

**PREPARATION OF SILVER-COPPER BIMETALLIC NANOPARTICLES
ADDED SILICA COATED-COBALT FERRITE MAGNETIC
NANOPARTICLES FOR HYDROGEN PRODUCTION FROM AMMONIA
BORANE**

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ABSTRACT

PREPARATION OF SILVER-COPPER BIMETALLIC NANOPARTICLES ADDED SILICA COATED-COBALT FERRITE MAGNETIC NANOPARTICLES FOR HYDROGEN PRODUCTION FROM AMMONIA BORANE

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Hydrogen known as one of the most important clean energy source and finding proper hydrogen storage material and method to generate hydrogen from it is one of the most difficult issue for mobile applications. There are a lot of publication in literature related to hydrogen storage materials like metal hydrides, chemical hydrides, organic molecules, metal organic frameworks and carbon nanotubes. Among them chemical hydrides has attracted great attention due to their high hydrogen storage capacity. Ammonia borane, with 19.6 wt % hydrogen content, known as the important hydrogen storage material besides stability and nontoxicity. By using proper catalyst it is possible to get three moles of hydrogen per mole of ammonia borane at mild conditions. The development of high-efficiency catalysts to improve the kinetic parameters in the hydrogen production from ammonia borane under mild conditions is so important for mobile application of hydrogen energy.

In this study, a facile way for preparing magnetically recyclable $\text{CoFe}_2\text{O}_4@\text{SiO}_2$ supported Silver-Copper nanoparticles as catalyst for hydrolytic dehydrogenation of aqueous AB by a wet impregnation method were reported.

The prepared catalysts show excellent catalytic activity toward the hydrolytic dehydrogenation of aqueous AB at room temperature. An initial turnover frequency (TOF) value is calculated as 146 min^{-1} . Furthermore, AgCuNPs which are loaded on $\text{CoFe}_2\text{O}_4@\text{SiO}_2$ support exhibit remarkable stability and reuse capability and keep almost their initial activity with total conversion after 10^{th} reuse in the hydrogen generation from ammonia borane.

Keywords: Hydrogen evolution, magnetic nanocatalyst, hydrogen energy, magnetic separation, ammonia borane



ÖZ

AMİN BORANDAN HİDROJEN ÜRETİLMESİ İÇİN ÜZERİNE BİMETALİK GÜMÜŞ-BAKIR NANOPARÇACIKLARI EKLENMİŞ SİLİKA KAPLI KOBALT FERRİT MANYETİK NANOPARÇACIKLARIN HAZIRLANMASI

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Hidrojen en önemli temiz enerji kaynaklarından biri olarak bilinmektedir ve mobil uygulamalar için hidrojen taşıyıcı sistemler ve bu sistemlerden hidrojen eldesini sağlayacak metodların geliştirilmesi çok önemlidir. Literatürde olarak metal hidrürler, kimyasal hidrürler, organik moleküller, metal organik kafes yapıları ve karbon nanotüpler gibi hidrojen depolama malzemeleri ile ilgili bir çok yayın bulunmaktadır. Bunlar arasında kimyasal hidrürler yüksek hidrojen depolama kapasiteleri sebebi ile büyük ilgi görmektedir. Kararlılığı ve toksik olmaması yanında kütlece 19.6 % oranında hidrojene sahip olması sebebi ile amin boran önemli bir hidrojen depolama malzemesi olarak bilinmektedir. Uygun katalizör kullanımı ile normal şartlarda 1 mol amin borandan 3 mol hidrojen eldesi mümkündür. Amin borandan hidrojen eldesinde kinetic parametrelerin iyileştirilmesi için yüksek etkiye sahip katalizörlerin geliştirilmesi, hidrojen enerjisinin mobil uygulamaları için çok önemlidir. Bunun yanında katalizörün reaksiyon ortamından ayrılması ve tekrar kullanımı, üstesinden gelinmesi gereken diğer önemli konulardır.

Bu çalışmada, amin borandan hidrolitik olarak hidrojen eldesin için katalizör olarak manyetik olarak ayrılabilen $\text{CoFe}_2\text{O}_4@\text{SiO}_2$ destek malzemesine ıslak emdirme yöntemi ile eklenmiş gümüş-bakır nanoparçacıklarının hazırlanması için kolay bir yöntem rapor edilmiştir. Hazırlanan katalizör oda sıcaklığında amin borandan hidrojen eldesi reaksiyonunda mükemmel katalitik aktivite göstermiştir. İlk çevrim frekansı 146 dk^{-1} olarak hesaplanmıştır. Buna ek olarak, $\text{CoFe}_2\text{O}_4@\text{SiO}_2$ destek malzemesi üzerine eklenmiş AgCu nanoparçacıklar, kaydadeğer kararlılık ve tekrar kullanılabilme kabiliyeti göstermiştir ve amin borandan hidrojen eldesinde 10. kullanımda bile tam çevrimde hemen hemen ilk aktivitesini korumuştur.

Anahtar Kelimeler: Hidrojen çıkışı, manyetik nanokatalizör, hidrojen enerjisi, dehidrojenlenme, manyetik ayırma, amin boran



To my Family

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LIST OF ABBREVIATIONS

AB	-	Ammonia Borane
APTMS	-	(3- aminopropyl) trimethoxysilane
BET	-	Brunauer- Emmett- Teller
BJH	-	Barret-Joyner-Halenda
E_a	-	Activation Energy
EDX	-	Energy Dispersive X-ray
FE-SEM	-	Field Emission Scanning Electron Microscopy
H_c	-	Coercivity
H_{sat}	-	Saturation Field
HR-TEM	-	High Resolution Transmission Electron Microscopy
ICP-OES	-	Inductively Couple Plasma- Optical Emission Spectroscopy
MSC	-	Magnetically Separable Catalyst
TEOS	-	Tetraethyl Orthosilicate
TOF	-	Turnover Frequency
TON	-	Turnover Number
XRD	-	X-ray Diffraction
XPS	-	X-ray Photoelectron Spectroscopy

CHAPTER 1

INTRODUCTION

It is an established fact that hydrogen is known as the cleanest and non-contaminating source of energy. This scientific reality nominates hydrogen as one of the most significant sources of renewable energy.¹ Recently, there has been an increasing necessity for both the effective production and storage of hydrogen. In addition, the materials that might facilitate the proper release of hydrogen have attracted a great deal of attention. As a result, one of the chemical compounds that have been chosen to serve this purpose is ammonia-borane (NH_3BH_3). It has been selected due to many reasons as for instance; its low molecular weight (30.9 g/mol), low reactivity under fuel cell applications, being nontoxic, and due to its higher hydrogen density which is nearly 19.6 wt % than the content with 9 wt % H_2 which is the target of 2015 U.S. Department of Energy.^{2,3}

The use of certain approaches such as thermal decomposition in solid state and dehydrocoupling/dehydrogenation in organic solvent by means of metal catalysis have shown that such approaches do stimulate the production of hydrogen from AB. However, in the case of catalyzing the transition metal, hydrogen production from NH_3BH_3 takes place and its concentration becomes higher owing to the fast hydrogen formation even though the conditions are considered to be mild.⁴

Studies have indicated that ~3 equivalence of H₂ per mole of NH₃BH₃ can be produced via aqueous solution reaction of NH₃BH₃ through utilizing active metal catalyst at room temperature. It has been stated, in some literature, that in the hydrolytic dehydrogenation of NH₃BH₃ several homogenous⁵ and heterogeneous⁶ catalysts can be utilized.

Even though, homogenous catalysts are known as effective for the hydrolytic dehydrogenation,⁵ at present, heterogeneous catalysts have certainly attracted significant prominence owing to their ease of separation and catalyst recovery properties.⁶

Furthermore, high catalytic activity in the hydrolytic dehydrogenation of NH₃BH₃ has been displayed by some noble metals such as Ru,⁷ Rh,⁸ Pd,⁹ Pt,¹⁰ and Au¹¹. However, from practical point of view, the development of low cost catalyst systems for this significant reaction is considered extremely vital. In recent times, 3rd transition metal catalysts namely Fe,¹² Co,¹³ Ni¹⁴, and Cu¹⁵ have shown that such metals can be utilized for the catalysis process of the hydrolytic dehydrogenation of NH₃BH₃. Nevertheless, low activities as well as 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.

The emphasis now has been shifted towards the utilization of non-costly metals such as Co, Ni, Fe, or Cu mixed with costly metals as bimetallic nanoparticles (Au-Ni, Pt-Co) aiming at lowering the cost and increasing the activity. Furthermore, simplicity in isolating such catalysts and the ease of their reusability encourage the application of the principle of sustainable chemical processes.

1.1 Hydrogen as a Source of Energy

In our world today, it is a fact that fossil fuels is covering above 80% of the world's energy supply today.¹⁶ In order to identify the effects of the use of fossil fuels as a source of energy on our environment and ecology systems, several studies have been conducted. Moreover, many issues are becoming the centre of scientific attention due to their seriousness such as exhaustion of reserves and raw materials, the influence of air pollution, the continues change in the atmosphere and its effects on the climate and health of human beings. When the fossil fuels are combusted to produce energy, greenhouse gases such as CO₂ are produced and as a result, the increase in the production of such gases has become a great concern.

In order to decrease the concerns of the environmental consequences and challenges in safety during the consumption of the fossil fuels, effective and inventive end-use technologies and unconventional energy investments such as solar, wind, hydropower energy is offered for future energy sources. Nevertheless, there are some challenges facing these new approaches, for instance, the issue of continuity of such energy sources as well as their high cost. The good news is that these undesired consequences and challenges could be eradicated by energy storage and here comes hydrogen as secure, plentiful, clean, and renewable source of energy.

Furthermore, hydrogen can be got from various sources. Naturally, hydrogen exists in a combination state with oxygen such as in water and it does have the capability to react with many other elements as for instance carbon, nitrogen, and oxygen as in living things and fossil fuels.¹⁷

Throughout the separation of hydrogen from other elements in order to obtain molecular hydrogen (H₂), an environment-friendly fuel is attained and during the combustion process with oxygen, the outcome is nothing more than water.¹⁷

To use hydrogen as a suitable energy carrier, various complications emerge in the way and they must be resolved competently. To keep the process of producing hydrogen at low cost and as economical as possible, four major features must be taken into account¹⁸:

- Production – Improvement of manufacturing approaches that drains less amount of energy in order to produce hydrogen. Moreover, sustainable production of large-scale hydrogen is an important measure towards lowering the cost of production.
- Storage – Ease of storing for both utilizing and transporting makes hydrogen an easily accessible source of energy.
- Power generation – Competent power generation scheme that eats up hydrogen for portable applications.
- Safety – Certain procedures and measurements for safety issues and concerns should be applied owing to the high degree of flammability of hydrogen, during the use of hydrogen, handling and storing. Furthermore, extremely harmless and safe approaches should be selected to produce and store hydrogen.

Despite the plentiful challenges and difficulty of production process of hydrogen, and its storing and utilization, hydrogen remains the most significant source of renewable energy for the future. However, it is worth mentioning that the accomplishment of anticipated schemes is usually evaluated through its efficiency. The price of the ending product concerning the monetary, resource, durability, stability of the process and its safety are further significant issues, which display the degree of success or failure of the suggested systems to utilize them as a part of hydrogen cycle.¹⁸

1.2 Types of Hydrogen Storage

One of the practical and technical issues that needs to be resolved when it comes to the production and facilitating the use of hydrogen, is the issue of storage. Most of hydrogen storing systems are experiencing deficiency of enough volumetric capacity and safety for mobile applications owing to high pressure and cryogenic storage.¹⁹ In the attempts to deal with this issue, many materials have been suggested for resolving the issue of storage such as metal hydrides²⁰, metal organic frameworks²¹, nanostructures²², and chemical compounds²³. These chemical hydrogen storage materials (Figure 1.1) have attracted great of attention owing to their high capacity of storage. This feature in turn have made such materials extremely suitable for usage in fuel cell applications under ambient conditions.

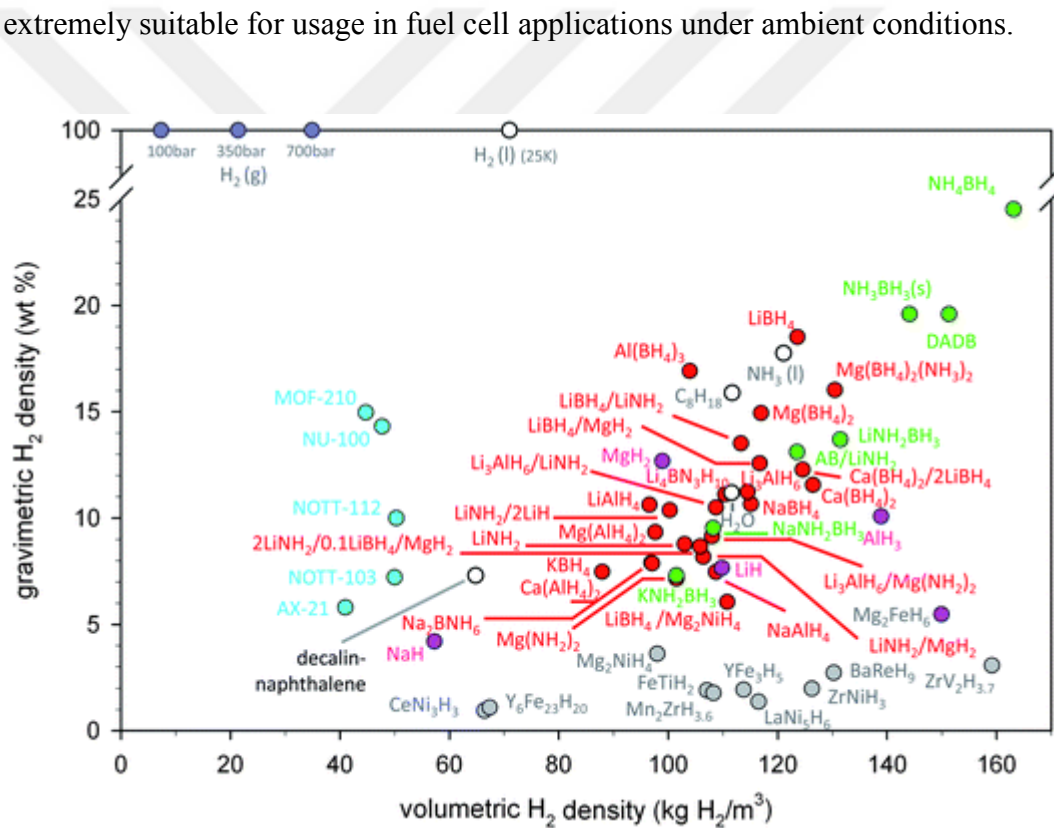
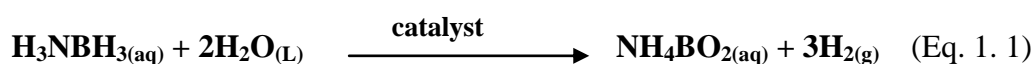


Figure 1.1 Hydrogen storage densities (volumetric and gravimetric) of different hydrogen storage materials.²⁴

1.3 Ammonia Borane as a Hydrogen Storage Material

Ammonia borane (NH_3BH_3) adduct is seen as one of the furthest capable complex in the group of boron hydride complexes for portable applications because of its great content of hydrogen. Moreover, other features of this adduct is its nontoxicity and high stability.²⁵ Furthermore, some other features have made this adduct extremely significant which are nontoxicity and high stability.²⁶ NH_3BH_3 is a tetragonal crystal having a white color and its melting point is larger than 110°C , at room temperature.

Both pyrolysis and solvolysis routes are utilized for the release of hydrogen stored in this adduct. By applying the method of thermal decomposition at 385 K , hydrogen release of $6.5\text{ wt } \%$ of the initial mass of NH_3BH_3 can be achieved. Nevertheless, the increase of hydrogen release requires high temperatures ($> 500^\circ\text{C}$)²⁷. However, it is worth mentioning that above the temperature of 125°C , volatile side products such as borazine, cycloborazanes, polyaminoborane, and ammonia are formed and such products can have some dramatic effects on the fuel cell by poisoning it²⁸. Consequently, the use of catalytic hydrolysis of NH_3BH_3 solution at room temperature by utilizing the appropriate catalyst is certainly the most practical and efficient way for attaining hydrogen virtually and professionally as given in Eq. 1.1.²⁹



1.4 Definition of Catalysis

A catalyst is a material that accelerates the chemical reaction without being exhausted or drained up stoichiometrically in the reaction. The use of a catalyst in a chemical reaction usually results in increasing the rate of the reaction. It also results in creating different mechanism with different transition state which in turn decreasing the activation energy, otherwise known as transition-state theory.

When a catalyst is used in a reaction, then the entropy of the activation in this reaction is usually less than that of the reaction, which is not catalyzed, according to the transition state theory. The reason being that the use of catalyst paralyzes the transition state on its surface by losing translational freedom. 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 1.2), 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.³⁰

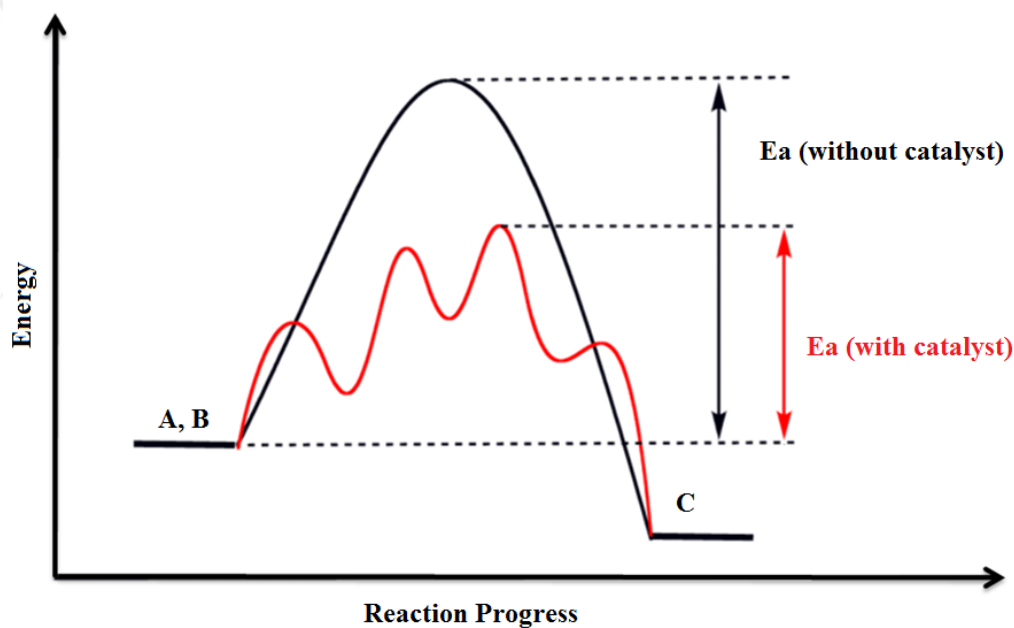


Figure 1.2 Potential energy diagram for an exothermic reaction with and without catalyst.³⁰

Even though, there are various kinds of catalysts such as Lewis acids, organometallic complexes, polymers, enzymes and so on, the main types of the catalysts can be categorized as heterogeneous catalysts, homogeneous catalysts, and biocatalysts.³⁰

Homogenous 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 homogenous catalysis. The homogenous 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, heterogeneous catalysts perform in different phase than reactants. In this category of catalysis process, the reactants diffuse to the surface of metal catalyst, and adsorption onto surface is carried out via chemisorptions.³⁰

The products of the reaction are released and separated from the surface of the catalyst, 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 attained countless prominence in numerous number of chemical and energy industries. Most of the catalytic processes, which are carrying out in nature, are very good illustrations and examples of heterogeneous type catalyst schemes comprising solid catalyst and gas or liquid phase reactants.³⁰

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.³⁰

1.5 Applications of Magnetic Nanoparticles

Magnetic nanoparticles display individual magnetic properties weighed against their bulk counterparts, and lately they have attained great deal of significance. This great reputation have paved the way for such nanoparticles to be used in various applications³¹ such as biotechnology, magnetic fluids, magnetic resonance imaging, data storage, environmental remediation, and catalysis.³²

Magnetic features of the nanoparticles can be adjusted and controlled by changing the size, shape, composition and crystal structure of these nanoparticles. However, it is not viable to regulate these aspects throughout the production of nanoparticles and make them accurately equal in their chemical composition and size, which in turn results in different property for the same type of nanomaterial.³³

1.6 Synthesis of Magnetic Nanoparticles

It is plausible to synthesis nanoparticles by a widespread variety of approaches by means of applying gas, liquid or solid phase production practices. In some scientific works, thermal decomposition, micro emulsion, hydrothermal and solvothermal techniques, sonochemical, polyol, and co-precipitation methods are utilized to manufacture nanoparticles with numerous compositions and phases.³⁴ Co-precipitation is a simple and practical technique for making the magnetic nanoparticles from aqueous solutions of salt precursors with a base as reducing agent at room or high temperatures. Moreover, some kinds of salts (e.g., chlorides, sulfates, nitrates) utilized for manufacturing, the ratio of the ions, the temperature, pH, ionic strength of the medium are all vital factors that deeply influence size, shape, and composition of manufactured nanoparticles. High scale synthesis and easiness make the process valuable for the manufacturing of magnetic nanoparticles.³⁴

1.7 Importance of Surface Coating of Magnetic Nanoparticles

There is a great need for a sizeable barrier to be there, in order to forbid the uninvited interactions between the magnetic core and molecular catalyst, which is attached to nanoparticle surface. Silica layer on magnetic nanoparticles inhibits unwanted interactions of catalyst with core and prevents agglomeration of particles. Additionally, silica coating owing to the existence of silanol groups on surface, offers surface alteration with several functional groups and nanoparticle adding to the surface easily.³⁵

Sol-gel technique is a wet-chemical method, which is extensively utilized for coating of silica on magnetic nanoparticles. This method depends on Stöber technique in which nanoparticles are concealed with silica layer³⁶ and hydrolysis reaction endures with the following condensation reaction of an alkoxide which acts as a silicon precursor (generally tetraethyl orthosilicate (TEOS)) in alcohol-water mixtures by using a base catalyst.

The thickness of the silica layer can be effortlessly managed throughout changing the reaction conditions. Xia and coworkers confirmed that by altering the concentration of TEOS added into water, isopropanol and ammonia (30 % v/v) solutions that contain magnetic fluids, the thickness of the silica layer can be managed and accustomed.³⁷ Consequently, the governing of the silica layer thickness (2-100 nm size range) on magnetic nanoparticles could be established by means of avoiding the homogeneous nucleation of silica nanoparticles.

1.8 Magnetically Separable Nanocatalysts

Green chemistry, also recognized as “sustainable chemistry”, is a branch of knowledge that deals with the process of designing chemicals and products. Moreover, green chemistry inspires the topic of minimizing the usage and generation of harmful substances to the lowest level possible.

Green catalysis is undoubtedly one of the most critical subjects of green chemistry. Recently, the improvement of maintainable and environment-friendly code to prohibit the practice of utilizing hazardous organic solvents, toxic chemicals, dangerous and violent reaction conditions have been observed. Furthermore, such practices help to tackle many serious issues in this field of study, as for instance, time-consuming and ineffective separation during synthesis.³⁸ Even though, catalysts are being utilized extensively in industry, the most central obstacles that are associated with their usage are namely the isolation and separation of the concluding product after the reaction has come to an end. Consequently, this position makes the entire procedure challenging and problematic.

Very small quantities of the catalyst that is measured in ppm or ppb can exist in the finishing product, even if it is segregated from the reaction mixture. Clearing away the catalyst is essential for avoiding metal contamination in the case of drugs and pharmaceutical products.

By designing a heterogeneous catalytic scheme that is through accomplishing the heterogenization of catalysis molecules it is conceivable to segregate and separate the catalysis effortlessly.³⁹ In heterogenization process, the attaching of active molecules can be succeeded at the surface or inside the pores of silica, alumina or ceria supports through entrapment or embedding methods.

Moreover, grafting takes place with the help of covalent binding or physical adsorption of catalytic molecules. However, in case of heterogeneous catalysts, accessing of the active sites is not an easy task to perform compared with the homogenous catalysts. Therefore, one can observe the decline in the activity of catalyst very easily. As a final point, a catalytic scheme should display both high degree of activity and selectivity as observed in homogenous systems. Furthermore, the separation and recovery should be easy as the case in the heterogeneous systems. All these objectives can turn into a world of reality through utilizing nanocatalysis systems. A nanocatalyst can enjoy all the gains of both heterogeneous and homogenous catalysts and preserve all the required attributes of both systems.

Nanocatalysts display few benefits when measured up against other renowned catalyst systems despite having the drawbacks of isolation and recovery from the reaction medium. Filtration and centrifugation are recognized as classical methods, which are not suitable due to small size of the catalyst. As a result, it is a bit of challenge to contribute to the economical use of nanocatalysts. This issue can be resolved by the utilization of magnetic nanoparticles.

The insolubility of particles and paramagnetic characteristics contribute to the subtraction of the catalyst from the reaction medium effortlessly and properly through an external magnetic field.

These reasonable properties make magnetic nanoparticles tremendously needed materials with greatly growing attention.⁴⁰ Magnetically separable catalysts (MSC) also provide imperative activities in a widespread variety of reactions because of their prospective for intended surface functionalities along with catalyst preparation.

1.9 Aim of the Study

In this thesis, magnetic support material, $\text{SiO}_2\text{-CoFe}_2\text{O}_4$, was used to add silver-copper bimetallic nanoparticles and form $\text{Ag}(0)\text{Cu}(0)/\text{SiO}_2\text{-CoFe}_2\text{O}_4$ nanocomposite material. In order to prepare $\text{Ag}(0)\text{Cu}(0)/\text{SiO}_2\text{-CoFe}_2\text{O}_4$ magnetic material, $\text{Ag}(\text{I})$ and $\text{Cu}(\text{II})$ ions were added by using wet-impregnation of on $\text{SiO}_2\text{-CoFe}_2\text{O}_4$ followed by *in-situ* reduction of the ions with NH_3BH_3 on the surface of magnetic $\text{SiO}_2\text{-CoFe}_2\text{O}_4$ particles. The prepared materials were characterized by using XRD, XPS, SEM, TEM, HR-TEM, EDX, ICP-OES and N_2 adsorption-desorption technique. Then the prepared catalyst was used in the hydrogen evolution from aqueous solution of ammonia-borane at room temperature. 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, silver nitrate, AgNO_3 , copper chloride, CuCl_2 , cobalt (II) chloride hexa-hydrate, $(\text{CoCl}_2 \cdot 6\text{H}_2\text{O})$, iron(III) chloride hexa-hydrate $(\text{FeCl}_3 \cdot 6\text{H}_2\text{O})$, tetraethylorthosilicate (TEOS), (3-Aminopropyl) trimethoxysilane (APTMS), ammonium hydroxide (NH_4OH), sodium chloride (NaCl), sodium hydroxide (NaOH) and ammonia borane (NH_3BH_3), 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 structural characterization of the nanocatalysts were investigated 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 investigated with energy-dispersive X-ray analyzer (EDX) coupled with SEM and TEM.

Rigaku Ultima-IV model X-ray diffraction (XRD) spectrometer was used to figure out the crystal structure of the catalyst prepared. XRD patterns of support, catalyst before and after usage were obtained in the range of $2\theta = 5- 60^\circ$.

Physical Electronics 5800 spectrometer equipped with a hemispherical analyzer was used to obtain XPS spectrum by using monochromatic Al-K α radiation. NOVA 3000 series instrument (Quantachrome Instruments) was used for the nitrogen adsorption/desorption isotherms at 77 K.

To find out the amount of metal loaded on to the magnetic support and leaching of loaded silver and copper was investigated by using Perkin Elmer inductively coupled plasma optical emission spectroscopy (ICP-OES).

Magnetic properties of the catalyst were revealed by using ADE Magnetics EV9 Model Vibrating Sample Magnetometer.

2.3. Synthesis of Silica Coated Cobalt Ferrite (CoFe₂O₄@SiO₂) Magnetic Nanoparticles and Formation Silver-Copper Bimetallic Nanoparticles Supported on Silica Coated Magnetic Nanoparticles

The preparation technique, which was implemented for the making of CoFe₂O₄@SiO₂, was basically the same technique published beforehand with some modifications.^{34,41} According to this procedures, , 10 mL of 0.4 M iron chloride and 10 mL of 0.2 M cobalt chloride solutions were mixed and stirred at a room temperature. At that point, in separate containers, 5 ml of 1.5 M sodium chloride and 10 mL of 3.0 M sodium hydroxide solution were made ready and gradually supplemented to the initial solution. Finally, a black suspension was acquired, immediately after addition of the NaOH aqueous solution. Continuous stirring had to be carried out for 1 hour at a temperature of 80°C under sonication.

Then the solution cooled to room temperature and the black precipitates were collected by using an external magnet. The supernatant was removed and the particles were washed 3 times with deionized water–ethanol solution and then the particles were dispersed in 20 ml of water.

After that, 80 ml ethanol, 250 μL TEOS and 40 μL APTMS were mixed in a beaker, and subsequently 20 ml cobalt ferrite colloid was added to the mixture and stirred for 4 hours at room temperature. After the formation the thick silica shell, particles were collected with a magnet and washed three times with deionized water.

The addition of silver (Ag^+) and copper (Cu^{2+}) metal ions on the $\text{CoFe}_2\text{O}_4@\text{SiO}_2$ support was performed by the wet-impregnation method.⁴² First, 100 mg $\text{CoFe}_2\text{O}_4@\text{SiO}_2$ nanoparticles were dispersed in 10 ml water. After that silver nitrate (AgNO_3) and copper chloride, CuCl_2 added to this dispersion. After 12 hour mixing, particles were separated by using external magnet and washed with deionized water several times. Actual loading of silver and copper ions on magnetic support was determined with ICP-OES measurements. Before using in the hydrolysis of AB, prepared catalyst were reduced by using NaBH_4 . After reduction was completed, particles were collected with external magnet and washed and then used in the hydrolytic dehydrogenation of AB.

2.4. Hydrolytic Dehydrogenation of Ammonia Borane

The activity of the prepared $\text{AgCuNPs}/\text{CoFe}_2\text{O}_4@\text{SiO}_2$ nanoparticles in the hydrolytic dehydrogenation of AB was evaluated by quantifying the rate of hydrogen production. In order to determine this, the system shown in Figure was used. Then, 25.0 mg $\text{AgCuNPs}/\text{CoFe}_2\text{O}_4@\text{SiO}_2$ (with 1.9 wt % Ag and 1.3 wt % Cu loading) was putted in to reaction bottle and 31.8 mg (1 mmol) AB was added after dissolving in 10 mL water. The temperature of the system was regulated at 25 $^\circ\text{C}$ with PL circulator. Then the reaction was started by opening the magnetic stirrer which was statted at 900 rpm.



Figure 2.1 System used for the hydrogen production from NH_3BH_3 .

The evolved hydrogen volume was measured by recording the water level change at every 30 s at a constant temperature and pressure until no more hydrogen evolution was observed.

2.5. The stability of magnetic support

After the hydrogen generation reaction was completed, another equivalent of AB (31.8 mg) was added into the reaction system and the released gas was monitored by the system defined at previous section. Also Powder XRD measurements were performed in order to find the stability of prepared catalyst before and after the hydrolysis reaction of AB.

2.6. Determination of Activation Energy (E_a) for the Reaction Catalyzed by AgCuNPs/CoFe₂O₄@SiO₂ nanoparticles

In order to find the catalytic parameters of the prepared catalyst (Activation energy (E_a)), catalytic activity of the catalyst was revealed by using 10 mg AgCuNPs/CoFe₂O₄@SiO₂ catalyst at different temperatures (20, 25, 30, 35 °C). In order to find the optimum amount of catalyst various amounts (10, 15, 20, 25 mg) of AgCuNPs/CoFe₂O₄@SiO₂ were performed in the hydrolysis of 10 mL of 100 mM (31.8 mg) NH₃BH₃ solution.

2.7. Recyclability Studies

At the end of the first run in hydrolysis reaction the particles were collected by onto the wall of the reactor by using external magnet. Then the particles were washed several times with water and then used again in the hydrolytic dehydrogenation of AB by addition of same amount of AB and water. This procedure was repeated ten times in order to find the reuse capabilities of the AgCuNPs/CoFe₂O₄@SiO₂ catalyst.

CHAPTER 3

RESULTS AND DISCUSSION

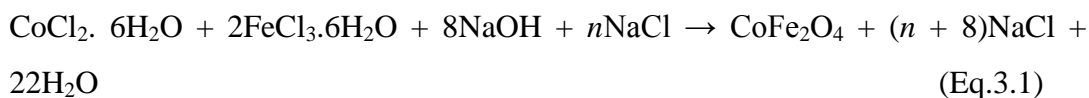
In this study, cobalt ferrite (CoFe_2O_4) magnetic nanoparticles were selected as a support material because of the easy preparation method. CoFe_2O_4 must be covered to prevent it against the leaching and agglomeration. Besides, silica layer provides the surface for addition of nickel and palladium nanoparticles. After loading the silica coated cobalt ferrite magnetic nanoparticles ($\text{CoFe}_2\text{O}_4@\text{SiO}_2$) with silver (Ag (I)) and copper (Cu (II)) ions (Ag (I) Cu (II)/ $\text{CoFe}_2\text{O}_4@\text{SiO}_2$), silver-copper bimetallic nanoparticles on silica coated cobalt ferrite magnetic nanoparticles ($\text{AgCuNPs}/\text{CoFe}_2\text{O}_4@\text{SiO}_2$) were *in situ* generated during the hydrogen production from NH_3BH_3 as a novel catalytic material.

Morphological and magnetic properties, surface area, crystal structure of the SiO_2 - CoFe_2O_4 magnetic supports were investigated. Then, morphological property, stability, catalytic activity, and reusability of the $\text{AgCuNPs}/\text{CoFe}_2\text{O}_4@\text{SiO}_2$ nanostructures were revealed.

3.1. Preparation of Silica Coated Magnetic Cobalt Ferrite ($\text{CoFe}_2\text{O}_4@\text{SiO}_2$) Nanoparticles as Support Material

In order to prepare magnetic support material, cobalt ferrite (CoFe_2O_4) nanoparticles, modified co-precipitation method were applied.

According to this method, highly dispersive small sized CoFe_2O_4 magnetic nanoparticles and their agglomerates were synthesized by using $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and NaOH as precursor in the presence of inert salt, NaCl . Equation 3.1 shown below gives the chemical reaction related to cobalt ferrite preparation.



Silica coating was performed over CoFe_2O_4 magnetic nanoparticles to prevent the attraction with the other particles which results agglomeration and to in bigger particle size and provides the surface for addition of nickel and palladium nanoparticles as a host material. The silica coating of magnetic CoFe_2O_4 nanoparticles were performed by using Stöber method explained in details in Experimental part.

The morphology and particle sizes of the support and catalysts were examined using high resolution transmission electron microscopy (HRTEM). Figure 3.1 shows the HRTEM images of the $\text{CoFe}_2\text{O}_4 @ \text{SiO}_2$ support.

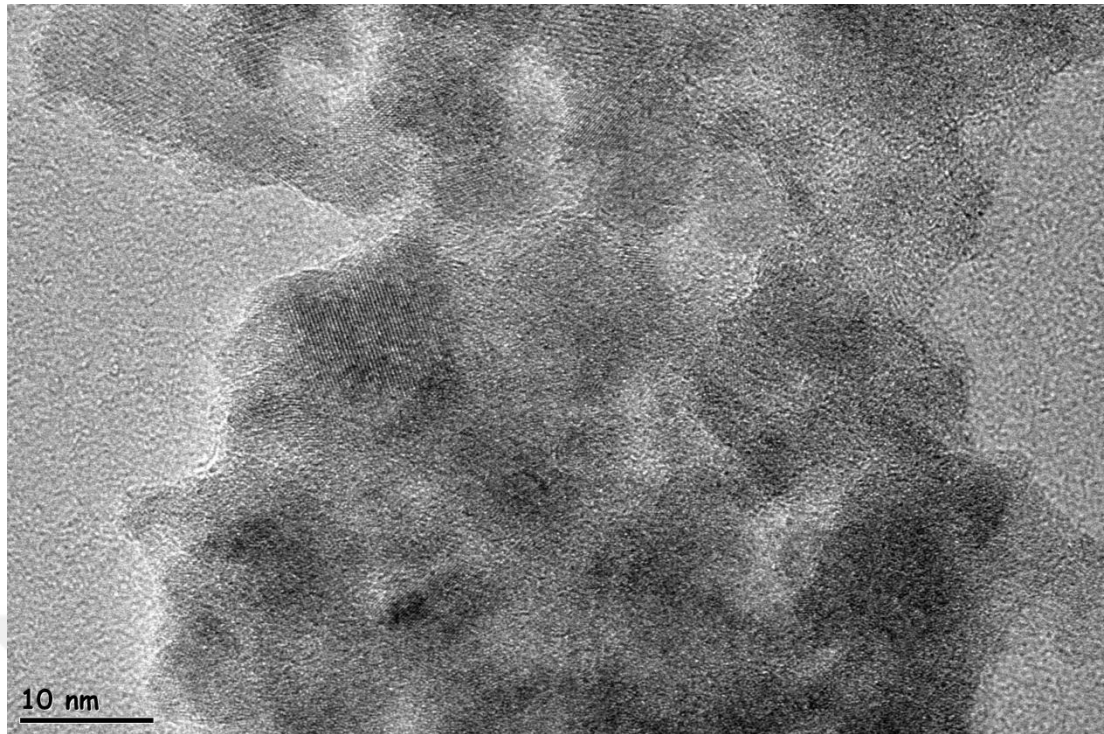


Figure 3.1 HRTEM images of bare CoFe₂O₄@SiO₂ nanoparticles.

The HRTEM images given Figure 3.21 reveal that the size of the support particles are made of about 12-18 nm with the size of CoFe₂O₄@SiO₂ aggregates about 150 nm

The elemental composition of the CoFe₂O₄@SiO₂ magnetic nanoparticles was determined by EDX measurement coupled with FE-SEM. Figure 3.2 shows the obtained EDX pattern. The EDX pattern confirms the presence of metals added to the structure in the preparation part.

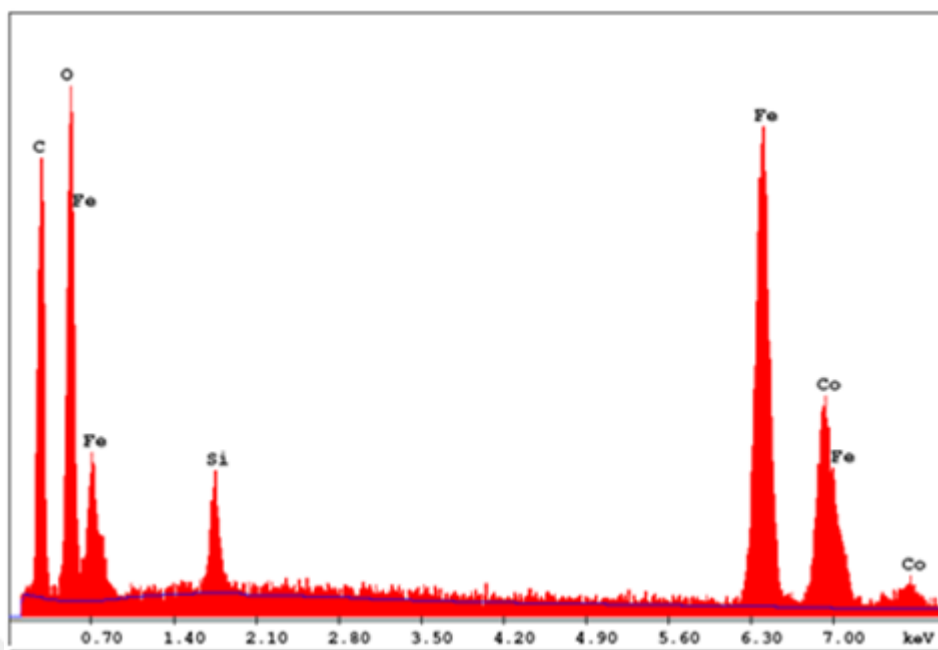


Figure 3.2 EDX pattern of CoFe₂O₄@SiO₂ magnetic nanoparticles.

3.2.Preparation and Characterization of AgCuNPs/CoFe₂O₄@SiO₂

As stated before, addition of metal ions onto the magnetic nanoparticles was performed with wet-impregnation method. After that metal ions were reduced by using sodium borohydride. The prepared AgCuNPs/CoFe₂O₄@SiO₂ nanoparticles were obtained from the reaction medium by using external magnet. The characterization of prepared catalyst were performed by using XRD, TEM, SEM, EDX, ICP-OES, XPS and BET techniques.

The morphological characterization of the prepared catalyst was investigated with HRTEM and EDX spectroscopy. Figure 3.3 shows the HRTEM images of AgCuNPs/CoFe₂O₄@SiO₂ with a silver and copper loading of 1.9 wt. % and 1.3 wt. % respectively which is figured out by inductively coupled plasma (ICP-OES) analyses.

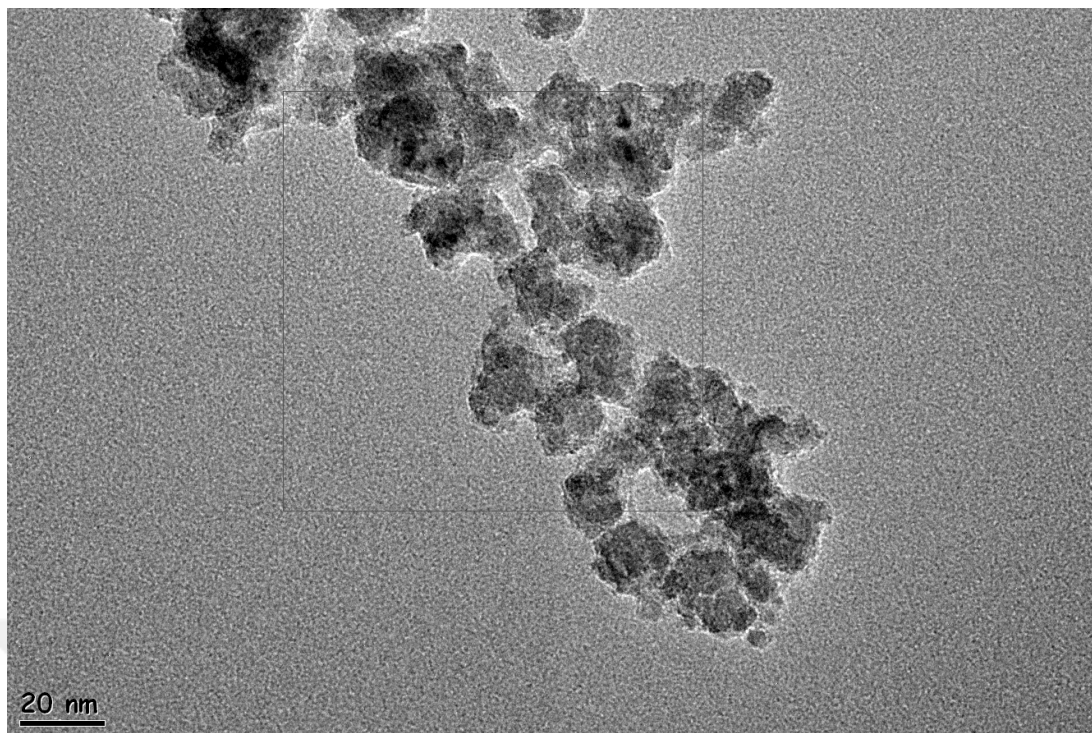


Figure 3.3 HRTEM images of AgCuNPs/CoFe₂O₄@SiO₂ nanoparticles.

Average particle size of silver-copper nanoparticles supported on CoFe₂O₄@SiO₂ lies in the range of 3-8 nm. Energy-dispersive X-ray spectroscopy (EDX) point analyses (Figure 3.4) of randomly chosen nanoparticles exhibit the presence of both Ag and Cu besides the Co, Fe and Si used for the preparation of magnetic support .

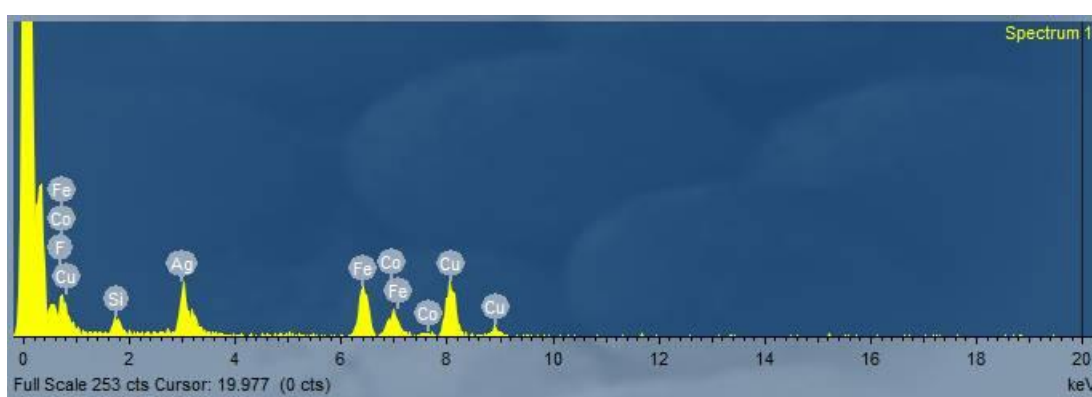


Figure 3.4 EDX pattern of AgCuNPs/CoFe₂O₄@SiO₂ nanoparticles.

The structural analysis of bare magnetic support $\text{CoFe}_2\text{O}_4@\text{SiO}_2$, Powder X-ray diffraction (XRD) was performed on all the as-synthesized nanoparticles. Figure 3.5 shows the X-ray diffraction pattern of the $\text{CoFe}_2\text{O}_4@\text{SiO}_2$ and $\text{AgCuNPs}/\text{CoFe}_2\text{O}_4@\text{SiO}_2$ catalyst after preparation and reuse study. XRD studies were performed in the 2θ range of $15\text{-}70^\circ$ and peaks at 30.3° , 35.8° , 43.3° , 57.4° and 62.5° were obtained and it is found to be that they are related to (220), (311), (400), (511) and (440) respectively (PDF Card 22-1086).

In the pattern no peaks were observed coupled to silver and copper metals because of the small size and low loading. These results were compatible with the TEM and ICP-OES results. A comparison of the XRD patterns shown in Figure 3.5 clearly indicates that the addition of small size Ag and Au nanoparticles on magnetic $\text{CoFe}_2\text{O}_4@\text{SiO}_2$ nano-support and hydrogen generation from ammonia borane did not make any change on the crystal structure of magnetic support material.

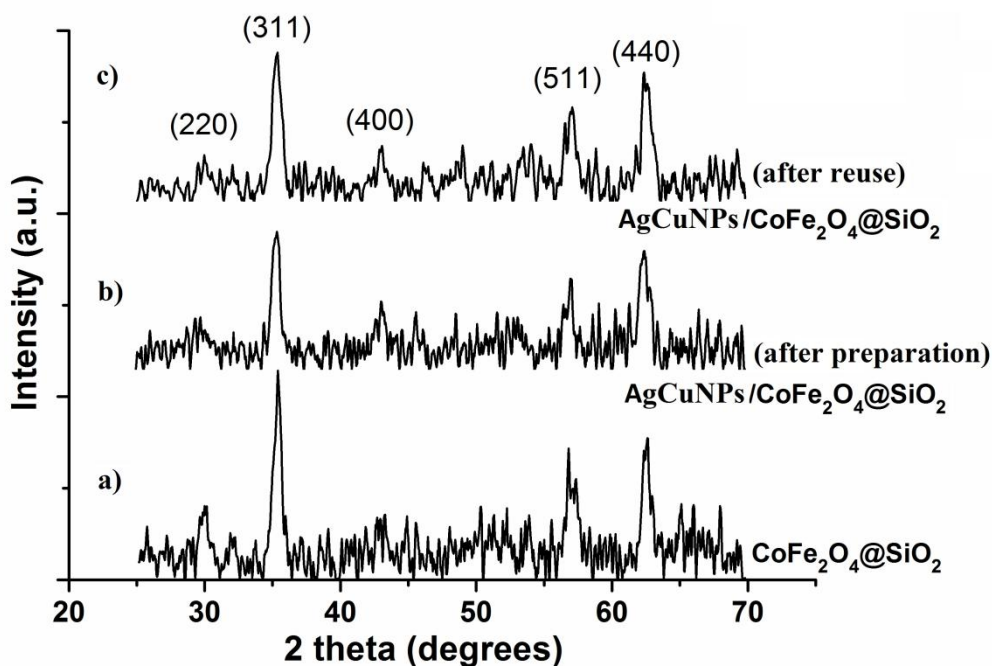


Figure 3.5 Powder XRD patterns of (a) $\text{CoFe}_2\text{O}_4@\text{SiO}_2$ (b) $\text{AgCuNPs}/\text{CoFe}_2\text{O}_4@\text{SiO}_2$ obtained after the hydrogen production from NH_3BH_3 and (c) $\text{AgCuNPs}/\text{CoFe}_2\text{O}_4@\text{SiO}_2$ after 10 reuse.

BET method was performed to find the specific surface areas of the bare magnetic support and metal nanoparticle loaded catalysts. Besides BJH (Barret-Joyner-Halenda) method were applied to figure out the pore size distribution Results are given in Table 3.1.

Table 3.1 The specific surface area, pore volume and pore radius of $\text{CoFe}_2\text{O}_4@\text{SiO}_2$ and $\text{AgCuNPs}/\text{CoFe}_2\text{O}_4@\text{SiO}_2$

Sample	Multi Point BET (m^2/g)	pore volume (cc/g)	pore radius (\AA)
$\text{CoFe}_2\text{O}_4@\text{SiO}_2$	178	0.369	42.7
$\text{AgCuNPs}/\text{CoFe}_2\text{O}_4@\text{SiO}_2$ (1.9% Ag and 1.3 Cu%)	169	0.293	8.5

The surface area and total pore volume of $\text{CoFe}_2\text{O}_4@\text{SiO}_2$ were calculated from BET (Brunauer–Emmett–Teller) plot and found to be $178 \text{ m}^2/\text{g}$ and $0.369 \text{ cc}/\text{g}$, respectively with a pore size of 42.7 \AA . The surface area decreases to $169 \text{ m}^2/\text{g}$ with the addition of the small size Ag and Cu metal nanoparticles respectively to the $\text{CoFe}_2\text{O}_4@\text{SiO}_2$ magnetic support besides the pore volume and pore size decrease which indicates the addition of Ag and Cu nanoparticles in the pores of support material.

The magnetic behavior of $\text{AgCuNPs}/\text{CoFe}_2\text{O}_4@\text{SiO}_2$ nanoparticles toward external magnetic field was initially tested by putting external magnet near to the sample holder. $\text{AgCuNPs}/\text{CoFe}_2\text{O}_4@\text{SiO}_2$ nanoparticles were collected in 3 seconds which is the indication of high magnetic behavior of the prepared catalyst.

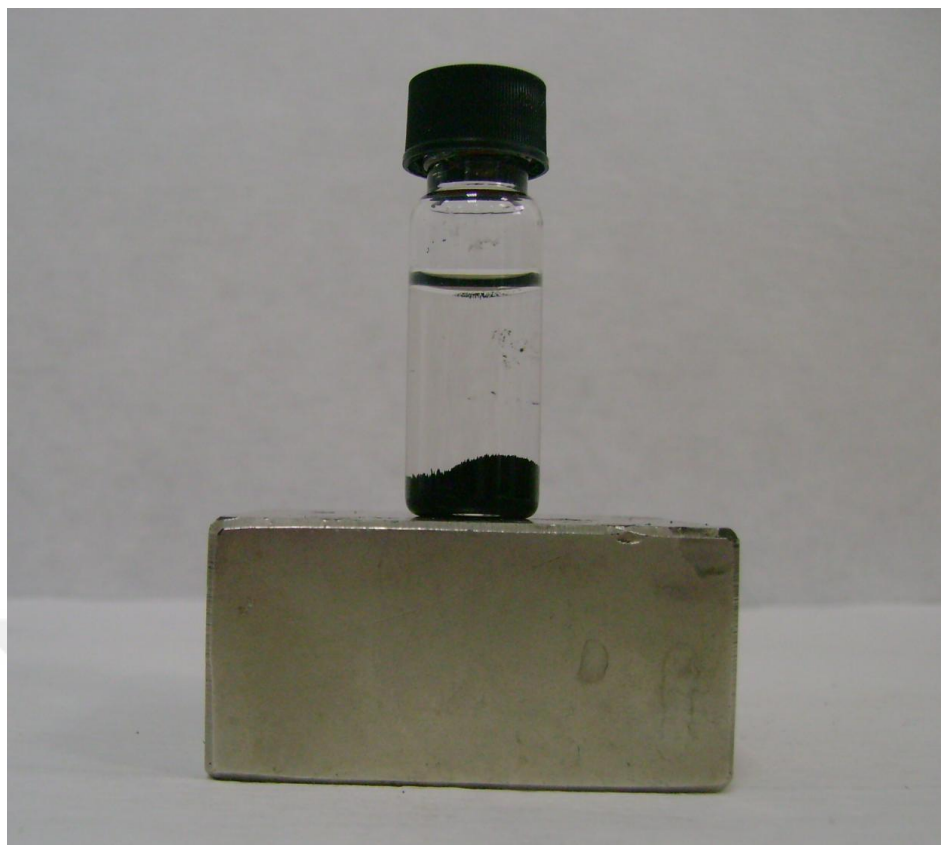


Figure 3.6 Collection of $\text{AgCuNPs/CoFe}_2\text{O}_4@\text{SiO}_2$ nanoparticles by using external magnet with 1.6 T magnetic field.

The magnetic property of $\text{AgCuNPs/CoFe}_2\text{O}_4@\text{SiO}_2$ catalyst was also characterized by using the vibrating sample magnetometer (VSM). According to the hysteresis curves recorded at 300K the saturation magnetization and coercivity values of the $\text{AgCuNPs/CoFe}_2\text{O}_4@\text{SiO}_2$ magnetic nano catalyst were 39.2 emu/g and 189 Oe respectively.

3.3. Catalytic Activity of Silver and Copper Nanoparticles Supported on Silica Coated Cobalt Ferrite ($\text{AgCuNPs/CoFe}_2\text{O}_4@\text{SiO}_2$) Nanoparticles

Initially the activity of $\text{CoFe}_2\text{O}_4@\text{SiO}_2$ was checked to see the effect on the hydrolysis of NH_3BH_3 . It was found that the magnetic support material ($\text{CoFe}_2\text{O}_4@\text{SiO}_2$) has no catalytic activity in the hydrogen production from NH_3BH_3 .

The catalytic activity of the AgCuNPs/CoFe₂O₄@SiO₂ towards the hydrolytic dehydrogenation of AB was evaluated in a system defined in the experimental part. Figure 3.7 shows the amount of H₂ generated as a function of reaction time at different catalyst concentrations under ambient conditions. The molar ratio of hydrolytically generated H₂ to the initial AB is close to 3.0, indicating dehydrogenation is completed. AgCuNPs/CoFe₂O₄@ (25 mg with a silver content of 1.9 wt. % and copper content of 1.3 wt. %) exert good catalytic activity in which the hydrolysis reaction of AB is completed within only 8 minutes.

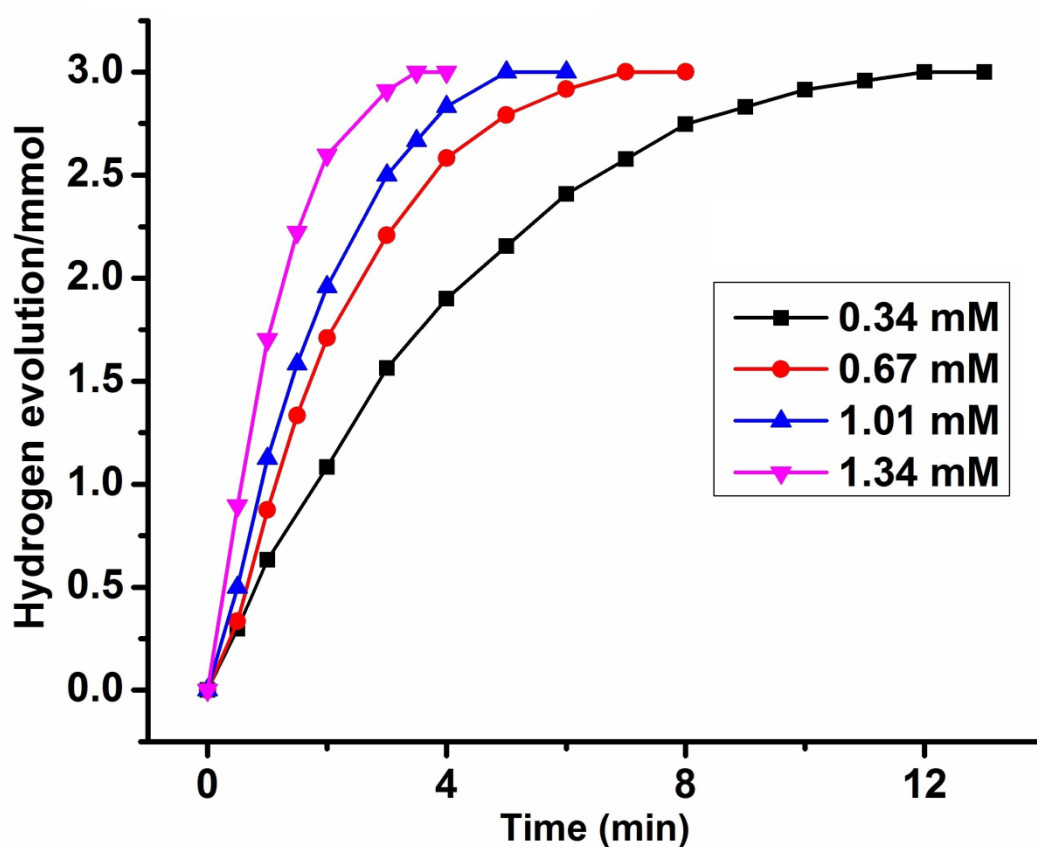


Figure 3.7 Hydrolytic dehydrogenation of AB (0.1 M, 10 mL) catalyzed by AgCuNPs/CoFe₂O₄@SiO₂ nanoparticles with a silver content of 1.9 wt. % and copper content of 1.3 wt. % respectively with different concentrations as given at 25.0 ± 1° C.

The TOF (turnover frequency) number is usually used in order to show the activities of the catalysts for reaction. It is calculated from the amount of hydrogen produced by a certain amount of catalyst in a given time ($\text{mol H}_2 \times \text{mol catalyst}^{-1} \times \text{min}^{-1}$). According to this definition, the highest initial TOF values of with a silver content of 1.9 wt. % and copper content of 1.3 wt. % catalyst calculated as 146 min^{-1} by using 0.67 mM catalyst.

The TOF number of the catalyst prepared with metals used in the hydrogen production from NH_3BH_3 are given in Table 3.2 in order to make comparison with prepared AgCuNPs/CoFe₂O₄@SiO₂ catalyst.

Table 3.2 TOF values of first row metals based catalysts reported in the literature for the hydrogen production from NH_3BH_3 .

Entry	Catalyst	TOF (min^{-1})	Ref.
1	Fe NPs	5	[43]
2	Co/Al ₂ O ₃	2	[44]
3	Ni/Al ₂ O ₃	2	[44]
4	Co NPs	38	[45]
5	Co/Zeolite	4	[46]
6	Ni NPs	5	[47]
7	Ni NPs	1	[48]
8	Ni NPs	9	[49]
9	Ni/Zeolite	5	[50]
10	Cu/Cu ₂ O	0.3	[51]
11	Cu/Zeolite	0.8	[52]
12	Cu/Co ₃ O ₄	18	[53]
13	CuNPs/SiO ₂ -CoFe ₂ O ₄	40	[54]
14	AgCuNPs/CoFe ₂ O ₄ @SiO ₂	146	This Study

^a TOF = $\text{mol H}_2 / \text{mol metal} \times \text{min}$; ^b

To figure out the catalytic parameters like activation energy, the catalytic activity of AgCuNPs/CoFe₂O₄@SiO₂ catalyst were tested at different temperature. Results are given in Figure 3.8.

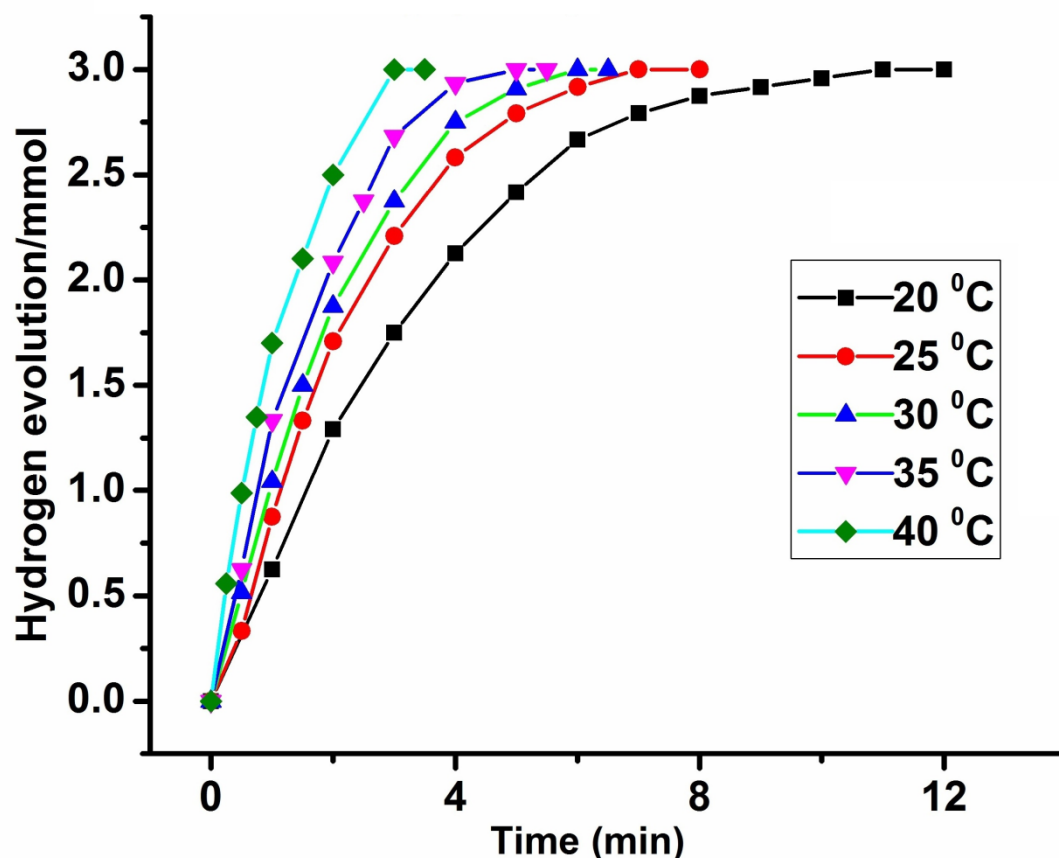


Figure 3.8 Hydrolytic dehydrogenation of AB (0.1 M, 10 mL) catalyzed by 0.67 mM AgCuNPs/CoFe₂O₄@SiO₂ nanoparticles with a silver content of 1.9 wt. % and copper content of 1.3 wt. % respectively at different temperature.

From the figure given above, the rate constants of hydrogen generation were calculated at five different temperatures in the range of 20-40 °C. From that value and by using Arrhenius plot, (lnk versus 1/T (K⁻¹)) activation energy (E_a) of the reaction catalyzed by AgCuNPs/CoFe₂O₄@SiO₂ nanoparticles was calculated. Results are given in Table 3.3.

Table 3.3 Activation energy of the reaction catalyzed by AgCuNPs/CoFe₂O₄@SiO₂ nanoparticles calculated from Arrhenius plot

T (C)	k (mol L ⁻¹ mol _{metal} ⁻¹ s ⁻¹)
20	53
25	73
30	86
35	110
40	164
E_a (kcal mol ⁻¹)	40.4

3.4. Stability and Recyclability Studies Performance of AgCuNPs/CoFe₂O₄@SiO₂ Catalyst

Stability is one of the important properties of catalyst in practical applications. In order to check the stability of prepared AgCuNPs/CoFe₂O₄@SiO₂ catalyst, they were tested in the hydrogen generation experiments from an aqueous solution of AB at sequential runs (5 runs) with the addition of same amounts of AB in to the system at room temperature. The results are given in Figure 3.9. As shown in Figure 3.9, even after 5 successive runs, the productivity of hydrogen remained almost unchanged, indicating that AgCuNPs/CoFe₂O₄@SiO₂ nanoparticles showed good stability in aqueous solution under ambient atmosphere.

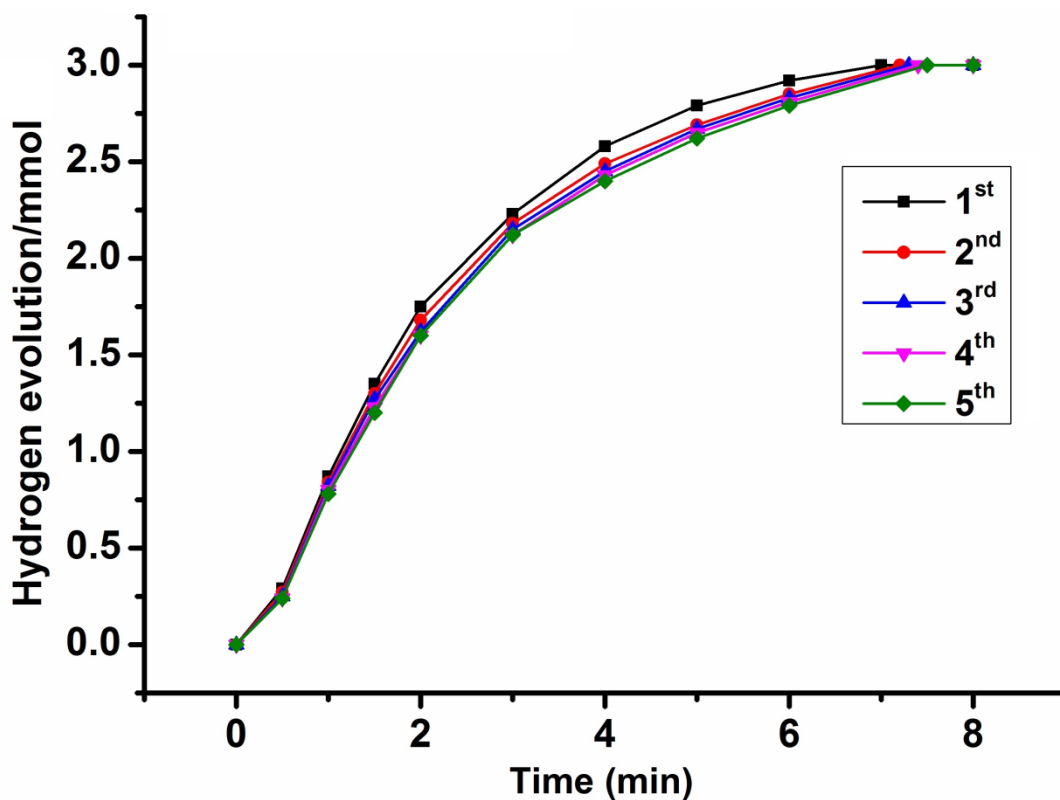


Figure 3.9 Generation of hydrogen from an aqueous solution of ammonia borane (0.1 M, 10 mL) catalyzed by 0.67 mM AgCuNPs/CoFe₂O₄@SiO₂ catalysts at sequential runs by the addition of equivalent amounts of ammonia borane.

Moreover, these high performance catalysts are magnetic and thus can be easily recovered by an external magnet after the reaction. So for the recyclability studies, AgCuNPs/CoFe₂O₄@SiO₂ catalysts were separated from the reaction solution and reused after washing as the catalyst for the hydrolytic dehydrogenation of AB. The hydrogen productivity of AgCuNPs/CoFe₂O₄@SiO₂ catalyst remains constant even after over 10 runs and there was no significant decrease (3%) in catalytic activity even after the tenth use (Figure 3.10).

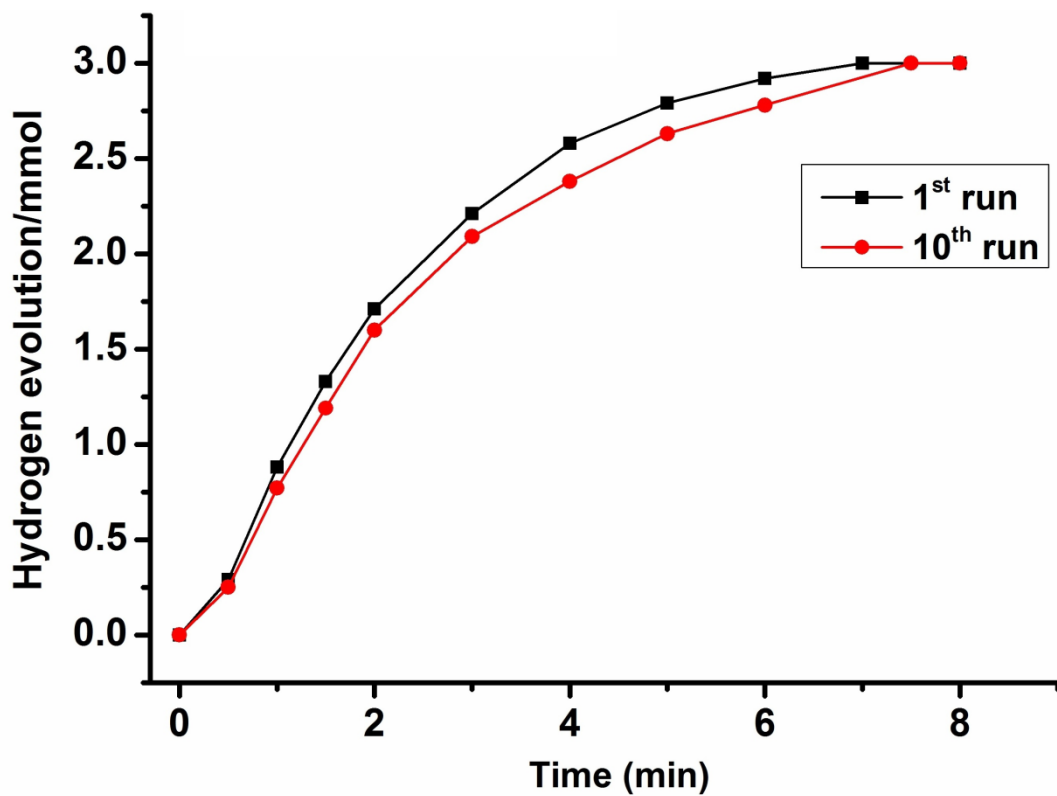


Figure 3.100 Catalytic performance of the AgCuNPs/CoFe₂O₄@SiO₂ catalysts at first and tenth run in generation of hydrogen from an aqueous solution of ammonia borane (0.1 M, 10 mL).

CHAPTER 4

CONCLUSION

In conclusion, by applying wet-impregnation technique, silver and copper ions were added on to the magnetic support material. After that the added metals were reduced and AgCuNPs/CoFe₂O₄@SiO₂ nanoparticles were obtained. Then the catalytic activity of the prepared catalyst was investigated in the production of hydrogen from ammonia borane. The obtained nanoparticles are magnetically recyclable and shows synergistically enhanced catalytic performance for hydrolytic dehydrogenation of ammonia borane at mild conditions. The TOF number of the prepared AgCuNPs/CoFe₂O₄@SiO₂ nanocatalyst was calculated as 146 min⁻¹ by using 0.67 mM catalyst. Besides high catalytic activity, prepared catalyst shows long term stability and high reuse capacity. They retain almost all of their initial activity even at the tenth catalytic run.

The detailed characterization of the AgCuNPs/CoFe₂O₄@SiO₂ nanocatalyst were done by using XRD, HRTEM, EDX, VSM, BET and ICP-OES. Besides the activation energy of the process performed by using AgCuNPs/CoFe₂O₄@SiO₂ nanocatalyst was also calculated.

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