

**PREPARATION AND CHARACTERIZATION OF PALLADIUM
NANOPARTICLES ADDED POLYTHIOPHENE FOR HYDROGEN
PRODUCTION FROM AMMONIA BORANE**

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ABSTRACT

PREPARATION AND CHARACTERIZATION OF PALLADIUM NANOPARTICLES ADDED POLYTHIOPHENE FOR HYDROGEN PRODUCTION FROM AMMONIA BORANE

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Nowadays, nanostructured catalysts gain great attention due to their high catalytic activities in various types of reactions. For this reason more efforts have been devoted to develop more efficient ways to produce catalysts with desired sizes. To prepare an effective nanocatalyst, one of the main parameter is to prepare proper support materials. It keeps the activity constant by preventing nanoparticles from agglomeration and increases the reuse performance by giving easy isolation properties. Among the support materials, polymers can be considered as good candidates due to their cheap and easy preparation ways and stabilites.

Hydrogen energy is considered as one of the most promising green energy resources. Therefore, the design and production of proper catalysts, which can be used in the production of hydrogen from the storage materials is so important. Among the solid hydrogen storage materials like metal hydrides, chemical hydrides, organic molecules, metal organic frameworks and carbon nanotubes, ammonia borane (AB) considered as one of the most effective hydrogen storage material. The hydrogen content of AB is 19.6 wt % and it is nontoxic and stable under air and water.

With the usage of suitable and effective catalyst, it is possible to take all hydrogen from AB at moderate conditions. For this reason, production of highly efficient catalysts to enhance the catalytic parameters in the production of hydrogen from AB is of great importance for the development of hydrogen energy and its extensive usage.

In this thesis, to produce catalyst for hydrogen generation from aqueous AB under mild condition a novel support material, polythiophene, was used to immobilize the palladium nanoparticles by using a wet impregnation method. The prepared catalyst shows good catalytic activity at 25 °C. An initial turnover frequency (TOF) value is calculated as 28.9 min⁻¹. Furthermore, PdNPs, which are loaded on polythiophene support, show high stability and reuse property.

Keywords: Polymer support, polythiophene, palladium nanoparticle, nanocatalyst, hydrogen production, ammonia borane

ÖZ

AMİN BORANDAN HİDROJEN ÜRETİLMESİ İÇİN PALADYUM NANOPARÇACIKLARI EKLENMİŞ POLİTİYOFENİN HAZIRLANMASI VE KARAKTERİZE EDİLMESİ

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Günümüzde nanoyapıya olan katalizörler katalitik etkinlikleri sebebi ile oldukça yüksek ilgiye sahiptirler. Bu nedenle istenilen büyüklüğe ve etkinliğe sahip katalizörlerin hazırlanmasına yönelik prosedürlerin geliştirilmesine yönelik oldukça fazla çaba sarfedilmektedir. Etkili bir katalizör hazırlamak için başlıca etkenlerden biri uygun destek malzemesinin hazırlanmasıdır. Uygun destek malzemesi nanoparçacıkların topaklaşmasını engelleyerek katalitik aktivitenin sabit kalmasını sağlar ve kolay ayrılması ile tekrar kullanım performansını artırır. Destek malzemeleri arasında polimerler ucuz olmaları, kolay hazırlanmaları ve kararlılıkları sebebi ile iyi birer aday olarak sayılmaktadır.

Hidrojen en önemli yeşil enerji kaynaklarından biri olarak bilinmektedir. Bu nedenle hidrojen depolama malzemelerinden hidrojen üretiminde kullanılmak üzere uygun katalizörlerin dizayn ve üretimleri oldukça önemlidir. Metal ve diğer kimyasal hidrürler, organik moleküller, metal organik kafes yapıları ve karbon nanotüpler gibi katı hidrojen depolama malzemeleri arasında amin boran (AB) yüksek hidrojen bileşenine (19.6 wt %) sahip olması, kararlılığı ve toksik olmaması sebebi ile en önemli hidrojen depolama malzemesi olarak bilinmektedir.

Uygun ve etkili bir katalizörün kullanılması ile yapıda bulunan tüm hidrojenin ılımlı şartlar altında alınması mümkündür. Bu sebeple amin borandan hidrojen eldesinde etkili katalizörlerin kullanımı için etkili katalizörlerin üretilmesi, hidrojen enerjisinin gelişmesi ve yaygın kullanımı için çok önemlidir.

Bu tezde, amin borandan hidrolitik olarak hidrojen eldesi için katalizör olarak politiyofen destek malzemesine ıslak emdirme yöntemi ile eklenmiş paladyum nanoparçacıklarının hazırlanması için kolay bir yöntem rapor edilmiştir. Hazırlanan katalizör oda sıcaklığında amin borandan hidrojen eldesi reaksiyonunda iyi bir katalitik aktivite göstermiştir. İlk çevrim frekansı 28.9 dk^{-1} olarak hesaplanmıştır. Buna ek olarak, politiyofen destek malzemesi üzerine eklenmiş Pd nanoparçacıklar, kaydadeğer kararlılık ve tekrar kullanılabilirlik kabiliyeti göstermiştir.

Anahtar Kelimeler: Polimer destek malzemesi, politiyofen, paladyum nanoparçacık, nanokatalizör, hidrojen üretimi, amin boran

To my Family

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LIST OF ABBREVIATIONS

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

CHAPTER 1

INTRODUCTION

Catalysis is known as the important chemical process in chemical industry and science. One of the main challenge in this field is the development of facile techniques in the controlling and manipulating of the activities and selectivities besides the stability of the prepared catalysts. Catalyst at nanometric scale exhibits superior chemical and physical properties due to high surface area when compared with the bulk forms. With the help of the developments in nanoscience and nanotechnology, production of nanocatalysts for a various chemical applications gained great importance and found extensive applications.

It is a well known fact that hydrogen energy is considered as one of the cleanest and renewable energy source¹. For this reason, research on production and storage of hydrogen effectively gained great importance. The envisaged target of 2015 by U.S. Department of Energy for hydrogen content was 9 wt % H₂ for hydrogen storage materials. With 19.6 wt % hydrogen content ammonia borane (AB) meets this target, besides its low molecular weight (30.9 g/mol), low reactivity under fuel cell applications and being nontoxic^{2,3}. Studies performed on the dehydrogenation of AB show that it is possible to get 3 moles of hydrogen from 1 mol of AB by using metal based homogeneous⁴ and heterogeneous⁵ catalysts under mild conditions.

Although, homogeneous catalysts are effective for the hydrolytic dehydrogenation studies, heterogeneous catalysts have considered as the suitable one due to their ease of separation and catalyst recovery properties. It is possible to use both transition metals based nanoparticles like Fe,⁶ Co,⁷ Ni⁸, and Cu⁹ and noble metal nanoparticles such as Ru,¹⁰ Rh,¹¹ Pd,¹² Pt,¹³ and Au¹⁴ to get the hydrogen from AB. In recent times, 3rd row transition metal catalysts can be utilized for the catalysis process of the hydrolytic dehydrogenation of NH₃BH₃. Nevertheless, low activities as well as poor reusability performance have been exhibited by most of them. Consequently, developing a metal catalyst that is economical as well as highly active has obviously become the centre objective for this essential reaction in addition to recovery and reuse.

1.1 The Definition of Catalysis

Catalysts have been known as accelerating materials used in chemical reactions without their interaction with reagents. Mentioned materials cooperate in reactions and bonds with the reagent molecules. Catalytic reagents allow cooperating in reaction to produce final product. The reaction products then detach from the catalyst and leave out reaction medium without direct transaction in process stages. In fact, catalytic reactions are cyclic stages processes with participating of catalytic reagents in first step and its recovering in next step from final products. A and B molecules interacts with each other through catalytic reaction to form P molecule as a final product via catalytic reaction. This reaction can be expressed in Equation 1.1 as below:



The initiation of reaction proceeds with the attraction of molecules A and B in the presence of catalyst. “A” and “B” reagents then participate in the reaction which resulted as final product so called “P, the final product is attached to the catalyst. Finally, product of the reaction and the catalyst are separated from the reaction medium.

In order to illustrate the catalyst role as reaction accelerator it is necessary compare the activation energy levels between the reagents and the products of reactions handled with and without catalyst. The comparison of the activation energy is given in Figure 1.1. For the reaction driven without catalyst, the figure can be defined as the simplest type of Arrhenius equation in which the reaction progressing when “A” and “B” reagents participate in reaction with reasonable energy level to overcome the activation barrier.

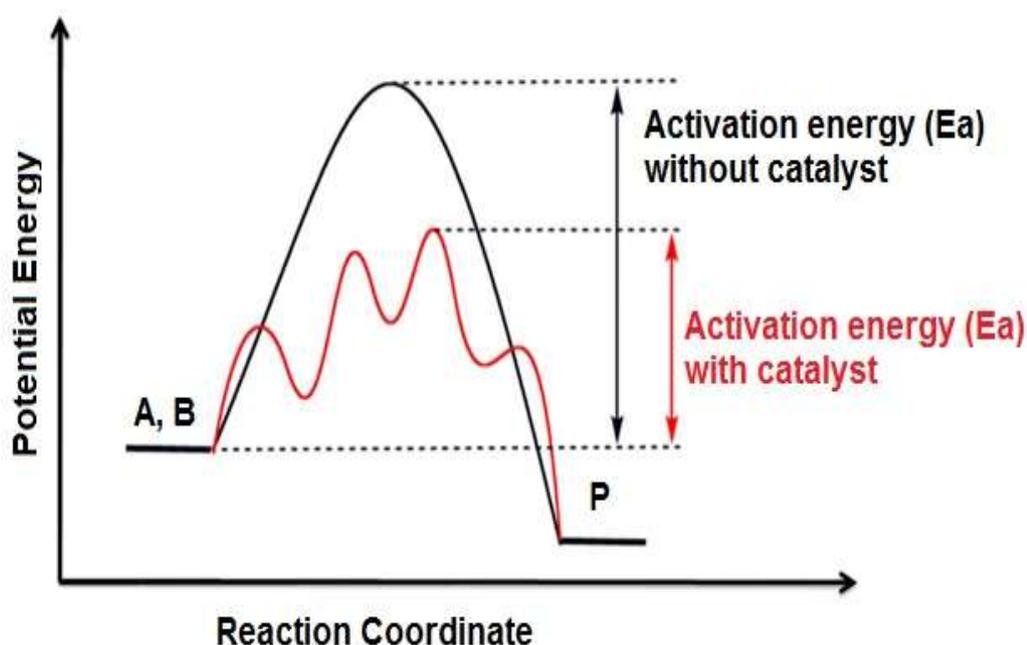


Figure 1.1 Potential energy diagram for an exothermic reaction performed with and without catalyst, respectively.

Based on that, the theory proclaims that the activation energy during the use of a catalyst should be less than that of the same reaction when a catalyst is not used (Figure 1.1), which increases the collisions between the molecules of the different reactants, thereby reducing the energy required to reach the final transition state. It is of a great significance to state that during the utilization of a catalyst, the extent of a reaction does not change at all. Thus, chemical equilibrium of a reaction is not disturbed owing to equal influence on the rate of both the forward and the reverse reaction.¹⁵

1.2 Homogeneous and Heterogeneous Catalysts

Homogeneous and heterogeneous catalysis are categorized as being unlike or same phase with reactants during the reaction process. When the catalyst has the same phase as the reactants and products, it is then called homogeneous catalysis. The homogeneous catalysts are composed of transition metals. Moreover, the stability of such transition metals is achieved by a ligand. The ligand binds the metal atoms. By changing the type of the ligands, the properties of catalyst can be changed. Additionally, the phase of heterogeneous catalysts is different than the phase of reactants. In this category of catalytic process, the reactants spread to the surface of metal catalyst, and adsorption onto surface is carried out via chemisorptions.

The products of the reaction are released and separated from the catalyst surface, as soon as the reaction is finalized. In case of the heterogeneous catalysts, availability of the catalyst sites is associated to the total exposed surface area of the catalyst. Furthermore, heterogeneous catalysts have attracted great attention and applied in numerous numbers of industrial applications. Most of the catalytic processes, which are carrying out in nature, are very good illustrations and examples of heterogeneous type catalyst schemes comprising solid type catalyst and reactants in gas or liquid phase.

Currently, most heterogeneous catalysts are greatly favored in industrial processes due to their properties such as ease of separation, reusability, solidity, low-price and low degree of toxicity. The comparison of the properties of homogeneous and heterogeneous catalysts is given in Figure 1.2.

Heterogeneous	Homogeneous
<ul style="list-style-type: none"> ▪ More stable / high reaction temp. possible. ▪ Product/catalyst separation is easy ▪ Poor degree of synthetic control. ▪ Challenging to study. 	<ul style="list-style-type: none"> ▪ Limited to lower reaction temperatures. ▪ Can design complex structures for specific jobs. ▪ Amenable to study and rational design. ▪ More selective / high reaction rates.

Figure 1.2 Properties of homogeneous and heterogeneous catalysts

1.3 Nanocatalyst

Nanocatalysts gain great importance, which involves the usage of nanomaterials in the form of catalysts in most reactions. The characteristics of nanocatalysts are given in Figure 1.3. Heterogeneous catalysis reactions are one of important target of commercial applications of nanotechnology where metallic nanoparticles, semiconductors, materials oxidized products and similar materials are widely used. Although surface studies have significant express principles of catalysis where most of these conventional catalysts are still prepared through simple reactions steps including mixing, stirring and baking stages with interaction of different reagents. However, their nanometric morphologies are not sufficiently controllable and the synthesis regard to their structure/performance dependencies are extremely confused.

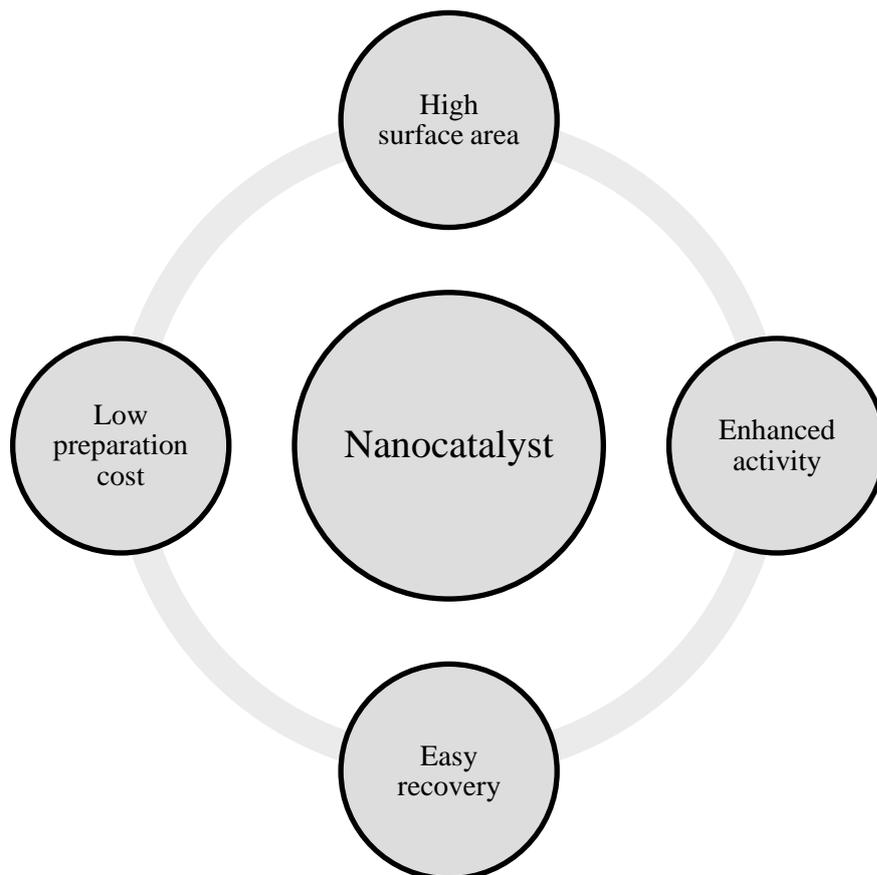


Figure 1.3 Characteristics of nanocatalysts

Because of their sophisticated physiochemical properties of conventional catalysts their characterizations in the active sites in nanometric scales are not achievable. High selectivity and activity property besides long lifetime and low energy consumptions considered as the key points of nanometric catalysis which can be obtained by controlling their porosity and particle characteristics. In order to obtain cost effective nanocatalyst, scientists try to replace high cost supports and metals with cheaper one. Besides they target to increase catalytic activity by accurate controlling of porous materials sizes, shapes and their spatial distribution beside surface composition.

Metal nanoparticles as colloidal solutions and supported on solid materials known as very attractive catalysts in various organic and inorganic reactions due to their high surface-to-volume ratio and very active surface atoms compared to bulk catalysts.

Figure 1.4 and Figure 1.5 show the common usage areas and benefits of nanocatalysts, respectively.

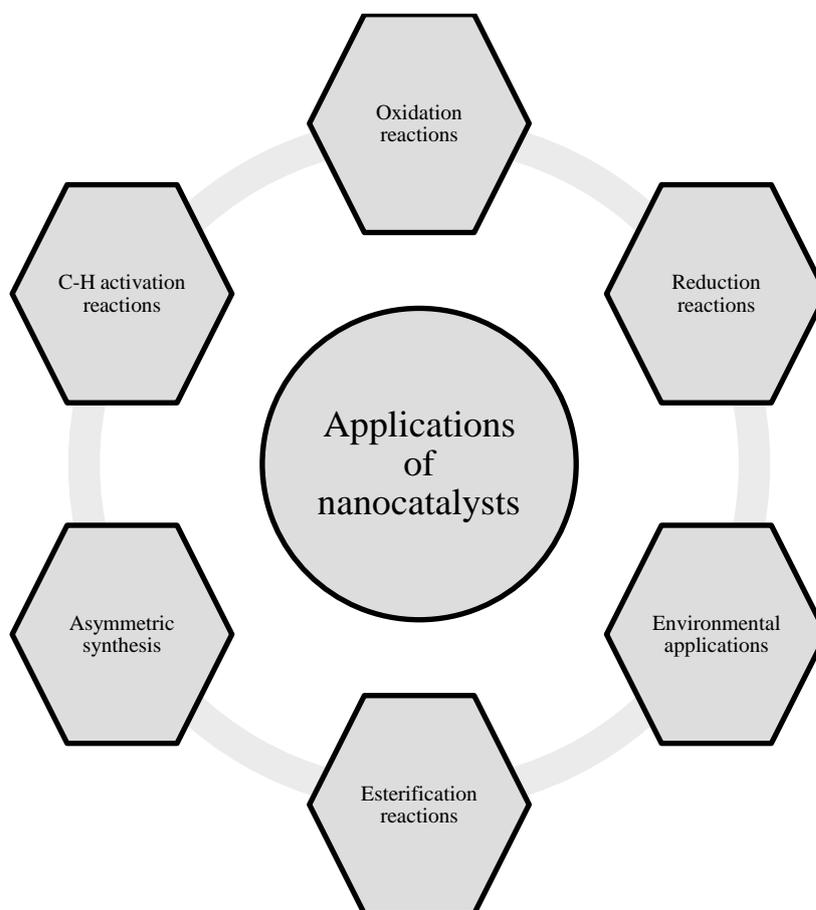


Figure 1.4 Application of nanocatalysts

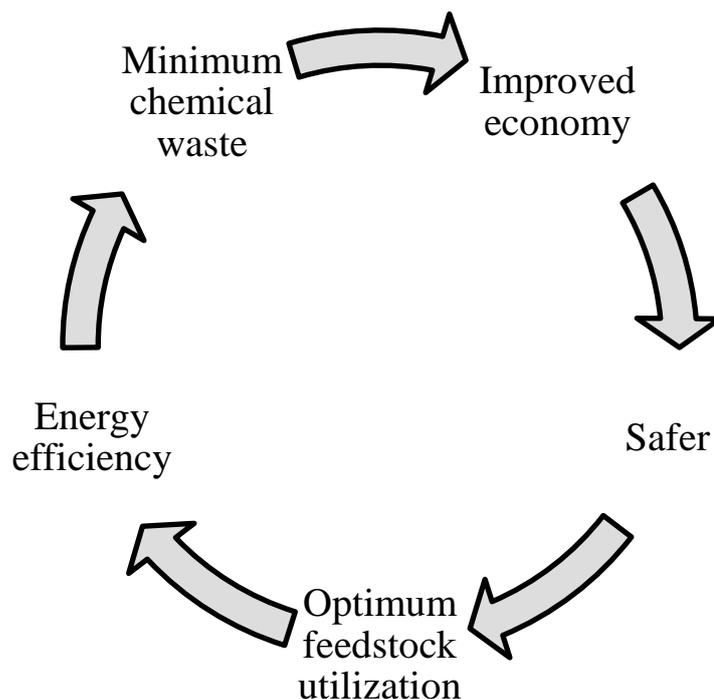


Figure 1.5 Benefits of nanocatalysts

Biological¹⁶, magnetic¹⁷ and carbon based^{18,19} materials and polymers²⁰ are considered as different types of support materials used for immobilization of noble metal nanoparticles. After immobilization of noble metal nanoparticles, they can be used as catalysts. The interaction of support and metal nanoparticles has a significant effect on catalytic activity by affecting the stabilization, formation and state of the metal in the structure.

1.4 Supported Metal Catalysts

Supported catalysts have highly impact in most of the processes applied in industry. The solid support materials allow the dispersion of active sites on metal nanoparticles properly due to their high surface area²¹.

Catalytic processes are generally occur in the form of dispersion with high surface per volume rate in the case of metallic oxides^{22,23}. This can be provided by interaction between metallic nanoparticles and the support chemical surfaces (metal/support interaction) which affects the electronic properties of the metal in bulk phase.

Both electronic and geometric effects may affect the catalytic performance of a supported metal catalyst (particle-size effect). Aggregation of the nanoparticles leads to serious decreasing in nanoparticles surface activation. So finding proper support material is so important in various types of catalytic applications.

1.5 Conjugated Polymers as Support Materials

Polymer based materials are widely used as support materials for metal nanoparticles due to easy functionalization property and highly porous structures. Their facile preparation techniques beside their different polymerization are considerable. They can be prepared by free-radical reactions²⁴ beside ionic polymerization²⁵ known as cost effective processes.

Solid polystyrene (PS) microgel particles, cross-linked poly (N-isopropyl acrylamide) (PNIPA) polymer, poly (methacrylic acid) microgels, are some of the examples applied to stabilize metal based nanocatalyst^{26, 27}. Besides, a modified poly (4-vinylpyridine) cryogels,²⁸ polymer dendrimers like poly (amidoamine) (PAMAM) and poly(propyleneimine) (PPI) are also applied to stabilize metal nanoparticles like Ag, Pt and Pd²⁹. Besides, a poly-(3,4)ethylenedioxythiophene (PEDOT) conjugated polymer was reported as a solid support material³⁰.

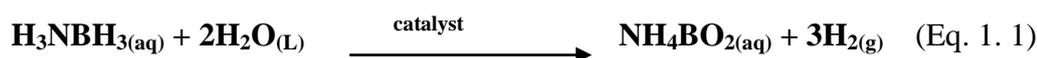
1.6 Supported Nanocatalysts for Hydrogen Generation from Ammonia Borane

Commonly hydrogen gas has been introduced as non-limited, non-pollutant green fuel energy source with a high energy content per mass (120 MJ/kg) compared to fossil fuel (44 MJ/kg). Hydrogen gas can be served as energy carrier in different mobile applications like hydrogen based fuel cells and portable electronics³¹.

The gravimetric and volumetric content of hydrogen at mild reaction conditions given by US Department of Energy (DOE) are 9.0 wt% and 81 g/L, respectively. To meet the targets applied by US DOE, different storage materials were developed^{32,33,34}. However, most of challenges have been remained without any solution. Chemical storage materials with low molecular weight and high hydrogen content feel to have high impact in promising of hydrogen sources^{35,36}. Particularly, ammonia borane (AB) and hydrazine borane (HB) are considered as good candidates. They can release their hydrogen through thermal dehydrogenation in solid state and solvolysis in solution³⁵.

Among the hydrogen storage materials, AB considered as one of the most important hydrogen storage material. It is a colorless crystalline chemical with 0.74 g cm⁻³ density under mild conditions. The total content of hydrogen is 19.6 % by weight. The hydrogen gas in AB can be released by applying different procedures. One of them is thermolysis reaction in which 6.5wt% H can be taken from one mole of AB by heating it at high temperature. Thermal decomposition of AB usually need a few amounts of heat energy require for initiation and propagation of reaction. Such reactions are relatively difficult to control.

The catalytic hydrolysis or methanolysis of AB, second and most effective way, is considered as more proper way to release hydrogen production from AB^{37,38}. In the presence of an effective catalyst, it is possible to produce 3 moles of hydrogen for each mole of AB in aqueous solution of AB at room temperature and pressure according to reaction given below³⁹:



In order to take the hydrogen from AB by using hydrolysis reaction, noble metal catalyst such as Pt, Ru, Rh and Pd are widely used. Different support materials like Al₂O₃, C, and SiO₂ are studied in hydrolysis reaction of AB molecules¹⁰.

Platinum based nanocatalysts were explored to have much more activity. Recently, ultrafine Platinum nanoparticles embedded into the metal-organic carriers (MIL-101) were prepared with high efficiency property in hydrolytic dehydrogenation from AB⁴⁰. Besides, transition metals based catalyst such as Fe, Co, Ni, and Cu also investigated in the hydrogen production from AB^{41,42,43,44}.

1.7 Aim of the Study

In this thesis, conjugated polymer, polythiophene, was used to add palladium nanoparticles and form Pd(0)/Polythiophene nanocomposite material. In order to prepare Pd(0)/Polythiophene material, Pd(II) ions were added by using wet-impregnation of on polythiophene. After that the reduction of the palladium ions was performed with NaBH₄ on the surface of polythiophene particles. The prepared catalyst was characterized by using SEM, TEM, HR-TEM, EDX, and ICP-OES techniques. Then the prepared catalyst was used in the hydrogen evolution from aqueous solution of AB at room temperature and pressure. The stability and reuse performance of the prepared catalyst were also investigated.

CHAPTER 2

MATERIALS AND METHODS

2.1. Chemicals and Materials

In this work, palladium nitrate hydrate, $(\text{Pd}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O})$, iron(III) chloride (FeCl_3), thiophene, dichloromethane, ammonia borane (NH_3BH_3) and methanol were purchased from Sigma-Aldrich in analytical grades and utilized as received from the source. Milli-Q water cleaning system was used to acquire deionized water. Washing of glassware's was accomplished using both ethanol and water.

2.2. Characterization

The morphological characterization of the prepared nanocatalysts were revealed by using 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).

Elemental composition of prepared samples was founded with energy-dispersive X-ray analyzer (EDX) coupled with SEM and TEM.

The palladium content of the nanocatalyst (assembled on polythiophene polymer support) and the leaching of ions into the solution after reaction were evaluated after analyzing by Perkin Elmer DRC II series of inductively coupled plasma mass spectroscopy (ICP-OES).

2.3. Preparation of Polythiophene Polymer Support Material

Chemical polymerization of thiophene was performed in order to prepare polythiophene. The preparation procedure is given in Figure 2.1. For this, initially 1.00 g anhydrous Iron (III) chloride (FeCl_3) and 10 ml of chloroform (CHCl_3) were mixed and stirred on magnetic stirrer for 5 min. In separate beaker 0.200 g 3-methylthiophene monomer and 10 ml of CHCl_3 were mixed and stirred on magnetic stirrer for 5 min. After that, initially prepared mixture was added drop by drop into the solution which contains monomer. The resulting mixture was stirred for 3 hours at room temperature for the complete polymerization.

At the end of this period 100 ml methanol was added into the mixture. In order to obtain precipitates of polythiophene final composition was stored in freezer for 24 h, and then formed were collected by filtration. After collecting the precipitate it washed with dichloromethane and methanol in Soxhlet apparatus for 3 days. Obtained polythiophene particles were dried at room temperature.

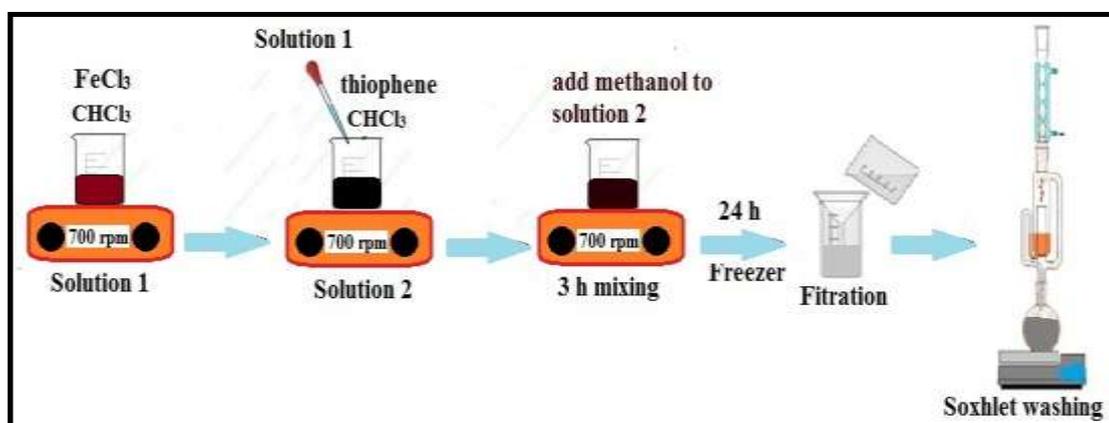


Figure 2.1 Preparation of polythiophene support material

2.4. Addition of Palladium Ions onto Polymer Support

Preparation of palladium ion (Pd^{2+}) added polythiophene was performed by using wet-impregnation technique. According to this method, initially 100 mg of polythiophene was dispersed in 10 mL water by using magnetic stirrer. Then, palladium nitrate was added in to dispersion. The mixture was stirred for 5 hours and palladium ion loaded polythiophene support materials were isolated from the solution by centrifuging the mixture. Preparation method is shown in Figure 2.2. After that the particles were rinsed with deionized water. The eluent and washing portion were kept to determine the amount of palladium added onto the polymer support by using ICP-OES.

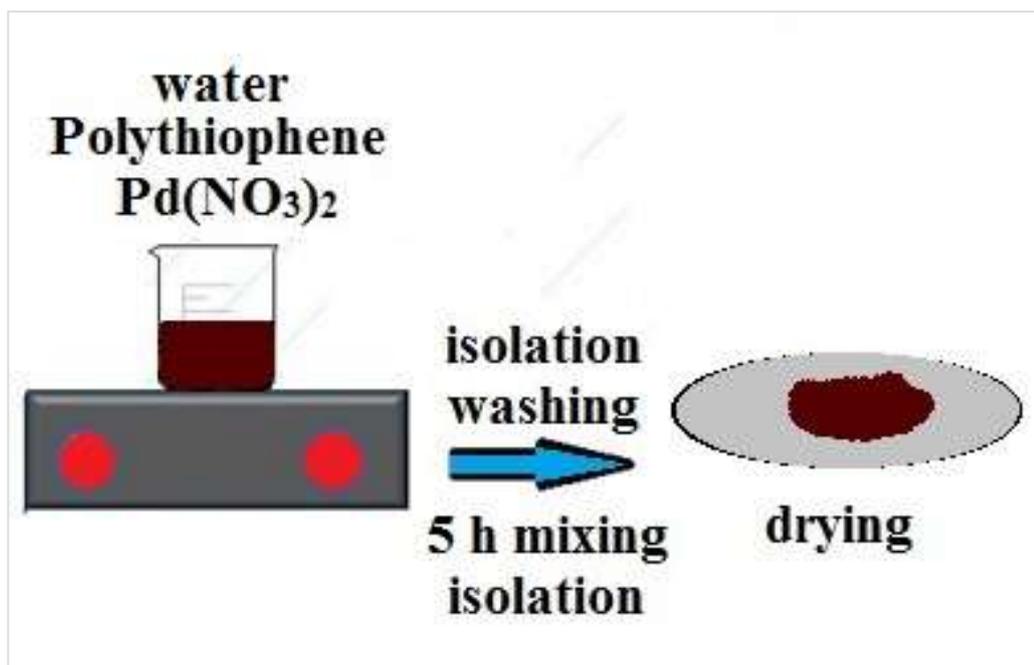


Figure 2.2 Addition of palladium ions onto polythiophene

2.5. Preparation of Palladium Ions onto Polymer Support

Palladium ions supported onto the polythiophene were reduced by using sodium borohydride (NaBH_4). Schematic representation of the production is given in Figure 2.3. For this 100 mg Pd ion added support was dispersed in 20 mL water. Then 50 mg NaBH_4 was added into solution and mixed by using magnetic stirrer. The reduction was completed in 1 h. Then the particles were collected and washed. After that particles were dried in oven.

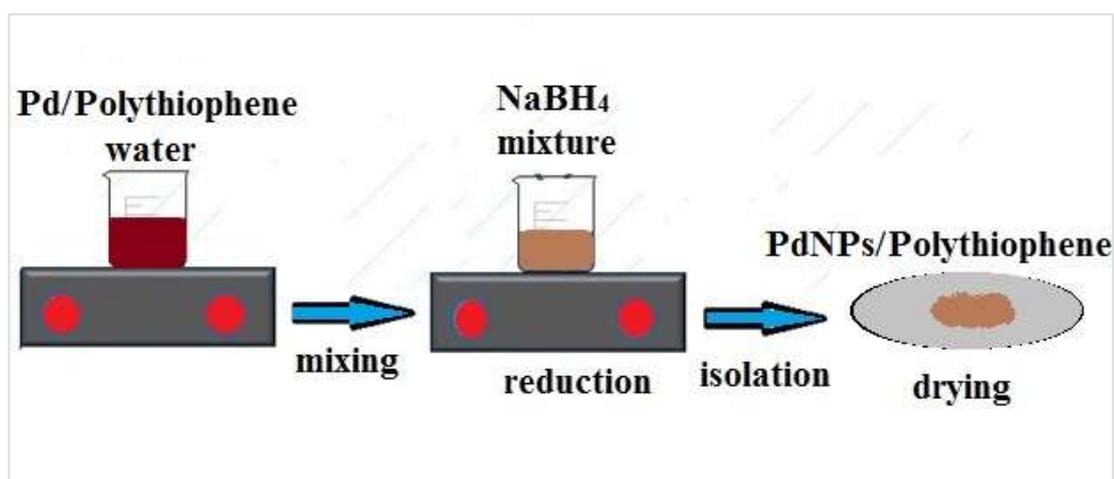


Figure 2.3 Preparation of palladium nanoparticles onto polythiophene

2.6. Hydrogen Generation Studies

The catalytic performance of the PdNPs/Polythiophene in the hydrogen generation from AB was revealed by finding the amount and rate of hydrogen production during the experiment. Catalytic activity measurements were performed with the system given in Figure 2.4. According to applied procedure, 20 mg of catalyst (with 1.15 wt % Pd loading) was dispersed in 10 mL water in to the reactor. After that, the temperature of the inside part of the reactor was adjusted to 25 °C by using circulator. Then 1mmol (31.8 mg) AB was added in to the reactor. With the addition of AB, reaction was started by opening the magnetic stirrer which was set to 700 rpm.



Figure 2.4 System used for the hydrogen generation studies

The amount of hydrogen generated was measured volumetrically by recording the change of water level on graduated part. The level change was recorded at every 30 s until the end of the reaction. The temperature and pressure were kept constant at the end of the reaction.

2.7. Reuse performance of the Prepared Catalyst

Finally the reuse capacity of the PdNPs/Polythiophene catalyst was investigated. For this, after the first try, the used catalyst was collected by using centrifuge and washed with water. Then they dispersed in another 10 mL portion of water and same procedure was applied at same conditions. The performance of the catalyst was checked in the hydrolytic dehydrogenation of AB by addition of 1mmol of AB. This was repeated five times and the reuse performance of the PdNPs/Polythiophene catalyst was found.

CHAPTER 3

RESULTS AND DISCUSSION

In this thesis, polythiophene polymer was chosen as a support material due to their easy preparation procedure and low cost and toxicity properties. They used as a host material for palladium nanoparticles which used as effective catalyst in the hydrogen generation from ammonia borane (AB). After loading the Pd ions onto polythiophene, PdNPs were formed by using strong reducing agent, sodium borohydride. Then the catalytic activity of the palladium nanoparticles added polythiophene (PdNPs/Polythiophene) in the hydrogen production from AB was revealed under mild conditions. Besides the catalytic performance, morphological properties, and reuse performance of the prepared catalyst were investigated. Obtained results were given below, respectively.

3.1. Preparation of Polythiophene

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 that obtained polymer was treated with hydrochloric acid in order to increase the surface area of it. Then 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.

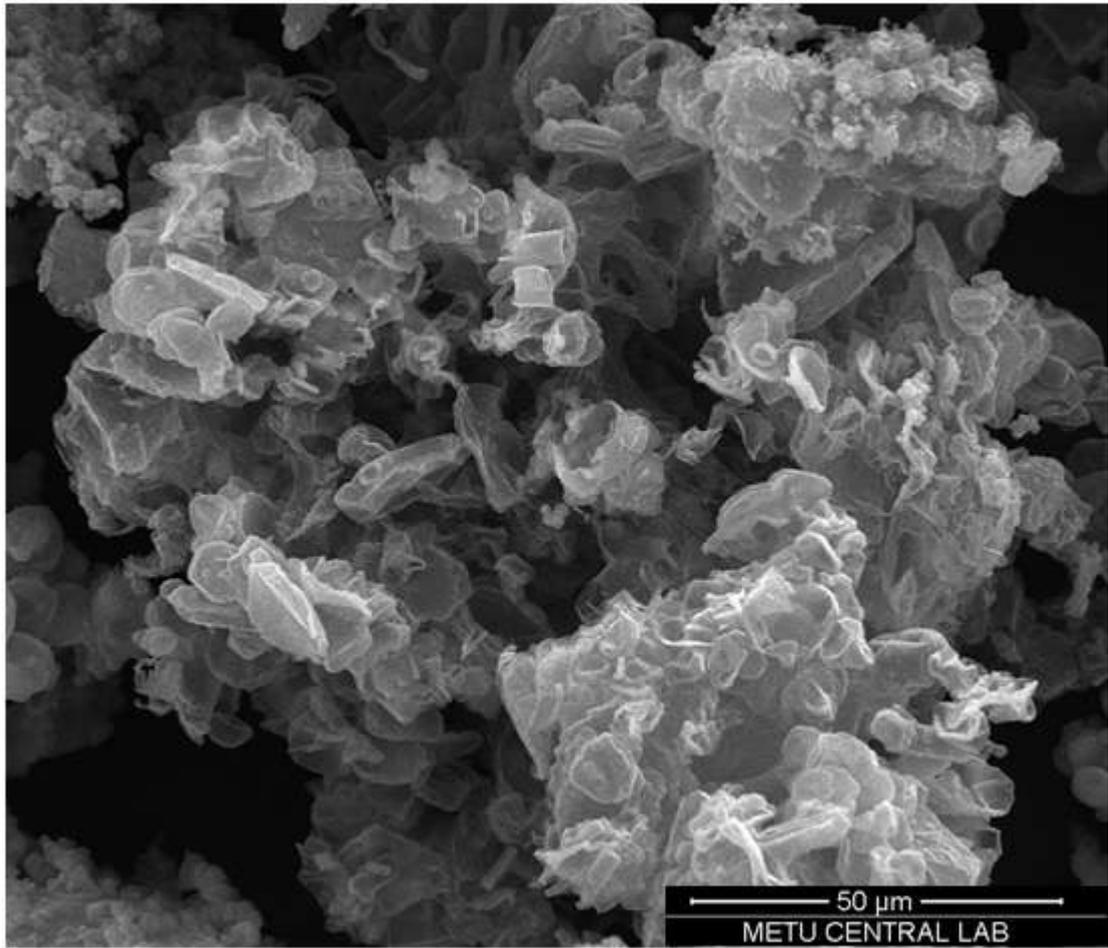


Figure 3.1 SEM images of bare polythiophene.

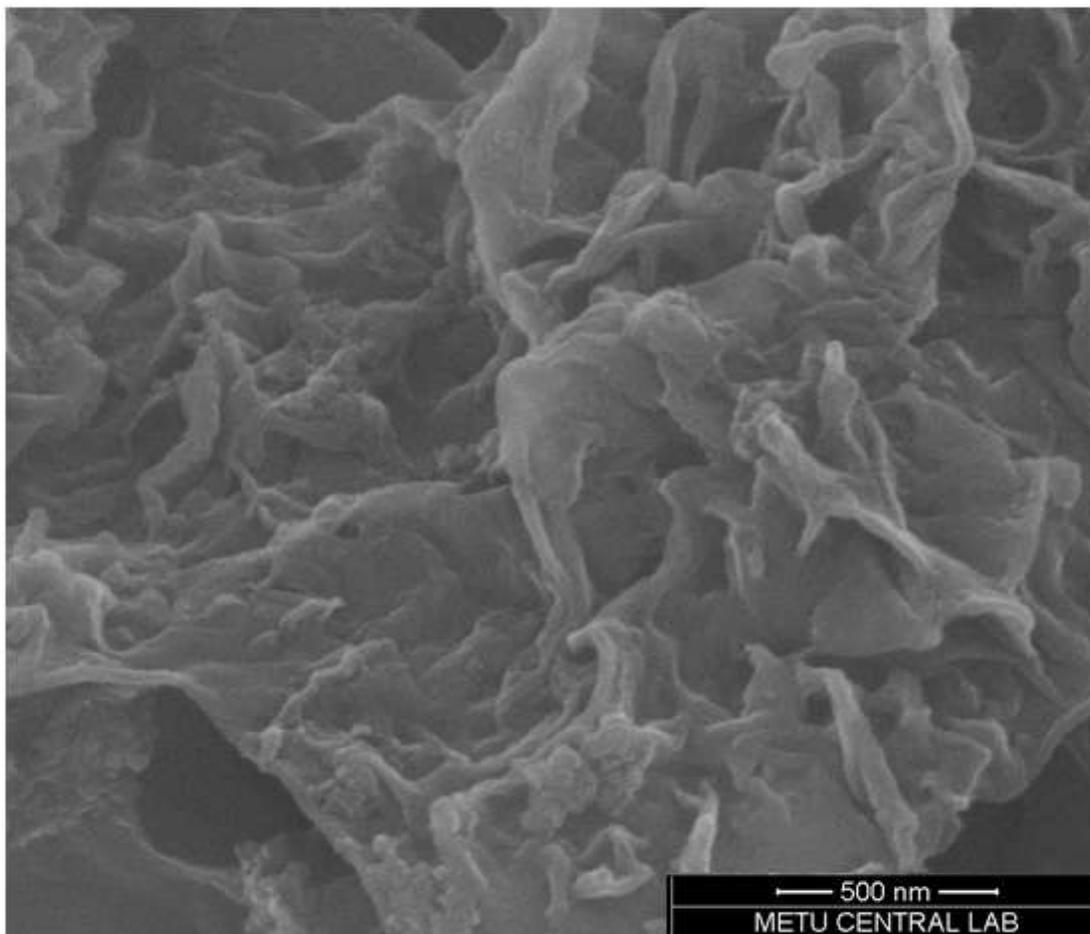


Figure 3.2 SEM images of bare polythiophene.

The SEM images provide that the polythiophene polymer support has high surface area and proper surface for the addition of ruthenium nanoparticles on it. The elemental composition of the polythiophene particles was examined by using EDX which is coupled with FE-SEM. The result of the measurement is given Figure 3.3. The obtained EDX pattern confirms the presence of elements founded in polythiophene and monomer used to prepare it.

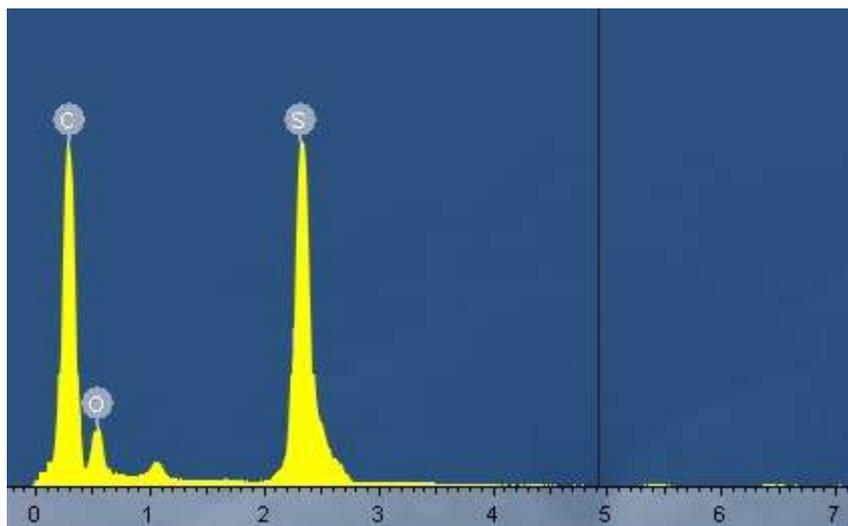


Figure 3.3 EDX pattern of polythiophene particles.

3.2.Preparation and Characterization of Palladium Nanoparticles Added Polythiophene

As mentioned before, palladium ion addition onto the polymer particles was performed by using a method known as wet-impregnation. After the impregnation of palladium ions, they were reduced to form palladium nanoparticles (PdNPs) by using sodium borohydride as reducing agent. After that the particles were isolated and used in the hydrogen generation and characterization studies. The characterization of the palladium nanoparticles added polythiophene was carried out by using HR-TEM, SEM, EDX, ICP-OES techniques.

The morphological properties, size and dispersion behavior of PdNPs supported onto polythiophene, of the prepared materials were revealed with HR-TEM and EDX spectroscopy. The obtained images are given in Figure 3.4 and 3.5, respectively. In the sample preparation for HR-TEM and EDX measurements, 1.15 wt. % Pd loaded polythiophene was used.

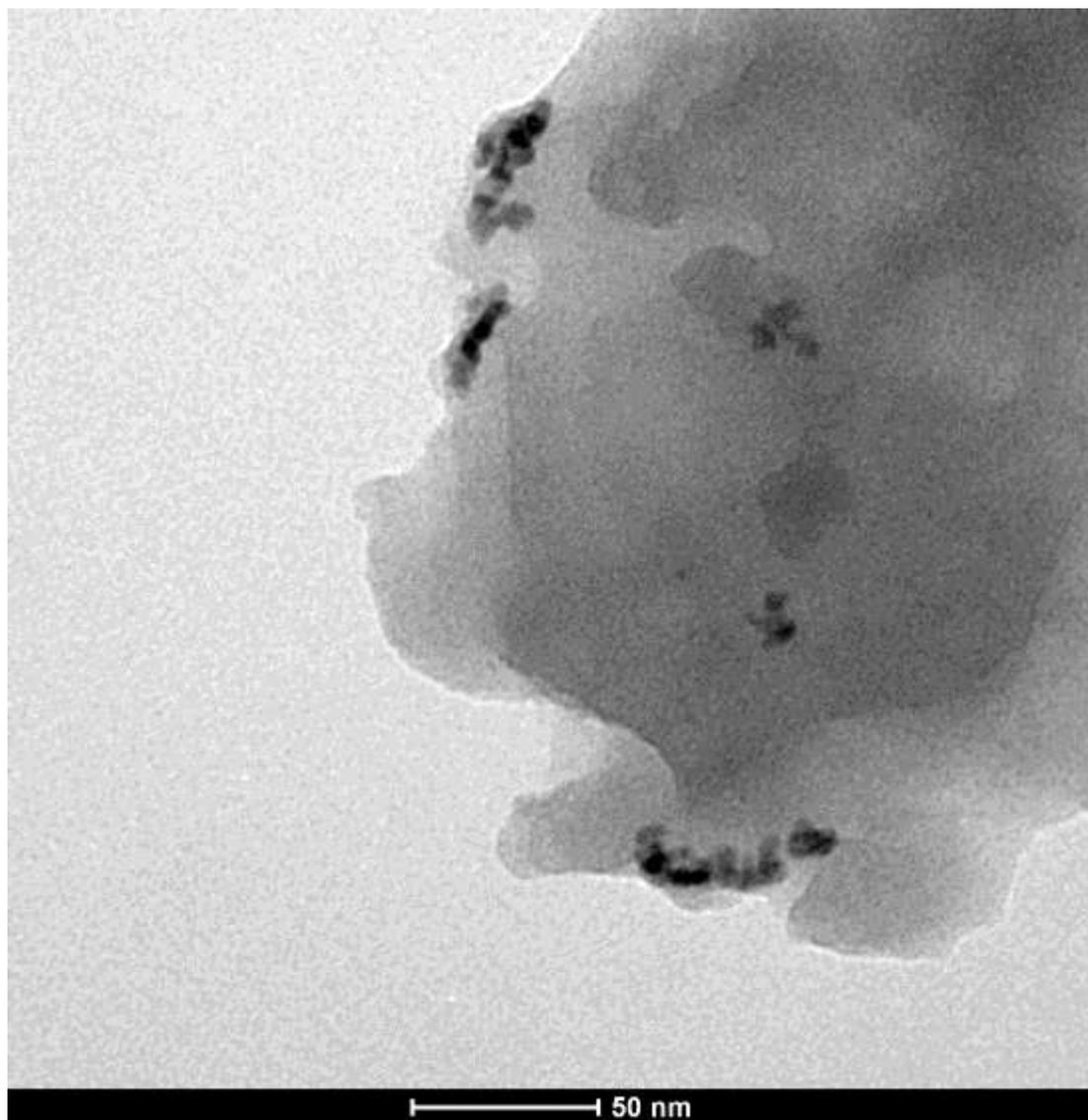


Figure 3.4 HRTEM images of PdNPs/Polythiophene particles.

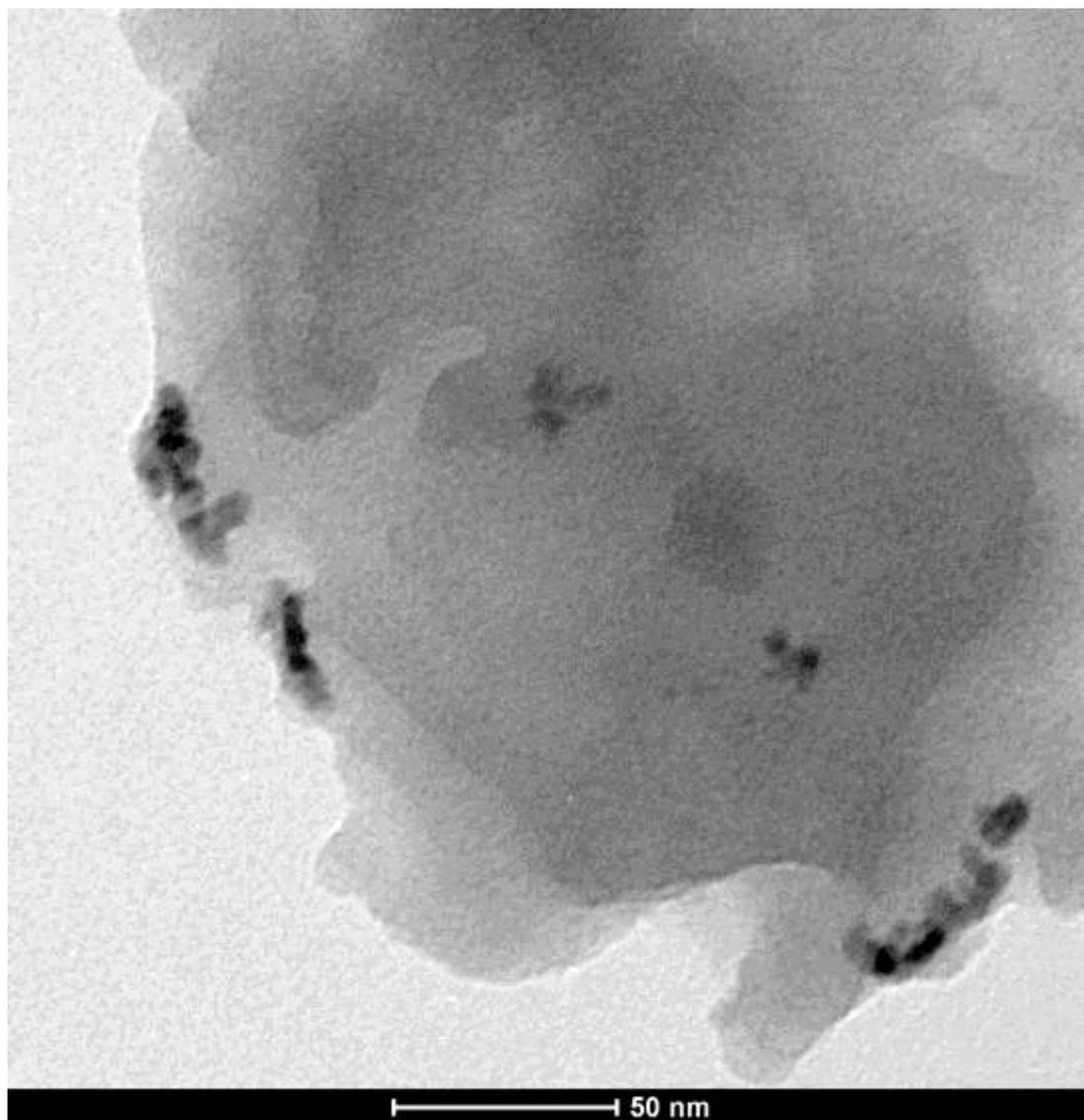


Figure 3.5 HRTEM images of PdNPs/Polythiophene particles.

From the figures given above, the particle size of PdNPs was laid between 7-15 nm. After that, EDX measurements were performed to prove the addition of palladium and formation of PdNPs on polythiophene support. The result is given in Figure 3.6.

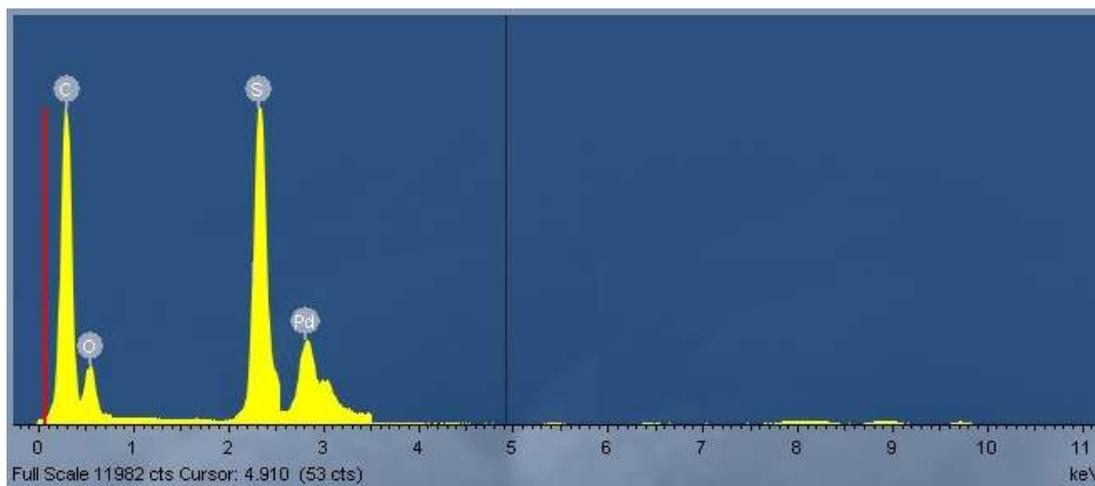


Figure 3.6 EDX pattern of PdNPs/Polythiophene particles.

According to EDX pattern given above, final structure contains palladium besides the elements founded in the structure of polythiophene. This results also supported by ICP-OES measurements. According to ICP-OES results, 1.15 wt. % palladium calculated on the polythiophene support material.

3.3. Investigation of the Catalytic Activity of Palladium Nanoparticles Added Polythiophene

The activity measurements were started with the bare polythiophene support material to check the effect on the reaction. For this 20 mg polythiophene without palladium content was used. The result showed that the polythiophene polymer support has no catalytic activity in the dehydrogenation reaction of ammonia borane (AB).

After that, the catalytic activity of the palladium loaded polythiophene catalyst was checked in the hydrogen production from AB according to procedure given in experimental part. In this experiment, hydrogen gas produced as a function of time was followed by using PdNPs/Polythiophene particles at a given temperature and pressure.

Obtained results were plotted as number of moles of hydrogen gas versus time. The molar ratio of hydrolytically generated H_2 to the initial AB is close to 3.0, indicating dehydrogenation is completed.

Initially, different amounts of palladium loading were investigated to find the optimum amount of loading on polythiophene support. For this initially 1%, 2% and 3% wt. palladium loading were tried. By using wet impregnation method mentioned amounts tried to load over polymer support. Loading amounts of palladium were investigated with ICP-OES and % loading of palladium founded as 0.61, 1.15 and 1.84, respectively. After that the catalytic activity of the prepared materials were investigated by applying the activity measurement procedure given in experimental section. Hydrogen evolution performance of the prepared catalyst with different Pd loading is given in Figure 3.7.

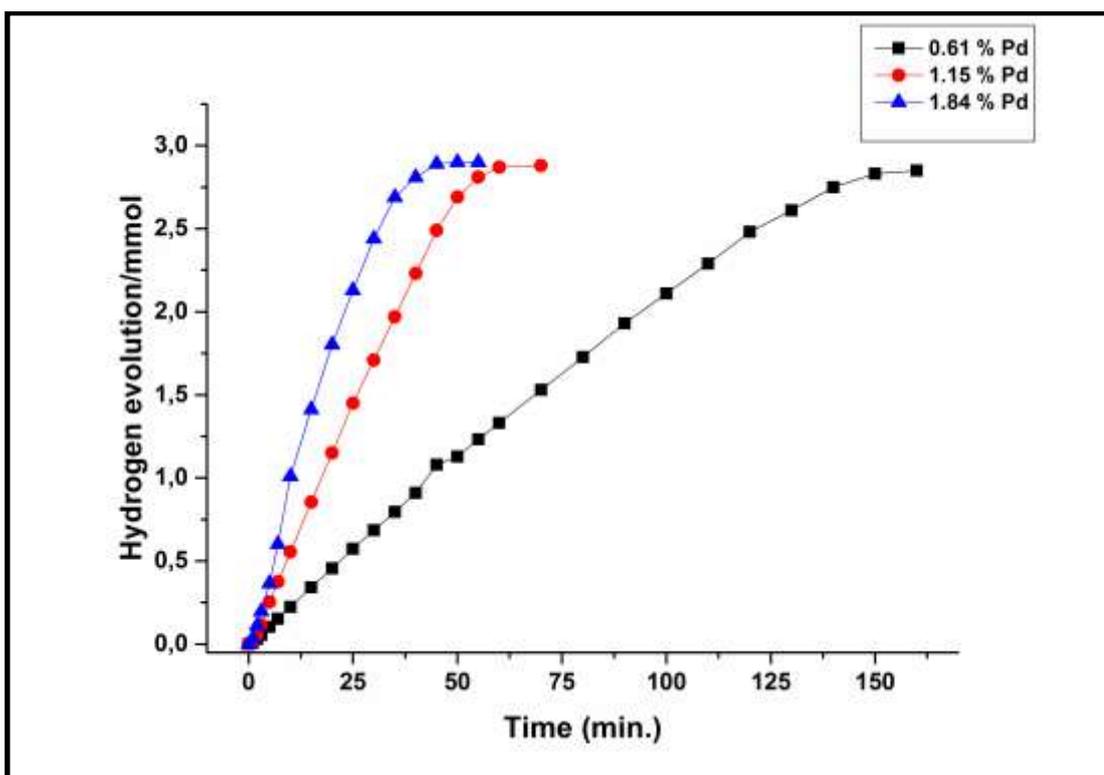


Figure 3.7 Hydrogen generation from AB (0.1 M, 10 mL) by using PdNPs/Polythiophene particles with different wt. % palladium content performed at $25.0 \pm 1^\circ C$.

The comparison of the turn over frequencies (TOF) obtained with the usage of different Pd amount is given in Figure 3.8.

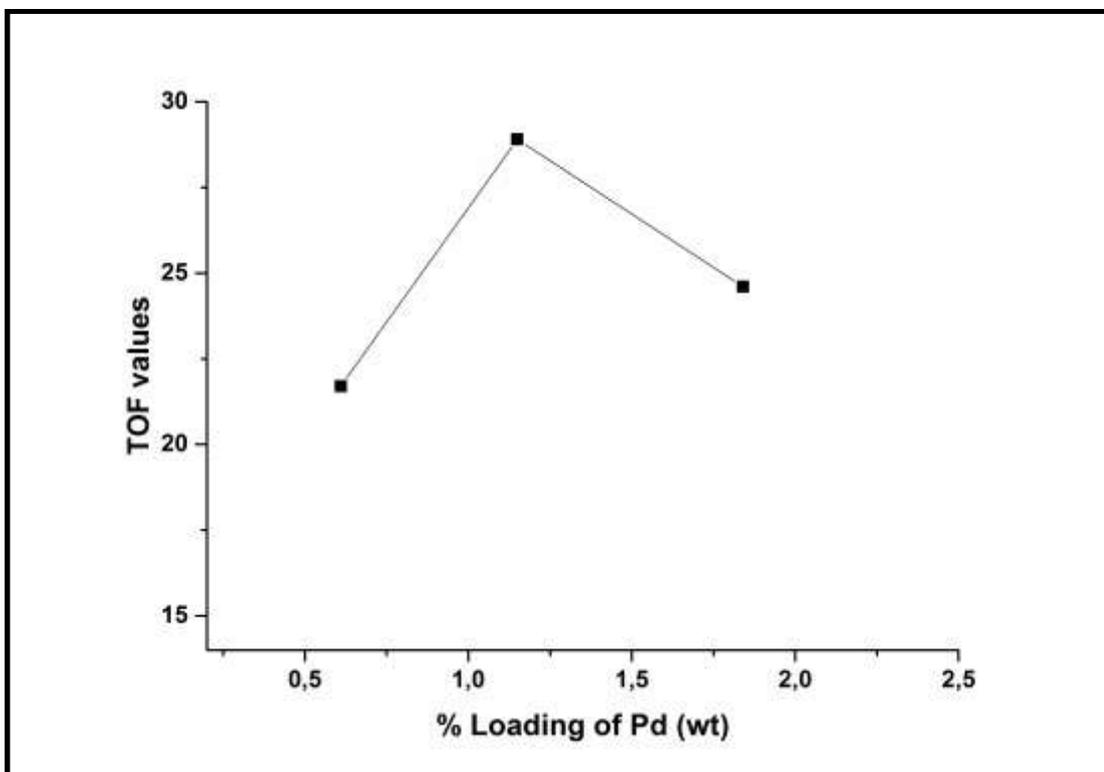


Figure 3.8 Comparison of the activities of the prepared catalyst contains different % loading of palladium (0.61, 1.15, 1.84 % palladium, respectively).

According to results given in Figure 3.7 and Figure 3.8, 1.15 % wt loading of palladium has the highest catalytic activity. So 1.15 % wt palladium loaded polythiophene was chosen as the best working catalyst and used through the study.

After that different catalyst concentrations were used to find the optimum amount of catalyst in this reaction. In all experiments 1.15 % wt palladium loaded polythiophene was used. The results are given in Figure 3.9.

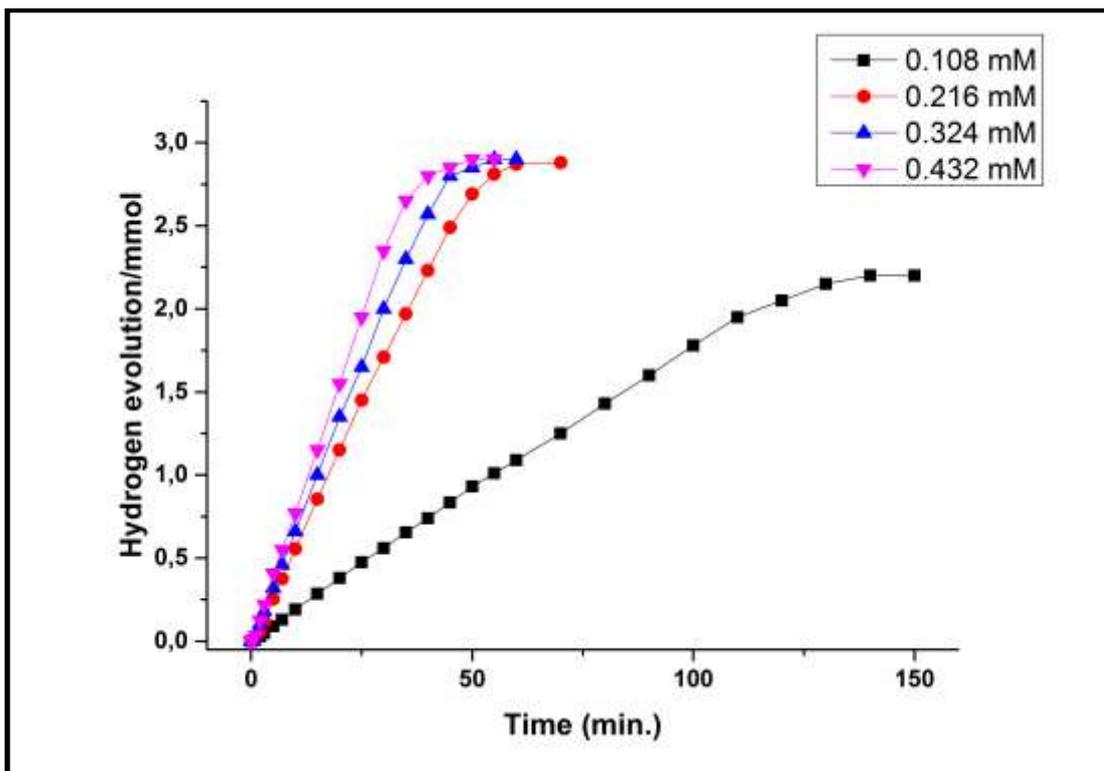


Figure 3.9 Hydrogen generation from AB (0.1 M, 10 mL) by using PdNPs/Polythiophene particles with a palladium content of 1.15 wt. % at different concentration of catalyst performed at $25.0 \pm 1^\circ \text{C}$.

Figure 3.9 shows the amount of H_2 generated as a function of reaction time at different catalyst amount under ambient conditions. According to results, 20 mg catalyst shows the best catalytic activity in the hydrolysis reaction of AB.

TOF (turnover frequency) numbers for each try were estimated from the total amount of hydrogen gas produced by a given amount of catalyst in a given time ($\text{mol H}_2 \times \text{mol catalyst}^{-1} \times \text{min}^{-1}$). The results are given in Figure 3.10.

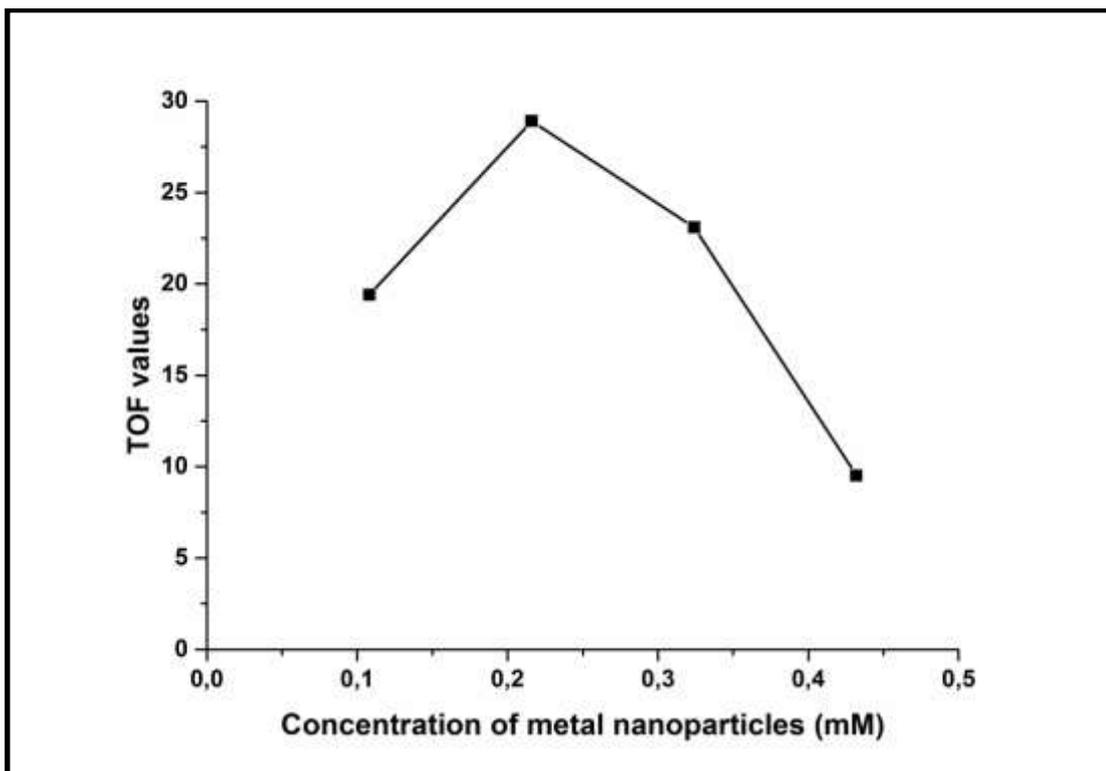


Figure 3.10 Comparison of the activities of the prepared catalyst with different concentration (0.108, 0.216, 0.324 and 0.432 mM, respectively).

The highest initial TOF vales of catalyst with a palladium content of 1.15 wt. % calculated as 28.9 min^{-1} by using 20 mg PdNPs/Polythiophene catalyst.

The comparison of the TOF value obtained with PdNPs/Polythiophene catalyst with the palladium based studies in literature used in the hydrogen production from AB is given in Table 3.1.

Table 3.1 TOF values of palladium based catalysts reported in the literature for the hydrogen production from AB.

Entry	Catalyst	TOF (min^{-1})	Ref.
1	Pd black	0.67	[45]
2	Pd/ γ - Al_2O_3	1.39	[45]
3	PSSA-co-MA-Pd	5	[46]
4	RGO/Pd	6.25	[47]
5	Pd/zeolite	6.25	[48]
6	Pd(0)-HAP	8.3	[12]
7	Pd(0)/ SiO_2	10	[49]
8	CDG-Pd	15.5	[50]
9	Pd@Co/graphene	37.5	[51]
10	Pd(0)/ SiO_2 - CoFe_2O_4	254	[49]
11	PdNPs/Polythiophene	28.9	This Study

TOF = $\text{mol H}_2 / \text{mol metal} \times \text{min}$

As seen from the table, PdNPs/Polythiophene can be considered as the good candidate for the hydrogen production from AB at mild conditions.

3.4. Reuse Performance and Stability of the PdNPs/Polythiophene Catalyst

In practical applications stability is considered as one of the important properties of catalyst. To find the stability and the reuse performance of prepared PdNPs/Polythiophene catalyst, it was tested in the hydrogen production experiments from an aqueous solution of AB at 5 sequential runs at room temperature. For the reuse performance, PdNPs/Polythiophene catalysts were separated from the solution at the end of the reaction. After washing they used again as the catalyst for the hydrolytic dehydrogenation of AB. The results are given in Figure 3.11.

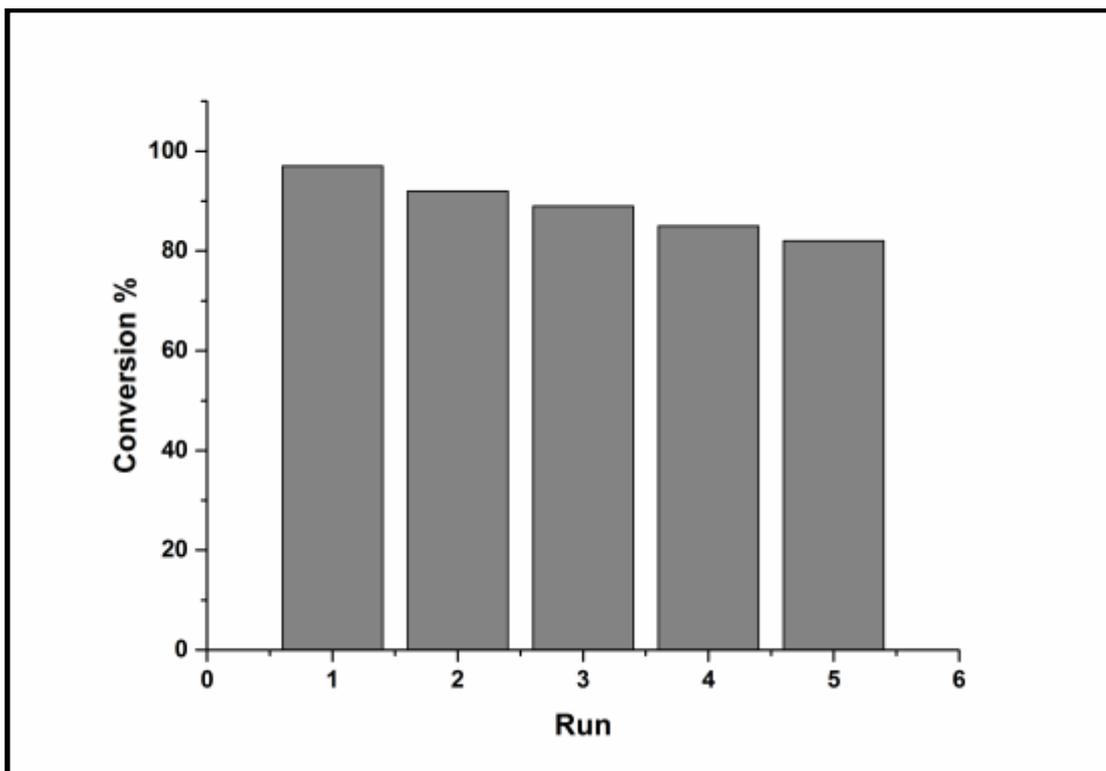


Figure 3.11 Conversion values 20 mg, 1.15 % Pd loaded polythiophene catalysts at 5 sequential runs in the hydrogen generation from an aqueous solution of ammonia borane (0.1 M, 10 mL) at room temperature

As shown in Figure 3.11, even after 5 successive runs, prepared catalyst worked properly and generation of hydrogen reduced only 10 % when compared to first run, indicating that PdNPs/Polythiophene catalyst showed good stability and reuse performance in the hydrogen production from AB under ambient conditions.

CHAPTER 4

CONCLUSION

As a conclusion, palladium ions were added on to the polythiophene support material by utilizing liquid impregnation technique. After that the palladium ions added onto polymer support were reduced to form palladium nanoparticles on polythiophene. Then the catalytic performance of the PdNPs/Polythiophene catalyst was investigated in the hydrogen production from ammonia borane. Addition of palladium nanoparticles onto the polymer support prevents the agglomeration of PdNPs and makes the isolation of catalyst easy from the reaction solution at the end of the process. The obtained nanoparticles are isolated easily by using centrifuge and reuse for hydrolytic dehydrogenation of ammonia borane at mild conditions.

The prepared catalyst showed good catalytic performance. The TOF number of the prepared PdNPs/Polythiophene catalyst was calculated as 28.9 min^{-1} with the usage of 1.15 % wt. PdNPs added polythiophene catalyst. The prepared PdNPs/Polythiophene catalyst shows high stability and reuse performance besides good catalytic activity. PdNPs/Polythiophene catalyst keeps nearly all of their initial activity with 83% conversion even at the fifth catalytic run. Besides the catalytic activity and reuse studies, the detailed characterization of the PdNPs/Polythiophene catalyst were done by using SEM, HRTEM, EDX, and ICP-OES.

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