

**PREPARATION OF COPPER NANOPARTICLES ADDED
POLYTHIOPHENE FOR DEHYDROGENATION OF AMMONIA BORANE**

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SALHA M. ALABLAQ

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Approval of the Graduate School of Natural and Applied Sciences, Atılım University.

Prof. Dr. İbrahim AKMAN
Director

I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Science.

Prof. Dr. Atilla CİHANER
Head of Department

This is to certify that we have read the thesis “Preparation of Copper Nanoparticles Added Polythiophene for Dehydrogenation of Ammonia Borane” submitted by “Salha M. Alablaq” and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

Assoc. Prof. Dr. Murat KAYA
Supervisor

Examining Committee Members

Asst. Prof. Dr. Ferdi KARADAŞ

Assoc. Prof. Dr. Seha TİRKEŞ

Assoc. Prof. Dr. Murat KAYA

Date: 22.06.2017

I declare and guarantee that all data, knowledge and information in this document has been obtained, processed and presented in accordance with academic rules and ethical conduct. Based on these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Name, Last name: Salha M. Alablaq

Signature:

ABSTRACT

PREPARATION OF COPPER NANOPARTICLES ADDED POLYTHIOPHENE FOR DEHYDROGENATION OF AMMONIA BORANE

ALABLAQ, Salha M.

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Supervisor: Assoc. Prof. Dr. Murat KAYA

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Nanocatalyst is the material with an increased catalytic activity due to their high surface-to-volume ratio. In the case of homogeneous nanocatalysis like colloidal metal nanoparticle suspensions, they are found in the same phase with precursors used for reaction and products. The main advantage of this type of catalyst can be considered as highly selective systems compared with heterogeneous ones. But low thermal stability, serious metal contamination and difficulty recovery of the catalyst are the main disadvantages of homogeneous catalyst. In order to overcome these problems, heterogeneous type nanocatalysts are widely used in reactions. In this type of catalyst, metal nanoparticles are immobilized onto support materials like silica, alumina, and carbon based materials. Nowadays, some polymer support gained great interest due to their facile and cheap methods to produce them.

Hydrogen energy is considered as one of the most important clean source. For this reason a lot of studies are performed to produce hydrogen storage materials like metal hydrides, chemical hydrides, organic molecules, metal organic frameworks and carbon nanotubes. Between these storage materials chemical hydrides has attracted great attention due to their high hydrogen storage capacity.

Among the chemical hydrides, ammonia borane (AB) gained great importance because of high hydrogen content (19.6 wt %), low toxicity and high stability. With the usage of appropriate catalyst it is possible to get three moles of hydrogen per mole of AB under mild conditions. For this reason, it is so important to produce a catalyst with high-efficiency and improved kinetic parameters in the hydrolysis of AB under mild conditions for hydrogen energy applications.

In this thesis, a facile way for preparing copper nanoparticle (CuNPs) supported on polythiophene as catalyst for hydrogen production from aqueous AB was presented. For this, initially polythiophene polymer support material was prepared. After that Cu (II) ions were added onto polymer support by utilizing wet impregnation method. Then copper ions were reduced by using sodium borohydride and copper nanoparticles were obtained. The catalytic activity of prepared nanocatalyst was revealed. An initial turnover frequency (TOF) value is founded as 11.8 min^{-1} . The stability and reuse capacity of the prepared catalyst were also investigated. The prepared catalyst shows good stability and reuse capacity. CuNPs added onto polythiophene shows nearly same activity after 5th reuse in the hydrolytic dehydrogenation of AB.

Keywords: Supported catalyst, metal nanoparticles, polymer support, hydrogen energy, ammonia borane

ÖZ

AMİN BORANIN DEHİDROJENLENMESİ İÇİN BAKIR NANOPARÇACIK EKLENMİŞ POLİTİYOFENİN HAZIRLANMASI

ALABLAQ, Salha M.

Yüksek Lisans, Kimya Mühendisliği ve Uygulamalı Kimya

Tez Yöneticisi: Doç. Dr. Murat KAYA

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Nanokatalizörler sahip oldukları büyük yüzey-hacim oranları sebebi ile yüksek katalitik aktivite gösteren malzemeler olarak bilinmektedirler. Koloidal nanoparçacıkların sulu çözeltileri gibi homojen nanokatalizörler ise reaksiyonun oluşması için kullanılan başlangıç maddeleri ve oluşan ürünler ile aynı fazda bulunmaktadır. Bu tip katalizörlerin heterojen katalizörlere karşı başlıca avantajı sahip oldukları yüksek seçicilik olarak sayılabilir. Ancak düşük termal kararlılıkları, ciddi metal kirliliği ve reaksiyon ortamından geri kazanımındaki zorluk homojen katalizörlerin karşılaştığı başlıca zorluklardır. Bu zorlukların üstesinden gelebilmek için heterojen nanokatalizörler yaygın olarak kullanılmaktadır. Bu tür katalizörlerde metal nanoparçacıklar silika, alüminyum ve karbon temelli malzemelerin üzerine sabitlenmektedir. Günümüzde ise bazı polimer destek malzemeleri kolay ve ucuz üretim metodları sebebi ile büyük ilgi toplamaktadır.

Hidrojen en önemli temiz enerji kaynaklarından biri olarak bilinmektedir. Bu sebeple metal hidrürler, kimyasal hidrürler, organik moleküller, metal organik kafesler ve karbon nanotüpler gibi hidrojen depolama malzemelerinin üretimi için birçok çalışma yapılmaktadır.

Bu hidrojen depolama malzemeleri arasında kimyasal hidrürler yüksek hidrojen depolama kapasitesine sahip olmaları sebebi ile büyük ilgi görmektedir. Kimyasal hidrürler arasından amin boran, yüksek hidrojen depolama kapasitesi (kütlece 19.6 %), yüksek kararlılık ve düşük toksisiteye sahip olması sebebi ile büyük önem kazanmıştır. Uygun katalizör kullanımı ile ılımlı şartlarda 1 mol amin borandan 3 mol hidrojen eldesi mümkündür. Amin borandan hidrojen eldesinde kinetik parametrelerin iyileştirilmesi için yüksek etkiye sahip katalizörlerin geliştirilmesi, hidrojen enerjisinin uygulamaları için çok önemlidir.

Bu tezde, amin borandan sulu ortamda hidrojen eldesi için politiyofen üzerine bakır nanoparçacıkların eklendiği katalizörün hazırlanması için uygun bir yöntem sunulmaktadır. Bunun için ilk olarak politiyofen destek malzemesi hazırlanmıştır. Daha sonra bakır iyonları ıslak emdirme yöntemi ile polimer destek malzemesinin üzerine eklenmiştir. Bu aşamadan sonra bakır iyonları sodyum borohidrür kullanılarak indirgenmiş ve bakır nanoparçacıklar elde edilmiştir. Daha sonra hazırlanan katalizörün katalitik aktivitesi ortaya çıkarılmıştır. İlk çevrim frekansı 11.8 dk^{-1} olarak bulunmuştur. Buna ek olarak, hazırlanan katalizörün kararlılığı ve tekrar kullanılabilme kapasitesi bulunmuştur. Hazırlanan katalizör oldukça iyi kararlılık ve tekrar kullanılabilme kapasitesine sahiptir. Bakır eklenmiş politiyofen katalizörü amin boranın hidrolitik olarak dehidrojenlenmesindeki beşinci tekrar kullanımından sonra benzer aktivite göstermiştir.

Anahtar Kelimeler: Destek yüzeyine eklenmiş katalizör, metal nanoparçacıklar, polimer destek malzemesi, hidrojen enerjisi, amin boran

To my Family

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LIST OF ABBREVIATIONS

AB	-	Ammonia Borane
E_a	-	Activation Energy
EDX	-	Energy Dispersive X-ray
FE-SEM	-	Field Emission Scanning Electron Microscopy
HR-TEM	-	High Resolution Transmission Electron Microscopy
ICP-OES	-	Inductively Couple Plasma- Optical Emission Spectroscopy
TOF	-	Turnover Frequency

CHAPTER 1

INTRODUCTION

Catalyst is a material that accelerates the rate of chemical reaction without occurring evident changes in its chemical structure. Catalysts are used in reactions to convert reactants into products by lowering the activation energy (E_a). By using a catalyst, the reaction progresses faster than reactions when compared with the one performed without catalyst¹. The working principle of catalyst is given in Figure 1.1. In the production of important products like fine chemicals, fuels, medicines, paints, polymers and other valuable products, it is essential to use catalyst in order to make the process feasible, green and sustainable².

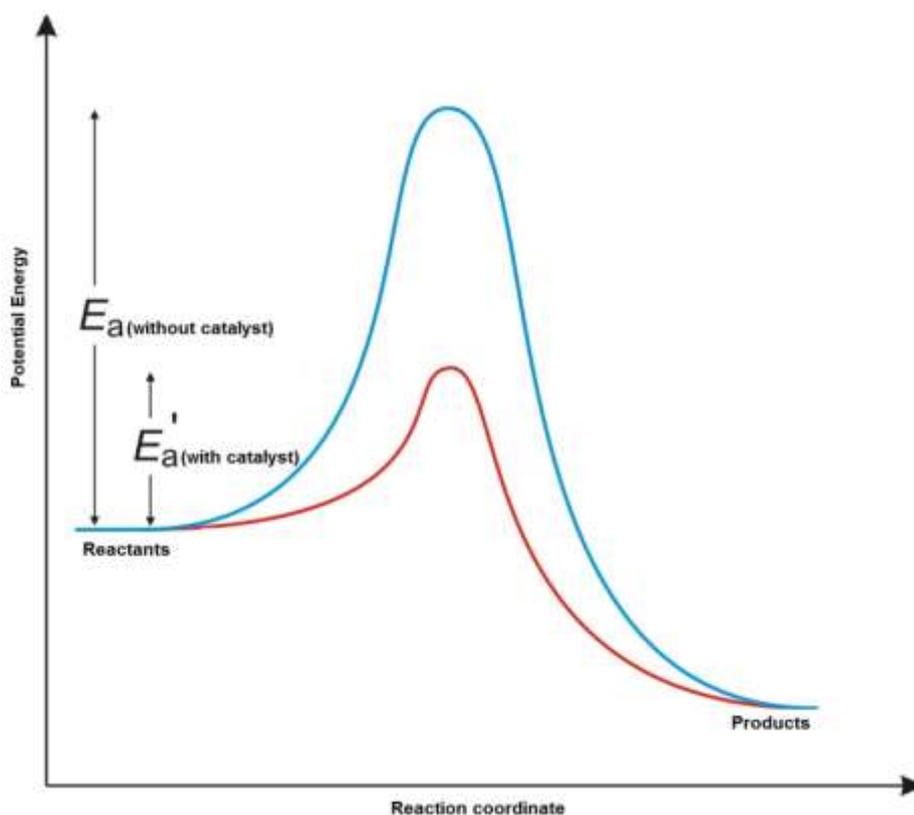


Figure 1.1 Potential energy diagram

Mainly there are three types of catalysis in action known as homogeneous, heterogeneous and enzymatic³ (Figure 1.2). The new type of catalyst named as nanocatalyst have gained great interest due to combined advantages of both the homogeneous and heterogeneous catalytic materials. It allows the chemical change selectively and rapidly with high yield besides easy separation and reuse capability. The most important advantage which supported nanocatalyst serves is the recovery of catalysts from the reaction medium. Due to high surface area the attraction between reactants and catalyst increases dramatically. With the help of insolubility in the reaction medium, they can be separated out from the reaction like heterogeneous catalysis^{4,5,6}.

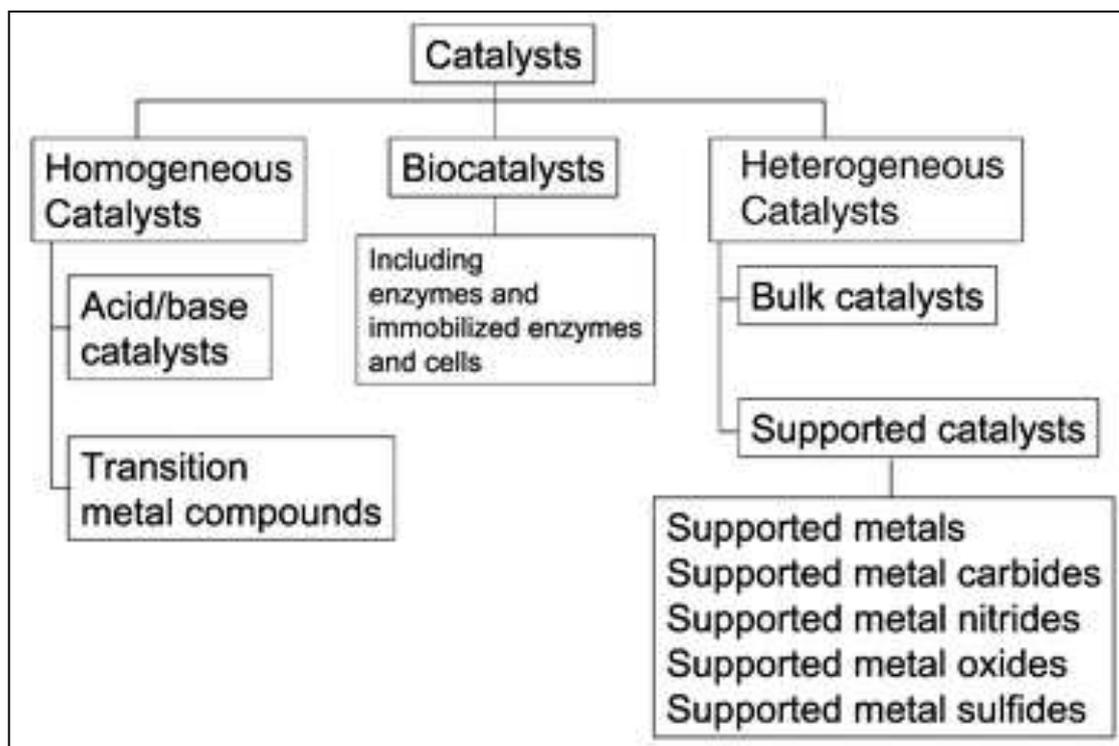


Figure 1.2 Main types of catalyst⁷

Nanocatalysts are very effective candidates in the field of photochemistry, nanoelectronics, and optic science as well. In order to maximize the conversion efficiency in catalytic reactions besides minimizing the total investment cost of the process researchers presented new generation of nanometric scale catalysts in which have more efficiency because of their high activity and conversion rate that results by surface area to volume ratio. Recent developments in synthesis of nanomaterials have produced new nanocatalysts with novel properties and reactivity⁸.

Nanoparticles because of their huge amount of active functional groups on their surface area, can improve catalytic activity. However, the problem in which this type of catalysts involves defines as their tending to aggregation in high temperatures in which reduce reaction surfaces which is hidden in the pores of the catalysts. In most of the cases, aggregation leads to lose of properties related to colloidal metal nanoparticles. During catalytic processes, aggregation or coagulation of metal nanoparticles causes significant decreasing in catalyst activity. The stability in colloidal metallic nanoparticles would also promote the catalysis activity as important aspect in synthesis of current catalysts⁹.

Besides stability, recovery of nanocatalyst from the reaction mixture for reuse is another important issue to overcome. Due to small size, it is very difficult to remove nanoparticles from a solution. In order to separate them, extra effort must be spent which makes the whole process complex and expensive. Besides them, it poses an environmental risk¹⁰. For this reason methods to prepare well-defined supported metal nanoparticle based catalysts are highly desired as well as new methods for catalyst separation and recycling.

Hydrogen is known as one of the most important sources of renewable energy¹¹. Recently, there has been an increasing demand for finding proper ways for producing and storing it. Also finding appropriate catalysts which promote the release of hydrogen is so important. Metal catalysis can stimulate the production of hydrogen gas from solid and liquid hydrogen storage materials¹². It has been stated in literature several homogenous¹³ and heterogeneous¹⁴ catalysts can be utilized to remove hydrogen from the storage materials. Although, homogenous catalysts are known as effective for the hydrolytic dehydrogenation¹³, nowadays, heterogeneous catalysts have certainly attracted significant importance due to their ease of separation and catalyst recovery properties¹⁴.

Noble metals such as Ru,¹⁵ Rh,¹⁶ Pd,¹⁷ Pt,¹⁸ and Au¹⁹ have high catalytic performance in the dehydrogenation of ammonia borane hydrolytically. However, from practical point of view, finding of catalyst with low cost for hydrogen generation from solid hydrogen storage materials is considered extremely important.

In recent times, 3rd transition metal catalysts namely Fe,²⁰ Co,²¹ Ni²², and Cu²³ have shown that such metals can be utilized for the catalysis process of the hydrolytic dehydrogenation. Nevertheless, low activities as well as reusability performance have been exhibited by most of them. For this reason, producing a metal catalyst that is economical as well as highly active has obviously become the main objective for this essential reaction besides to recovery and reuse.

1.1 Preparation of Metal Nanoparticles

Metal nanoparticles can be synthesized by using various methods. These methods are the part of two main classifications known as top-down and bottom-up approaches. In top-down approach of nanomaterial synthesis, the bulk reagents are used as initiator which is passed from physically treatment such as sputtering techniques²⁴ mechanical alloying²⁵, and mechanical grinding²⁶.

The nanoparticles produced by mentioned synthesis technique generally have a wide range of size distribution²⁷ and defects.

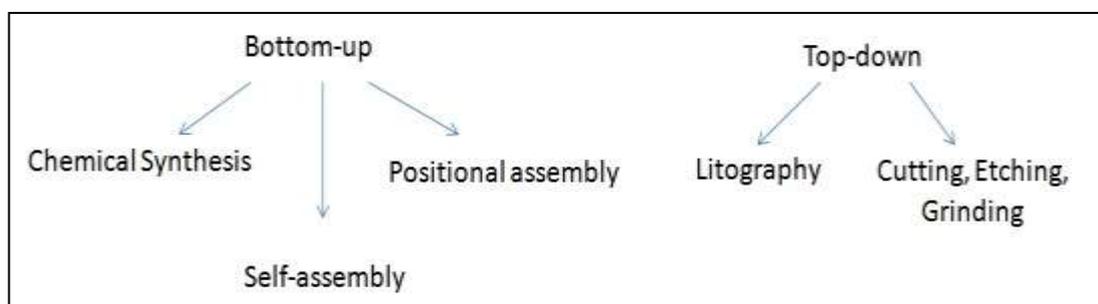


Figure 1.3 Preparation of nanoparticles

In the bottom-up synthesis, the single atoms or ions are allowed to grow into clusters or nanoparticles introduced as wet chemical reactions such as chemical reduction of metallic salts²⁸, decomposition of precursors using thermal²⁹, photolytic³⁰ or sonochemical processes³¹. Chemical synthesis way known as more proper way to produce metal nanoparticles due to better size and shape control.

Chemical reduction of metal salts is the most widely used techniques for the production of nanoparticles^{28,32}. In this method, the metal salts participated to form metallic ions. The metallic ions are reduced by a reducing agent to form metallic based nanoparticles subsequently. Synthesized nanoparticles were immersed by using a surfactant type solution to protect the nanoparticles dispersion from undesired agglomeration. The most common reduction agents are normally including the solvents such as alcohol³³ salts such as sodium borohydride³⁴ and sodium citrate³⁵ and gases such as carbon monoxide³⁶ and hydrogen³⁷. Borohydrides are the most common agents are used in redox reactions in colloidal metallic nanoparticles synthesis³⁸. Aliquot amount of sodium borohydride is dissolved in aqueous solution and used immediately to avoid decomposition of borohydride to borane and gaseous hydrogen that could escape from the reaction medium. Sodium borohydride is also used as a reduction agent in Platinum and Copper nanoparticles synthesis³⁹.

1.2 Supported Metal Nanoparticles as Catalyst

The colloidal dispersions of metal nanoparticles have high catalytic activity and they are widely used in various types of chemical processes such as hydrogenations⁴⁰, dehydrogenations^{41,42} and oxidation reactions⁴³. Generally it is difficult even in some cases impossible to separate and recover the catalysts from the reaction environment which is containing reagents and products mixture. Furthermore, metallic nanoparticles are tending to form aggregates or coagulate in which leads to the loss of catalytic activity during catalytic reaction.

To overcome this problem, metallic nanoparticles can be immobilized onto solid support materials. The supported metallic nanocatalysts have advantages such as activity enhancements, proper selectivity also aggregation preventing capability by immobilizing onto the surface of solid support substrates. Several different alternative ways have been proposed for the synthesis of supported metallic nanoparticles. Among them saturation method is commonly applied for the synthesis of supported metallic catalysts. This process involves in dissolution of solid support with precursor metal salts in aqueous environment⁴⁴.

The supported catalysts synthesized by this method resulted in polydisperse mixture with wide range of size distribution and dispersivity ratio depends on the nature of metal, loading ratio and amount of support material.⁴⁵.

Precipitation or co-precipitation also known as desorption is another technique used in metal catalysts synthesis⁴⁶. This method initiate with precursor metallic salt dissolution in sufficient amount of solvent⁴⁷. The both size distribution profile and dispersion rate of nanoparticles depend on the nature of the support, reaction environment, pH, concentration of precursor and temperature used for drying and calcinations as well⁴⁶.

Grafting is another technique used in preparing supported metallic catalysts⁴⁸. This method begins with formation of covalent bounds between metallic precursor and the functional groups of support material^{49,50}. Microwave exposures classification is the other category of metallic catalysts synthesis methods⁵¹. This method has short reaction duration compared to the conventional heating methods with long-time duration. This method also allows the formation of much more small particles and narrow particle size distributions profile⁴⁵.

1.3 Support Materials Used in the Production of Catalyst

In order to immobilize the metal nanoparticles to use as nanocatalyst, a variety of support materials can be used like carbon, silica, alumina and titania^{52,53,54}. Carbon based support materials are most widely used in broad range in metallic nanoparticles applications because of their low preparation costs also their high thermal and chemical stability. Because of surface chemical properties of carbon can offer different services such as acidic and thermal treatments to optimize catalyst support interactions. Various morphologies of carbon supports are used in many industrial applications such as carbon nanotubes⁵⁵, carbon black⁵⁶ nanoporous carbon structures. Activated charcoal is the most widely used carbon support for the synthesis of supported metallic nanocatalysts^{57,58}. Metallic nanoparticles supported on metal oxides can be used in a variety of organic reactions as catalyst agent. Metal oxides supports have high surface areas, high thermal stabilities and engineered pore structures.

Silica⁵⁹, alumina⁶⁰, and titania⁶¹, are the most common metal oxide nanoparticles which are applying as support platforms. Other variants of silica supports can be used to in catalytic reactions. These materials are including silica gel⁶², silica monoliths⁶³, mesoporous silica^{54,59}. Silica supported metallic nanoparticles can be employed in catalytic reactions such as hydrogenations⁶⁴, Heck cross coupling reactions⁶⁵.

Due to advanced physical properties like high resistivity and thermal stability, low solubility and easy functional group addition polymers can be considered as the proper candidate among the support materials. Highly porous surface of the polymer can host metal nanoparticles to increase the catalytic activity besides reuse performance⁶⁶.

1.4 Hydrogen as an Energy Carrier

Fossil based fuels known as the main source of the world energy. This energy type has high impact on ecological and environmental issues⁶⁷. Efforts in finding new sources of fossil fuels and usage of it also cause global warming. Greenhouse gas emissions, especially CO₂ resulted in the combustion steps of fossil fuels are one of the main environmental problems in which researchers focused on. In order to reduce the environmental risks, different alternative energy sources can be considered instead of fossil fuels. Solar, wind, and hydropower energy are different samples of energy in which can be used by end-users. It has been proposed to use novel energy forms with no environmental problems that cause challenges in fossil fuel consumption.

Limited fossil fuel energy due to finite amounts of oil reservoirs in addition high extraction investments are the disadvantages of this type of energy so these advantages push the researchers to use renewable unlimited energy sources, such as wind and solar energy where always available. But, these new sources of energy facing with some difficulties like the issue of continuity of such energy sources as well as their high cost. These problems can be solved by finding proper energy storage ways. In this concept hydrogen can be considered as the best alternative due to being a secure, plentiful, clean, and renewable source of energy⁶⁸. Additionally, it is possible to get hydrogen from various sources.

Naturally, hydrogen exists in a combination state with oxygen such as in water and it can react with many other elements like carbon, nitrogen, and oxygen⁶⁸. With the separation of hydrogen from the complex, it is possible to obtain green source of energy and at the end of the combustion with oxygen, product is water⁶⁸. In order to use hydrogen sources as a green energy, various problems must be overcome and main features must be taken into account⁶⁹. These features can be summarized as the improvement of the production techniques that reduces the demand of energy in the generation of hydrogen in large scale and low cost, finding easy storage and transportation way for easy access, construction of power generation units, and meet safety issues during the use, handling and storage of hydrogen. Although having a various challenges and difficulty in production, storage and use of hydrogen, it is considered as the most significant source of renewable energy for the future⁶⁹.

1.5 Types of Hydrogen Storage

During the production and use of hydrogen the most important issue needs to be resolved is considered as the storage of it. Hydrogen gas can be stored under high pressure and low temperature⁷⁰. But these conditions are not feasible and safe for mobile applications. In order to solve these problems many novel materials have been suggested like metal hydrides⁷¹, metal organic frameworks⁷², nanostructures⁷³, and chemical compounds⁷⁴. These are known as chemical hydrogen storage materials (Figure 1.3) and they have appealed great of interest due to their high hydrogen storage capacity. They can be considered as the proper materials for mobile applications and usage fuel cells under mild conditions safely.

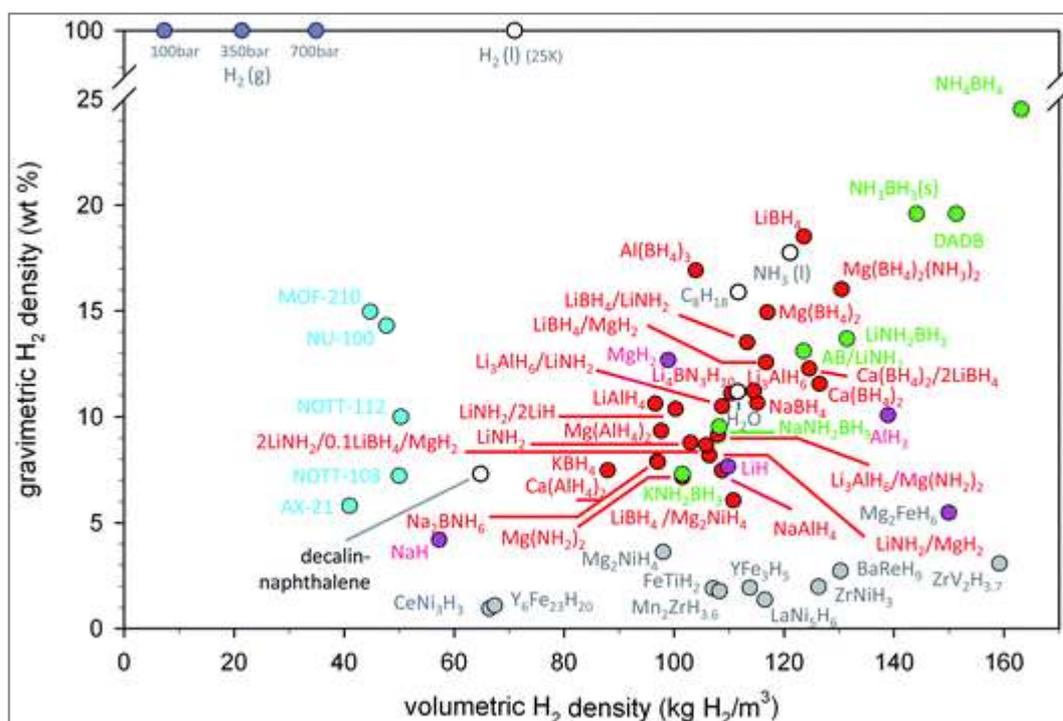


Figure 1.4 Related hydrogen storage densities of storage materials⁷⁵

1.6 Ammonia Borane as a Hydrogen Storage Material

Among the solid hydrogen storage materials, amine boranes attracted great interest because of their high hydrogen storage capacity. With the 19.6% (w/w) hydrogen content, ammonia borane (AB) great interest, besides stability and non-toxicity under mild conditions. Ammonia borane is a colorless solid chemical with 110 °C – 114 °C melting point and stable at room temperature⁷⁶. It is possible to take the hydrogen from AB by applying both pyrolysis and solvolysis methods.

In the case of thermal decomposition method at least 385 K heat must be applied to AB to release of 6.5 wt % hydrogen gas. To take 3 moles of hydrogen from 1 mole of AB requires high temperatures (> 500 °C)⁷⁷. Besides, over the 125°C, volatile side products such as borazine, cycloborazanes, polyaminoborane, and ammonia are formed which has serious effects on the system by poisoning it⁷⁸.

Therefore, the use of hydrolysis of AB by using proper catalyst is the most practical and efficient way for hydrogen production at room temperature. In this way it is possible to get hydrogen from AB at room temperature as given in Eq. 1.1⁷⁹.



For this reason finding proper catalyst to increase the rate of hydrogen evolution is so important. In order to meet this requirement, researchers have focused on the search for the preparation methods of metal catalysts^{80,81}.

1.7 Aim of the Study

In this thesis, initially polythiophene was prepared to use as solid support to immobilize the copper nanoparticles (CuNPs). After that Cu (II) ions were loaded onto the polymer support by using wet-impregnation method. Finally CuNPs were formed by reduction of the Cu ions with sodium borohydrides. The prepared materials were investigated by using SEM, TEM, HR-TEM, EDX and ICP-OES techniques. Then obtained catalyst was used in the hydrogen evolution from aqueous solution of AB at room temperature. Besides, the stability and reuse performance of the prepared catalyst were investigated.

CHAPTER 2

MATERIALS AND METHODS

2.1. Chemicals and Materials

In this work, in order to prepare polythiophene support material and copper nanoparticles, copper chloride, (CuCl_2), iron(III) chloride (FeCl_3), sodium borohydride (NaBH_4), thiophene, chloroform (CHCl_3), methanol and ammonia borane (NH_3BH_3) were purchased from Sigma-Aldrich. They are in reagent grades and used as received. Deionized water used in experiments was obtained by using Milli-Q water cleaning system. All glassware were cleaned both ethanol and water before use.

2.2. Characterization

QUANTA 400F Field Emission Scanning Electron Microscope (FE-SEM), JEOL JEM-2010F (FEG, 80-200 kV) transmission electron microscopy (TEM) and high resolution-TEM (HR-TEM) were used to perform morphological characterization of the prepared nanocatalysts.

The presence of the elements used in the production of copper nanoparticles added polythiophene was verified by utilizing energy-dispersive X-ray analyzer (EDX) coupled with SEM and TEM.

Percent amount of copper added onto polythiophene support material and the leaching of ions into the solution after reaction were revealed by Perkin Elmer DRC II series of inductively coupled plasma mass spectroscopy (ICP-OES).

2.3. Preparation of Polythiophene as Polymer Support Material

The preparation technique, which was implemented for the making of polythiophene, was basically the same technique published beforehand with some modifications. Preparation method is given in Figure 2.1. According to this method polythiophene was prepared by using chemical polymerization method with some modification which is given in Figure 2.1. According to given procedure, 1.00 g Iron (III) chloride (FeCl_3) and 10 ml of CHCl_3 were mixed in a beaker by using magnetic stirrer for 5 min. In separate beaker 0.200 g thiophene was dispersed in 5ml CHCl_3 and resulting solution were mixed on magnetic stirrer for 5 min. After that, iron solution was added drop by drop into the solution which contains monomer solution. Then, the final mixture was stirred at room temperature for 3 hours under nitrogen atmosphere for polymerization. At the end of 3 hours 100 mL methanol was added into the mixture and putted it in freezer for 24 h. After this period formed precipitates of polythiophene were collected by filtration and washed with dichloromethane and methanol by using Soxhlet apparatus for 3 days. Finally obtained polymer was dried at room temperature.

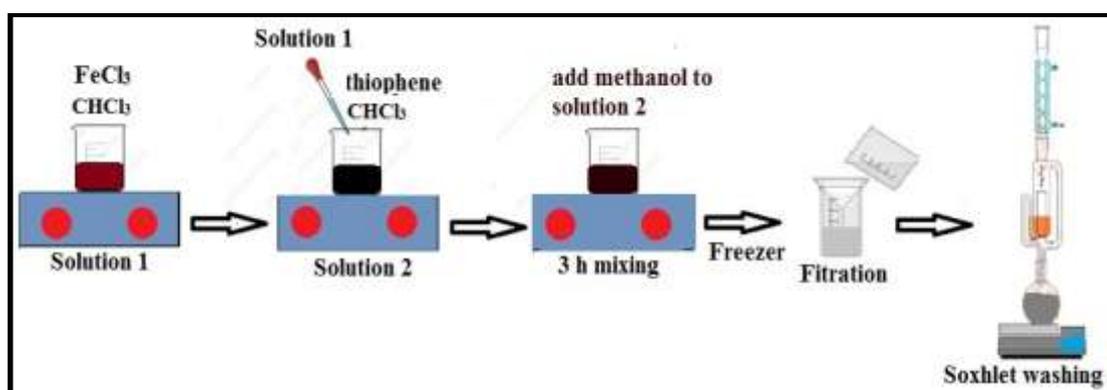


Figure 2.1 Preparation of polythiophene support material

2.4. Immobilization of Copper Ions onto Polymer Support

Addition of Copper ions (Cu^{2+}) onto polythiophene solid support was done by applying wet-impregnation technique. For this, initially 100 mg of polythiophene was dispersed in 10 mL water initially and stirred 5 min by using magnetic stirrer. After that, certain amount of chloride salt of copper was added in to polythiophene water mixture. The mixture was stirred for 5 hours to impregnate the copper ions onto the polymer support. After that period copper ion loaded polythiophene particles were collected from the mixture with centrifugation at 5000 rpm for 15 min. After that the particles were washed with deionized water several times to get rid of copper ions which are not supported onto polymer. ICP-OES measurements were performed to determine the percent loading of copper onto the polythiophene support by using eluent obtained from isolation part and washing portion. The whole preparation procedure is given in Figure 2.2.

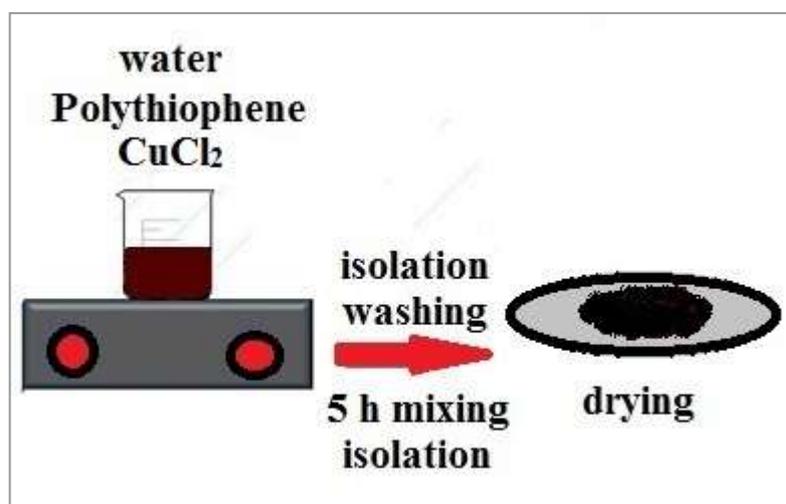


Figure 2.2 Impregnation of copper ions onto polythiophene support material

2.5. Preparation of Copper Ions onto Polymer Support

Preparation of copper nanoparticles which are supported onto polythiophene (CuNPs/Polythiophene) was performed with reduction of copper ions by using sodium borohydride as reducing agent. Initially 100 mg Cu ion added polythiophene support was dispersed in 20 mL water. After well mixing, 50 mg sodium borohydride was introduced into the mixture contains copper ions. The mixture was stirred until the complete reduction was obtained. Reduced particles supported onto polymer were collected with centrifuge. Then obtained catalysts were washed with deionized water and then dried in oven. Schematic representation of the production is given in Figure 2.3.

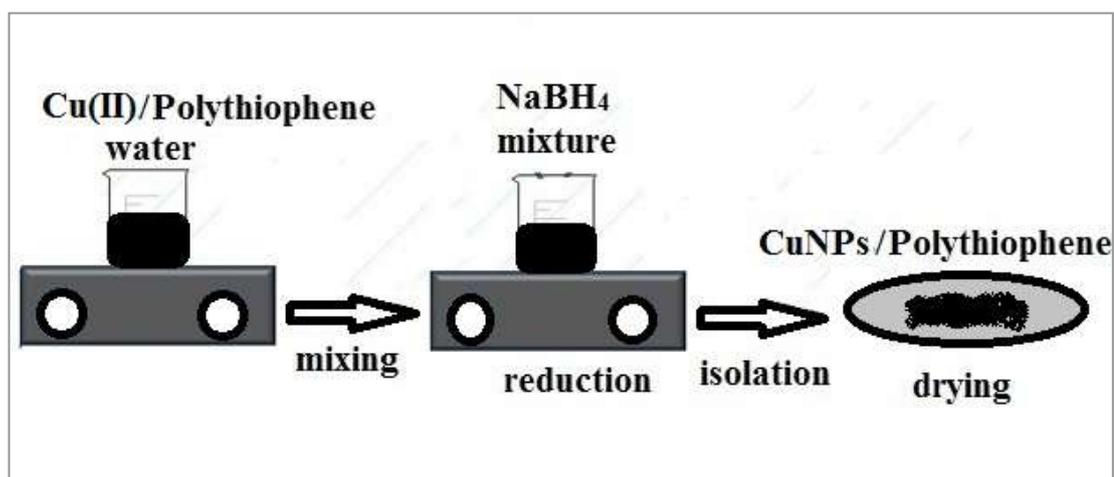


Figure 2.3 Conversion of copper ions into nanoparticles by reduction

2.6. Hydrogen Generation Studies

The catalytic performance of the obtained catalyst CuNPs/Polythiophene in the hydrogen generation from AB was revealed by finding the amount and rate of hydrogen production during the experiment by using the experimental setup given in Figure 2.4.



Figure 2.4 System used for the hydrogen generation studies

In order to measure the catalytic activity of CuNPs/Polythiophene catalyst initially 20 mg of catalyst (with 0.65 wt % Cu loading) was putted in 10 mL water in to the reactor and mixed by using magnetic stirrer. Then magnetic stirrer was closed and the temperature of the mixture in the reactor was adjusted to 25 °C by using water circulator. After that 32 mg (1mmol) ammonia borane was added in to the reactor and closed with rubber septum. Finally, reaction was started by operating the magnetic stirrer and the hydrogen gas evolved was noted at certain times.

The volumetric amount of hydrogen gas obtained from the reaction was measured by recording the change of water level on graduated part of the system. The level change in water was recorded until no more hydrogen evolution was observed. The temperature and pressure were kept constant during the reaction.

After that the optimum amount of catalyst was founded by performing hydrogen generation reaction by using different amounts of CuNPs/Polythiophene nanostructures in the reaction at same conditions.

2.7. Reuse Performance of the Prepared Catalyst

In this part several experiments were performed to find the stability and reuse performance of CuNPs/Polythiophene catalyst. For this, at the end of the first run of reaction, the used catalyst was isolated by using centrifuge and washed with water. Then used CuNPs/Polythiophene catalyst dispersed in another 10 mL portion of water and same procedure was applied under the same conditions. The performance of the catalyst was checked in the hydrolytic dehydrogenation of AB by addition of 1mmol of AB. This procedure was repeated five times and the stability and reuse performance of the CuNPs/Polythiophene catalyst was revealed.

CHAPTER 3

RESULTS AND DISCUSSION

In this study, copper nanoparticles were immobilized on polymer support material, polythiophene. Polythiophene support material was selected due to their low cost procedure and low toxicity properties. Copper nanoparticles known as effective catalyst in the dehydrogenation of ammonia borane (AB), also gained easy separation property after loading then onto polythiophene solid support. Initially copper ions were loaded onto polythiophene solid support by utilizing wet impregnation method. Then reduction of copper ions was performed by using strong reducing agent, sodium borohydride to obtain copper nanoparticles (CuNPs).

The characterization of CuNPs was performed with SEM, TEM, EDX and ICP-OES. Upon reduction of copper ions, the catalytic activity of the copper nanoparticles added polythiophene (CuNPs/Polythiophene) was tested in the hydrogen generation reaction of ammonia borane in water under room temperature and pressure. Then optimization studies were performed in order to find the concentration in which the highest activity was observed. Besides the catalytic activity, stability and reuse performance of the prepared catalyst were investigated.

3.1. Preparation of Polythiophene Solid Support

Polymer support material was prepared according to the procedure given in experimental part. According to that procedure, monomer (thiophene) polymerized with anhydrous iron trichloride in chloroform. After the preparation of polythiophene, scanning electron microscopy (SEM) was used to investigate the morphological properties of the support material. The obtained SEM images at different magnifications are given in Figure 3.1 and Figure 3.2 respectively.

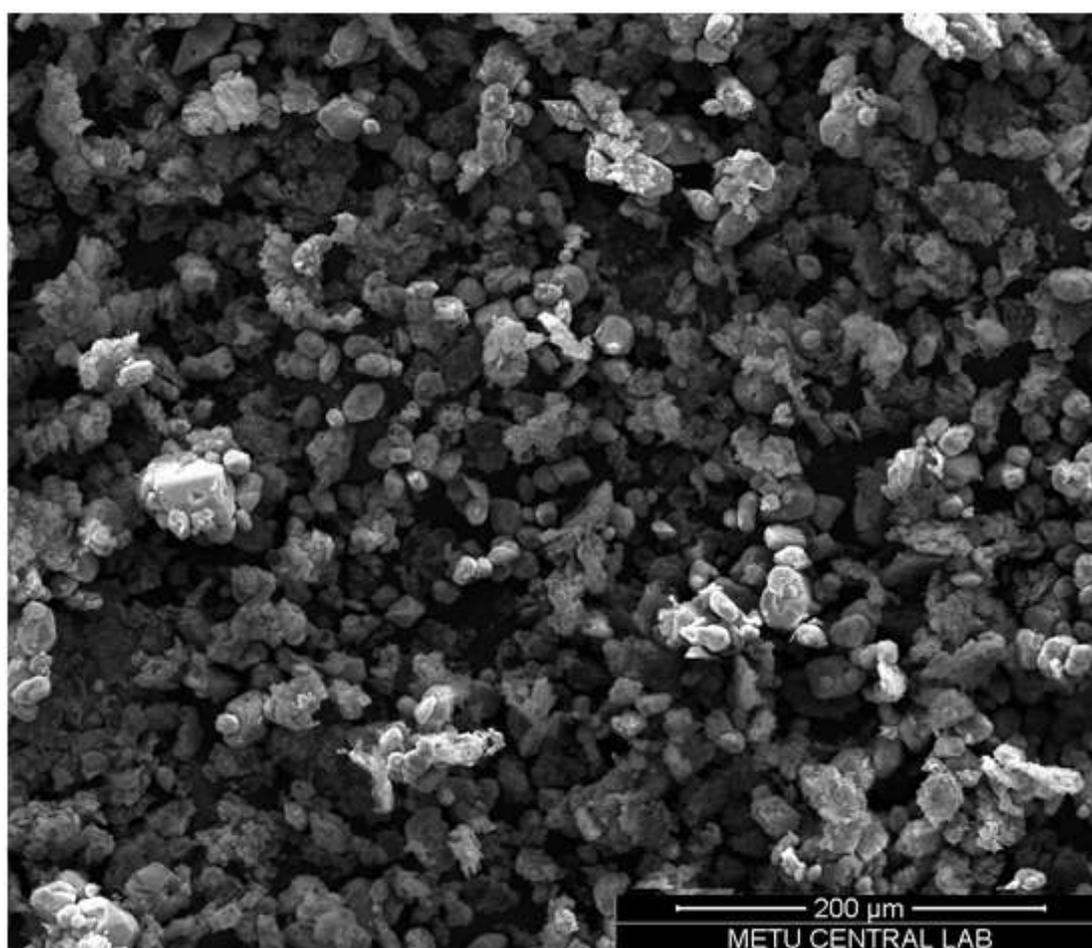


Figure 3.1 SEM image of bare polythiophene solid support

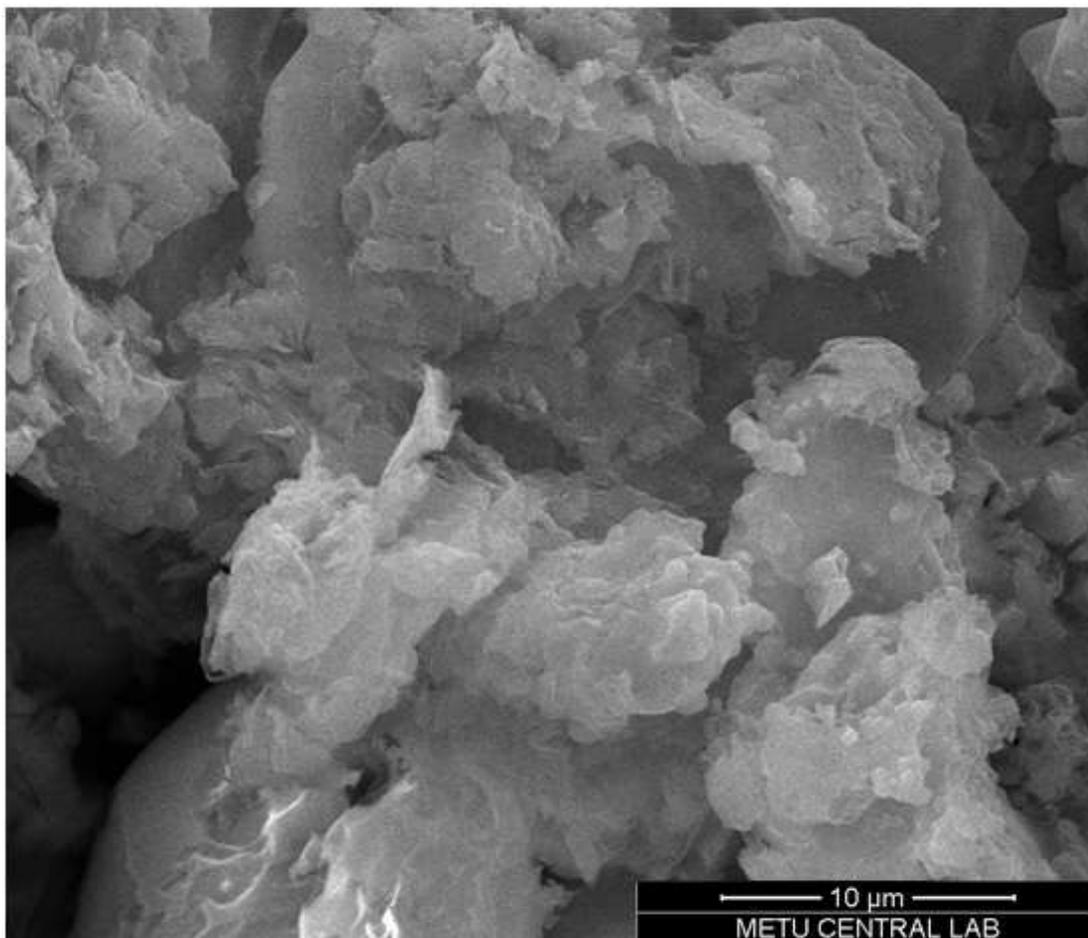


Figure 3.2 SEM image of bare polythiophene solid support.

The SEM images provide that the polythiophene polymer support has high surface area and proper surface for the addition of copper nanoparticles on it. Besides EDX pattern of polythiophene polymer was also taken by using EDX which is coupled with TEM to prove the presence of precursors. The EDX pattern is given in Figure 3.3.

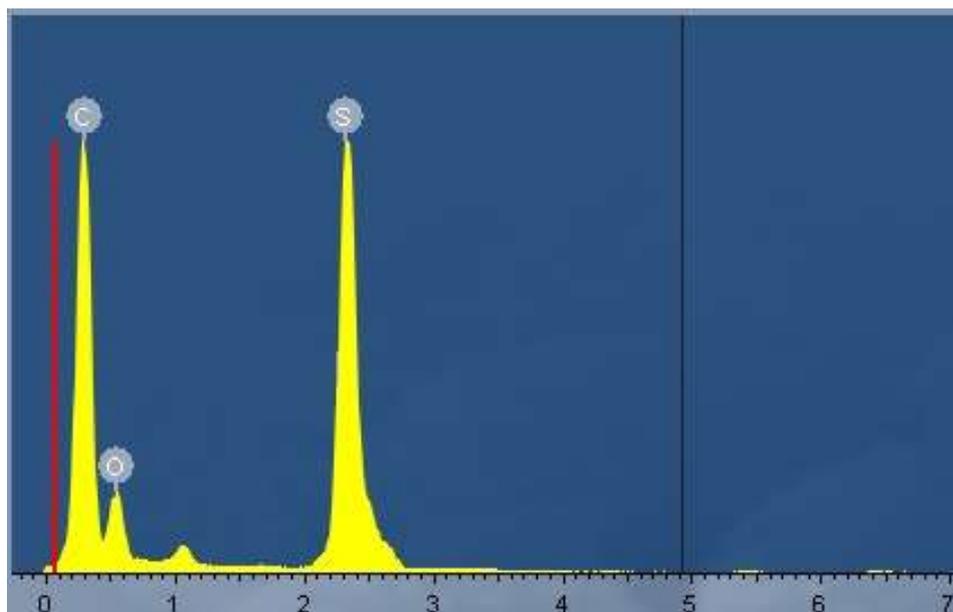


Figure 3.3 EDX pattern of polythiophene.

As can be seen from the EDX pattern, final structure contains only the elements founded in monomer.

3.2.Preparation of Copper Nanoparticles Added Polythiophene Catalyst

After getting the polythiophene polymer support, addition of copper ions onto solid support was done by using wet-impregnation method. Detailed procedure was given in experimental part of the study. According to given procedure, initially polythiophene polymer particles were dispersed in certain amount of water. After that chloride salt of copper was added into the solution and mixed 5 hours. At the end of this period particles were isolated and washed. Copper ions were converted into nanoparticles by using sodium borohydride as reducing agent. Finally copper nanoparticles added polythiophene polymer supports were isolated, washed and dried before catalytic activity experiments.

The characterization of copper nanoparticles added onto polymer support was performed by using HR-TEM, EDX coupled to TEM and ICP-OES. Initially the morphological property of the prepared catalyst was investigated with HR-TEM to find the size and dispersion behavior of CuNPs added onto polythiophene support. The obtained result is given in Figure 3.4 and Figure 3.5 respectively. HR-TEM and EDX measurements were performed by using 0.65 wt. % Cu loaded polythiophene samples.

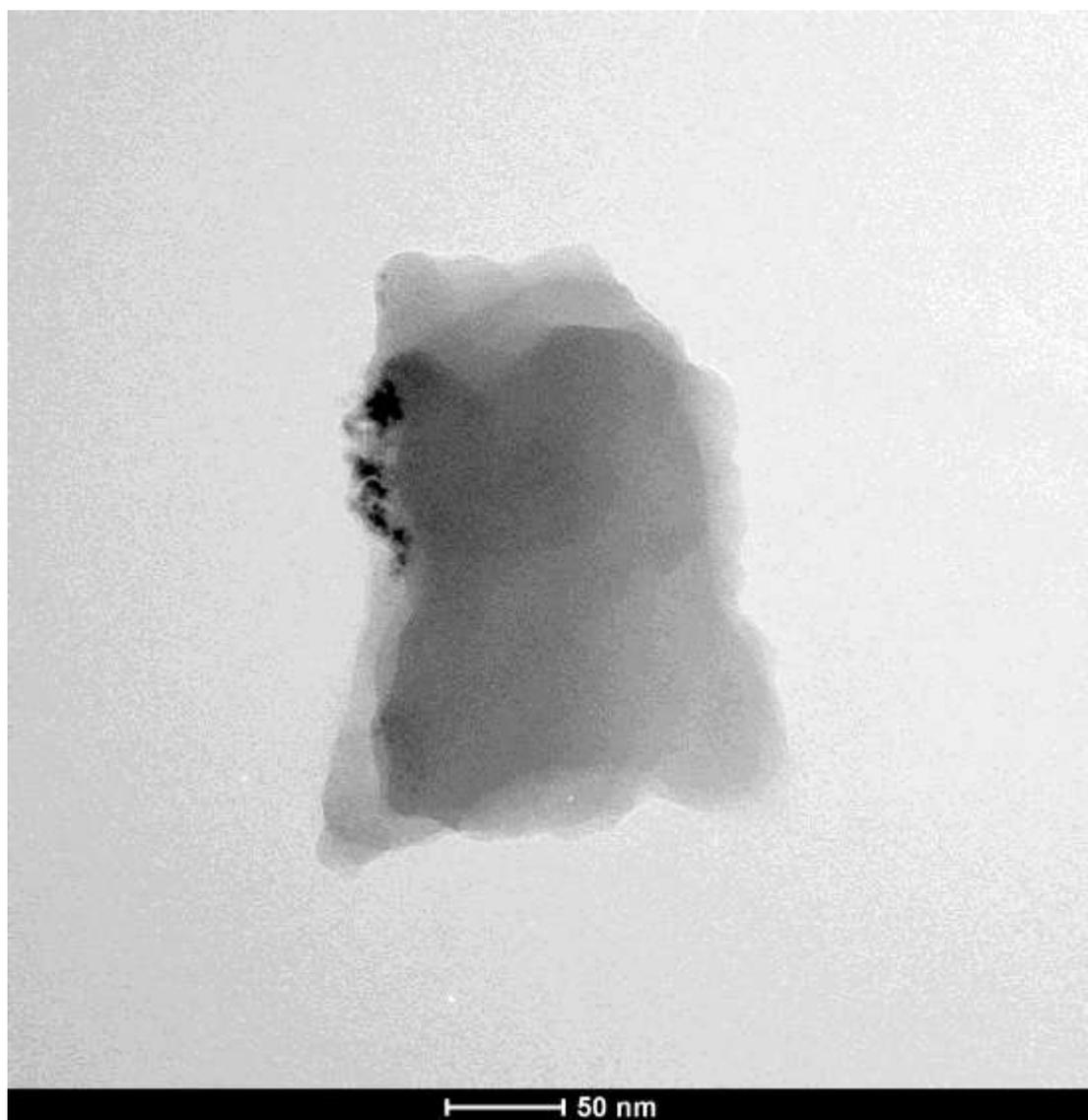


Figure 3.4 HRTEM images of CuNPs/Polythiophene particles.

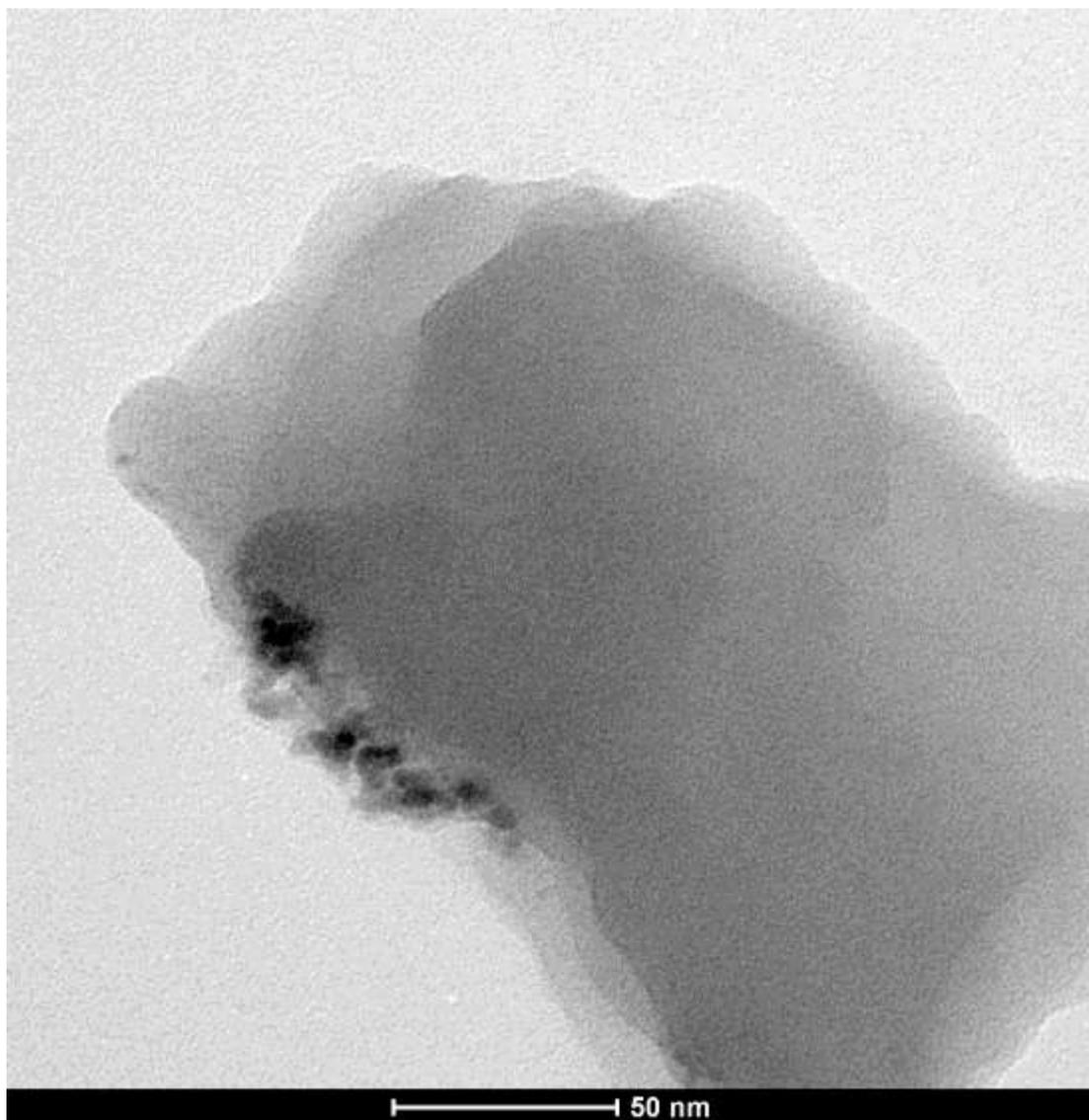


Figure 3.5 HRTEM images of CuNPs/Polythiophene particles.

From the TEM images given above, the average particle size of CuNPs was calculated as 11 ± 5 nm. After that, EDX measurements were performed to prove the addition of copper on polythiophene support. The result is given in Figure 3.6.

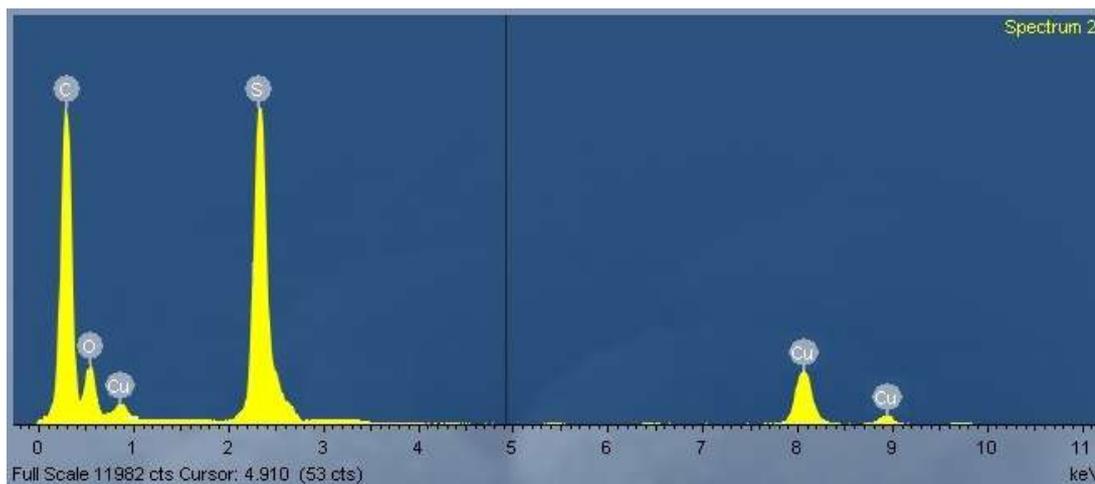


Figure 3.6 EDX pattern of CuNPs/Polythiophene particles.

EDX pattern shows the successful addition of CuNPs onto the polythiophene. Also the presence of copper in the final structure proved with the ICP-OES measurement.

3.3. Catalytic Activity Measurements of Prepared Catalyst

Before starting to catalytic activity measurements of copper added polythiophene catalyst, activity measurement of the bare polythiophene support material was performed to see the effect of it on the hydrogen production reaction. For this 20 mg bare polythiophene support material was used. At the end of the experiment, no activity was observed in the dehydrogenation reaction of ammonia borane (AB).

After that, in order to find the catalytic activity of the copper loaded polythiophene catalyst, hydrogen production from AB reaction was performed by using it according to procedure given in experimental part. During the experiment, hydrogen evolution was followed as a function of time by at a given temperature and pressure.

After getting the data, they were plotted as number of moles of hydrogen gas versus time. 3.0 molar ratio of generated hydrogen to the initial concentration of ammonia borane (AB) considered as the complete conversion point. The sample graph is given in Figure 3.7.

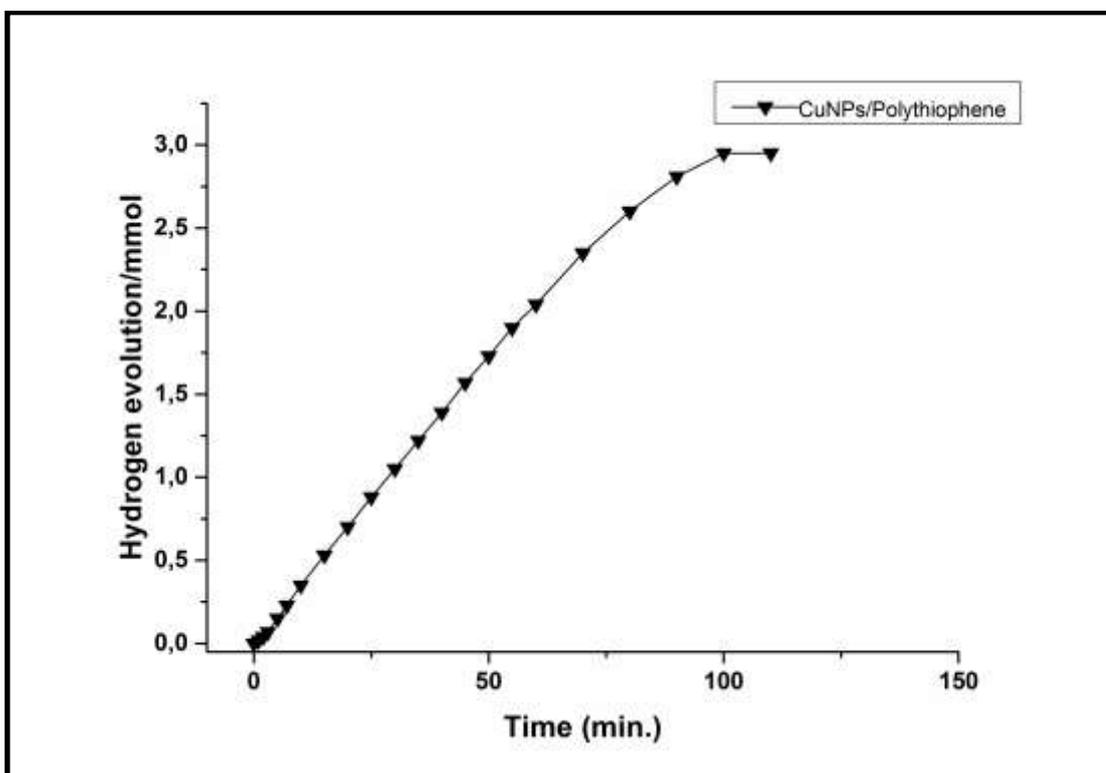


Figure 3.7 Hydrogen evolution versus time graph obtained from 0.1 M, 10 mL AB utilizing 40 mg CuNPs/Polythiophene particles with a copper content of 0.65 wt. % at $25.0 \pm 1^\circ \text{C}$.

% 98 conversions was obtained in 30 minutes by using 40 mg CuNPs/Polythiophene particles with a copper content of 0.65 wt. % at room temperature.

After that the effect of % copper loading onto polythiophene support was investigated. For this different % copper loading on polythiophene support were tried to find the best catalytic activity. To find the optimum copper loading, initially 0.5%, 1%, 2% and 4% wt. percent loading were tried. By using wet impregnation method mentioned amounts tried to load over polythiophene support.

Final loading amounts of copper were revealed with ICP-OES measurements. % addition of copper metal founded as 0.35, 0.65, 1.13 and 2.84 respectively. In order to find the effect of % loading of copper over polythiophene support material, catalytic activity of the catalyst contains different % copper were investigated in the hydrolytic dehydrogenation of ammonia borane at room temperature and pressure. The hydrogen evolution performance and calculated TOF values are given in Figure 3.8 and Figure 3.9, respectively.

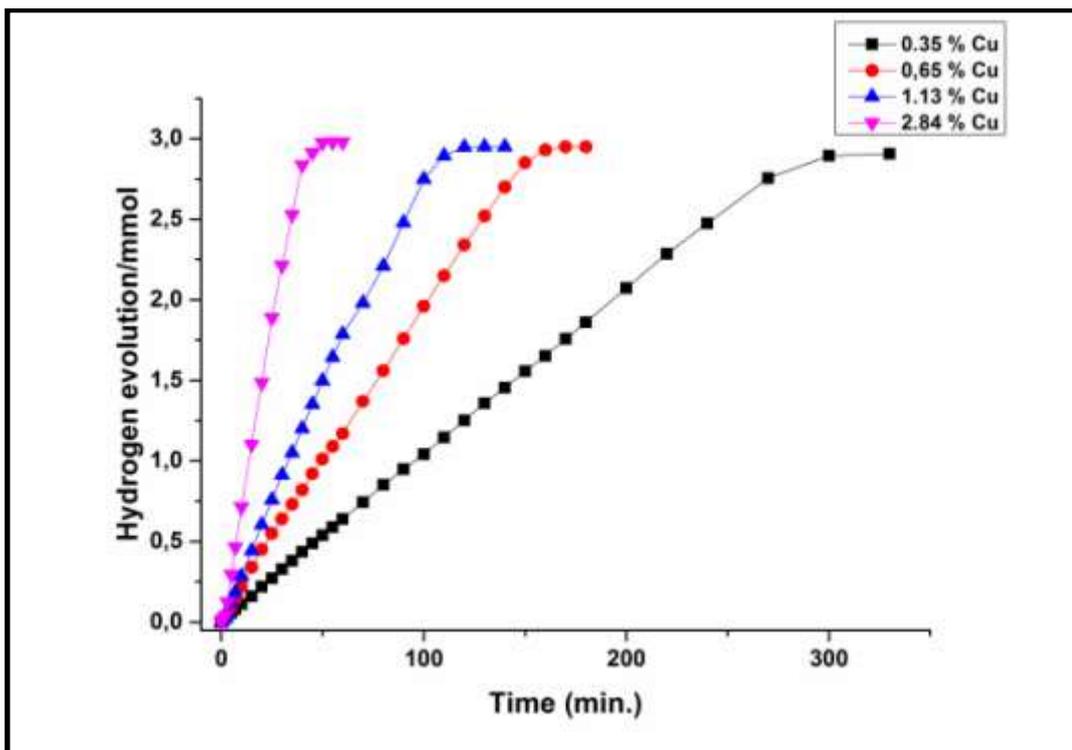


Figure 3.8 Hydrogen evolution versus time graph obtained from 0.1 M, 10 mL AB utilizing 20 mg CuNPs/Polythiophene particles with a different wt. % copper content at $25.0 \pm 1^\circ \text{C}$.

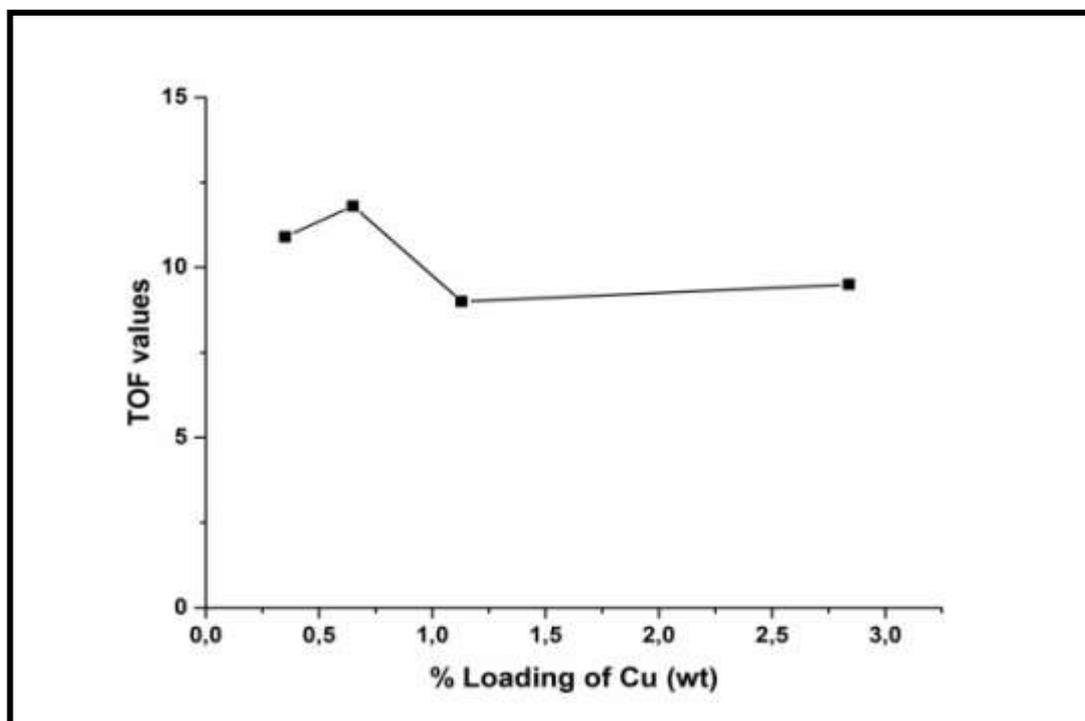


Figure 3.9 Comparison of the activities of the prepared catalyst contains different amount of copper (0.35, 0.65, 1.13, and 2.84 % wt respectively).

According to results given in Figure 3.8 and Figure 3.9 0.65 % wt loading of copper shows the highest catalytic activity. For this reason 0.65 % wt loading was used through the study.

3.4. Optimization of the Amount of the CuNPs/Polythiophene Catalyst

To find the optimum concentration of CuNPs/Polythiophene catalyst in the hydrolytic dehydrogenation of AB, different amounts of catalyst were tried by keeping the reaction conditions constant. In these experiments 0.65 % wt copper loaded polythiophene was used. The results are given in Figure 3.10.

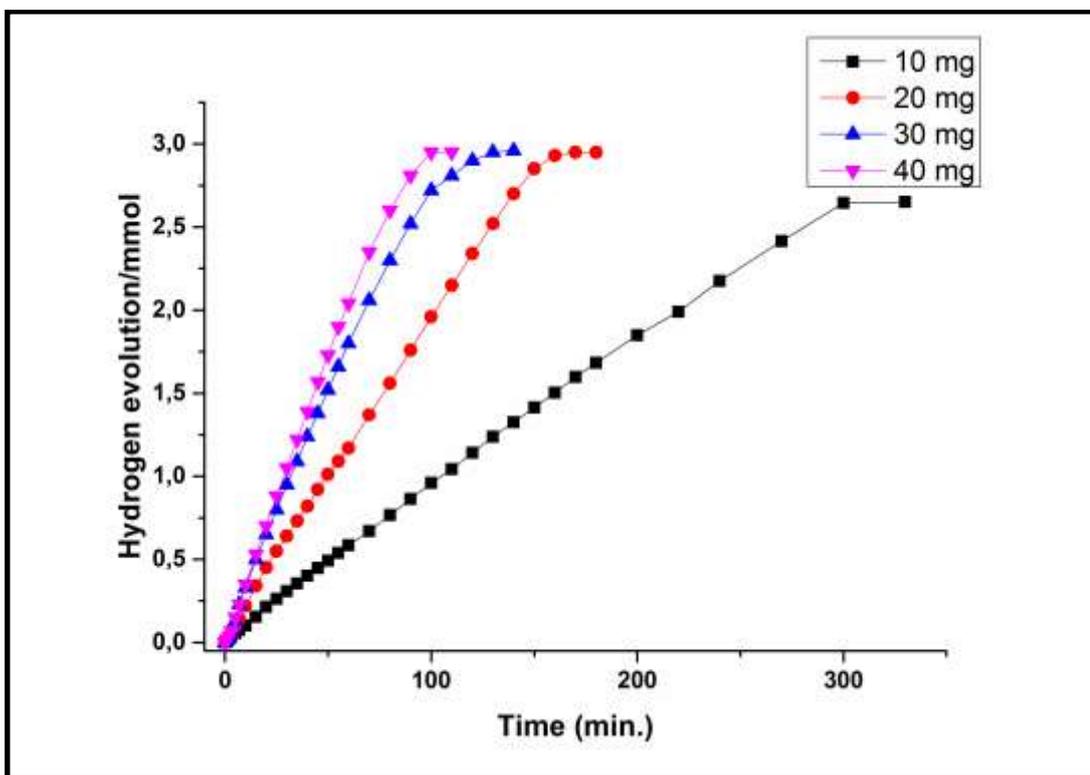


Figure 3.10 Hydrogen evolution versus time graph obtained from 0.1 M, 10 mL AB utilizing CuNPs/Polythiophene particles with different amount as catalyst (copper content is 0.65 wt. %) at $25.0 \pm 1^\circ \text{C}$.

TOF value is calculated from the amount of hydrogen evolved by a certain amount of metal content of catalyst in a given time ($\text{mol H}_2 \times \text{mol catalyst}^{-1} \times \text{min}^{-1}$). After finding the optimum amount of catalyst, turnover frequency number (TOF), which

shows the catalytic activity of the prepared catalyst was calculated by using the data which shows the best performance of the catalyst. Results are given in Figure 3.11.

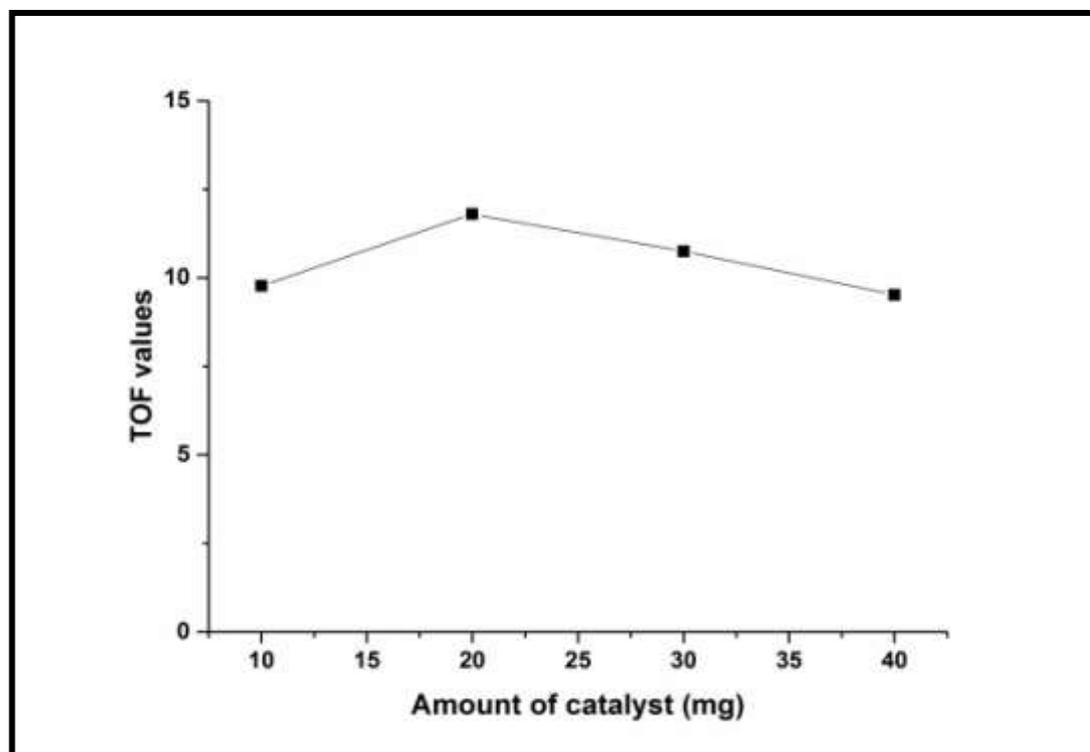


Figure 3.11 Comparison of the activities of the prepared catalyst with different amount (10, 20, 30, and 40 mg respectively)

According to this information, TOF values were calculated for each catalyst concentrations given in Figure 3.10 and the highest initial TOF value is founded as 11.8 min^{-1} for the CuNPs/Polythiophene catalyst with 20 mg 0.65 %wt loading.

It can be concluded from the results given in Figure 3.10 and Figure 3.11, 20 mg CuNPs/Polythiophene catalyst contains 0.65 wt. % copper shows the best catalytic activity in the hydrogen evolution reaction.

The comparison of the TOF value obtained with CuNPs/Polythiophene catalyst with the copper and other first row transition metal based studies in literature used in the hydrogen production from AB is given in Table 3.1.

Table 3.1 TOF values of first row transition metal based catalysts reported in the literature for the hydrogen production from AB.

Entry	Catalyst	TOF (min^{-1})	Ref.
1	Fe NPs	4.7	[20]
2	Co NPs	14	[82]
3	Ni NPs	10	[83]
4	Co/ Al_2O_3	2.1	[84]
5	Ni/ Al_2O_3	2.3	[84]
6	Co/ SiO_2	20	[85]
7	Ni/Zeolite	5.1	[86]
8	Cu@Cu ₂ O	0.25	[87]
9	Cu/Zeolite	0.78	[88]
10	Cu/ Co_3O_4	18	[23]
11	CuNPs@SCF	40	[89]
12	CuNPs/Polythiophene	11.8	This Study

TOF = mol H₂ / mol metal×min

It can be stated from the table that, CuNPs/Polythiophene can be considered as a high performance catalyst in the hydrogen generation process from ammonia borane under mild conditions.

3.5. Reuse Performance and Stability of the CuNPs/Polythiophene Catalyst

As mentioned in the introduction part, it is very hard to isolate nanocatalyst from the reaction medium at the end of the reaction. By immobilizing the nanoparticles onto solid support, the isolation and reuse capacity can be improved dramatically.

In this study, it is aimed to increase reuse capacity and stability by preventing them from agglomeration. For this reason copper nanoparticles were supported onto polythiophene support material.

After that the effect of polymer support on stability and reuse performance were investigated. For this CuNPs/Polythiophene catalyst was tested in the hydrogen production experiments from an aqueous solution of AB for five sequential runs at room temperature.

For this, after checking the catalytic activity of CuNPs/Polythiophene catalysts, they were separated from the solution by centrifuge after the reaction was completed. Then they washed with water and redispersed with water in the reactor and used again as the catalyst for the hydrolytic dehydrogenation of AB. The results are given in Figure 3.12.

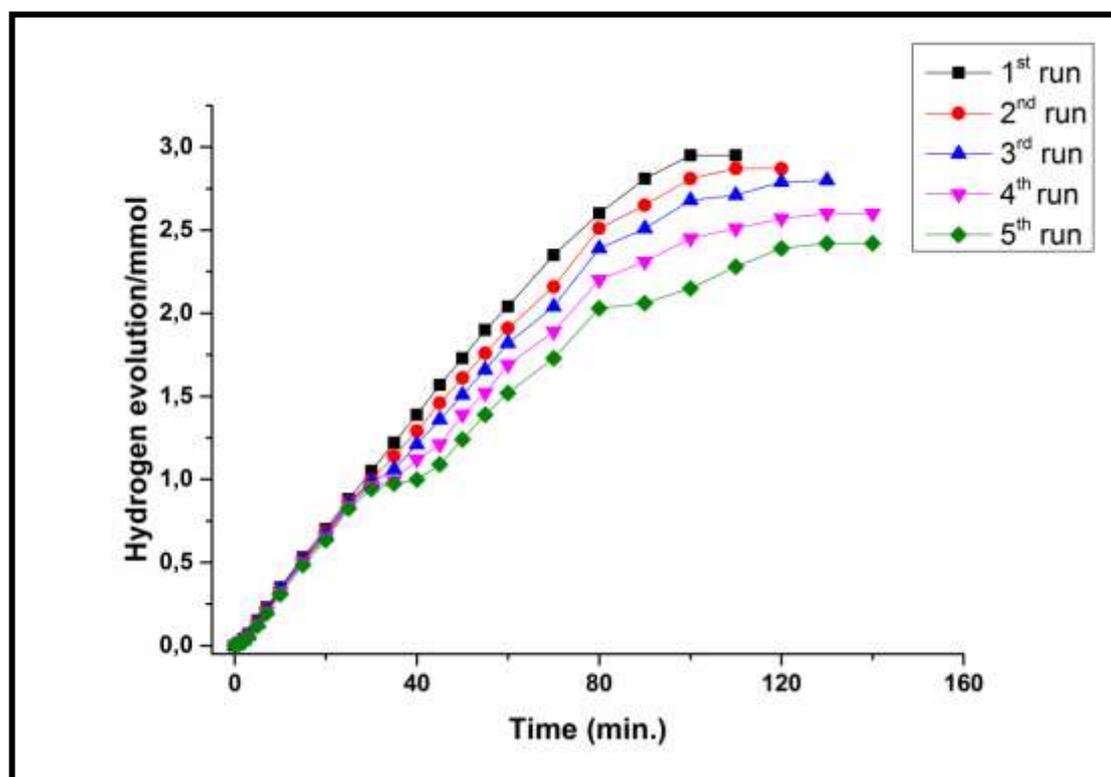


Figure 3.12 Hydrogen evolution versus time graph for five sequential run obtained from 0.1 M, 10 mL AB utilizing 40 mg CuNPs/Polythiophene particles (copper content is 0.65 wt. %) at room temperature.

According to results given in Figure 3.12, the catalytic activity of CuNPs/Polythiophene catalyst in the dehydrogenation of ammonia borane founded nearly as the same after 5 successive runs. This result shows the stability and reuse performance of the CuNPs/Polythiophene catalyst in the hydrogen production from AB under ambient atmosphere. The conversion capacity of the catalyst for each run is given in Figure 3.13 to support the reuse performance of the CuNPs/Polythiophene catalyst.

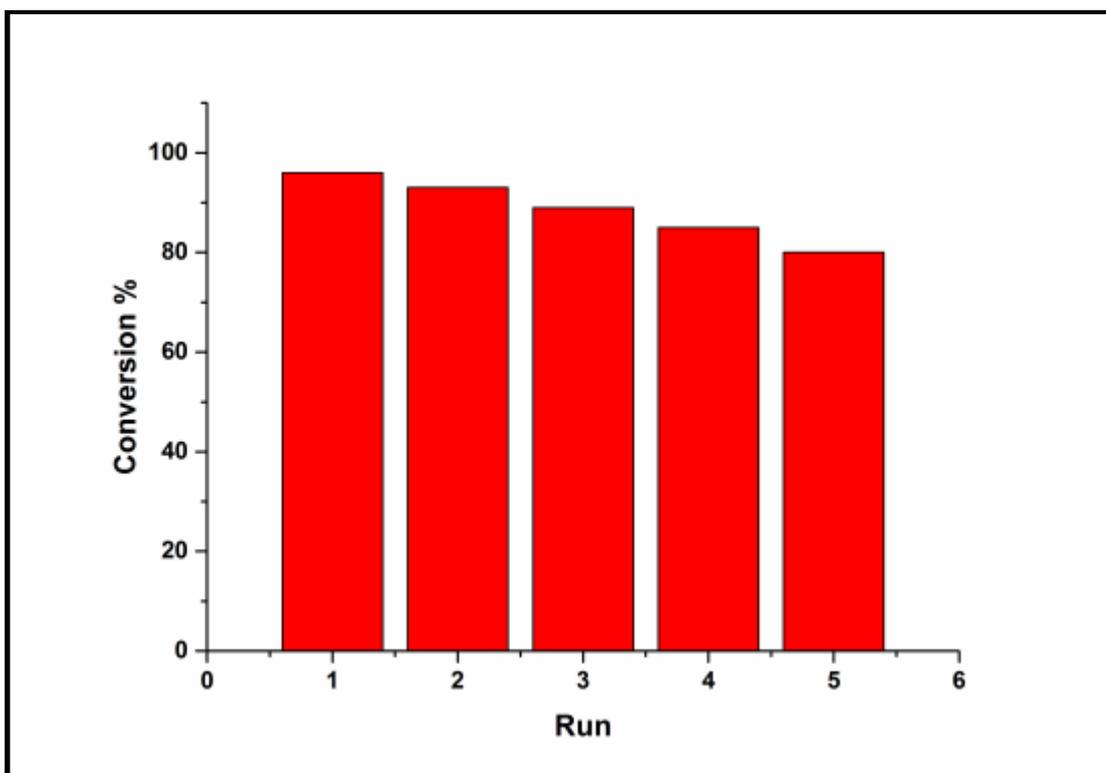


Figure 3.13 % Conversions for each run performed with CuNPs/Polythiophene catalyst

As can be seen from the Figure 3.13, CuNPs/Polythiophene catalyst keeps 80% of their initial conversion after fifth use.

CHAPTER 4

CONCLUSION

In conclusion, in this study copper nanoparticles immobilized on polythiophene support material was prepared as catalyst for the hydrolytic dehydrogenation of ammonia borane at room temperature and pressure. For this, initially copper ions were impregnated on to the polythiophene support material in water. After that the copper ions immobilized onto polythiophene were reduced by using sodium borohydride to obtain copper nanoparticles. The characterization of prepared particles was performed with SEM, TEM, EDX and ICP-OES. The average particle size of the copper nanoparticles was founded as 11 ± 4 nm.

After the optimization studies, the optimum % loading of copper was founded as 0.65% wt and the highest activity was observed with the usage of 20 mg CuNPs/Polythiophene particles. The highest initial turn over frequency was calculated as 11.8 min^{-1} by using 20 mg and 0.65% wt copper metal loaded catalyst.

In this study, in order to isolate copper nanoparticles and prevent them from agglomeration, polythiophene polymer was used as a support material. The final structure can be isolated from the reaction medium easily by using centrifuge in a short time. So it can be used again in the hydrolytic dehydrogenation of ammonia borane at mild conditions. In order to show it, stability and reuse performance of the catalyst studied. CuNPs/Polythiophene catalyst showed high stability and reuse performance besides good catalytic activity. It kept nearly all of their initial activity even at the fifth try in the same reaction without leaching of copper metal. Due to properties mentioned above, polythiophene polymers can be considered as a good candidate for the stabilization of metal nanoparticles used as catalyst in various reactions.

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