, as it is one of the dangerous and flammable gases quickly when combined with oxygen in the air, and to reduce the risks generated by the combustion and explosion accompanying the aforementioned process, scientists have resorted to storing hydrogen in solid, stable and storable states under normal conditions.

1.1.4. Solid State Hydrogen Storage

The garage of H_2 received through the adsorption approach on Carbone substances and/or through absorption in chemical substances has unique in protection, wherein a few shape as transformation or electricity enter for supply the hydrogen in subsequent utilize. Widespread research were procedure cutting-edge hydrogen-garage structures as steel imides, steel nitrides, steel hydrides, steel imides, steel nitrides, clathrate hydrates, carbon , zeolites, steel natural, frameworks (MOF)

primarily and doped polymers, based totally substances. In garage of strong status, hydrogen is banded through chemical forces including in imides, nitrides and hydrides or carbon and physically, e.g. MOF primarily fundamentally substances.

1.1.5. Amine Boranes & DMAB as Hydrogen Storage Materials

Amine borane is one of the strong solid-state of hydrogen compounds including coordinate covalent bond inter the nitrogen and boron atoms have been currently received a interest. They will be employed as H_2 store substances due to their highly hydrogen gage. Dimethylamine borane is a one of the primary B-N compound with low molecular weight (58.9 g mol-1) and excessive H_2 gas capacity (16. 9 % wt.) that has a great heed in hydrogen store applications because of as a promising boron-primarily foundation totally compound. It is especially substantial that the H_2 gas liberation from the dehydrogenation of dimethylamine borane with the use of suitable catalysts under mild conditions.

1.2. Transition Metal (0) Nanoparticles as Catalyst

1.2.1. Homogeneous Versus Heterogeneous Catalysis

Heterogeneous and homogeneous catalysts are the two basic kinds of catalysts. The catalyst in a heterogeneous reaction is in a different phase than the reactants Because of the reactants, the catalyst is inside the equal phase in a homogeneous reaction. A homogeneous catalyst is one in which the reactants and catalyst are in the same phase. Heterogeneous catalysis now has a significant lead over homogeneous catalysis, accounting for more than 85% of all industrial processes.

The surface area of the heterogeneous catalyst influences the number of active reaction sites, making it possible to monitor and perhaps restrict the number of reaction sites. It can, however, be isolated from the reaction mixture in a clean way, such as by filtering. As a result, costly catalysts may be readily recovered, which is vital for industrial production operations.

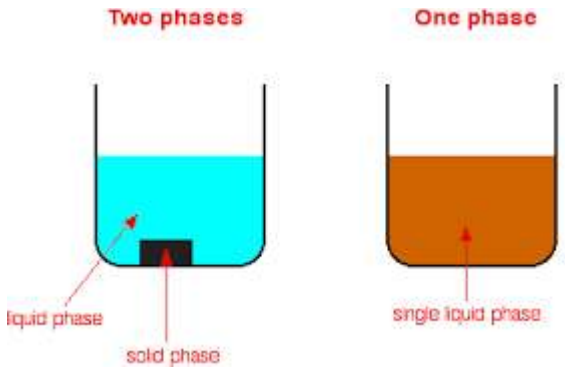


Figure 1.2.Types of Catalysts.

1.1.1. Catalysis

Catalysis is described as growing the rate of a chemical reaction via the advent of a catalyst. A catalyst in turn is a substance that is not consumed by a chemical reaction, but that lowers the activation energy of the reaction. In different words, the catalyst is a reactant and the made from a chemical reaction. Normally, only a very small amount of catalyst is required in order to catalyze a reaction. The activation energy of a reaction is described as the minimum amount of energy required to obtain a reaction. Catalysts supply the molecular interaction between the reactants and decrease the activation energy. Meaning the catalyst lower the energy of the transition state and the equilibrium state stays untouched.

1.1.2. Nano-Catalysis

Nanomaterials are important in a variety of fields, from basic research to numerous projects in electronics, biological sensors, catalysis, and energy. As a robust immoderate surface area, heterogeneous catalysts, and catalytic support, they have emerged as viable alternatives to standard chemicals. Nano-sized particles increase the exposed surface area of the catalyst's active factor, drastically improving interaction between reactants and catalyst and simulating homogenous catalysts. This review focuses on the application of Nano-catalysis for novice chemical development, including the method of combining Microwave heating with Nano-catalysis in safe aqueous reaction medium, which produces a powerful synergistic effect with more capacity than those three additives alone. To illustrate the proof-of-

idea of this “inexperienced and sustainable” approach, consultant examples are mentioned on this article.

1.1.3. Transition Metal Nanoparticles as Catalysts

Nano catalyst is an unexpectedly developing discipline that includes using NPs as catalysts for a number of natural and inorganic reactions. Chemical reduction strategies like an alcohol reduction, (29, 30) hydrogen reduction, (31, 32) sodium borohydride reduction, etc. had been maximum, not unusual place methods of synthesizing colloidal metal NPs. In additional, reduction approaches like electrochemical (33), Photochemical and chemical reduction techniques had been utilized to a least range. Many distinct stabilizers had been employed like covering factors for synthesize of colloidal metallic Nano-catalysts which includes polymers, dendrimers, block copolymer micellar (34) Surfactants, etc. Supported metallic Nano catalysts had been organized via way of means of the adsorption of the colloidal metallic Nano-catalysts into the support, grafting of the NPs into the support, etc. Supported metallic Nano-catalysts likewise can be lithographically fabricated the use of electron beam lithography.

Cross-coupling reactions, oxidations, hydrogenations, electron-transfer reactions, fuel cell reactions (35), and a numerous of other reactions have been catalyzed by utilize of colloidal and supported metal Nano-catalysts. Transition metal NPs appear to be so appealing to apply as catalysts because of their highly surface-to-extent ratio and surface energy that gets their surface atoms extremely activity. Furthermore, the presence of a large number of active surface atoms may cause the nanoparticles to be unsettled in terms the direction of their catalytic functional. This increases queries about whether or not the surface atoms are very active that they bring about adjustments withinside the volume and form of the transition metal NPs throughout their catalytic functional. Consequently, this leading to inquiries about the recycling ability of the transition metal nanoparticles.

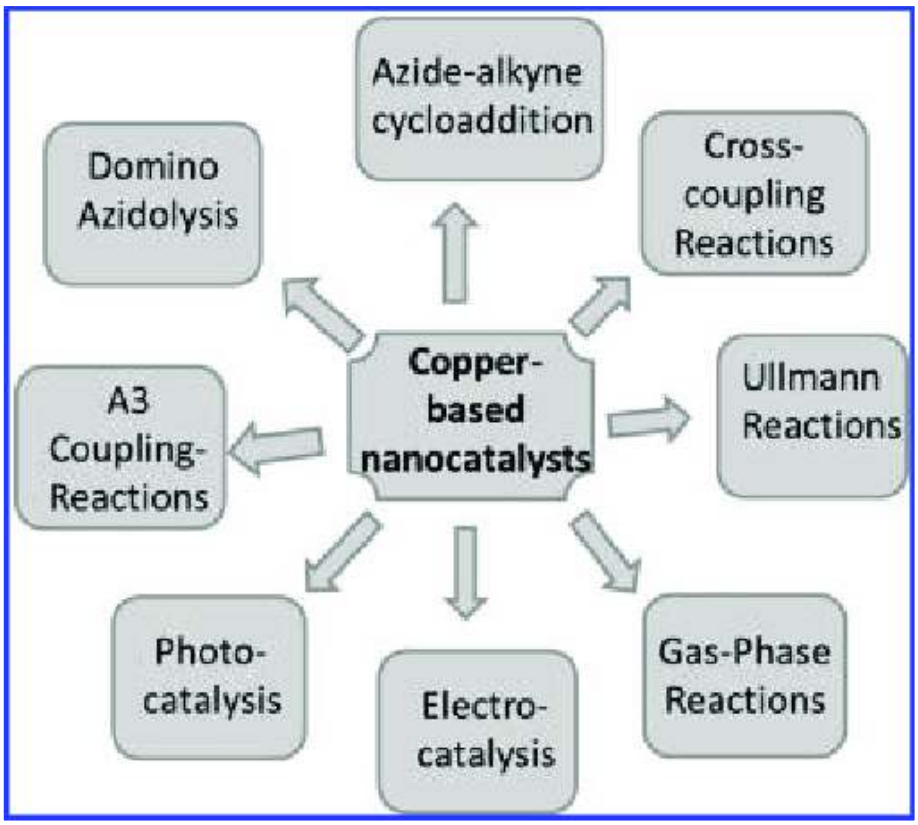


Figure 1.3. Applications of Cu-based nanocatalysts

2. AIM AND SCOPE OF THE STUDY

The primary intent of this work is to prepare and study the catalytic usage of Cu^0 supported on tungsten (VI) oxide in the dehydrogenation dimethylamine borane. Cu^0 NPs are precipitated on the surface of WO_3, which were constructed by the reduction of copper (II) 2-ethylhexanoate through H_2 gas evolution from dimethylamine borane at 60.0 ± 0.5°C. Cu^0/WO_3 catalyst was characterized by using TEM, UV–vis, and XPS procedures after the dehydrogenation reaction of DMAB. Cu^0/WO_3 nanoparticles are less expensive than other noble metals that generate H_2 from dimethylamine borane. Tungsten oxide (IV) supported copper (0) NPs are efficient catalysts with the top turnover frequency registered ($38h^{-1}$) by emitting 1.0 equivalent of hydrogen (g) per mole of dimethylamine borane. The Leaching and reusability tests of the catalyst copper nanoparticles supported tungsten as an active catalyst in the dehydrogenation of DMAB. This report also gives kinetic study of hydrogen generation from dimethylamine borane catalyzed by Cu^0/WO_3 nanoparticles reliant on a catalyst concentration, the activation parameters, and temperature substrate concentration catalytic reaction was calculated from kinetic date.

3. MATERIALS AND METHODS

3.1 Materials.

Dimethylamine borane $(CH_3)_2NHBH_3$, 97%), Copper (II) 2-ethylhexanoate (Cu $[CH_3 (CH_2)_3CH (C_2H_5) CO$, Tungsten (VI) oxide ($WO_3$, 99.99%) and toluene (99.9%) were purchased from Sigma–Aldrich. After the toluene solvent was purified over metallic sodium, stowed under an inert N_2 atmosphere, all glassware was dried in oven at 150°C, and vacuumed for 20 min to eliminate vestiges of O_2 and moistness before using in an experimental process.

3.2 In Situ Generation Copper (0) Supported on Tungsten Oxide (IV) Nanoparticles During H_2 (g) Generation from DMAB.

In order, the reduction of copper (II) 2-ethylhexanoate by DMAB and dehydrogenation of DMAB ensue within same catalytic reaction. All the reactions were conducted under an inactive nitrogen gas atmosphere. The equipment was vacuumed under high vacuum for 20 min to remove oxygen and moistness pre-use. Dissolve 91.81 mg (0.218 mmol) copper (II) 2-ethylhexanoate in 15 mL toluene to equip the stock solution. In a specific reaction, 7 ml from stock solution was conveyed to reaction flask having 100mg WO_3, and the suspension was mixed for 75 min to assure Cu^{+2} ion impregnated on WO_3 at 25.0 ± 0.5 °C. A 60.2mg from dimethylamine-boran was dissolved in 3 ml toluene through raising the temperature to 60.0°C ,and added to the reaction, including the stock solution (17.49mMCu) tungsten oxide (IV) by utilizing the syringe at 60.0 ± 5.0°C. The color of reaction mixture was altered within 5 minutes from light green to dark blue after adding DMAB into the reaction mixture. The reduction of copper (II) ions supported WO_3 to Cu^0/WO_3 and started hydrogen releasing from dimethylamine borane. The volume of H_2 (g) is gauged by revising the water level at constant pressure, whereby the complete transformation of dimethylamine-boran to 1.0 equivalent of hydrogen per mol of dimethylamine borane. The reaction stops when there is no further additional H_2 (g) evolution is noticed.

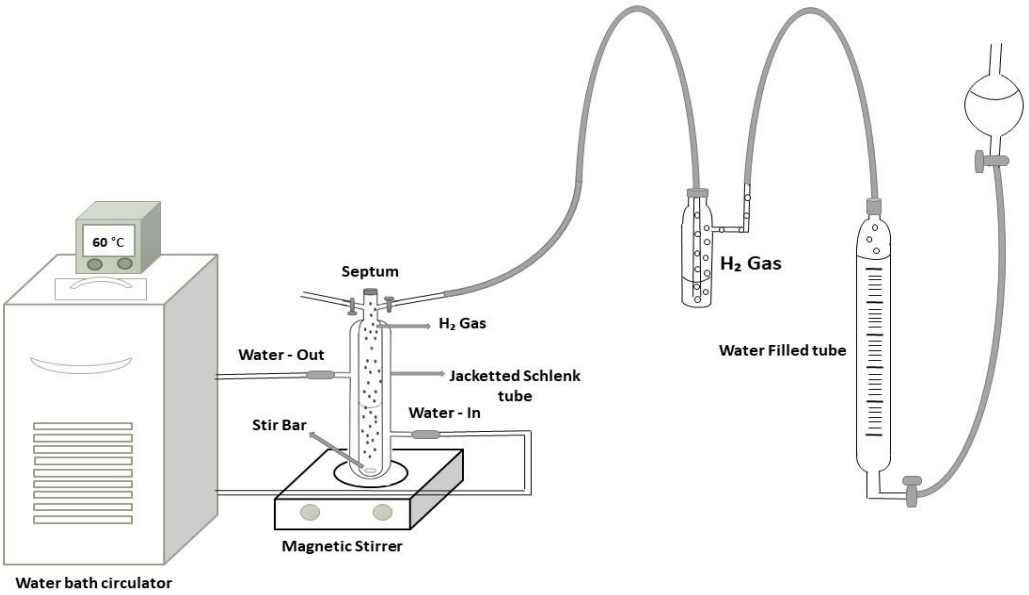


Figure 3.1. The diagram displays the reaction setup used for releasing H_2 from the dehydrogenation of dimethylamine borane in dehydrogenation reaction.

3.3 Determination of Most Effective Cu Loading for Cu^0/WO_3 NPs.

Samples of Cu^0/WO_3 catalyst with various Cu loadings (2.0, 4.0,6.0,8.0% wt) were experimented starting with 6.56 mM Cu and 100 mM DMAB at 60.0±5.0°C in dehydrogenation of DMAB. 4.0 % by weight Cu loaded on 100 mg Tungsten oxide (IV) the most catalytic activity was achieved for Cu^0/WO_3 nanoparticles. Copper 4.0 wt. % was utilized for all the experiment's catalytic reactions.

3.4 Effect of Kinetic Parameters in H_2 Generation from $(CH_3)_2NHBH_3$ Catalyzed by Cu^0/WO_3.

A typical experiment was accomplished with 100mg Cu^0/WO_3 (4.0% wt.) and a steady concentration of DMAB (100mM, 60.11 mg DMAB) in 10ml toluene solution at different temperatures (60, 55, 50, 45 °C) in order to get the activation parameters of the reaction.

3.5 Leaching Performance of Cu^0/WO_3 NPs in H_2 (g) Production from DMAB.

After finishing the first run of releasing H_2 from dimethylamine borane (100mM), the catalyst (Cu^0/WO_3, 4%wt.Cu, 6.54mM) on 100mg tungsten oxide at 60 ± 5.0 °C was permitted to settle down. Reverse filtration was used to transport the liquid portion of the solution into the reaction flask, quit the solid part in the main flask under an inactive gas. The insulated solid and the filtrate was tested for catalytic efficiency in the dehydrogenation of dimethylamine borane by adding a new bunch of dimethylamine borane (60.11mg, 100mM) under the same reaction conditions.

3.6 Recyclability Test of Cu^0/WO_3 NPs in the Hydrogen Generation from $(CH_3)_2NHBH_3$.

The catalytic performance of Cu^0/WO_3 NPs in subsequent runs of the reaction was tested in H_2(g) production from dehydrogenation of dimethylamine borane by starting with 100 mg Cu^{+2}/WO_3 (4% wt. Cu) and 100 mM DMAB at 60.0 ± 0.5°C. The same approach was used for the second run of the reaction and performance of the catalyst was evaluated with determining turnover frequency.

3.7 Characterization of Tungsten (IV) Oxide Supported Cu^0 NPs.

Cu^0 supported on WO_3 NPs catalyst were distinguished by using UV-vis techniques, (XPS), (TEM), and (XRD) and) at the end of hydrogen gas production from dimethylamine borane.

(XPS)- X-ray Photoelectron Spectroscopy: After the completion of the DMAB catalytic reaction, XPS analysis of Cu^0/WO_3 NPs was performed utilizing monochromatic Al K radiation on K-alpha spectrophotometer-equipped hemispherical analyzer.

(TEM) Transmission Electron Microscopy Analysis: TEM images were obtained by diluting 0.2 mL of the Cu^0/WO_3 solution formed in situ in the end of DMAB dehydrogenation reaction with 1 mL ethanol and then transferring it into a glass vial. 2 mL colloidal solution was dropped for five seconds on a carbon-coated copper grid

and dried in an inert environment. Hitachi HT-7700 operating at 120kV was used to test the sample.

Ultraviolet-Visible Spectroscopy (Uv-Vis.): The sample were acquired for UV-Visible by taking 100-µL solution in a 1cm quartz cuvette with utilize a Shimadzu 2540double-beam spectrometer in the range of 200–800 nm at room temperature.

(XRD) X-ray Diffraction: XRD for the samples were registered one the Cu-Ka radiation(λ = 1.5418 Å) in the Rigaku Multiflex 2 kW diffractometer with range 22 = 10–90° at a scan of 5°/min at room temperature.

4. RESULT AND DISCUSSION

4.1 Formation Tungsten Oxide (IV) Supported Cu^0 NPs Concomitant in Releasing H_2 from DMAB.

Cu^0/WO_3 NPs were produced by reduction of copper (II) on the surface of WO_3 supporting material and tested catalytically in H_2 (g) generation from DMAB. However, catalytic activity of bare Cu(II) ions were determined without using any stabilizer in dehydrogenation reaction before using WO_3 as a supporting material for Cu^0 NPs. Figure 4.1 shows the hydrogen evolution graphs from DMAB in the presence of bare Cu(II) ions and WO_3 supported Cu^0 NPs. The same amount of Cu concentration was used in both experiments to compare each other. Although hydrogen evolution starts within a few minutes, Cu^0 NPs lose their catalytic activity after 20 minutes as a result of the agglomeration of Cu^0 NPs through the reaction path for the bare Cu^0 NPs. In the reaction, the solution contains copper(II) 2-ethylhexanoate as the only stabilizer in the reaction medium that could not prevent the agglomeration of Cu^0 NPs. On the other hand, Cu^0 NPs supported on WO_3 show high catalytic activity release 1.0 equivalent of hydrogen production from DMAB at 60.0 ± 0.5°C. In this case, WO_3 was used as a supporting material for Cu^0 NPs obtained from in-situ reduction of Cu (II) ions. The comparison of bare Cu^0 NPs and WO_3 supported Cu^0 NPs in Figure 1 indicates that WO_3 could be prevents the agglomeration of Cu^0 NPs during the reaction course.

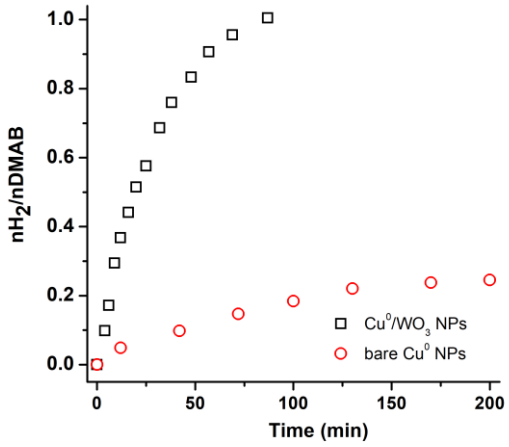


Figure 4.1. Plots of mol H_2/mol DMAB versus time for H_2 production reaction catalyzed by bare Cu^0 NPs and WO_3 supported Cu^0 NPs at 60.0±0.5°C.

As indicated in Figure 4.1, the rate of H_2 (g) generation decreases with continuing the reaction, which implies the Cu^0 NPs are not stabilize. Cu^0 nanoparticles formation from the reduction of Cu^{+2} through the H_2 generation from dimethylamine borane, as exposed tend to collect the bulk metal at the terminus of reaction due to use the only stabilizer existent in the toluene solution is a 2-ethylhexanoate ion. It does not supply sufficient stabilization for Cu^0 NPs to prevent agglomeration when releasing H_2 from DMAB (19). Therefore, copper (0) nanoparticles need a stabilizer by using support with the large surface area.WO_3 Nano powder was trialed as a support for copper (0) NPs against agglomeration when releasing H_2 from DMAB. Cu^0 NPs supported on Cu^0/WO_3 were produced by reduction of Cu^{+2} to Cu^0/WO_3 through the catalytic dehydrogenation of DMAB. After addition, dimethylamine borane in suspension contains Cu^{+2} impregnated on the surface of supporting material WO_3, and the evolution of hydrogen observed after four mints.

Dehydrogenation experiments were carried out starting with 6.65 mM copper(II) 2-ethylhexaonate, 100 mg WO_3 in 10 mL of toluene at 60.0 ± 0.5 °C. After addition of dimethylamine borane to the reaction, the color of the solution changes from green to dark brown approximately in fifteen mints. The change of the color in the solution can be pursued by using UV-vis spectroscopy. In Figure 4.2, displays the UV-Vis of WO_3 supporting material for Cu^0 nanoparticles solution before and after

addition of dimethylamine borane. In beginning, the UV-Vis spectrum was taken for Cu^{+2} ions was showed a sharp absorption band 280 nm and a broad band at around 662 nm. While the sharp absorption band at 280 nm is attributed to LMCT, the other band at 662 nm shows the d-d transition of the copper salt used as a precursor in this study. The Ultraviolet-visible spectroscopy of the solution taken after the reaction is complete shows that the bands at around 280 and 662 nm vanish and a new band at 285 nm appears. The new band at 285 nm exhibits characteristic Mie scattering for Cu^0 NPs, implying that Cu^{2+} ions are reduced to Cu^0 via a catalytic mechanism in the dehydrogenation of DMAB.

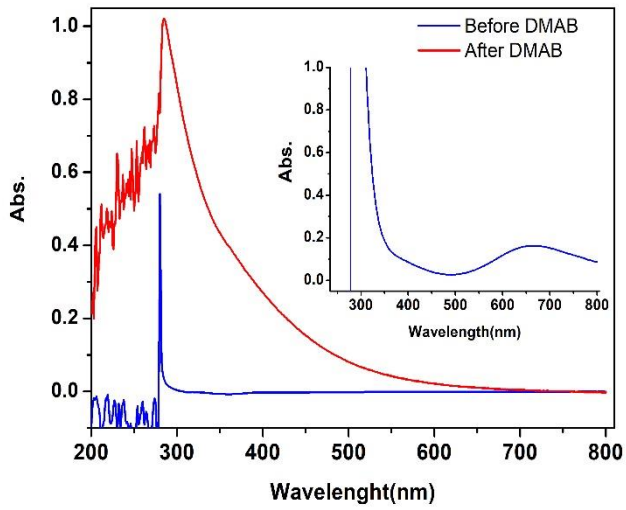


Figure 4.2. Uv-vis spectrum of precursor solution of Cu (II) 2-ethylhexanoate in toluene (a) before and (b) after addition of 100 Mm dimethylamine borane.

4.2 Characterization of Cu^0/WO_3 Catalyst in H_2 (g) Production from DMAB.

After being insulated Cu^0/WO_3 Nps catalyst were characterized from the reaction solution by utilizing advanced analytical techniques (TEM, XRD, and XPS). Figure.4.3 TEM image displays taken from the sample of Cu^0/nanoWO_3 sample with 4.0% Cu loaded after the catalytic dehydrogenation of DMAB at different magnifications. Figure.4.3.a-c shows the dispersion of WO_3 as a supporting material for Cu^0 nanoparticles. Figure.4.3.d displays the particle size histogram by counting

more than 100 non-touching particles and mean diameter of Cu^0 NPs was found as (4.6 ± 1.0) nm.

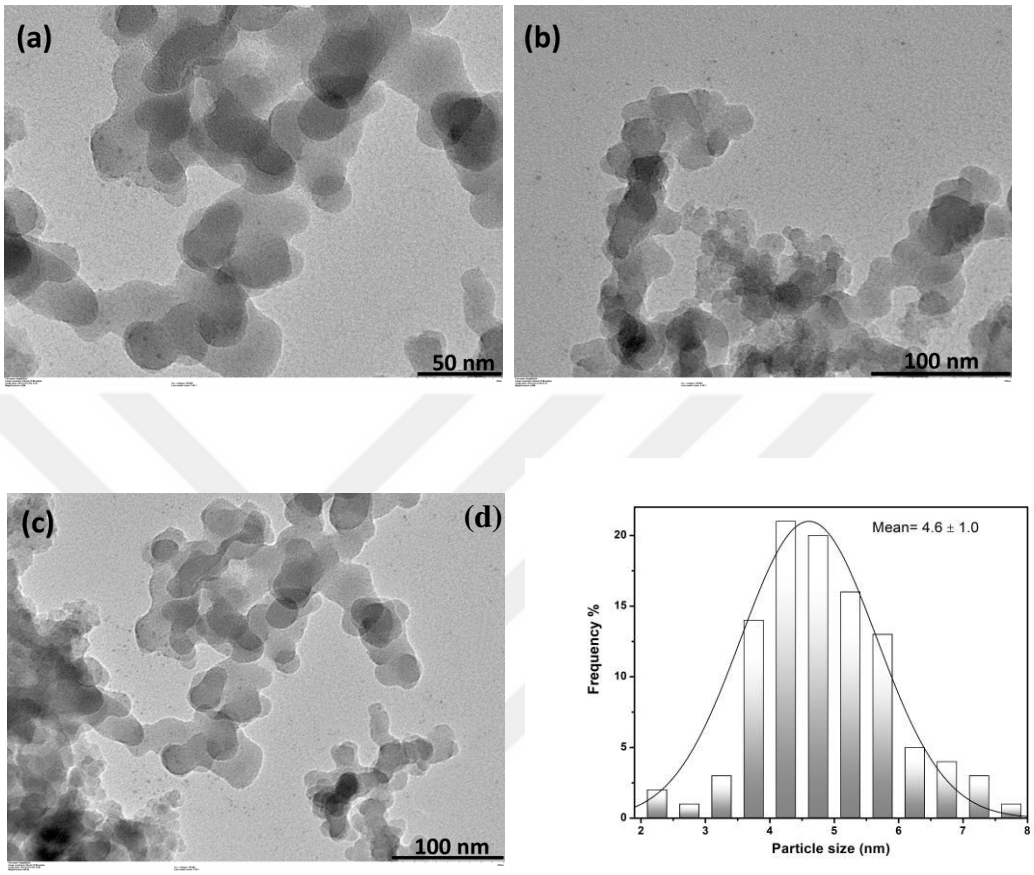


Figure 4.3.(a, b, c)TEM image of Cu^0/WO_3 with Cu 4.0 % loading after dehydrogenation of DMAB in different magnifications 50, 100 nm d) The histogram of Cu^0 NPs.

Figure.4.4. the XRD patterns were taken for bare tungsten (IV) oxide and Cu^0/WO_3 nanopowder with 4.0% wt. Cu loading for various diffraction peaks. Both samples appear the same diffraction peaks of the XRD pattern, which belong to WO_3 (ICDD Card No: 43-1035). These peaks approve:(i) there is no clear peak that could be attributed to Cu, probably being to lower metal loading and (ii) Notice the presence of Cu^{2+} ions on the surface of WO_3 and their reduction to Cu^0 does not change the crystallinity and lattice of tungsten oxide (IV). Moreover, no alteration in the

positions of the WO_3 diffraction peaks was notice, indicating that Cu loading has no effect on the infrastructure for support.

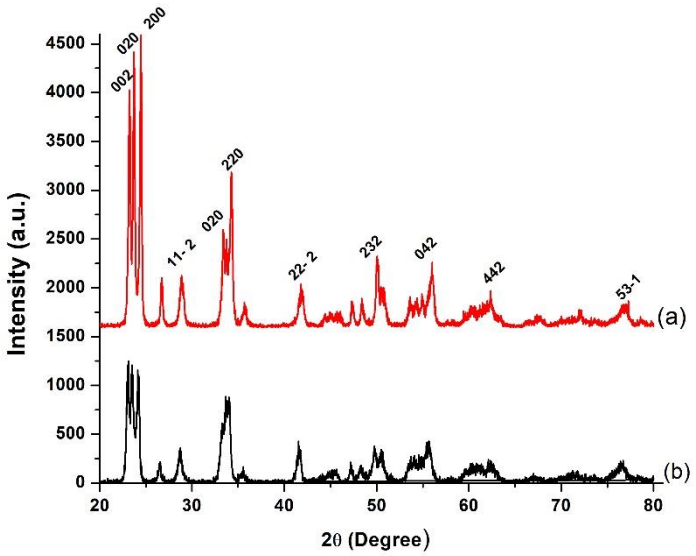


Figure 4.4. The powder XRD pattern of a) Bare WO_3 (red line) ,b) Cu^0/WO_3 with Cu loading of (4.0 wt.%Cu) (black line).

XPS analysis makes important insights for the surface architecture of Cu^0/WO_3 and the oxidation state of Cu metal in the catalyst sample. The survey analysis of Cu^0/WO_3 with (4.0% wt.) with a metal loaded in Figure 4.5. Shows the Cu element with the framework elements of WO_3. High-resolution spectrum of Cu 2p bands indicates two prominent peaks at 932.8 and 952.7 eV belong to metallic Cu $2p_{3/2}$ and $Cu2p_{1/2}$ respectively. XPS analysis is an evidence of the reduction of Cu^{2+} ions used as a precursor and existence of metallic Cu as a Cu^0 form in the catalyst sample.

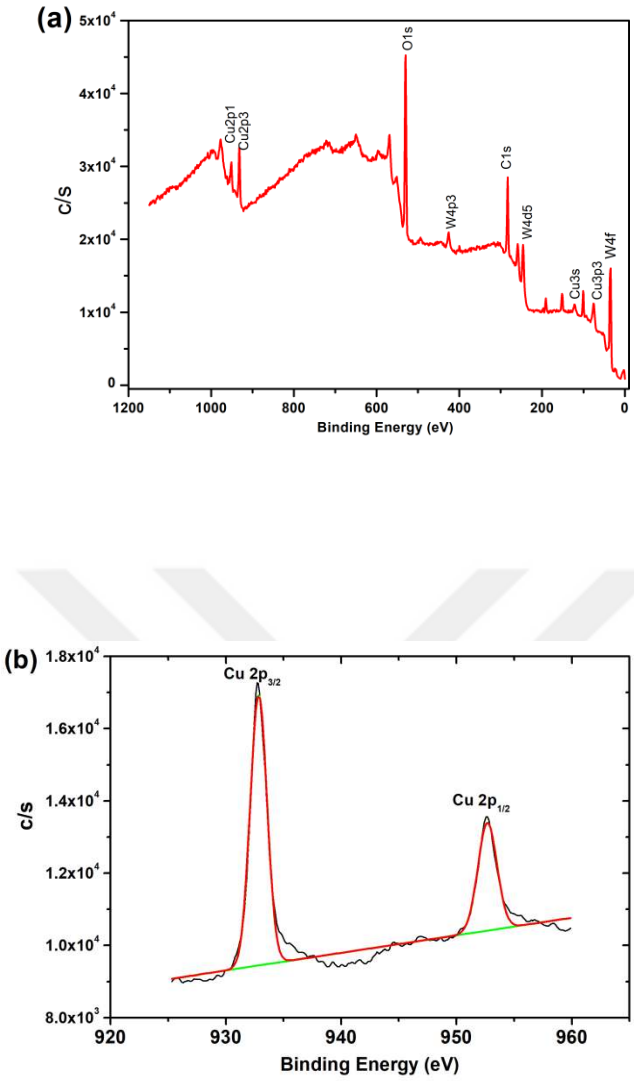


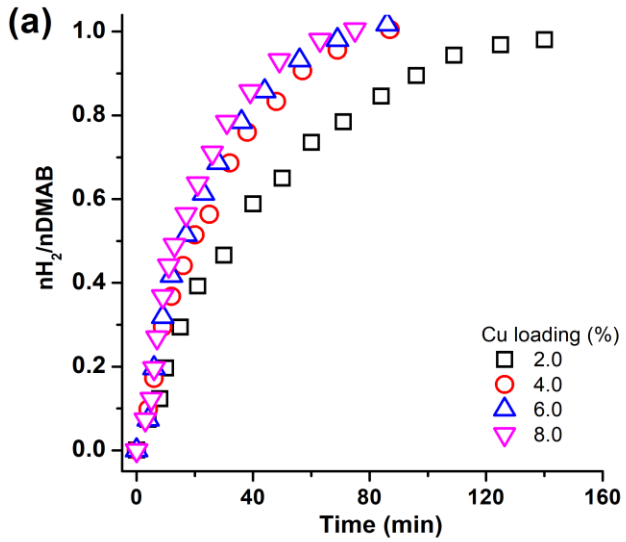
Figure 4.5.(a)XPS analysis survey scan, (b) The high-resolution Cu 2p XPS spectra of Cu^0/WO_3 nanoparticles with Cu loading (4.0 wt.%).

4.3 Catalytic Performance of Cu^0/WO_3 in H_2 (g) Generation from Dimethylamine Borane.

In the beginning, the study starting with 100 mg of bareWO_3 in 10 mL of toluene solution at 60.0 ± 0.5°C to test its efficiency in hydrogen released from DMAB, no hydrogen gas evolution was obtained, which approve the bare WO_3 does not produce H_2 from dimethylamine borane. WO_3 supported Cu^0 NPs was tested in hydrogen generation from dimethylamine borane at with different Cu loadings. Figure.4.3.1a shows the releasing of H_2 from dimethylamine borane in the presence

of Cu^0/WO_3 catalyst with various Cu loading in the ranging 2 to 8 wt.% Cu to find the most effective Cu loading on the catalytic activity of WO_3 supported. H_2 evolution starting initiates instantly after adding 100 mM dimethylamine borane into the solution and continues until 1.0 equiv gas evolved from the catalytic reaction.

The turnover frequency (TOF) values for Cu^0/WO_3 NPs in the dehydrogenation of DMAB were obtained from the diagrams in (Figure.4.6.a) for Cu^0/WO_3 as a (2, 4, 6 and 8 wt. % Cu). Figure.4.6.b illustrates the graph for TOF values that determined to be 36, 39, 24, and 32 h^{-1}versus different Cu loading which was afforded a shape disparity Cu^0 NPs supported on tungsten (IV) oxide in releasing H_2 from dimethylamine borane. A shape disparity with increase in the Cu loading most probably being to the agglomeration of Cu^0 NPs on the surface of WO_3 or with increases of Cu loading on the surface of supporting material ensuing decrease in surface area and failure to reach active sites of the catalyst. The premier activity of the catalyst was observed as 38 h^{-1} for Cu^0/WO_3 NPs with 4.0% wt. Cu. As seen in Table 1.the comparison of TOF values of the copper (0) NPs with different metal nanoparticles in the various heterogeneous catalysts. The Cu^0/WO_3 samples with a ratio of 4.0 wt. % Cu were usage as the more optimal ratio for all the further experiments in this work.



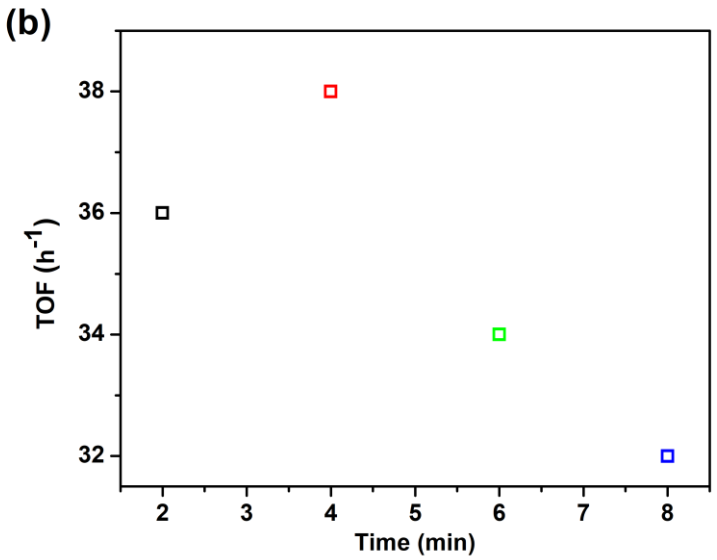
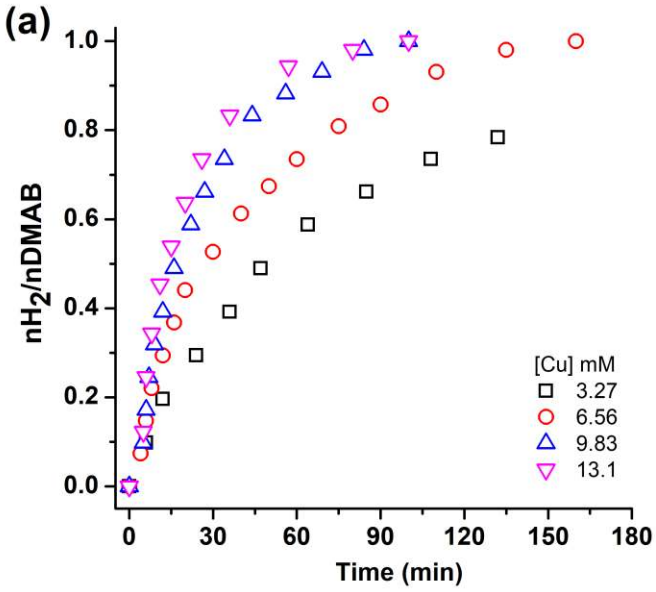


Figure 4.6.(a) Plots of mol H_2/mol DMAB versus time for the hydrogen generation from dimethylamine borane, with 100Mm DMAB in various copper loadings (2, 4, 6, and 8%wt. Cu). (b)TOF values versus Cu loadings of catalyst Cu^0/WO_3.

Pre- catalyst	Solvent	T(°C)	Particle Size(nm)	Ea(KJ/mol)	TOF(h^{-1})	Ref.
OAM-stabilized Ru^0 NPs	Toluene	25	1.8	29	137	(36)
Pt^0 NPs/AA	THF	25	3.3	64	15	(37)
Cp_2Ti	Toluene	20	-	-	12.3	(38)
Rh(0) Nanoclusters	Toluene	25	1.9	34	60	(39)
Cu^0/WO_3	Toluene	60	4.6	37	39	This study
Pd(0)/MOF	Toluene	25	4.3	173.5	75	(40)
Cu(0) NPs	Toluene	60	3.1	76	40	(41)
Rh^0/WO_3NPs	Toluene	60	1.92	45	2816	(42)
$Ru@Al_2O_3$NCs	-	35	11.9	25	51	(43)
$Pd(0)/Al_2O_3$	Toluene	25	7.1	36	73	(44)
$[Ru(H)(PMe_3)(N(C_2H_4P^iPr_2))_2]$	THF	25	-	-	1.5	(45)
Pt(0)/TBA	THF	25	3.9	46.7	31	(46)

Table 1. Catalysts tested in terms of the TOF and Ea for dehydrocoupling of DMAB from SciFinder literature search.

A string of experiment were carried out to learn the influence of catalyst concentration on the reaction kinetics of dimethylamine borane dehydrogenation, beginning with 100 mM DMAB in the existence of copper loading (4.0 %wt.) in various amounts of the tungsten (IV) oxide supporting. Figure. 4.7.a displays the plots of H_2 (g) evolution from dimethylamine borane using Cu^0/WO_3 NPs with different copper concentrations (3.27, 6.56, 9.83 and 13.06 mM) as catalysts. As shown in Figure.4.7.b obtained straight line with a slope of 0.96 indicates that hydrogen evolution from dimethylamine borane is a first-order reaction concerning to catalyst concentration.



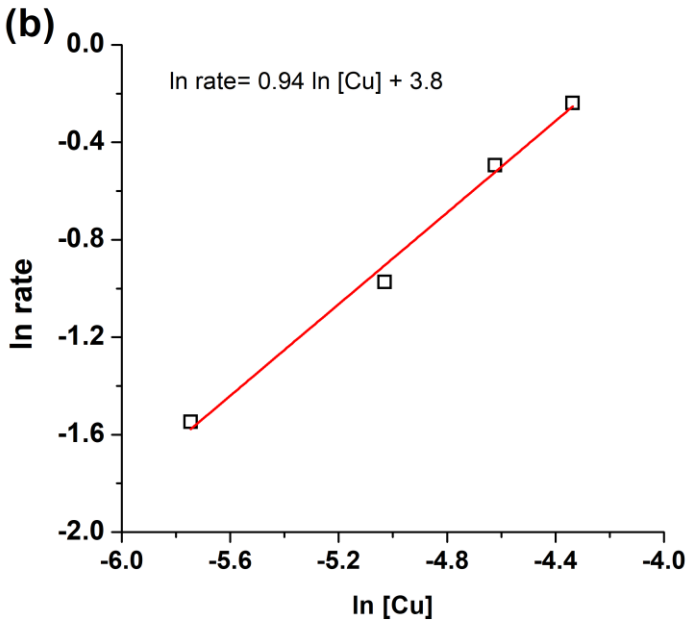
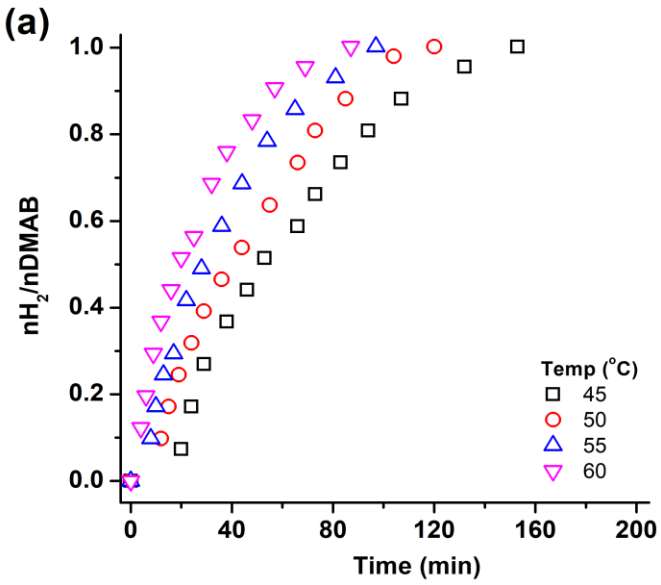
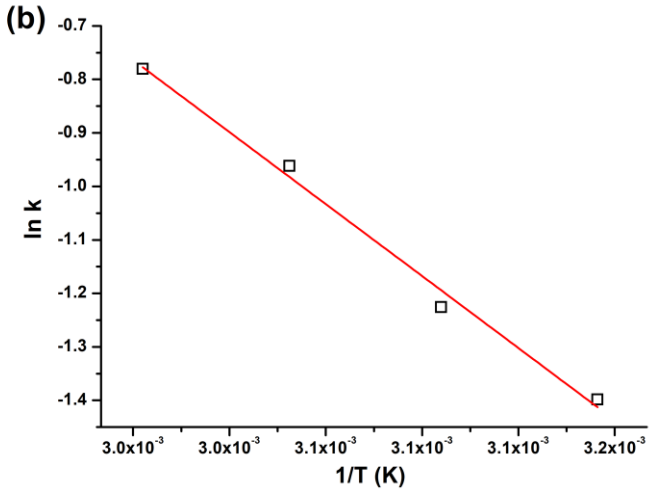


Figure 4.7.a)The graph shows mol H_2/mol DMAB versus time for releasing hrdrogen from 100 mM DMAB in different Cu concentrations, b)The logarithmic plot of the initial rate of hydrogen evolution versus copper concentration.

The dehydrogenation experiments were also repeated at different temperatures in the ranging from 45 to 60 ^{o}C to determine the activation parameters of the reaction. Figure 4.8 depicts the evolution of hydrogen gas from dimethylamine borane in the presence of Cu^0/WO_3 nanoparticles as a catalyst at various temperatures. The experimental data was used to calculate the rate constant for each plot that then used to draw the Arrhenius and Eyring graphs. The slopes of the Arrhenius and Eyring plots yielded the activation energy and entropy of the catalytic reactions as Ea=37±2 kJ/mol, $\Delta H^{\#}$=35±2 kJmol^{-1} and $\Delta S^{\#}$=−148±2 JK^{-1}mol^{-1} respectively, which are comparable to the formerly published in the literature. The activation energy Ea was also comparison with the different catalytic in table 1.


(a)
1.0
0.8
0.6
0.4
0.2
0.0
nH2/nDMAB
0
40
80
120
160
200
Time (min)
Temp (°C)
45
50
55
60


(b)
-0.7
-0.8
-0.9
-1.0
-1.1
-1.2
-1.3
-1.4
ln k
3.0x10-3
3.0x10-3
3.1x10-3
3.1x10-3
3.1x10-3
3.2x10-3
1/T (K)

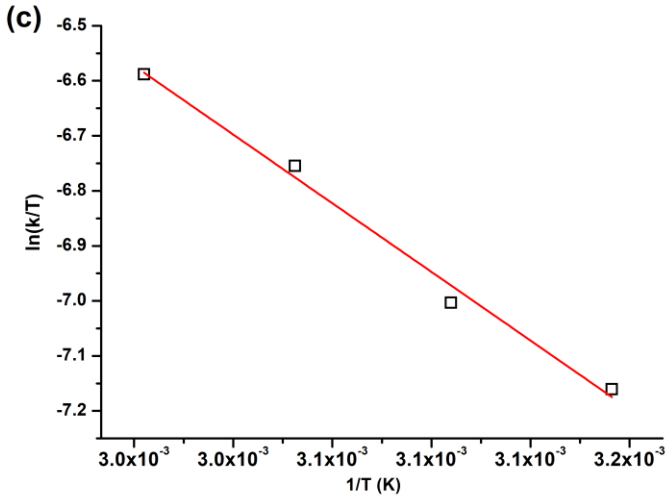


Figure 4.8.a) H_2 evolution graph of DMAB for the catalytic dehydrogenation of 100 mM dimethylamine by Cu^0/WO_3NPs (%4.0 Cu wt.) at various temperatures in the range (45-60 ̊C), b) Arrhenius and c)Eyring plots.

The leaching test was carried out under the same conditions for Cu^0/WO_3 catalyst to learn the catalytic activity in H_2 evolution from DMAB. After first run is end, the suspension was filtered and the insulated solid part from the filtration part under inert gas. The same amount of dimethylamine borane was added to the reaction. The resulting showed there is no leaching of copper on the surface of tungsten oxide (IV) through the dehydrogenation reaction for the filtration part as reported in previous study.

The catalytic functioning of Tungsten (IV) oxide supported Cu^0 NPs in hydrogen generation from DMAB was also tested in following runs of the reaction in terms recyclability. After the first run of the reaction, same amount of dimethylamine borane was added to reaction medium and hydrogen evolution was followed for the subsequent runs of the catalytic reaction. It was seen in Figure.4.9.Cu^0/WO_3 NPs catalyst are still active in releasing H_2 from DMAB even after third cycle of the reaction. The decrease in catalytic activity of the Cu^0/WO_3 NPs could be associated with the agglomeration of Cu^0 nanoparticles on the surface of WO_3.

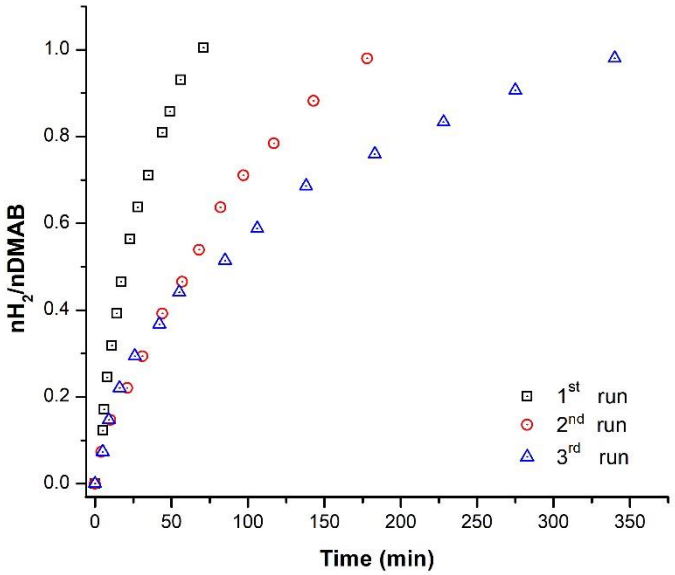


Figure 4.9. Dehydrogenation plots of DMAB catalyzed by Cu^0/WO_3 nanoparticles in subsequent runs.

5. CONCLUSION

The primary purpose of our study is to prepare and characterize tungsten oxide (IV) supported copper (0) nanoparticles and used as a heterogeneous catalyst in hydrogen generation from dimethylamine borane that resulted to the following finding:

1. Cu^0 NPs were obtained from the reduction of Cu^{2+} ions on the surface of WO_3, and subsequently tested as a catalytically in H_2 (g) evolution from DMAB. While the bare Cu^0 NPs does not show catalytic activity, WO_3 supported Cu^0 NPs found as efficient catalyst with a value of TOF (39 h^{-1}) for evolution the hydrogen gas from dimethylamine borane at 60.0±0.5°C.
2. After insulation of Cu^0/WO_3 NPs, they characterized after completion dehydrogenation of DMAB using advanced techniques (XRD, TEM, XPS, and Ultraviolet-visible spectroscopy). The results approved the Cu^0 NPs on the surface of WO_3 with a mean particle size of 4.6 ± 1.0 (nm).
3. The results of Cu^0/WO_3 catalyst in the kinetic study at different catalyst concentrations is found to be first-order in the dehydrogenation of DMAB.
4. Recyclability tests clarified that Cu^0/WO_3 NPs catalyst is active even after the third cycle of dehydrogenation reactions. The decreased activity of the Cu^0/WO_3 catalyst in sequent runs could be being to the agglomeration of nanoparticles on the surface of tungsten oxide (IV).
5. Relatively high activity, low cost, and the simple preparation of Cu^0/WO_3 catalyst make the Cu^0 NPs a promising contender to be utilize as attractive catalysts in evolving an efficient hydrogen generation system by employing DMAB as solid H_2 (g) storage materials.

6. REFERENCES

"Vancouver citation system was used in this thesis."

1. Ausfelder F, Beilmann C, Bertau M, Bräuninger S, Heinzel A, Hoer R, Koch W, Mahlendorf F, Metzelthin A, Peuckert M, Plass L. Energy storage as part of a secure energy supply. ChemBioEng Reviews. 2017 Jun;4(3):144-210.

2. Karaboga S, Özkar S. Ceria supported ruthenium nanoparticles: Remarkable catalyst for H2 evolution from dimethylamine borane. International Journal of Hydrogen Energy. 2019 Oct 8;44(48):26296-307.

3. Akbayrak S, Özkar S. Ammonia borane as hydrogen storage materials. International Journal of hydrogen energy. 2018 Oct 4;43(40):18592-606.

4. Yao Q, Lu ZH, Huang W, Chen X, Zhu J. High Pt-like activity of the Ni–Mo/graphene catalyst for hydrogen evolution from hydrolysis of ammonia borane. Journal of Materials Chemistry A. 2016;4(22):8579-83.

5. Staubitz A, Robertson AP, Manners I. Ammonia-borane and related compounds as dihydrogen sources. Chemical reviews. 2010 Jul 14;110(7):4079-124.

6. Hamilton CW, Baker RT, Staubitz A, Manners I. B–N compounds for chemical hydrogen storage. Chemical Society Reviews. 2009;38(1):279-93.

7. Marder TB. Will we soon be fueling our automobiles with ammonia–borane?. Angewandte Chemie International Edition. 2007 Nov 5;46(43):8116-8.

8. Van den Berg AW, Areán CO. Materials for hydrogen storage: current research trends and perspectives. Chemical Communications. 2008(6):668-81.

9. Langmi HW, McGrady GS. Non-hydride systems of the main group elements as hydrogen storage materials. Coordination Chemistry Reviews. 2007 Apr 1;251(7-8):925-35.

10. Caliskan S, Zahmakiran M, Durap F, Özkar S. Hydrogen liberation from the hydrolytic dehydrogenation of dimethylamine–borane at room temperature by using a novel ruthenium nanocatalyst. Dalton Transactions. 2012;41(16):4976-84.

11. Pun D, Lobkovsky E, Chirik PJ. Amine borane dehydrogenation promoted by isolable zirconium sandwich, titanium sandwich and N 2 complexes. Chemical communications. 2007(31):3297-9.

12. Turner J, Sverdrup G, Mann MK, Maness PC, Kroposki B, Ghirardi M, Evans RJ, Blake D. Renewable hydrogen production. International journal of energy research. 2008 Apr;32(5):379-407.

13. Jaska CA, Temple K, Lough AJ, Manners I. Transition metal-catalyzed formation of boron− nitrogen bonds: catalytic dehydrocoupling of amine-borane adducts to form amino boranes and borazines. Journal of the American Chemical Society. 2003 Aug 6;125(31):9424-34.

14. Lee J, Kong KY, Jung CR, Cho E, Yoon SP, Han J, Lee TG, Nam SW. A structured Co–B catalyst for hydrogen extraction from NaBH4 solution. Catalysis today. 2007 Feb 28;120(3-4):305-10.

15. Amendola SC, Sharp-Goldman SL, Janjua MS, Spencer NC, Kelly MT, Petillo PJ, Binder M. A safe, portable, hydrogen gas generator using aqueous borohydride solution and Ru catalyst. International Journal of Hydrogen Energy. 2000 Oct 1;25(10):969-75.

16. Stephens FH, Pons V, Baker RT. Ammonia–borane: the hydrogen source par excellence?. Dalton Transactions. 2007(25):2613-26.

17. Mohajeri N, Ali T, Adebiyi O. Hydrolytic cleavage of ammonia-borane complex for hydrogen production. Journal of power sources. 2007 May 15;167(2):482-5.

18. Fernandes R, Patel N, Miotello A. Hydrogen generation by hydrolysis of alkaline NaBH4 solution with Cr-promoted Co–B amorphous catalyst. Applied Catalysis B: Environmental. 2009 Oct 19;92(1-2):68-74.

19. Yan JM, Zhang XB, Han S, Shioyama H, Xu Q. Synthesis of longtime water/air-stable Ni nanoparticles and their high catalytic activity for hydrolysis of ammonia− borane for hydrogen generation. Inorganic chemistry. 2009 Aug 3;48(15):7389-93.

20. Patel N, Fernandes R, Guella G, Miotello A. Nanoparticle-assembled Co-B thin film for the hydrolysis of ammonia borane: A highly active catalyst for hydrogen production. Applied Catalysis B: Environmental. 2010 Mar 12;95(1-2):137-43.

21. Özkar S, Finke RG. Nanocluster formation and stabilization fundamental studies: ranking commonly employed anionic stabilizers via the development, then application, of five comparative criteria. Journal of the American Chemical Society. 2002 May 22;124(20):5796-810.

22. Tosheva L, Valtchev VP. Nanozeolites: synthesis, crystallization mechanism, and applications. Chemistry of materials. 2005 May 17;17(10):2494-513.

23. Castillejos E, Debouttière PJ, Roiban L, Solhy A, Martinez V, Kihn Y, Ersen O, Philippot K, Chaudret B, Serp P. An efficient strategy to drive nanoparticles into carbon nanotubes and the remarkable effect of confinement on their catalytic performance. Angewandte Chemie International Edition. 2009 Mar 23;48(14):2529-33.

24. El-Shall MS, Abdelsayed V, Abd El Rahman SK, Hassan HM, El-Kaderi HM, Reich TE. Metallic and bimetallic nanocatalysts incorporated into highly porous coordination polymer MIL-101. Journal of Materials Chemistry. 2009;19(41):7625-31.

25. Akbayrak S. Decomposition of formic acid using tungsten (VI) oxide supported AgPd nanoparticles. Journal of colloid and interface science. 2019 Mar 7;538:682-8.

26. Mazloomi K, Gomes C. Hydrogen as an energy carrier: Prospects and challenges. Renewable and Sustainable Energy Reviews. 2012 Jun 1;16(5):3024-33.

27. Momirlan M, Veziroglu TN. The properties of hydrogen as fuel tomorrow in sustainable energy system for a cleaner planet. International journal of hydrogen energy. 2005 Jul 1;30(7):795-802.

28. Schulz M, Karnahl M, Schwalbe M, Vos JG. The role of the bridging ligand in photocatalytic supramolecular assemblies for the reduction of protons and carbon dioxide. Coordination Chemistry Reviews. 2012 Aug 1;256(15-16):1682-705.

29. Li Y, Boone E, El-Sayed MA. Size effects of PVP− Pd nanoparticles on the catalytic Suzuki reactions in aqueous solution. Langmuir. 2002 Jun 11;18(12):4921-5.

30. Shiraishi Y, Hata S, Okawauchi Y, Oshima K, Anno H, Toshima N. Improved thermoelectric behavior of poly (3, 4-ethylenedioxythiophene)-poly (styrene sulfonate) using poly (n-vinyl-2-pyrrolidone)-coated geo2 nanoparticles. Chemistry Letters. 2017 Jul 5;46(7):933-6.

31. Ahmadi TS, Wang ZL, Green TC, Henglein A, El-Sayed MA. Shape-controlled synthesis of colloidal platinum nanoparticles. Science. 1996 Jun 28;272(5270):1924-5.

32. Narayanan R, El-Sayed MA. Effect of colloidal nanocatalysts on the metallic nanoparticle shape: the Suzuki reaction. Langmuir. 2005 Mar 1;21(5):2027-33.

33. Reetz MT, Quaiser SA. A new method for the preparation of nanostructured metal clusters. Angewandte Chemie International Edition in English. 1995 Nov 3;34(20):2240-1.

34. Bronstein LM, Chernyshov DM, Volkov IO, Ezernitskaya MG, Valetsky PM, Matveeva VG, Sulman EM. Structure and properties of bimetallic colloids formed in polystyrene-block-poly-4-

vinylpyridine micelles: catalytic behavior in selective hydrogenation of dehydrolinalool. Journal of Catalysis. 2000 Dec 10;196(2):302-14.

35. Moore JT, Corn JD, Chu D, Jiang R, Boxall DL, Kenik EA, Lukehart CM. Synthesis and characterization of a Pt_3Ru_1/Vulcan carbon powder nanocomposite and reactivity as a methanol electrooxidation catalyst. Chemistry of materials. 2003 Aug 26;15(17):3320-5.

36. Duman S, Özkar S. Oleylamine-stabilized ruthenium (0) nanoparticles catalyst in dehydrogenation of dimethylamine-borane. international journal of hydrogen energy. 2013 Aug 12;38(24):10000-11.

37. Sen F, Karatas Y, Gulcan M, Zahmakiran M. Amylamine stabilized platinum (0) nanoparticles: active and reusable nanocatalyst in the room temperature dehydrogenation of dimethylamine-borane. Rsc Advances. 2014;4(4):1526-31.

38. Clark TJ, Russell CA, Manners I. Homogeneous, titanocene-catalyzed dehydrocoupling of amine− borane adducts. Journal of the American Chemical Society. 2006 Aug 2;128(30):9582-3.

39. Zahmakiran M, Ozkar S. Dimethyl ammonium hexanoate stabilized rhodium (0) nanoclusters identified as true heterogeneous catalysts with the highest observed activity in the dehydrogenation of dimethylamine− borane. Inorganic chemistry. 2009 Sep 21;48(18):8955-64.

40. Gulcan M, Zahmakiran M, Özkar S. Palladium (0) nanoparticles supported on metal organic framework as highly active and reusable nanocatalyst in dehydrogenation of dimethylamine-borane. Applied Catalysis B: Environmental. 2014 Apr 5;147:394-401.

41. Tanyıldızı S, Morkan I, Özkar S. Ceria supported copper (0) nanoparticles as efficient and cost-effective catalyst for the dehydrogenation of dimethylamine borane. Molecular Catalysis. 2017 Jun 1;434:57-68.

42. Karaboğa S. Tungsten (VI) oxide supported rhodium (0) nanoparticles; highly efficient catalyst for H2 production from dimethylamine borane. International Journal of Hydrogen Energy. 2021 May 17;46(34):17763-75.

43. Bukan B, Duman S. Green dehydrogenation of dimethylamine-borane catalyzed by in situ generated ruthenium nanoclusters in presence of various supporters and its comparison with classical methods. International Journal of Hydrogen Energy. 2018 Apr 26;43(17):8278-89.

44. Karaboga S, Özkar S. Nanoalumina supported palladium (0) nanoparticle catalyst for releasing H2 from dimethylamine borane. Applied Surface Science. 2019 Sep 1;487:433-41.

45. Friedrich A, Drees M, Schneider S. Ruthenium-Catalyzed Dimethylamineborane Dehydrogenation: Stepwise Metal-Centered Dehydrocyclization. Chemistry–A European Journal. 2009 Oct 12;15(40):10339-42.

46. Erken E, Pamuk H, Karatepe Ö, Başkaya G, Sert H, Kalfa OM, Şen F. New Pt (0) nanoparticles as highly active and reusable catalysts in the C1–C3 alcohol oxidation and the room temperature dehydrocoupling of dimethylamine-borane (DMAB). Journal of Cluster Science. 2016 Jan;27(1):9-23.