

BOLU ABANT IZZET BAYSAL UNIVERSITY
THE GRADUATE SCHOOL OF NATURAL AND APPLIED
SCIENCES



STABILIZED METAL(0) NANOPARTICLES AS AN ACTIVE
CATALYST IN DEHYDROGENATION OF
DIMETHYLAMINE BORANE

MASTER OF SCIENCE

YEŞİM ÖZTÜRK KARACAN

BOLU, AUGUST 2019

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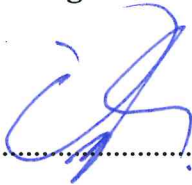
APPROVAL OF THE THESIS

STABILIZED METAL(0) NANOPARTICLES AS AN ACTIVE CATALYST IN DEHYDROGENATION OF DIMETHYLAMINE BORANE submitted by **Yeşim ÖZTÜRK KARACAN** and defended before the below named jury in partial fulfillment of the requirements for the degree of **Master of Science in Department of Chemistry, The Graduate School of Natural and Applied Sciences of Bolu Abant Izzet Baysal University** in **19.08.2019** by

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Yeşim ÖZTÜRK KARACAN

ABSTRACT

STABILIZED METAL(0) NANOPARTICLES AS AN ACTIVE CATALYST IN DEHYDROGENATION OF DIMETHYLAMINE BORANE

MSC THESIS

YEŞİM ÖZTÜRK KARACAN

BOLU ABANT İZZET BAYSAL UNIVERSITY GRADUATE SCHOOL OF
NATURAL AND APPLIED SCIENCES

DEPARTMENT OF CHEMISTRY

(SUPERVISOR: PROF. DR. İZZET AMOUR MORKAN)

BOLU, AUGUST 2019

Energy, which has an important place in human life, has become the most important need in developing countries as well as in developed countries. However, energy production and consumption started to be a criterion that determines the level of development of countries. The need for energy increases day by day in parallel with the increase in population and technological developments. Today, the majority of energy resources are fossil fuels. Depending on the reasons such as the gradual decrease in fossil fuel reserves, the continuous increase in prices, the negative effects on human health and the environment; There are renewable energy sources in the world and especially in developing countries. Of these renewable alternative energy sources, hydrogen is undoubtedly the fuel of the future. Although many methods are proposed for the production of hydrogen gas, hydrolysis of alkali metal hydrides is often preferred. The use of dimethylamine borane is quite common due to the high percentage of hydrogen (wt 17%) it contains. In the appropriate solvent and catalyst environment, all of the hydrogen contained in the dimethylamine borane can be released, and in these reactions transition metal-based catalysts are generally preferred. In this thesis, heterogeneous catalyst is preferred because of its high stability and reusability properties, and copper is used as transition metal because of low cost and high amount of nature. The effect of titanium dioxide on hydrogen production performance, which is used as support material in order to increase the surface area and prevent agglomeration, was investigated in the production of hydrogen from the dimethylamine borane. In addition, the preparation, characterization analyses and the experiments of the catalytic efficacy Cu(0) NPs loaded on the surface of TiO₂ were investigated. Copper nanoparticles fixed on metal oxide UV-visible region electronic absorption spectroscopy (UV-Vis), transmission electron microscopy (TEM), Brunauer-Emmett-Teller (BET), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and infrared spectroscopy (FT-IR).

KEYWORDS: Dimethylamine borane, dehydrogenation, copper, titanium dioxide, heterogeneous catalyst, nanoparticles.

ÖZET

**DİMETİLAMİN BORANIN DEHİDROJENLENMESİNDE AKTİF BİR
KATALİZÖR OLARAK METAL NANOPARÇACIKLAR
YÜKSEK LİSANS TEZİ
YEŞİM ÖZTÜRK KARACAN
BOLU ABANT İZZET BAYSAL ÜNİVERSİTESİ
FEN BİLİMLERİ ENSTİTÜSÜ
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(TEZ DANIŞMANI: PROF. DR. İZZET AMOUR MORKAN)**

BOLU, AĞUSTOS - 2019

İnsan hayatında önemli bir yeri olan enerji, gelişmiş ülkelerde olduğu gibi gelişmekte olan ülkelerde de önemli bir ihtiyaç halini almıştır. Ayrıca enerji üretimi ve tüketimi ülkelerin gelişmişlik düzeylerini belirleyen bir ölçüt olmaya başlamıştır. Enerjiye olan ihtiyaç, nüfusun artması ve teknolojik gelişmelere paralel olarak günden güne artmaktadır. Günümüzde enerji kaynaklarının büyük çoğunluğunu fosil yakıtlar oluşturmaktadır. Fosil yakıt rezervlerinin giderek azalması, fiyatlarının sürekli artması, insan sağlığı ve çevre üzerindeki olumsuz etkileri gibi nedenlerden dolayı tüm dünya ve özellikle de gelişmekte olan ülkelerde yenilenebilir enerji kaynakları konusunda çalışmalar yapılmaktadır. Bu yenilenebilir alternatif enerji kaynakları içerisinde hidrojen şüphesiz geleceğin yakıtı olarak anılmaktadır. Hidrojen gazı üretimi için birçok metot önerilmesine rağmen, çoğunlukla alkali metal hidrürlerin hidrolizi tercih edilmektedir. İçerdiği kütlece yüksek hidrojen yüzdesi (ağırlıkça %17) sebebiyle dimetilamin boran kullanımı oldukça yaygındır. Uygun çözücü ve katalizör ortamında dimetilamin boranın içerdiği tüm hidrojen açığa çıkarılabilmekte ve bu reaksiyonlarda genellikle geçiş metal esaslı katalizörler kullanılmaktadır. Bu çalışmada, yüksek kararlılık ve tekrar kullanılabilirlik özelliklerinden dolayı heterojen katalizör tercih edilerek, düşük maliyetli ve doğada fazla miktarda bulunmasından dolayı da geçiş metali olarak bakır kullanılmıştır.

ANAHTAR KELİMELER: Dimetilamin boran, dehidrojenlenme, bakır, titanyum dioksit, heterojen katalizör, nanoparçacıklar.

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LIST OF ABBREVIATIONS AND SYMBOLS

CBN	: Carbon-boron-nitrogen
DMAB	: Dimethylamine borane
wt	: Weight
eq	: Equation
AB	: Ammonia Borane
TON	: Total Turnover Number
NPs	: Nanoparticles
BET	: Brunauer–Emmett–Teller
XRD	: X-ray Diffraction
UV-Vis	: Ultraviolet-Visible
FT-IR	: Fourier Transform Infrared Spectrophotometer
TEM	: Transmission Electron Microscopy
XPS	: X-ray Photoelectron Spectroscopy
nm	: Nanometer
°C	: Degree Celsius
mL	: Milliliter
mg	: Milligram
rpm	: Revolution per minute
min	: Minute
a.u.	: Atomic Unit
deg	: Degree
mM	: Millimolar
eV	: Electronvolt
kV	: Kilovolt
kW	: Kilowatt
P/P_o	: Sound pressure per reference pressure
h	: Hour
K	: Kelvin
TON	: Turnover number

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1. INTRODUCTION

In our planet, oil, gas, coal called as fossil fuels that are used as an energy sources are depleting with the increasing population. The extreme use of carbon-based fuels is adding enormous amount of green house gases in the atmosphere and causes to raise the temperature of the planet (Hansen, 2007). In the near future, people will begin to perceive the importance of energy sources, the worth renewable energy as opposed to getting energy from sources that don't naturally regenerate. Hydrogen is accepted as an alternative energy carrier in the depletion of fossil fuels (Züttel, 2004). Hydrogen is the most promising candidate because it has light-weight, and environmentally friendly (Feng et al., 2019). It is the most abundant element with the highest percentage in the earth and an important component of vital activities like proteins, carbonhydrates etc.

1.1 Hydrogen storage materials

Hydrogen is a reactive element because of this it is not suitable to make use of its energy. Hydrogen must be liberated from renewable energy sources and after producing, there are three steps like storage, distribution and conversion to energy. These steps can be collected under the same title which is hydrogen economy (Turner, 2004). Here, a critical point is the storage of hydrogen. It can be stored physically (e.g. compressed gas) and chemically in some solid substances e.g. metal nitrides, amines (P. Chen, Xiong, Luo, Lin, & Tan, 2002), carbon nanotubes (Bacsa, Laurent, Morishima, Suzuki, & Le Lay, 2004), carbon-boron-nitrogen compounds (Huang & Autrey, 2012). The researchs show that among solid carbon-boron-nitrogen (CBN) compounds ammonia borane, dimethylamine borane, hydrazine borane take an important place because of their low weight and high hydrogen content (Sakintuna, Lamari-Darkrim, & Hirscher, 2007). Among these substances dimethylamine borane (DMAB, Me_2NHBH_3) has been sought after as its 17% hydrogen content (wt.), stability at room temperature and nontoxicity (Akbayrak, Tonbul, & Özkar, 2016). Moreover, DMAB can liberate 1 equivalent H_2 in the

presence of proper catalyst shown in equation 1 (eq. 1) (van den Berg & Areán, 2008).



DMAB undergoes thermally stimulated hydrogen generation at 130 °C in the solution to obtain the cyclic ammonia borane (AB) dimer $[\text{Me}_2\text{N-BH}_2]_2$ (Jaska, Temple, Lough, & Manners, 2003). In order for performing H_2 evolution of DMAB under suitable condition, a proper catalyst is required.

1.2 Definition and classification of catalysis

A catalyst that is used in a reaction has some features as following:

- accelerates the speed of a reaction, and it also improves the yield of the intended product.
- takes part in the reaction even though it itself is not consumed or used up during the reaction.
- makes the reaction faster by supplying an alternative pathway by reducing activation energy.
- is reaction-specific. It may not be efficient in another reaction even if the two reactions are of similar type.
- accelerates both the forward and the reverse reactions in a reversible reaction.

So, the inclusion of a catalyst does not alter the equilibrium constant of a reversible reaction. Figure 1.1 is an example for the effects of a catalyst to a reaction mechanism.

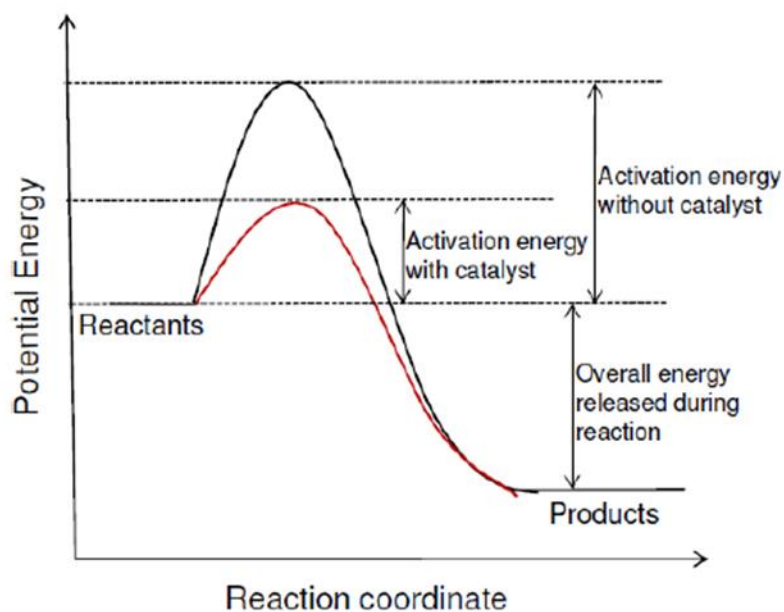


Figure 1.1. Energy diagram of an exothermic chemical reaction showing the difference in the energy of activation in two types reactions as a catalyzed and an uncatalyzed ones

In order to determine the efficiency of a catalyst TTON (total turnover number) is evaluated with the following equation 2:

$$\text{TTON} = \frac{\text{mol of product}}{\text{mol of catalyst}} \quad (2)$$

For the catalytic efficiency TOF (turnover frequency) is calculated as below: For instance, when the chemical reaction of the change of A to the product B in the existence of catalyst with a rate of v occurs, the below relation is used for TOF value



Catalysts can be classified in three groups as shown in Figure 1.2.

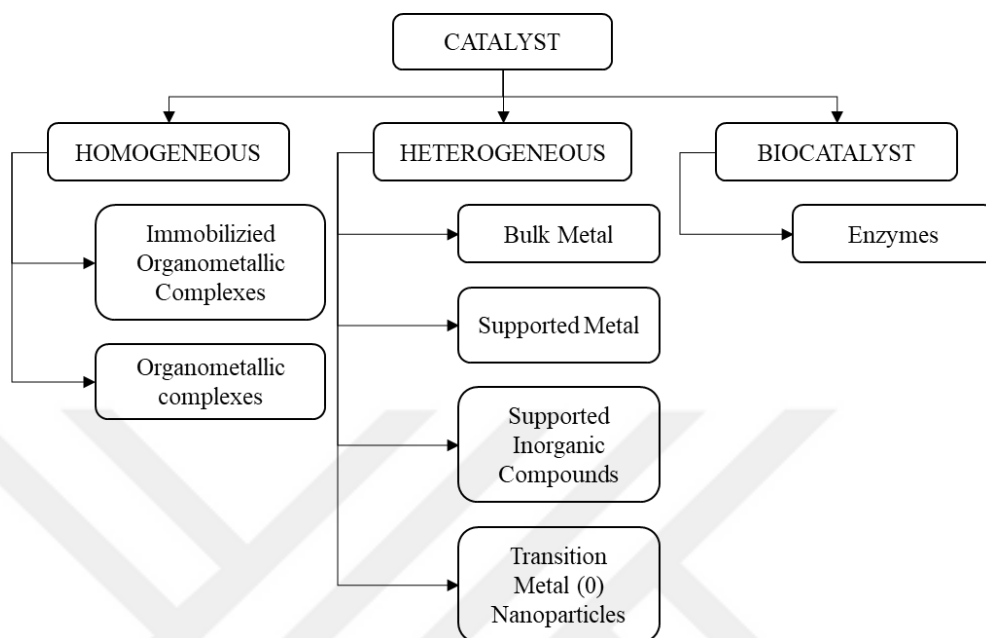


Figure 1.2. The classification of catalysts

1.3 Transition metals as catalyst

In a catalytic reaction, nanoclusters that are monodispersed particles that have less than 10 nm diameter in general (Aiken III, Lin, & Finke, 1996) can be used as a catalyst. Metal nanocrystals have unrivalled chemical and physical characteristics. This can be seen in Figure 1.3. It indicates that the large numbers of the metal atoms lie on the surface, which means that the reducing in particle size effects the increasing in the atom numbers on surface (Schmid, 1990). Thus, the activity of catalyst is increased.

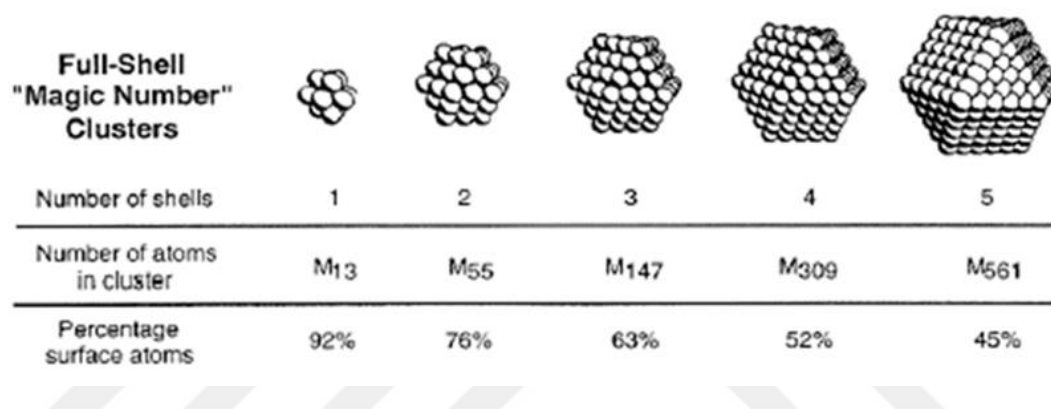


Figure 1.3. The correlation between the total number of atoms in clusters and the proportion of surface atoms (Schmid, 1990)

Besides, homogeneous and heterogeneous transition metal catalysts have been performed in many catalytic reactions of dehydrogenation of DMAB (Tanyıldızı, Morkan, & Özkar, 2017). Especially, because of their catalytic activity, the using of heterogeneous catalysts has been became popular. In addition, heterogeneous catalysts can be separated easily from the reaction media (Thomas, Thomas, Anderson, & Boudart, 1997) and minimizing the grain size of nonhomogeneous catalyst can support a remarkable going up in its activity as the fraction of surface atoms raising (Zahmakıran & Özkar, 2009).

Some of transition metals like Pt, Pd, Rh, Ru are expensive but, copper that is non-noble transition metal is low-cost and most abundant in Earth. Enhancement of the non-noble transition metal activity, solid supports can be used because copper-bare nanoparticles show larger particles during reaction (Fang et al., 2018). In

Table 1.1. various catalysts were studied in hydrogen generation of DMAB in solution of toluene.

Table 1.1. H₂ generation of DMAB in solution of toluene to yield [Me₂N-BH₂]₂ using different catalysts of transition metals (Jaska et al., 2003)

Catalyst	T(°C)	Mol % catalyst	T(h)	Yield (%)
None	45		168	0
[Rh(1,5-cod)(μ-Cl)] ₂	25	0.5	8	100
[Rh(1,5-cod)(μ-Cl)] ₂	45	0.5	2	90
[Rh(1,5-cod)(μ-Cl)] ₂	25	5.0	<2	100
[Rh(1,5-cod)(μ-Cl)] ₂	45	5.0	<2	100
[Ir(1,5-cod)(μ-Cl)] ₂	25	0.5	136	95
RhCl ₃	25	0.5	22.5	90
RhCl ₃ .3H ₂ O	25	0.5	64	90
IrCl ₃	25	0.5	160	25
RhCl(PPh ₃) ₃	25	0.5	44	95
[Cp*Rh(μ-Cl)Cl] ₂	25	0.5	112	100
[Rh(1,5-cod) ₂]OTf	25	0.5	7.5	95
[Rh(1,5-cod)(dmpe)]PF ₆	25	0.5	112	95
HRh(CO)(PPh ₃) ₃	25	0.5	160	5
<i>trans</i> -RuMe ₂ (PMe ₃) ₄	25	0.5	16	100
<i>trans</i> -PdCl ₂ (P(<i>o</i> -tolyl) ₃) ₂	25	0.5	160	20
Pd/C (10%)	25	0.5	68	95
Cp ₂ TiMe ₂	25	0.5	160	0
B(C ₆ F ₅) ₃	25	0.5	96	0

According to the Table 1.1., in the absence of catalyst, H₂ generation of DMAB not make an observation by self. The usage of transition metal complexes showed awesome diversity in efficiency hinging on reaction temperature, time and mol percentage of catalyst.

1.4 Support material for stabilization of transition metal

In the hydrogen generation of DMAB, transition metal nanoparticles are not stable thermodynamically as they have high surface energies and high surface areas. During a catalytic reaction, metal catalysts can be agglomerated and to prevent this problem, metal oxides can be used as solid supporting materials (Metin, Özkar, & Sun, 2010).

One of metal oxides, TiO_2 with large surface area ranging from 10 to 300 m^2/g , can be used as a support material to prevent the aggregation of metal NPs. Due to its nontoxicity and high stability characteristics, it is a good catalyst for environmental applications (Varghese, Paulose, LaTempa, & Grimes, 2009).

In this study, we state the preparation, some tests and characterization of the Cu(0) nanoparticles (NPs) that were doped on the surface of TiO_2 nanopowders by using wet impregnation process. The TOF of Cu(0)/ TiO_2 is four times more when compared with copper-bare nanoparticles in obtaining 1 equivalent of pure $\text{H}_2/(\text{CH}_3)_2\text{NHBH}_3$ (DMAB) at $60.0 \pm 0.5^\circ\text{C}$. The applied tests which are catalytic lifetime, leaching and reusability show that Cu(0)/ TiO_2 is significantly productive catalyst in hydrogen generation from dimethylamine borane.

2. AIM AND SCOPE

In the world the most of the energy needs are met from fossil sources and the resources may be sufficient for future generations. However, since fossil fuels will be depleted over time, and pollute the nature, people have started to search a new way for renewable energy sources (S. Chen, Xiao, Liu, & Li, 2018; Dresselhaus & Thomas, 2001). Among renewable energy sources, there is a growing considerable interest in hydrogen energy due to its non-toxicity, renewability and being more efficient than fossil fuels (Christopher, Dimitrios, & Science, 2012). The researchs reveal that solid carbon-boron-nitrogen (CBN) take a significant place because of their low in weight and high content of hydrogen (Sakintuna et al., 2007). As one of the hydrogen carrier materials, dimethylamine borane contains 17% wt. of hydrogen and can be liberated 1 equivalent of H₂ in the existence of a proper catalyst (Sen, Kuzu, Demir, Akocak, & Sen, 2017).

It is quite common to use transition metals as catalysts for the hydrogen generation of DMAB. Copper, which is a transition metal, is inexpensive and most abundant in nature and has played a major role in the selection of the catalyst as the active ingredient. However, the use of transition metal as the catalyst raises the problem of agglomeration and the efficiency of the catalyst reduces because of this agglomeration. The use of support material to raise the activity of the metal used by preventing agglomeration is considered the right choice. Metal oxides are commonly used as support materials and titanium dioxide is very common in this field. In this study, the interaction of copper and titanium dioxide was observed and copper loaded titanium dioxide was used as catalyst in the light of positive results.

The catalyst synthesized in situ was characterized by TEM, XRD, XPS, UV-Vis, FT-IR and BET technique. The results obtained were interpreted and compared with the literature data and Cu(0) NPs doped on TiO₂ surface were reduced in the presence of DMAB to play a role as a catalyst in the liberation of 1 equivalent of H₂, the efficiency of the catalyst was investigated and given in Section 3. As a conclusion, according to the studies for the hydrogen generation of DMAB in the presence of Cu(0)/TiO₂ catalyst, when TOF value as 59.9 h⁻¹ was compared with

the other studies of Cu(0) NPs in the literature, the results were observed to be an important position.



3. EXPERIMENTAL SECTION

3.1 Materials

In the study, copper bis(2,2,6,6-tetramethyl-3,5-heptanedionate) ($\text{Cu}(\text{OCC}(\text{CH}_3)_3\text{CHCOC}(\text{CH}_3)_3)_2$, 99%), dimethylamine borane ($(\text{CH}_3)_2\text{NHBH}_3$, DMAB, 97%), titania (TiO_2 , anatase, spec. surface area $65\text{-}75\text{ m}^2/\text{g}$ (BET) as a support, toluene ($\text{C}_6\text{H}_5\text{CH}_3$, anhydrous, 99.8%) as a solvent were used and purchased from Sigma Aldrich. Toluene was made purify under N_2 atmosphere by a specific system that contains metallic sodium. All labwares and magnetic stir bar which is teflon coated rinsed with deionized water and acetone before making dry in the oven at $120\text{ }^\circ\text{C}$.

3.2 Production of Cu(0) NPs and concomitant catalytic H_2 generation of DMAB

Schlenk system was used in all catalytic experiments to prevent the oxidation of metal during the reactions. Typical schlenk tube was vacuumed at least 30 min before using in catalytic reaction and purged with dry nitrogen gas. Reaction tube was circulated with water at a constant temperature. The outgasing part of the schlenk was linked to a graduated column filled with water. The bubbler with octane was utilized to follow H_2 gas evolution from the reaction medium. Stock solution of copper(II) ions which was containing 10% by weight (189.9 mg of copper(II) complex) was prepared in 25 ml of fresh toluene. In a typical reaction, 5.74 mL of stock solution and 2.16 mL of toluene were added into the reaction medium containing 100 mg of titania. Then, the system was set to 60°C by circulating the water around the reaction flask. 60.1 mg of DMAB dissolved in 3 ml of fresh toluene and injected to reaction media by a gastight syringe. H_2 liberated from the reaction was measured by following the displacement of water in the graduated column. When there is no hydrogen evolved from reaction, the experiment was stopped

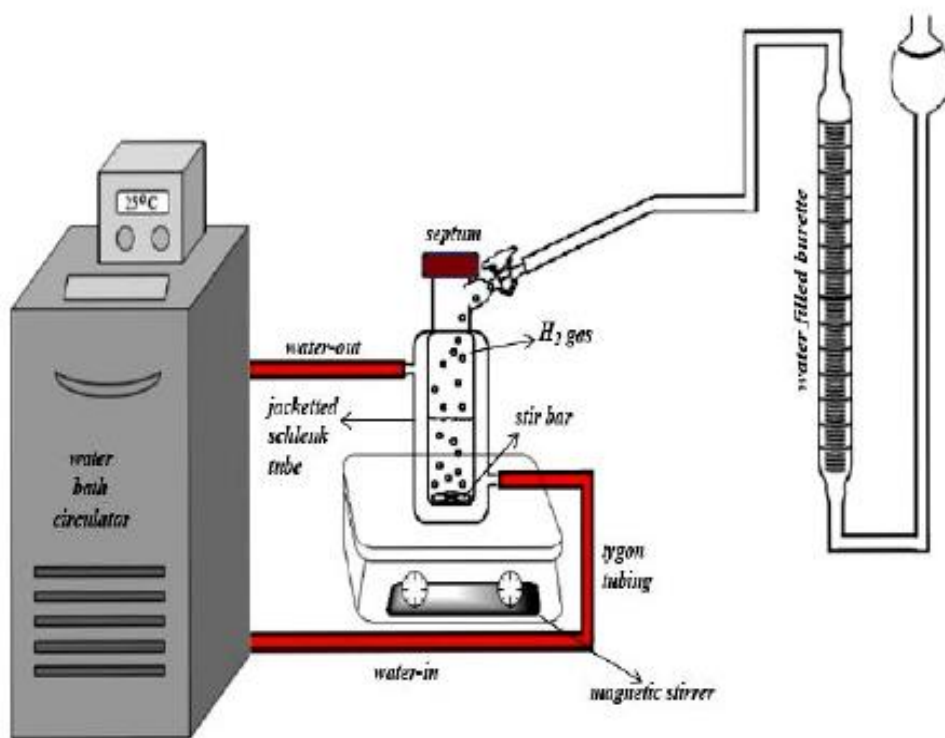


Figure 3.1. Experimental mechanism used for specifying H₂ generation through reactions

3.3 Specification of the loading of most dynamic copper for Cu(0)/TiO₂ in the hydrogen generation of DMAB

To determine the best effective copper on the surface of titania for the catalyst several loadings of copper were tested from 4.0 to 7.0 wt. in percentage beginning with 6.56 mM Cu and 100 mM DMAB in 10 mL solution of toluene at 60.0 ± 0.5 °C. The high efficiency was attained by using 6.0 wt.% copper impregnated on 100 mg TiO₂. In all of studies, 6.0 wt.% Cu was used unless anything else reported.

3.4 Preparation method of Cu²⁺ ion loaded on nanotitania surface

An aliquot solution of copper(II) ions was taken from the stock solution and added into schlenk tube including 100 mg of nanotitania. The resulting mixture was

stirred for 1 h to make sure an absolute adsorption of Cu^{2+} ions on the nanotitania at 25.0 ± 0.5 °C.

3.5 Specification of activation variances for H_2 evolution of DMAB catalyzed by $\text{Cu}(0)/\text{TiO}_2$

To find activation variances, catalytic hydrogen generation experiment of 100 mM of DMAB was studied starting with 10.04 mM of Cu (6.0 wt.%) at different temperatures (30, 40, 50, 60 °C). The rate constants of the catalytic reactions were calculated and used to estimate the energy of activation, enthalpy and change of entropy of the reaction by drawing Eyring–Polanyi plots.

3.6 Kinetic efficiency and leaching test of $\text{Cu}(0)/\text{TiO}_2$ in the dehydrogenation of DMAB

Afterwards the first run of hydrogen generation, the reaction flask containing 6 wt.% Cu/TiO_2 was settled down of copper(0) nanoparticles. Either the separated solid and liquid part were tested using previous procedure in dehydrogenation reaction of DMAB. The filtrate solution was silent for dehydrogenation reaction indicates that no leaching copper metal to the reaction medium during the dehydrogenation.

3.7 Recoverability of TiO_2 provided $\text{Cu}(0)$ NPs in the catalytic H_2 generation of DMAB

After the complete dehydrogenation of DMAB, 100 mM DMAB (60.12 mg) was put into to the flask without moving away nothing from the flask. This was repeated until completely 1 mol of H_2 releasing observed. This test is the answer of that question “ How many times the catalyst can help the releasing of 1 mol of hydrogen gas from DMAB?”.

3.8 Specification of catalytic time of life of Cu(0)/TiO₂ in the H₂ generation of DMAB

In order to calculate the catalytic time of life of Cu(0)/TiO₂ in the hydrogen generation of DMAB, the hydrogen evolution reaction was started containing 10.04 mM Cu(II), 100 mg TiO₂ and 150 mg DMAB in 10 mL toluene. The addition of DMAB was repeated till no more hydrogen released.

4. RESULTS AND DISCUSSIONS

4.1 Cu(0)/TiO₂ Nanoparticles

4.1.1 In situ formation of Cu(0) NPs fixed on TiO₂

In the hydrogen generation of DMAB in toluene solution, copper bis(2,2,6,6-tetramethyl-3,5-heptanedionate) was used as a precursor catalyst. In situ occurrence of Cu(0) NPs by reducing Cu²⁺ ions and interdependent H₂ evolution from the catalytical hydrogen generation of DMAB occurred in the same reaction media. As shown in Figure 4.1, a fast hydrogen releasing initiates instantly without induction time, when DMAB is put in to the toluene solution of copper bis(2,2,6,6-tetramethyl-3,5-heptanedionate) at 60.0 ± 0.5 °C.

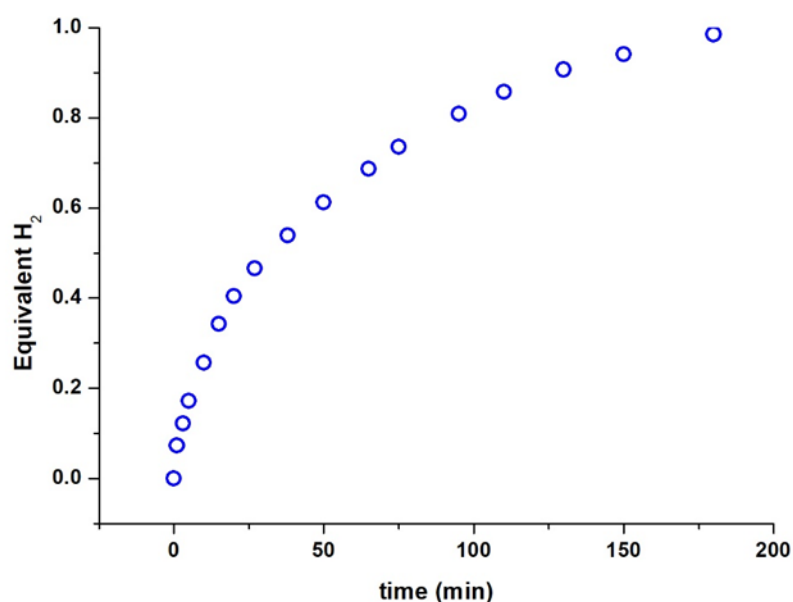


Figure 4.1. The graph of mole H₂/mole of DMAB versus time for hydrogen generation of DMAB beginning in 10.0 mL solution of toluene 10.04 mM Cu, 100 mM DMAB at 60.0 ± 0.5 °C.

However, the H₂ liberation decelerates after the liberation of approximately 0.6 equivalence H₂ per 1 mole of DMAB referring deactivation of the catalyst occurred. The solution color changes from greenish-blue to dark red in less than ten minutes referring the occurrence of Cu(0) NPs in the reduction of Cu(OCC(CH₃)₃CHCOC(CH₃)₃)₂. The changing in color signalize that the reaction can be followed by using UV-vis spectrophotometer. The starting solution including 10 mM Cu²⁺ ions in toluene solution shows an absorption band which is intense at $\lambda_{\text{max}} = 301$ nm and a broad absorption band at $\lambda_{\text{max}} = 680$ nm which refers to d-d transition when it is compared with the literature (Carlin, 1969) in the following spectrum (Figure 4.2).

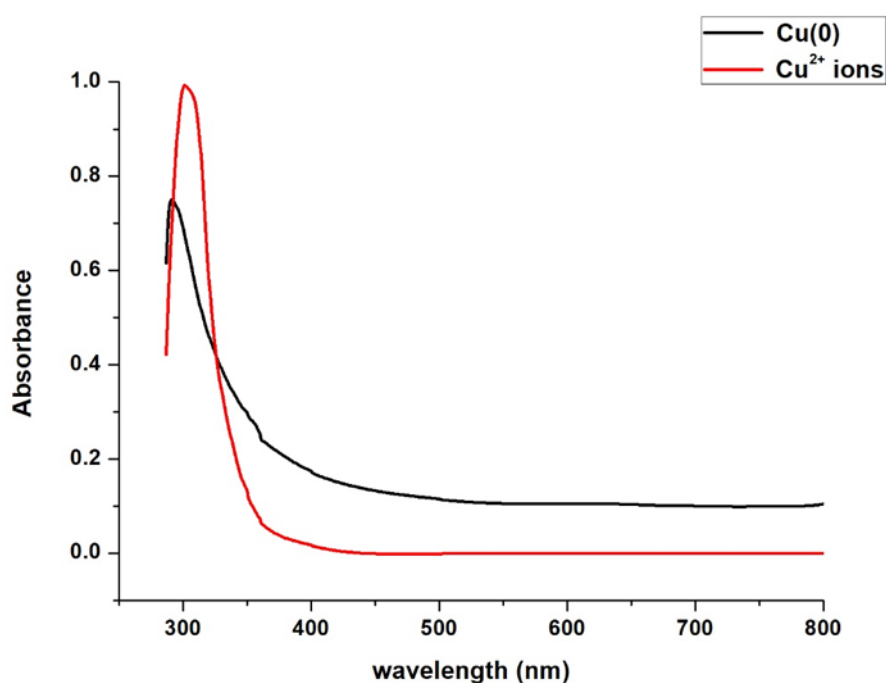


Figure 4.2. UV-Vis spectrums represent that the solutions including 10 mM Cu²⁺ in toluene before addition 100 mM of DMAB in the reaction flask (red line) and Cu(0) NPs after addition DMAB solution (black line)

When DMAB is added to the reaction media, this spectral property changes suddenly and a new band appears at 291 nm.

Moreover, the existence of Cu(0) NPs can be proved by using FTIR spectroscopy. In figure 4.3, there are aliphatic carbons peaks in the Cu(0)/TiO₂

spectrum, it can be said that these peaks come from the precursor substance which is called as copper bis(2,2,6,6-tetramethyl-3,5-heptanedionate). In other words, these aliphatic carbon peaks represent the occurrence of Cu(0) NPs without no change in the structure of TiO₂.

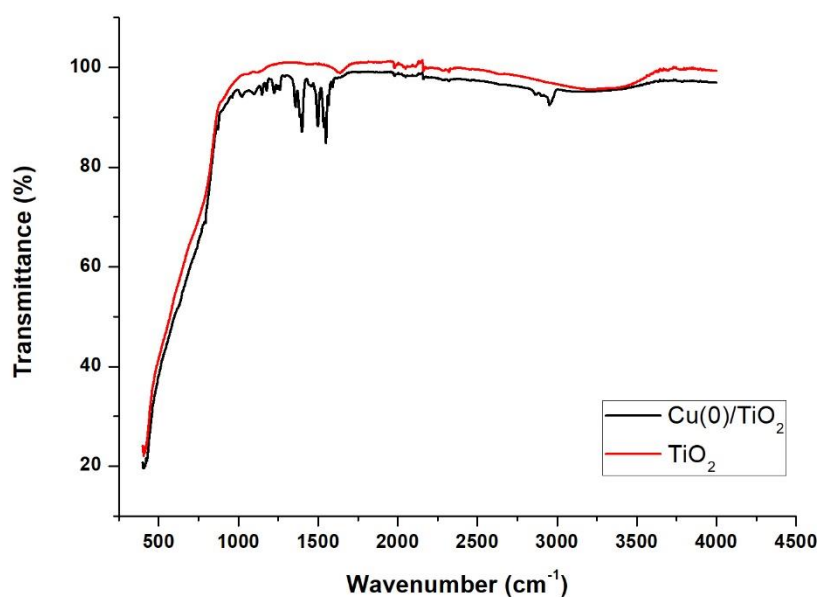


Figure 4.3. FTIR spectrums of Cu(0)/TiO₂ (black line) and pure TiO₂ (red line)

Figure 4.4 is an another evidence for the decreasing in catalytical activity of Cu(0) NPs. In order to prevent the agglomeration of that Cu(0) NPs they were loaded on TiO₂ surface. Cu(0) NPs loaded on nanotitania (Cu(0)/TiO₂) were occurred in situ by reducing Cu²⁺ ions doped on nanotitania (Cu²⁺/TiO₂) in the catalytic hydrogen generation of DMAB. Both the forming of Cu(0) NPs and catalytic hydrogen generation of DMAB occur simultaneously, when DMAB is added to the reaction media. These formations of DMAB and Cu(0) NPs was observed by recording the volume of released H₂ evolved. Then, it was changed into the equivalent H₂ per mole of DMAB with the ratio of 1:1 H₂/((CH₃)₂NHBH₃) (eq. 1). Figure 4.4. is the graph of mol H₂/mol DMAB versus time for the hydrogen generation of DMAB beginning with Cu²⁺/TiO₂ and 100 mM of DMAB in 10 mL solution of toluene at 60.0 ± 0.5 °C.

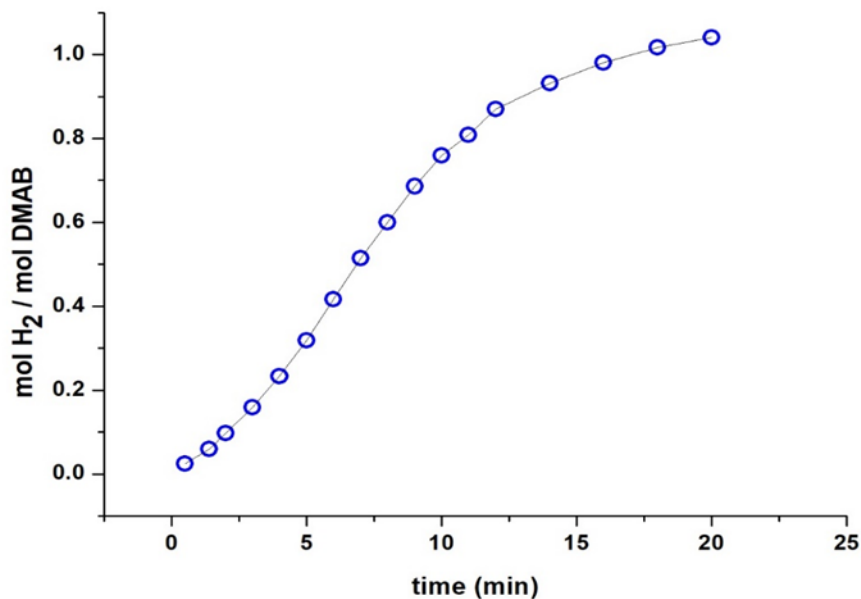


Figure 4.4. The liberation of mol H₂/mol DMAB versus time plot for the hydrogen generation of DMAB starting with Cu²⁺/TiO₂ precatalyst 10.04 mM and 100 mM DMAB at 60.0 ± 0.5 °C.

In the Figure 4.3. the sigmodial curve of the dehydrogenation is so forceful proof of the obtaining of metal(0) NPs catalyst.

4.1.2 Characterisation of Cu(0) NPs loaded on TiO₂

Copper(0) NPs impregnated on TiO₂, in situ occurred by the reduction of Cu²⁺ ions along the hydrogen generation of DMAB, were taken from the solution and characterized by using XRD, TEM, XPS, BET and FT-IR techniques.

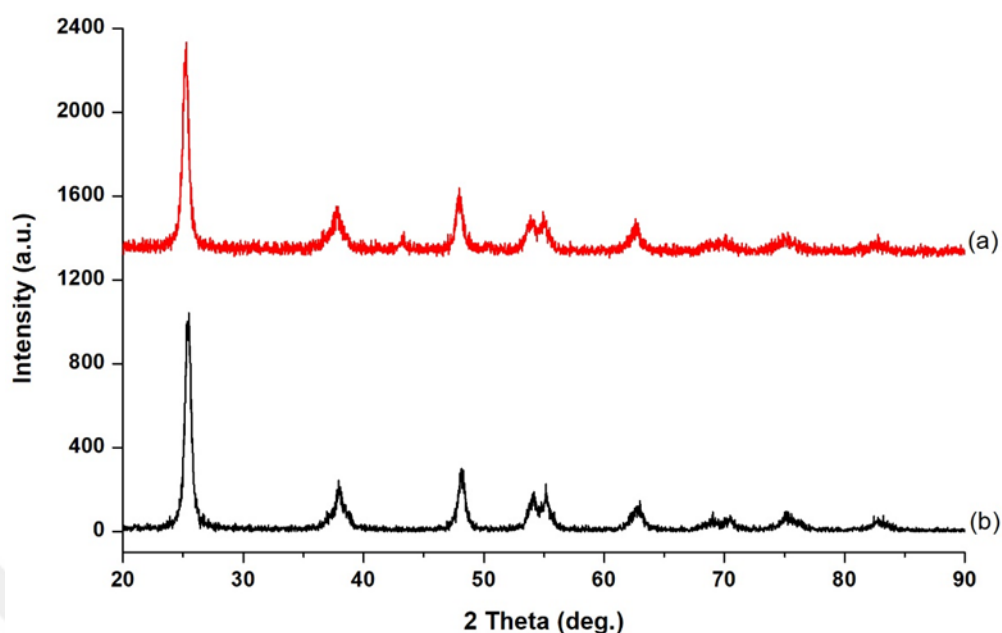


Figure 4.5. XRD patterns of powder (a) Cu(0)/TiO₂ and (b) pure TiO₂ including 6.0% Cu loading

X-ray diffraction; is a qualitative analysis that gives information about the crystallographic structure, and physical properties of materials, chemical content (Fernandes, 2010). It is a widely used method for the identification of solids and the determination of crystals in their structures. Especially, it is used to understand the changes in the crystal structure of the support material which is TiO₂ affected by Cu loading (Kavitha, Ramesh, & Geetha, 2016). XRD analysis was performed in the range of $2\theta=10-90^\circ$ for TiO₂ and Cu(0)/TiO₂. The XRD patterns of Cu(0)/TiO₂ and pure TiO₂ with a copper loading 6.0% wt. Cu is plotted in Figure 4.5. as a and b respectively. The distinctive peaks of the anatase phase of TiO₂ (JCPDS card no. 21-1272) NPs at 25.2° , 38.54° , 48.4° , 53.9° , 55.0° , 62.5° , 68.7° , 70.0° , 76.0° , 83.1° designated to the (101), (112), (200), (105), (211), (204), (220), (215), (301), (312) reflections of TiO₂. The numbers in the parenthesis represent the hkl values. This refers that TiO₂ NPs continue its crystallinity after loading Cu NPs during the hydrogen generation of DMAB. Thus, the conclusion is that copper loading does not affect the TiO₂ structure as there is no refraction peak which would be ascribable to Cu(0) NPs. The average crystallite size were calculated as 19.5 nm and 20.9 nm for

pure TiO₂ and Cu(0)/TiO₂ with 6.0% Cu loading respectively according to Debye Scherrer Equation (eq 4).:

$$D = K\lambda / \beta \cos\theta \quad (4)$$

where λ is wavelength of CuK α source, K (the Scherrer constant) depends on the how the width is evaluated, the shape of the crystal, and the size distribution, β is peak width (Speakman, 2019).

In order to calculate the particle size of copper NPs supported on the nanotitania surface, TEM was performed. Figure 4.6. indicates the images of TEM of Cu(0)/TiO₂ with loading 6.0% Cu that was taken after the catalytic reaction. To make the histogram of Cu(0) NPs, from TEM images more than 100 non-touching particles were measured. As seen from TEM images, the support supplies a large partition of active surface sites for Cu(0) NPs catalytically.

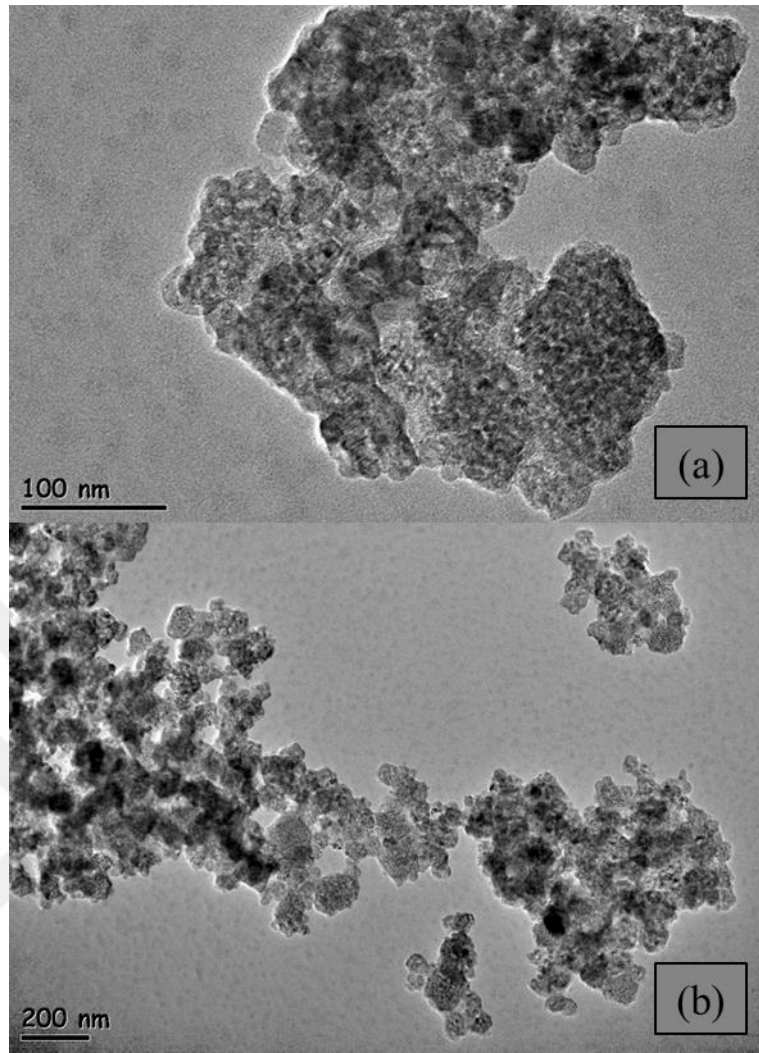


Figure 4.6. The images of TEM of Cu(0)/TiO₂ with loading 6.0% wt.copper in two different upsizing scales (a) and (b).

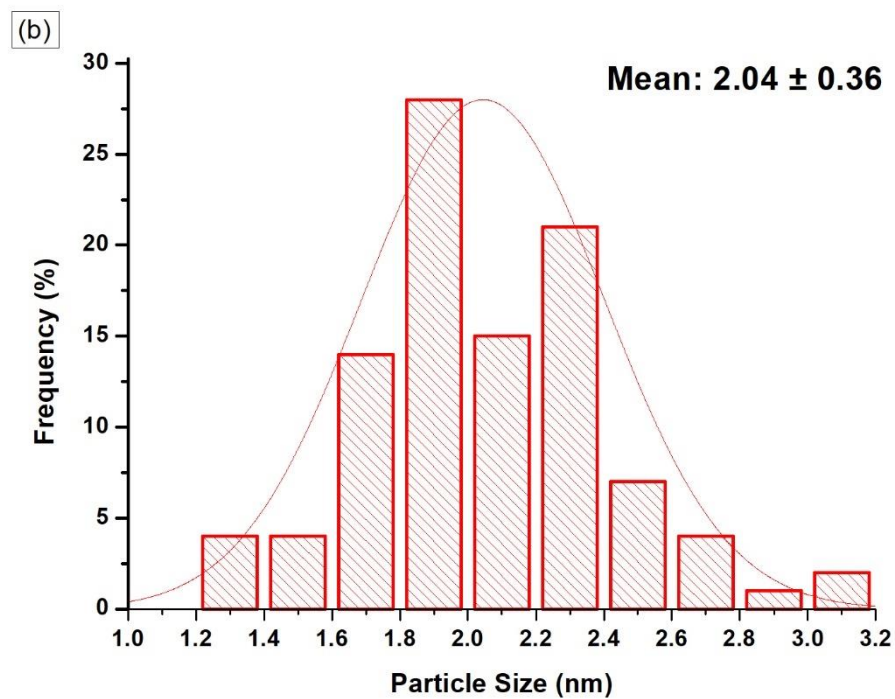
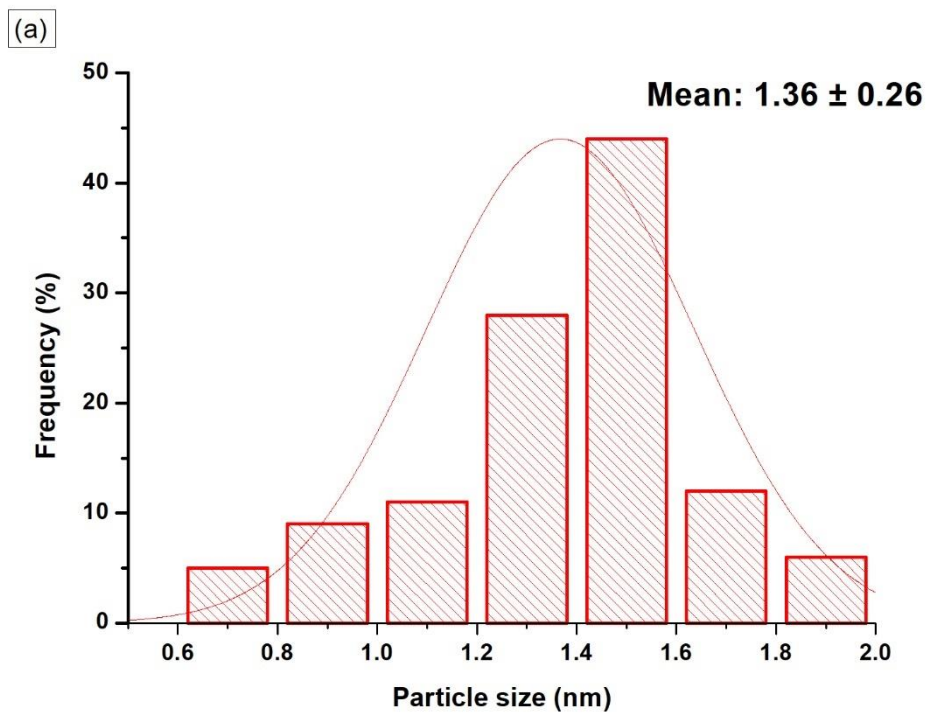


Figure 4.7. (a) the distribution of particle size histogram for Cu(0) for the first run (b) the distribution of particle size histogram for Cu(0) for the second run

In Figure 4.7a, the histogram shows the dispersion of the Cu(0) NPs on TiO₂ surface with the range 0.6-2.0 nm and Figure 4.7b indicates the Cu(0) NPs dispersion after adding second batch of DMAB with the range of 1.2-3.2 nm. For the first and second run, the average particle sizes were measured as 1.36±0.36 and 2.04±0.36 nm respectively. BET technique that is another way to show the presence of Cu(0) NPs was performed according to the capacity of N₂ adsorption and desorption of the samples as in the Figure 4.8. and the surface areas of TiO₂ and Cu(0)/TiO₂ containing 6.0% wt. copper was determined as 44 m²/g and 109 m²/g respectively. The raise in TiO₂ surface area which has Cu(0) loading refers the existence of Cu(0) NPs on the surface of TiO₂. This raise in the surface area of the support material loading by 6.0% wt Cu can be attributed to the occurrence of small copper NPs, which are weakly bound on the TiO₂ surface. Thus, the occurrence of Cu(0) NPs does not lead to a remarkable content of the TiO₂ surface but generates excess surface area (Kalkan, Akbayrak, & Özkar, 2017).

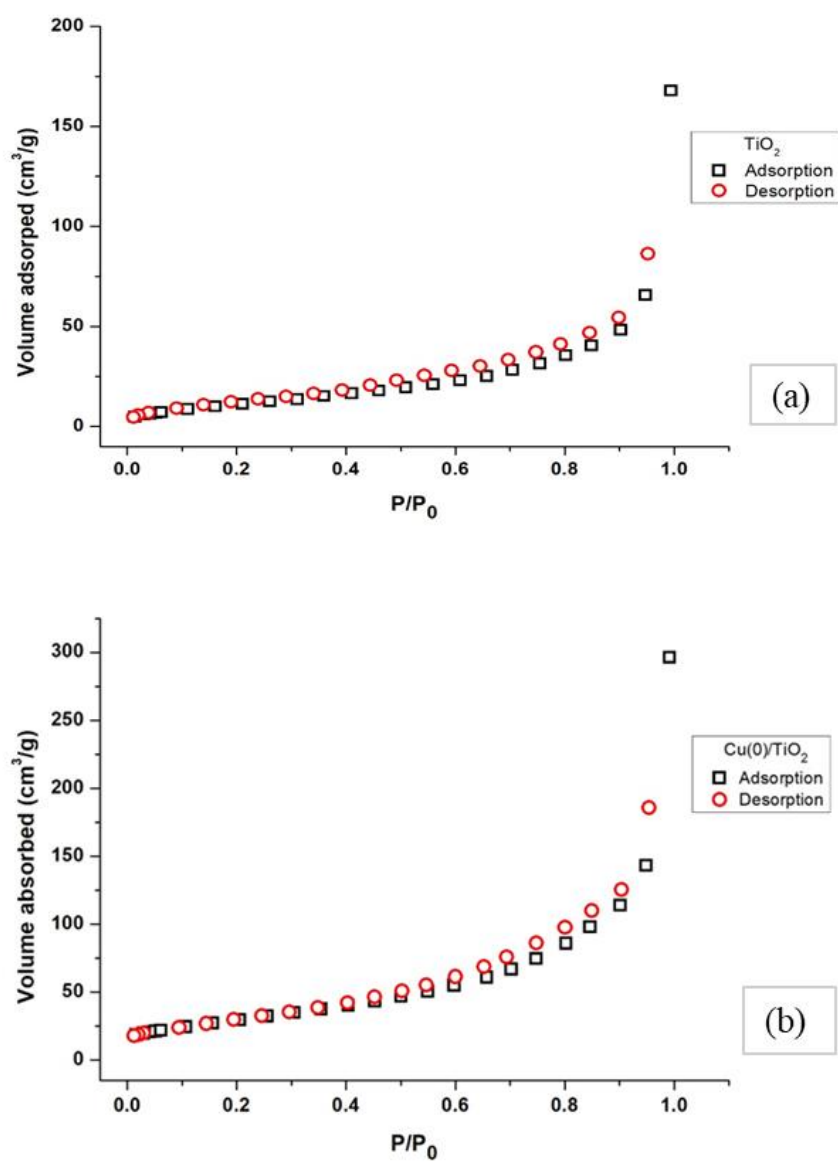


Figure 4.8. N₂ adsorption-desorption isotherms of (a) TiO₂ and (b) Cu(0)/TiO₂

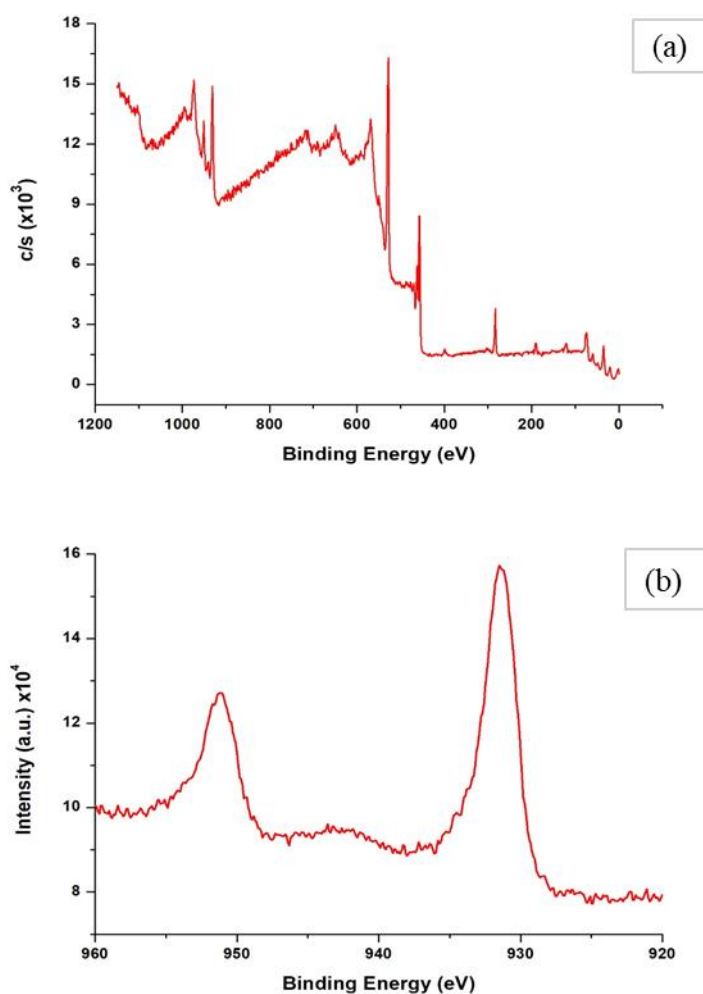


Figure 4.9. (a) The survey scan XPS spectra of Cu(0)/TiO₂ with the loading of wt. 6.0% copper (b) the high resolution scan of Cu 2p band.

In order to analyse the surface property of Cu(0)/TiO₂ NPs and the oxidation potential of copper, XPS characterization (Figure 4.8) was studied. As a result of the surface scan XPS spectrum which is including 6.0% weight of copper it can be concluded that only copper element is detected in the environment in Figure 4.9a. During the analysis, copper oxides (CuO and Cu₂O) can be occurred due to contacting with air (Ghodselahe, Vesaghi, Shafiekhani, Baghizadeh, & Lameii, 2008). Moreover, the high resolution spectra with 6.0% wt. of copper loading samples are shown in Figure 4.9b. In this spectra, the two peaks are depicted for Cu 2p core of the catalyst (Cu(0)/TiO₂) at 933 and 952 eV which are referred to Cu(II) 2p_{3/2} and 2p_{1/2} respectively (Tanyıldızı et al., 2017).

4.1.3 Catalytic activity of Cu(0)/TiO₂ in hydrogen generation of DMAB

In order to determine the catalytic efficiency of the support material which is called as nanotitania in hydrogen generation of DMAB, firstly a checking experiment was studied starting with 1.0 mmol DMAB and 100 mg of nanopowder of TiO₂ in 10 mL of toluene solution at 60.0 ± 0.5 °C. After 3 hours, no hydrogen gas releasing was observed referring that the support material is inactive for the dehydrogenation of DMAB. Next, by following the same procedure as in the control experiment, the copper loading with the range 4-7% wt. and 100 mg TiO₂ was studied in 10 mL solution of toluene at 60.0 ± 0.5 °C. According to the results of these experiments, Cu(0) NPs was determined to be significantly effective catalyst in hydrogen generation of DMAB. Figure 4.10a refers the mol H₂ / mol DMAB versus time μ s bound up with the copper loading in the range 4-7% wt. of Cu(0)/TiO₂ for the dehydrogenation of DMAB (100 mM) at 60.0 ± 0.5 °C.

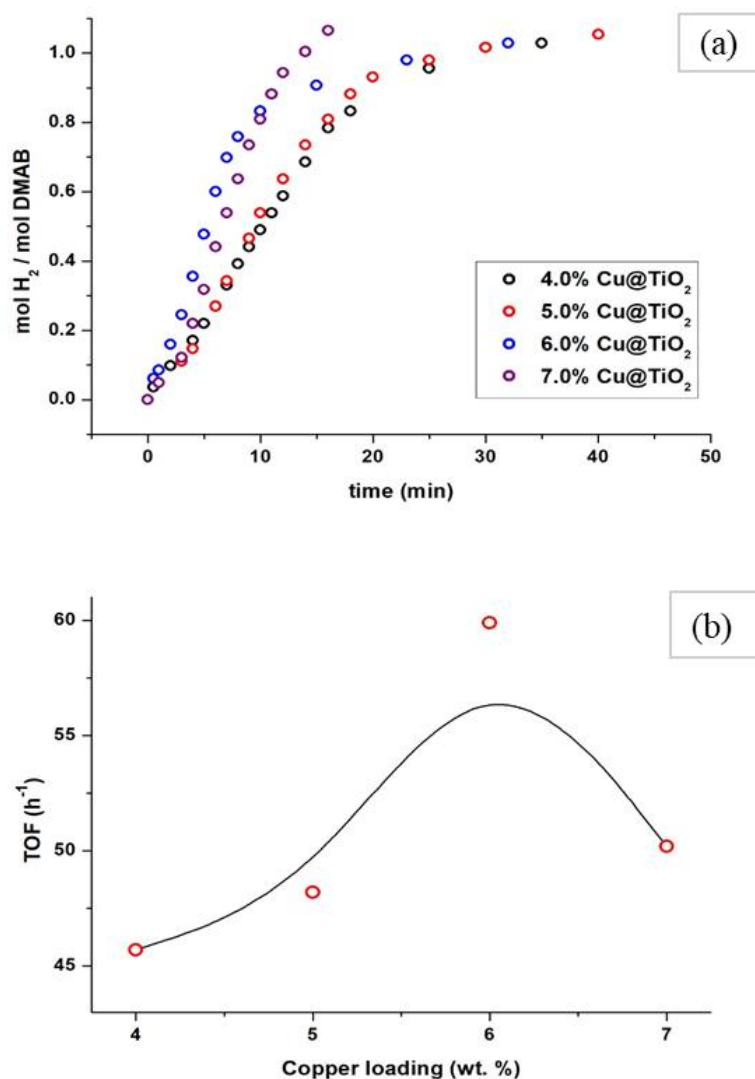


Figure 4.10. (a) mol H₂ / mol DMAB versus time graph depending on the copper loading in the range 4-7% wt of Cu(0)/TiO₂ for the hydrogen generation of DMAB (100 mM) at 60.0 ± 0.5 °C. (b) TOF values of the catalyst including copper loadings in the range 4-7% wt.

The turnover frequency (TOF) values were evaluated by concerning the linear part of the lines of the slope of each plot of the different copper loading and recorded as 45.7, 48.2, 59.9 and 50.2 h⁻¹ for Cu(0)/TiO₂ catalysts including 4.0, 5.0, 6.0, and 7.0 Cu respectively. The plot of TOF versus copper loading shows that the catalytical efficiency of Cu(0) NPs loaded on the nanopowders of titania in the generation of hydrogen of DMAB at 60.0 ± 0.5 °C (Figure 4.10b). As a result, the highest TOF value that is 59.9 h⁻¹ was succeeded at the end of the experiment containing 6.0% wt.

copper loading on the surface of titania. Over 6.0% copper loading, the catalytical efficiency of the used catalyst reduces with rising copper loading most likely because of the agglomeration of the copper NPs. When all the results were examined, 6.0% wt. of copper loading was determined that the best result was taken in this study.

After that, in order to evaluate the order of reaction and the formation rate of H₂, the catalytic hydrogen generation of DMAB was performed including various copper concentrations (5.02, 7.54, 10.04, and 12.60 mM) at 60.0 ± 0.5 °C (Figure 4.11a). To calculate the occurrence rate of H₂, the linear part of the each line was taken in consideration. As shown in the Figure 4.11b, the slope of the linear line was evaluated as 1.39 that means the order of the hydrogen generation reaction is first in compliance with the concentrations of the catalysts.

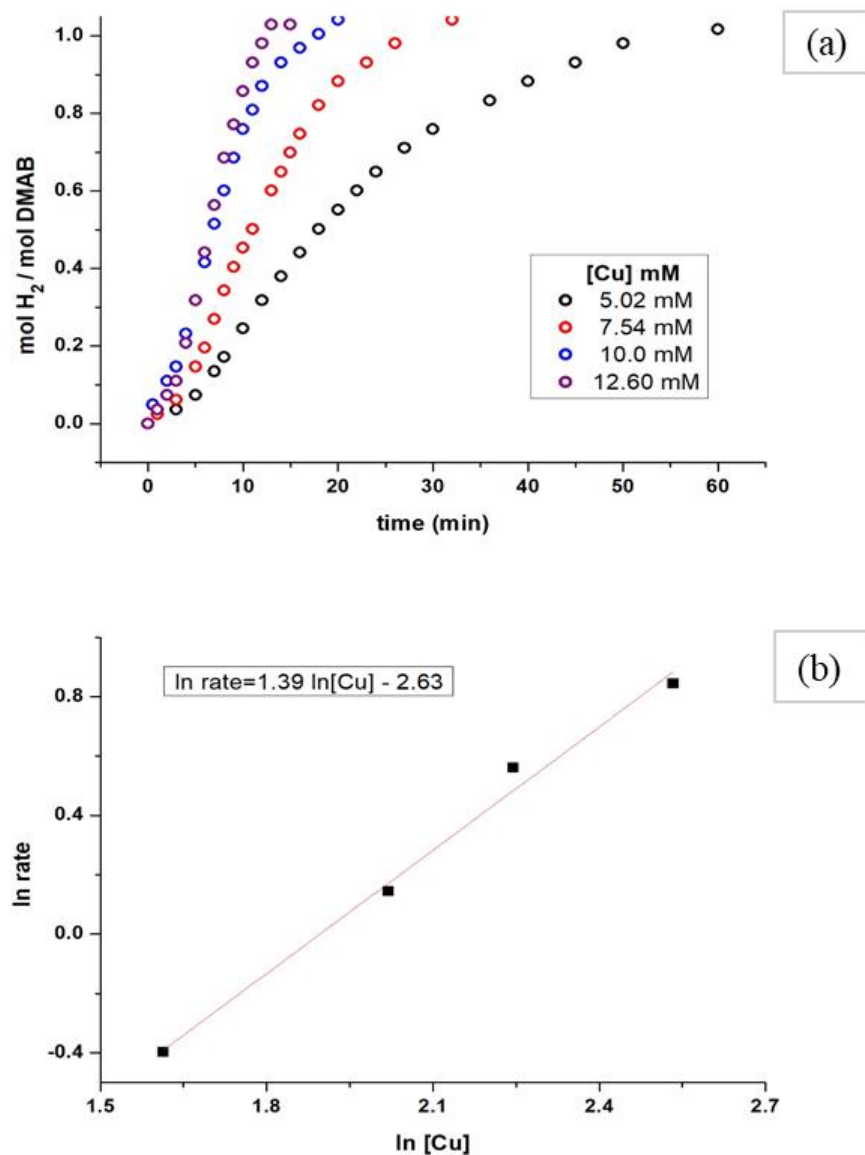


Figure 4.11. (a) 1 mol H_2 per 1 mol DMAB versus time graph depending on the different copper concentrations in $\text{Cu}(0)/\text{TiO}_2$ for the hydrogen generation of DMAB (100 mM) at 60.0 ± 0.5 °C. (b) The plot of H_2 formation rate versus copper concentration where both in logarithmic scale.

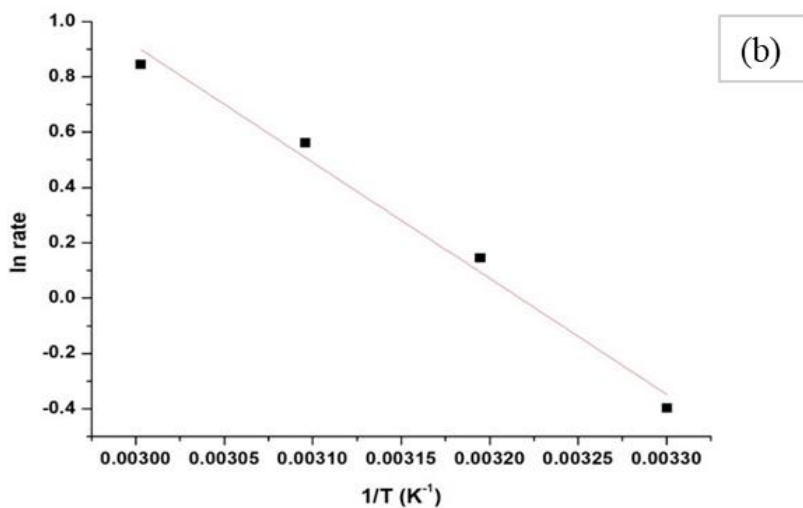
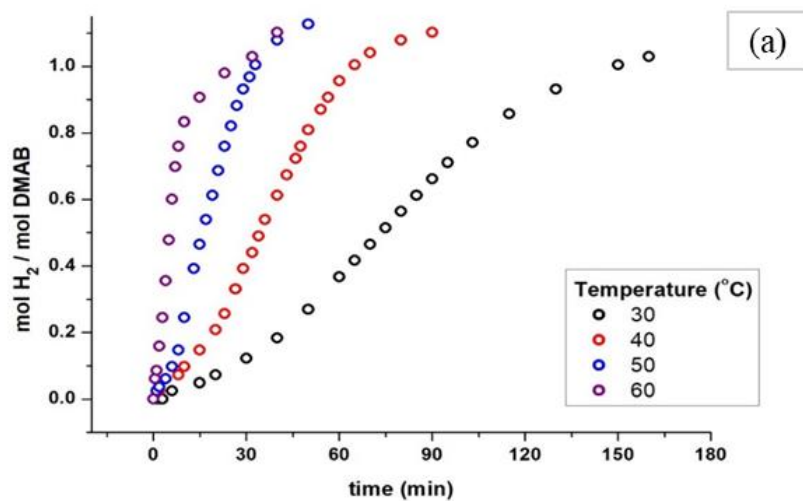


Figure 4.12. (a) mol H₂/mol DMAB vs time graph for the catalytical hydrogen generation of DMAB at different temperatures in the range 30-60 °C with constant concentration of DMAB and copper 100 mM and 10.04 mM respectively (b) Arrhenius Plot

From the linear part of each plot, the rate constants for the hydrogen generation of DMAB were evaluated at 30, 40, 50 and 60 °C which are shown in Figure 4.12a. after that, ln k versus 1/T was plotted and calculated the activation energy by using Arrhenius equation (Laidler, 1987) as following:

$$\ln k = -\frac{E_a}{RT} + \ln A \quad (5)$$

In Figure 4.12b, as the slope of the plot gives the term of E_a/RT , the activation energy for the hydrogen generation of DMAB was found as 34.96 ± 2 kJ/mol.

4.1.4 Leaching test experiment

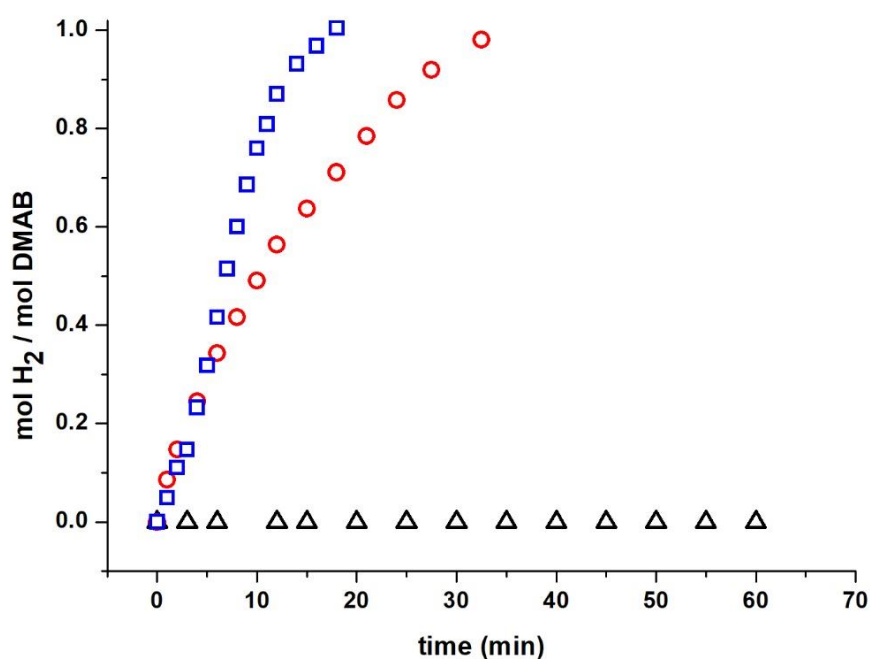


Figure 4.13. 1 mol of H₂ per 1 mol of DMAB vs time graph for the catalytic hydrogen generation of DMAB (100 mM) of first run reaction including Cu²⁺/TiO₂ (square, □), Cu(0)/TiO₂ solid part after first run (circle, o), filtrate solution obtained after filtration for first run (triangle, Δ) at 60.0 ± 0.5 °C.

After the all catalytic activity reaction of the hydrogen generation of DMAB, the leaching experiment was carried out to determine the type of the catalyst as well as to check whether there was a leakage into the liquid part. The first run was performed starting with 6.0% wt of copper and 100 mM of DMAB at 60.0 ± 0.5 °C in 10 mL toluene. Then, the suspension was allowed to rest for a while and both obtained mother liquid and isolated solid were performed to observe for their catalytic activity in the hydrogen generation of DMAB under the same circumstances

by adding 100 mM DMAB. The results were plotted as shown in Figure 4.13 and we can conclude that as no copper leakage observed in the mother liquid along the reaction, the catalyst used in all reactions is a heterogeneous type of catalyst.

4.1.5 Recyclability experiment of nanotitania supported of Cu(0) NPs

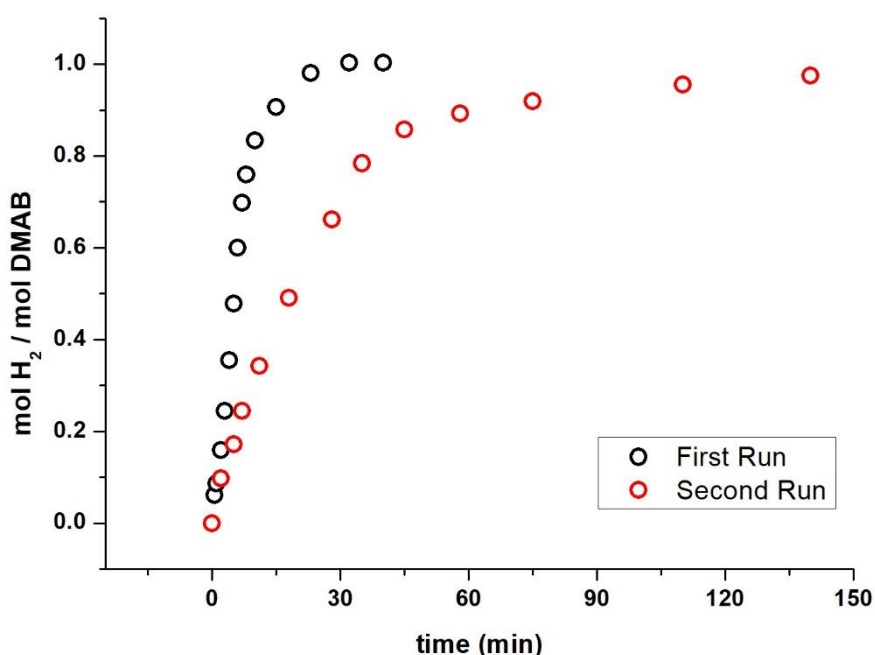


Figure 4.14. mol H₂ / mol DMAB vs time plot for the catalytic hydrogen generation of DMAB (100 mM) of first run reaction and the catalytic activity reaction after adding a new batch of DMAB (100 mM)

After the catalytic activity experiments for the hydrogen generation of DMAB were completed, a new control experiment was performed. Firstly, the experiment was carried out in 10 ml of toluene solution with 10.04 mM Cu(0)/TiO₂ and 100 mM DMAB. After, making sure that all hydrogen release is over, a new part of DMAB solution was put in to the reaction media directly and during this treatment, anything was not removed from the flask. As in previous experiments, hydrogen release was also monitored here. With the second addition of DMAB a decrease was observed in catalytic activity (Figure 4.14). But, 1 equivalent of H₂

generation was recorded as well. The reason of this decrement in second run of the hydrogen generation can be agglomeration of the Cu(0) NPs.

4.1.6 Catalytic lifetime experiment of Cu(0) NPs doped on the surface of TiO₂ for the hydrogen generation of DMAB

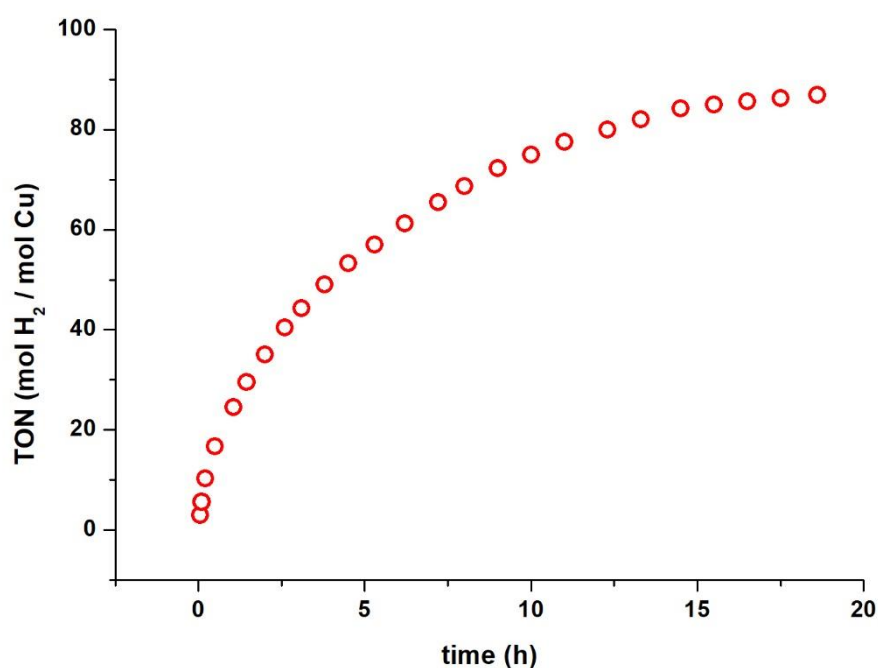


Figure 4.15. the graph of total turnover number (TTO) versus time for the hydrogen generation of DMAB in 10.0 mL the solution of toluene including 6.0% wt. of Cu supported on the surface of TiO₂, with 100 mM DMAB (for each run) at 60.0 ± 0.5 °C

The catalytic time of life of Cu(0)/TiO₂ was calculated by determining the total turnover number in hydrogen generation of DMAB. The experiment of lifetime was studied beginning with 10 mL solution including 10.04 mM Cu(II) loaded on the surface of nanotitania and 100 mM DMAB at 60.0 ± 0.5 °C. When all DMAB in the reaction media was totally dehydrogenated, a new part of DMAB was put in the solution and the reaction was kept going by this way till no H₂ releasing was monitored. Cu(0)/TiO₂ with 6.0% wt. of Cu supports 86.85 turnovers throughout the

lifetime experiment approximately 19 h in the hydrogen generation of DMAB at 60.0 ± 0.5 °C. before the inactivation of the catalyst (Figure 4.15).



5. CONCLUSIONS

To sum up, the preparation and characterization of the catalyst Cu(0)/TiO₂ for the hydrogen generation of DMAB has referred to the following deductions;

- Starting with the copper bis(2,2,6,6-tetramethyl-3,5-heptanedionate), Cu²⁺ are reduced to Cu(0) for the hydrogen generation of DMAB at at 60.0 ± 0.5 oC in 10 mL toluene. But, it is clearly seen that Cu(0) NPs is not stable in the reaction media and the particles come together in the process of time.
- In order to stabilize Cu(0) NPs, any support material is needed. For this reason, TiO₂ nanopowder is preferred to perform on its surface during the treatment of the reduction of Cu(II) to Cu(0). According to the results, the catalyst is an active one and provides 1 equivalent of the hydrogen generation of DMAB.
- According to the characterizons, the occurrence of Cu(0) NPs which has high degree of dispersion on the surface of TiO₂ is found out.
- The highest activity is achieved by TiO₂ supported Cu(0) NPs with 6.0% wt. of copper loading and TOF value is recorded as 59.9 h⁻¹ in the hydrogen generation of DMAB.
- Titania supported Cu(0) NPs are regarded as heterogeneous and kinetically qualified catalysts in the hydrogen generation of DMAB.
- As copper is a lowcost, most abundant in Earth, and high catalytical efficiency of nanotitania doped Cu(0) NPs make it up-and-coming candidate for the hydrogen generation of DMAB.
- Cu(0) NPs loaded on the surface of TiO₂ can support 86.85 turnovers in the hydrogen generation of DMAB at 60.0±0.5 °C before no hydrogen gas was monitored when a new batch of DMAB was added. Thus, the catalytic lifetime of Cu(0)/TiO₂ NPs (86.85 TTO) is considerably lower than the other ones reported for the valuable metal catalysts. However, Cu(0)/TiO₂ NPs can be regarded as cheap catalyst in comparison with other valuable transition metals catalyst.

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