

POLY(*N*-VINYL-2-PYRROLIDONE) STABILIZED NICKEL(0) NANOPARTICLES
AS CATALYST FOR HYDROGEN GENERATION FROM THE METHANOLYSIS
OF AMMONIA BORANE

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NANOPARTICLES AS CATALYST FOR HYDROGEN GENERATION FROM
THE METHANOLYSIS OF AMMONIA BORANE**

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ABSTRACT

POLY(*N*-VINYL-2-PYRROLIDONE) STABILIZED NICKEL(0) NANOPARTICLES AS CATALYST FOR HYDROGEN GENERATION FROM THE METHANOLYSIS OF AMMONIA BORANE

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This dissertation includes the preparation and characterization of poly(*N*-vinyl-2-pyrrolidone) stabilized nickel(0) nanoparticles, and investigation of their catalytic activity in hydrogen generation from catalytic methanolysis of ammonia-borane (AB). PVP-stabilized nickel(0) nanoparticles were prepared from the reduction of nickel(II) ethylhexanoate in the presence of PVP as stabilizer, by hydrazine borane at room temperature. PVP-stabilized nickel(0) nanoparticles were isolated from reaction medium by centrifugation and characterized using UV-vis spectroscopy, TEM and XPS techniques. PVP-stabilized nickel(0) nanoparticles have an average particle size of 3.0 ± 0.7 nm. PVP-stabilized nickel(0) nanoparticles were found as highly active and stable catalyst with 5300 turnovers over 52 hours in hydrogen generation from the methanolysis of ammonia borane at room temperature. Carbon disulfide poisoning test was performed to show that PVP-stabilized nickel(0) nanoparticles are true heterogeneous catalyst for the methanolysis of AB. This report also includes the kinetic studies of methanolysis of AB catalyzed by PVP-stabilized nickel(0) nanoparticles for understanding the effects of substrate concentration, catalyst concentration, and

temperature. Activation parameters (E_a , ΔH and ΔS) of catalytic methanolysis reaction of AB were calculated from the evaluation of kinetic data.

Keywords: Nickel Nanoparticles, Poly(*N*-vinyl-2-pyrrolidone), Catalyst, Methanolysis of Ammonia Borane, Hydrazine Borane, Hydrogen Generation

ÖZ

AMONYAK BORANIN METANOLİZİNDEN HİDROJEN ÜRETİMİNİ KATALİZLEYEN POLİ(N-VİNİL-2-PIROLİDON) İLE KARARLILAŞTIRILMIŞ NİKEL(0) NANOKÜMELERİ

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Bu tez poli(*N*-vinil-2-pirolidon) ile kararlılaştırılmıř nikel(0) nanoparçacıklarının hazırlanmasını, karakterizasyonunu, amonyak-boranın (AB) metanolizinden hidrojen salınımındaki katalitik aktifliğinin sınanmasını içermektedir. PVP ile kararlılaştırılmıř nikel(0) nanoparçacıkları nikel(II) etilhekzonatın kararlılařtırıcı olarak PVP varlığında hidrazin-boranın metanolizi sırasında indirgenmesinden hazırlanmıřtır. PVP ile kararlılaştırılmıř nikel(0) nanoparçacıkları santrifüjleme yöntemiyle reaksiyon ortamından izole edildi ve izole edilen nanoparçacıklar UV-görünür, TEM ve XPS teknikleri kullanılarak karakterize edildi. PVP ile kararlılaştırılmıř nikel(0) nanoparçacıkları 3.0 ± 0.7 nm ortalama parçacık boyutuna sahiptir. PVP ile kararlılaştırılmıř nikel(0) nanoparçacıkların, 52 saat boyunca amonyak-boranın methanolizinden hidrojen salınımında 5300 çevrim sayısıyla oldukça yüksek katalitik aktiviteye ve stabiliteye sahip oldukları bulundu. PVP ile kararlılaştırılmıř nikel(0) nanoparçacıkların amonyak-boranın metanolizi için uygun heterojen katalizör olduğunu göstermek için karbon disülfür zehirleme testi uygulandı. Bu tez, aynı zamanda katalizör derişiminin, tepken derişiminin ve sıcaklığın tepkime hızına etkisini anlamak için

yapılan amonyak-boranın metanoliz tepkimesinin kinetiğini de içermektedir. Elde edilen kinetik sonuçlardan AB'nin katalitik metanoliz tepkimesinin aktivasyon parametreleri (E_a , ΔH and ΔS) hesaplandı.

Anahtar Kelimeler: Nikel Nanoparçacıkları, Poli(*N*-vinil-2-pirolidon), Katalizör, Amonyak Boranın Methanolizi, Hidrazin Boran, Hidrojen Üretimi

To My Family,

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LIST OF ABBREVIATIONS

NPs	: Nanoparticles
PVP	: Poly(N-vinyl-2-pyrrolidone)
HB	: Hydrazine Borane
AB	: Ammonia Borane
TOF	: Turnover Frequency
TTON	: Total Turnover Number
E_a	: Energy of Activation
ΔH	: Activation enthalpy
ΔS	: Activation entropy
k	: Rate Constant
TEM	: Transmission Elektron Microscopy
XPS	: X-ray Photoelectron Spectroscopy

CHAPTER 1

INTRODUCTION

Carbon-based energy sources which are referred fossil fuels have been used to produce around 80% of the world energy [1]. However, these sources are depletable [2] and the combustion of them causes global warming due to the greenhouse gases released into atmosphere [3]. Therefore, renewable energy sources have been studied as an alternative source to fossil fuels. However, renewable energy sources have discontinuity problem and also on-going major problems such as low efficiency and high cost [4]. In this regard, the use of hydrogen as an energy carrier is expected to enable transition from fossil fuels to the renewable energy sources, on the way towards a sustainable energy future. Hydrogen is globally enrolled clean fuel which reduces environmental pollution.

If there is oxygen in the medium, it reacts with it and after reaction, energy and water occur [5]. Production, storage and use are the main challenges for common usage of hydrogen [6]. Renewable energy sources such as wind, solar, hydropower, and geothermal can be used for the production of hydrogen. However, such kinds of sources are costly, and also they have discontinuity problem. Therefore, in the production part, electrolysis, pyrolysis, photolysis, thermochemical cycles and biomass can be utilized due to incorporation of hydrogen with other elements [7].

The storage of hydrogen is very challenging technical and economical issue. Although there are some problems related to storage, some methods are available. Hydrogen alters its state conditions and with this way, it can be stored physically (compressed gas or liquid hydrogen). However, these processes have high cost and also extremely high pressure and low temperature are needed [8]. Another method is the chemical storage of hydrogen in various solid compounds like carbon nanostructures,

metal hydrides, metal organic frameworks, zeolites, organic polymers, and carbon-boron-nitrogen compounds. Among these hydrogen storage materials, boron-based compounds have recently drawn attention due to their high hydrogen content, low molecular weight, safe storability, and easy H₂ release under mild conditions [9].

According to the results of recent studies, ammonia-borane (AB, NH₃BH₃) and hydrazine-borane (HB, N₂H₄BH₃) are the most promising B-N compounds for efficient hydrogen storage owing to high hydrogen content which have 19.6 wt. % and 15.4 wt. % H₂, respectively; which satisfy 2015 targets of U.S. Department of Energy (U.S. DOE) (9 wt % H₂) [10].

Ammonia borane (AB, NH₃BH₃) is a leading candidate as hydrogen storage medium because of low molecular weight (30.9 gmol⁻¹) and high gravimetric hydrogen capacity (19.6 wt. %). Moreover, ammonia borane is stable in both solid state and solution under ambient conditions. Besides, it has solubility in some polar solvents. Recently, another B-N compound, hydrazine borane (HB, N₂H₄BH₃) has been introduced as a promising chemical hydrogen storage material. Since, it has low molecular weight (45.8 gmol⁻¹) and high hydrogen content (15.4 wt. %). There are two types of hydrogen that can be released. Four of them are protic (N-H, H^{δ+}) and three of them are hydridic (B-H, H^{δ-}) [11,12,13].

Hydrogen stored in ammonia borane can be released by using different kinds of reactions such as thermolysis [14, 15], dehydrocoupling in non aqueous medium [16, 17], hydrolysis [18] or methanolysis [19, 20]. Among these processes, thermolysis is not preferred due to the use of high temperature. When high temperature is utilized in hydrogen generation reaction, the control of reaction becomes difficult. Hydrolysis reaction is well-studied and favored process due to high hydrogen generation rate under ambient conditions. The least investigated one is the methanolysis of ammonia borane. Nevertheless, methanolysis of ammonia borane has a series of advantages that make process valuable. Boron based compounds have high solubility in methanol [21]. Moreover, they have high stability in methanolysis under mild conditions [22]. It means

that they do not go to self-methanolysis reaction. Methanolysis reaction of ammonia borane can be initiated at temperatures below 0 °C in the presence of suitable catalyst [23]. Pure hydrogen can be produced during methanolysis of AB, whereas the concomitant release of ammonia at high AB concentrations is the most frequently encountered problem from the hydrolysis of AB [24]. Tetramethoxyborate compound is formed after methanolysis reaction of ammonia borane and this by-product makes easier recycling process [25].

Suitable catalyst is needed to catalyze the methanolysis of ammonia borane releasing 3.0 equivalents of H₂:



Many homogeneous and heterogeneous catalysts have been employed in the catalytic methanolysis of ammonia borane and hydrazine borane. Many different catalyst have been developed for the methanolysis of AB such as RuCl₃, RhCl₃, PdCl₂ [26], copper nanoparticles [27], polymer stabilized palladium (0) [28] and ruthenium (0) nanoparticles [29], Co-Co₂B, Ni-Ni₃B, Co-Ni-B nanocomposites [30], zeolite confined rhodium(0) nanoparticles [31] and MMT-immobilized ruthenium(0) nanoparticles [25]. Additionally, nickel (0) nanoparticles have been reported to catalyze the methanolysis of HB releasing 3.0 equivalents of H₂ [32, 33]. Heterogeneous catalyst is preferred in many applications due to their separation, reusability, and stability [34]. In catalytic processes, metal nanoparticles are very efficient because of special and unique physical and chemical properties based on their nanosize. Since, they have high surface-volume ratio and large number of active atoms lying on the surface. The critical issue in the application of nanoparticles is the production of size and shape controllable nanoparticles. These factors are very important for the selectivity and activity of catalyst [35]. Metal nanoparticles are thermodynamically instable and tend to agglomerate in the reaction medium. The prevention of agglomeration is so crucial in order to retain their higher surface area, high activity, and lifetime [36]. Therefore, metal nanoparticles must

be stabilized kinetically. Water soluble polymers are widely used for stabilization of transition metal nanoparticles in aqueous solutions.

Poly(*N*-vinyl-2-pyrrolidone) (PVP) (Figure 1) has been investigated in stabilizing the transition metal nanoparticles because of nontoxicity, stability and solubility in many polar solvents [37]. In addition to these, it has a nonionic character and high protective function against agglomeration.

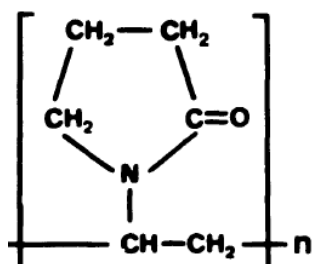


Figure 1. Poly(*N*-vinyl-2-pyrrolidone) (PVP) [38].

In the broadly accepted method, transition metal(0) nanoparticles are obtained from the reduction of transition metal ion in the reaction medium by using stabilizer or supporting agent which prevent agglomeration [39]. Normally, transition metal ions are reduced during dehydrogenation by substrate if it is a strong reducing agent such as sodium borohydride [40]. It has been observed that ammonia borane does not have capability to reduce nickel(II) ions during the hydrolysis [41]. Therefore, additional stronger reducing agent usually sodium borohydride is used to reduce nickel(II) metal ions. However, sodium borohydride causes some complications during the catalytic dehydrogenation because of the fact that it releases hydrogen as well. On the other hand, hydrazine borane reduce nickel(II) ions without using additional reducing agent [42, 43, 44]. The differences between the reducing abilities of ammonia borane and hydrazine borane show difference in their oxidation/reduction potential hydrazine borane has higher reducing ability than ammonia borane in methanol solution [45].

The aim of the study is to prepare of nickel(0) nanoparticles and to stabilize of nickel(0) nanoparticles by using steric stabilizer and their catalytic employment in hydrogen generation from the methanolysis of ammonia-borane. This report includes i) the *in-situ* generation of nickel(0) nanoparticles stabilized by poly(*N*-vinyl-2-pyrrolidone) (PVP) from the reduction of nickel(II) ions by hydrazine borane in methanol solution, and ii) their use as catalyst in hydrogen generation from the methanolysis of ammonia borane. Firstly, PVP-stabilized nickel(0) nanoparticles were generated during the methanolysis of hydrazine-borane. During the methanolysis reaction of HB, nickel(II) ethylhexanoate was reduced to nickel(0) nanoparticles in the presence of PVP stabilizer. Then, PVP-stabilized nickel(0) nanoparticles were isolated by centrifugation and characterized using UV-vis electronic absorption spectroscopy, transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). The isolated and characterized PVP-stabilized nickel(0) nanoparticles were used as catalyst in the methanolysis of ammonia borane. PVP-stabilized nickel(0) nanoparticles are stable in the reaction medium and have high catalytic activity in the methanolysis reaction of AB. In the kinetic part of the experiments, the methanolysis reaction was performed using different catalyst concentrations, substrate concentrations and temperatures to investigate their effect on the hydrogen liberation rate. Additionally, activation parameters (E_a , ΔH and ΔS) were determined from the temperature dependent kinetic data for the catalytic methanolysis of AB. The carbon disulphide poisoning experiment shows that the catalytic methanolysis of HB and AB is heterogeneous. This research has been already published [46].

CHAPTER 2

HYDROGEN

2.1. Hydrogen energy

Today, all over the world fossil fuels, coal and oil were being used to provide energy. However, these energy sources will start to cause some problems in time because of the fact that they produce pollution, their reserves are finite, the development of countries provokes request for energy more than compared to previous years and these reserves are in the critical places such as Arabian countries which can trigger war. Harmful effects of fossil fuels create a demand for renewable energy. There are some advantages of renewable energy. Renewable energy sources are sustainable and also there are no waste products like carbon dioxide. Although renewable energy has some advantages, it has disadvantages. Renewable energy sources provide less energy than our need. Another disadvantage is reliability of supply. Moreover, renewable energy sources are so costly. Therefore, alternative resources are researched and as a result of this research, hydrogen is seen the solution of the energy problem for the today's world (Figure 2) [47].

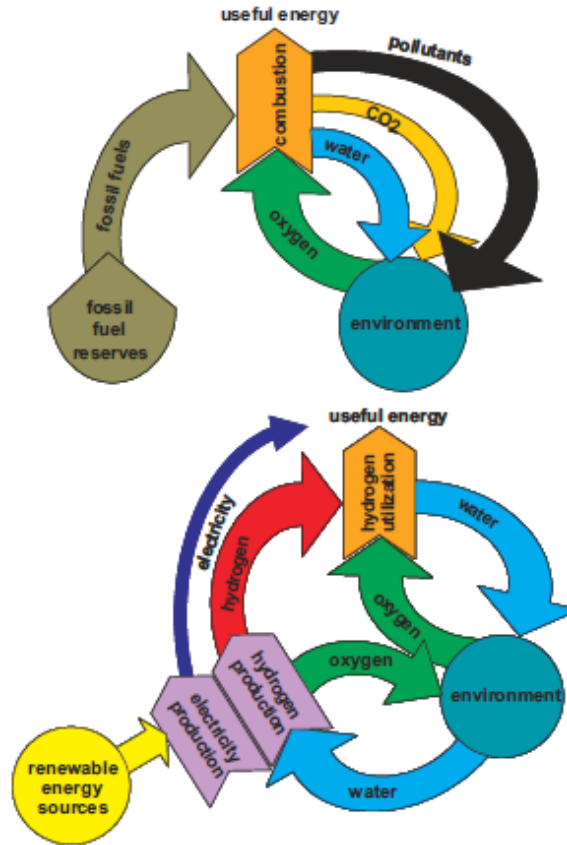


Figure 2. System representation of the present unsustainable energy system based on fossil fuels (a) and a future sustainable energy system based on renewable energy sources and hydrogen and electricity as energy carriers (b)

Hydrogen is critically important for future of the world. It has big power, which will satisfy the world's need. It is nontoxic and there is non-polluting. Basically, if there is oxygen in the medium, hydrogen reacts with it to form water and energy occur after the reaction. Moreover, hydrogen provides renewable and sustainable energy. The energy system, which uses hydrogen as an energy carrier, is called hydrogen economy. The aim of this system is to reduce the CO₂ amount that is released from the other energy sources. In the late of 1800s, the profile of usage of energy started to change. In that years, coal (25.8 g/MJ), oil (20.1 g/MJ) and gas (15.3 g/MJ), which have low carbon intensity, were using. The present years, the demand for natural gases starts to reduce (Figure 3) [48].

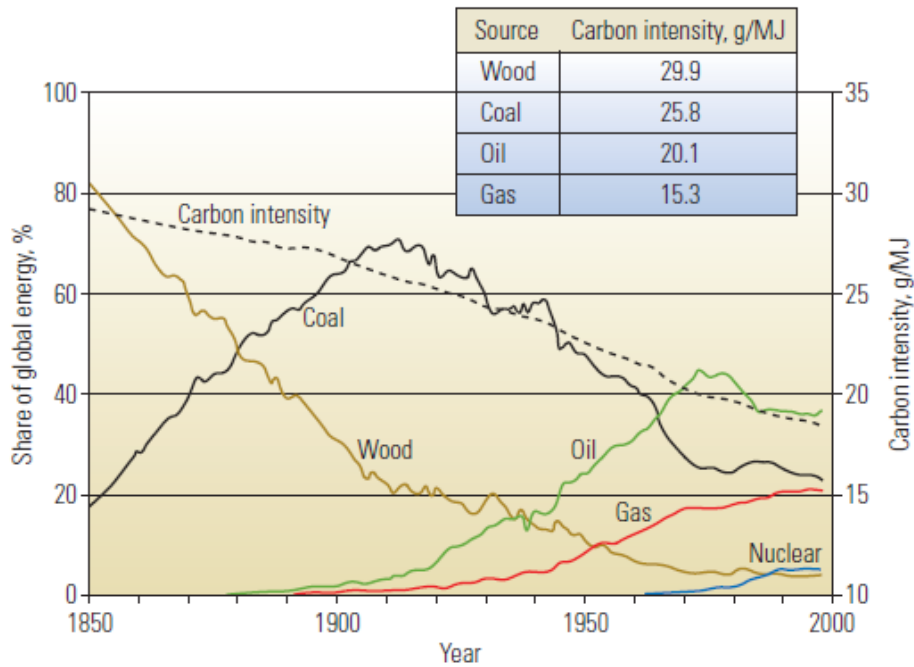


Figure 3. Decarbonization of energy sources

The energy system of world has some problems. Hydrogen economy is so important for handling with these problems. Since it has some critical benefits to worldwide; hydrogen prevents pollution because after its reaction, CO₂ is not produced and there is only water in the reaction medium. As a result of usage of hydrogen, there will be a hydrogen water cycle. Therefore there will be no greenhouse gases. Hydrogen is everywhere so economic dependency about energy will disappear. Because of these reasons, world is interested in hydrogen economy [49].

Another very significant point about hydrogen economy is the hydrogen. In the world, hydrogen element is abundant. On the other hand, the amount of the hydrogen gas is so low. How is the hydrogen gas obtained? What is the source of hydrogen?

There are numerous methods for obtaining hydrogen gas (Figure 4);

- **Electrolysis of water**

This method can be applied anywhere and any water source can be used. Water is split into oxygen and hydrogen, by using electricity. If the renewable sources are used such as wind or solar power, sustainable energy is obtained.

- **Reforming organic substances**

A special device is used and it is called Reformer. By this device, hydrogen can be generated from hydrocarbons and other molecules, which consist of hydrogen and carbon.

- **Reforming biomass**

Hydrogen is produced using natural wastes, such as garbage, agricultural wastes.

- **Pyrolysis**

In this method, oxidant free chamber is used. It is heated and hydrogen is separated from carbon based molecule. Hydrogen, which is obtained, is used to build wind and wave turbine [50].

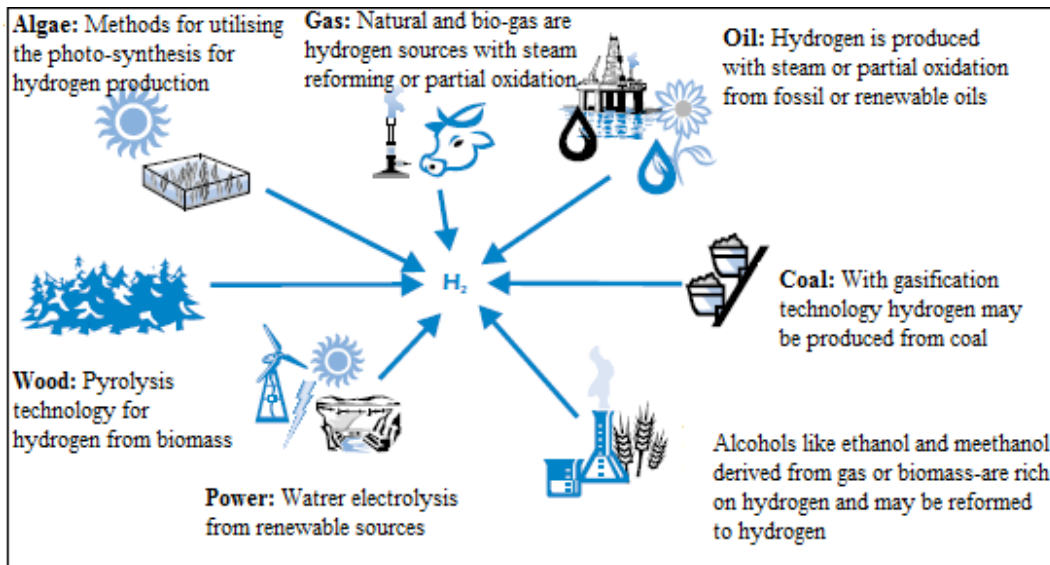


Figure 4. The methods of production of hydrogen [51].

These offers make the hydrogen so valuable, important for carbon-low energy systems. It has a lot of applications and is obtained from a lot of sources. Moreover, it is so significant for the chemical industry. Hydrogen can help world for carbon free energy system. For all these reasons, according to many experienced people, carbon free system, which has low cost, is possible with hydrogen [52].

2.2. Hydrogen storage

Hydrogen economy has a key role for future energy system and it can easily eliminate negative effects of today's energy system. Production of hydrogen is critically important. However, hydrogen can be easily obtained from different energy sources. Otherwise, hydrogen storage is a key part of the hydrogen economy [53]. Hydrogen is the source of huge energy compared to other energy sources. Because of this property, hydrogen is suitable for transportation fuel. However, to acquire satisfactory amount of hydrogen is difficult because of the fact that it is the lightest element. Hence, there are some challenges about the hydrogen storage [54]. Although there are some problems related to storage, some hydrogen storage methods are available:

- Hydrogen storage in compressed form ,
- Hydrogen storage in liquid form,
- Storage of metal hydride,
- Storage of chemical hydride [55].

Table 1. Storage methods of hydrogen

Storage Method	ρ_m [mass %]	ρ_v [kg H ₂ m ⁻³]	T [°C]	P [bar]	Phenomena and remarks
High pressure gas cylinders	13	<40	RT	800	Compressed gas (molecular H ₂) in light weight composite cylinders (tensile strength of the material is 2000 MPa)
Liquid hydrogen in cryogenic tanks	size dependent	70.8	-252	1	Liquid hydrogen (molecular H ₂) continuous loss of a few %per day of hydrogen at RT
Adsorbed hydrogen	≈2	20	-80	100	Physisorption (molecular H ₂) on materials e.g. carbon with a vey large specific surface area, fully reversible
Absorbed on interstitial sites in a host metal	≈2	150	RT	1	Hydrogen (atomic H) intercalation in host metals, metallic hydrides working at RT are fully reversible
Complex compunds	<18	150	>100	1	Complex compounds ([AlH ₄] ⁻ or [BH ₄] ⁻) desorption at elevated temperature, adsorption at high pressure
Metals and complexes together with water	<40	>150	RT	1	Chemical oxidation of metals with water and liberation of hydrogen, not directly reversible?

The technology of hydrogen storage is an major issue from the point of hydrogen power systems such as transportation and portable applications [56, 57].

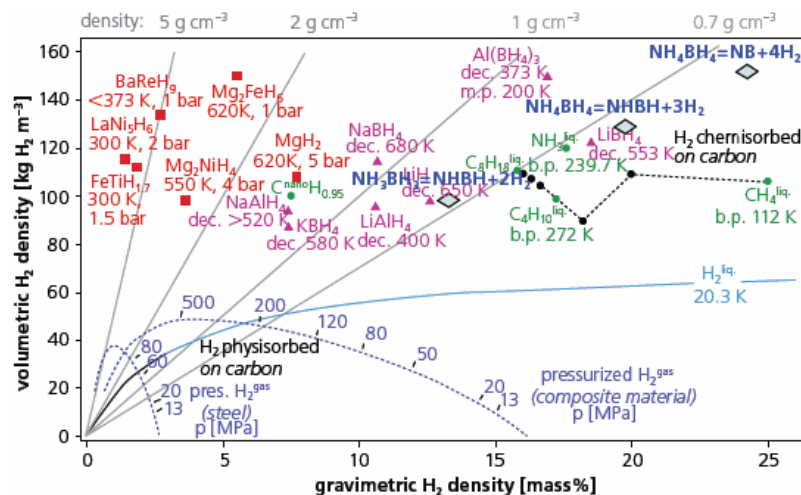


Figure 5. Comparison of gravimetric and volumetric densities of various hydrogen storage materials [58].

Chemical hydrides are the most preferable substances for hydrogen storage. Since, chemical hydrides have high hydrogen storage capacity [59]. Among chemical hydrides, boron based solid materials, which have low molecular weight and high gravimetric hydrogen capacity, are so suitable for hydrogen storage (Figure 5). Especially, sodium borohydride, lithium borohydride, ammonia borane and hydrazine borane are the most attractive hydrogen rich materials and they release hydrogen easily [20]. LiBH_4 and NaBH_4 have high hydrogen content (18 wt %) and (10.3 wt %). Although LiBH_4 has high hydrogen capacity, NaBH_4 is more popular than LiBH_4 because of safety and proper cost. However, NaBH_4 is unstable substance and because of this it goes self-hydrolysis during the reaction. It means that NaBH_4 behaves as catalyst while there is a catalyst in the medium. Therefore, it is not suitable for fuel cell applications [60]. These hydrogen storage materials are incapable for requirements of the hydrogen storage. Therefore, new sources of hydrogen were searched and B-N compounds were found as suitable hydrogen source. B-H bond is hydridic and N-H bond is protic [61]. If there are the multiple nature bonds in the substances, hydrogen generation becomes so successful. For this reason, ammonia borane (19.6 wt %) and

hydrazine borane (13.4 wt %) are commonly used material for hydrogen generation [62].

2.3. Ammonia borane and Its Methanolysis Reaction

One of the most important hydrogen generation power is the ammonia borane with high hydrogen capacity (19.6 wt %) and hydrogen storage density (2.74 kWh/L). Hence, it is suitable for some applications with these properties [63]. Besides these, AB is stable in air, water and also methanol. It is solid at room temperature (25°C). Furthermore, it is very friendly for environment and nontoxic material. It is not self-flammable because of chemical stability in the air. Thus, it is preferred for fuel cell applications instead of di-borane [64]. The chemistry of ammonia borane (Figure 6) with multiple kinds of hydrogens, protic N-H and hydridic B-H, is amazing.

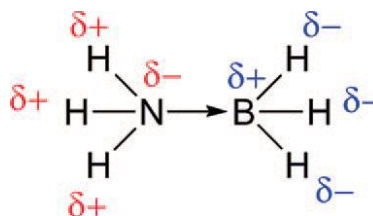
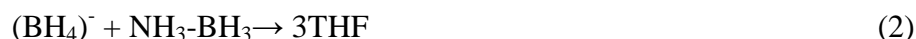
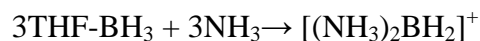


Figure 6. N-H and B-H bond polarizations in ammonia borane [65].

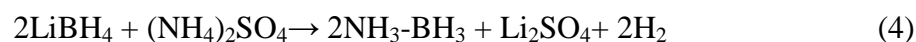
The mechanism of polarization of hydridic and protic hydrogens is explained by electronegativity of boron and nitrogen and also, it demonstrates the 3D stabilization systems of AB in details [66].

There are lots of production mechanisms of AB.

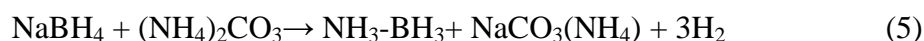
- The most favorite method is mixing ammonia (NH_3) and THF-borane (BH_3) solution (Equation 2).



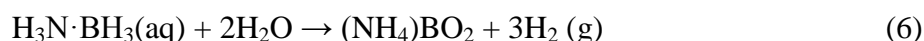
- Another method is that the reaction becomes between the lithium borohydride (LiBH_4) and ammonium salts (NH_4Cl (Equation 3)) and $(\text{NH}_4)_2\text{SO}_4$ (Equation 4).



However, NaBH_4 is preferred instead of LiBH_4 due to the fact that the reaction of AB production becomes less costly. NH_4Cl , $(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)_2\text{CO}_3$ can be used as ammonium salts (equation 5) [67].



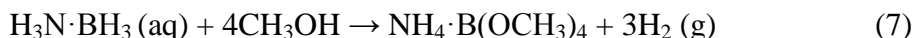
To release hydrogen which is stored in ammonia borane, thermolysis, hydrolysis and methanolysis can be used. However, the method of thermolysis is not common because the high temperature is needed. Hydrolysis process is well-known and efficient but after this process, ammonium gas is released when the high concentration of ammonia borane is used. The hydrolysis reaction is given below (Equation 6)



As a result of this, ammonium borate (NH_4BO_2) is formed in the medium and this causes some problems in practical applications. Although methanolysis reaction is the least investigated one, it is preferred because of its advantages. In methanol, ammonia borane has high solubility (23 wt. %) at 23°C. Methanolysis reaction provides high stability for ammonia borane and hydrazine borane. It means that they do not undergo self-methanolysis. Pure hydrogen is released in the methanolysis reaction. It means that

there is no ammonium gas during methanolysis reaction of ammonia borane. When the suitable catalyst is used, methanolysis reaction of ammonia borane takes place below 0°C. Moreover, ammonium tetramethoxyborate is formed in the medium and the recycling becomes easier due to this byproduct.

- The methanolysis reaction is given below (Equation 7) [19].



2.4. Hydrazine borane and Its Methanolysis Reaction

Hydrazine borane is a hot topic in terms of hydrogen storage issue. After ammonia borane, hydrazine borane is explored for satisfying the need of fuel cell and transport applications. Since, NH_3 gas can not form in the released H_2 during the reaction. This is important in terms of catalyst. If there is NH_3 in the reaction medium, catalyst is poisoned and the needed hydrogen can not be obtained for applications [68].

According to 2015 objective of U.S. Department of Energy (DOE), 9 wt. % hydrogen capacity provides convenience about applicability. Hydrogen capacity of hydrazine borane is greater than that of the target of DOE. Moreover, the released hydrogen equivalent can be raised if complete hydrolysis of hydrazine borane takes place by using proper catalyst [69].

Hydrazine borane (HB) has high gravimetric hydrogen capacity (15.4 wt. %). It also has both protic and hydridic protons. It has 4 protic (N-H , $\text{H}^{\delta+}$) and 3 hydridic (B-H , $\text{H}^{\delta-}$) protons different from ammonia borane, which has 3 hydridic, 3 protic protons [70].

The preparation of hydrazine borane is so simple and there are many methods for preparation. One of these methods is given below (Equation 8) [71]:

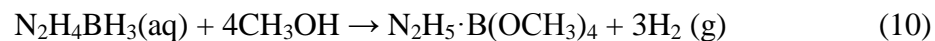


The liberation of hydrogen from hydrazine borane is possible by using thermolysis and solvolysis (hydrolysis or methanolysis) methods. Thermolysis is a critical and impractical method because high temperature is needed. However, when high temperature is used, high amount of H_2NNH_2 occurs in the reaction medium. This causes that the equivalent of H_2 is obtained lower than expecting equivalent. Instead of thermolysis, hydrolysis or methanolysis is preferred [72,73].

- Hydrolysis reaction of HB (Equation 9):



- Methanolysis reaction of HB (Equation 10) [74]:



CHAPTER 3

TRANSITION METAL(0) NANOPARTICLES; AS CATALYSTS

3.1. Catalysis

Catalysis is the most important part of the chemical conversion. This importance is explained in two facts: (i) there is no life without enzymes in the world (ii) no actual development exists for society without catalysts. In ancient times, catalysts are used for different procedures, e.g. wine production. However, that times, the mechanism of catalyst were not known and explained [75].

First of all, Berzelius suggested the term of ‘catalysis’ in 1835. He explained some reaction mechanism by using the definition of catalysis and supposed that the catalyst so powerful substances, which can affect the reaction route. Today, Ostwald’s definition is valid. According to Ostwald’s definition, some substances, which are in the reaction medium, make faster the reaction and these substances can not change after entering the reaction [76].

Catalysts are needed for many applications, reactions and syntheses. For example, ‘catalysis’ is key technology for industrial synthesis, many biological reactions and also automobiles converter. Moreover, this process is so important for protection of environment. Catalysis processes form about 85-90 % of the chemical reaction in the industry.

Simply, catalysts are substances that accelarate the reaction. Furthermore, they are not affected during the reaction. They stay in the medium without being consume at the end of the reaction (Figure 7).

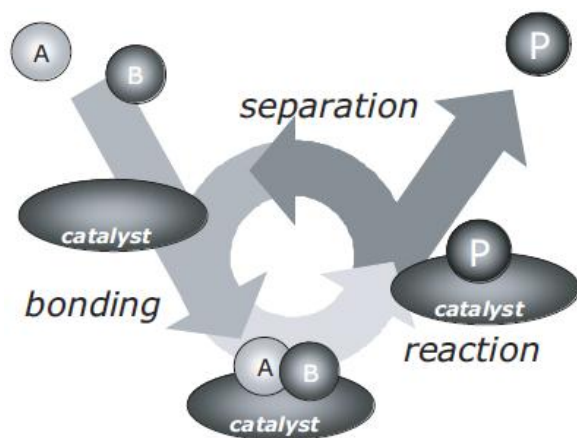


Figure 7. Catalytic cycle

The activation energy of uncatalyzed reaction is much higher compared to catalyzed reaction so the reaction rate is faster in the catalyzed reaction. The equilibrium constant for the overall reaction is not affected by the catalysts. While the catalysts affect the kinetics, thermodynamics do not. They accelerate the formation and composition reaction at the same proportion (Figure 8) [77].

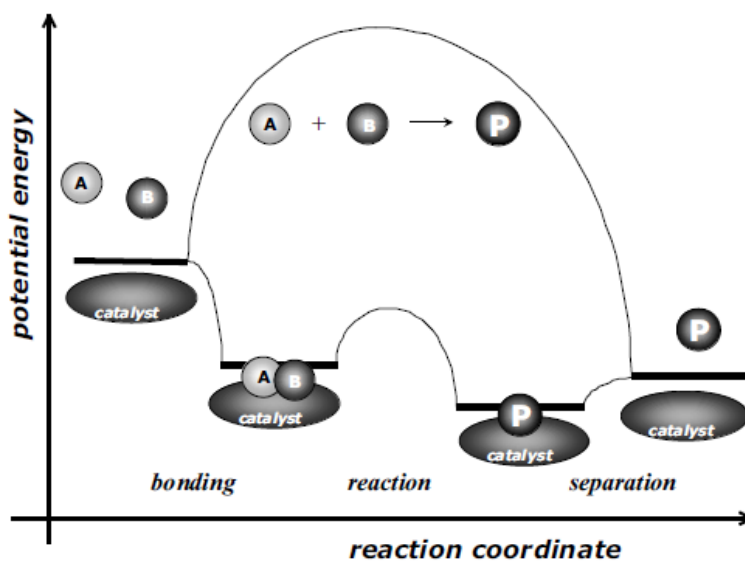


Figure 8. Potential energy diagram of catalyzed and uncatalyzed reactions

There are some critical factors of catalysts for the processes in order to get better results:

- activity
- selectivity
- stability

Catalyst activity can be measured by the term of turnover number (TON), the number of substances which can be converted by using one mole of catalyst. Total turnover number (TTON) is the maximum use of catalyst in a special reaction (Equation 11).

$$\text{TON} = \frac{\text{moles of product}}{\text{moles of catalyst}} \quad (11)$$

Catalytic efficiency is important and it is explained by turnover frequency (TOF). It measures the specific activity of the catalyst by the number of product which occurs at the per unit time (Equation 12).

$$\text{TOF} = \frac{\text{rate of reaction (v)}}{\text{moles of catalyst}} \quad (12)$$

Another important parameter is the selectivity. Selectivity of the reaction is the ratio of the starting material to the desired product. Stability is so critical for the catalyst. The life time is detected by the different kind of stability of catalyst.

Because of some reasons, selectivity is the head of modes of catalysts. After selectivity, stability comes and activity is the least important mode of catalyst [78].

3.1.1. Classification of Catalysts

There are many types of catalysts which are known today. These can be categorized according to some properties [79]:

- Structure
- Composition
- Area of application
- Aggregation

Generally, catalysts are classified by state of aggregation. According to this, there are three main classes in the classification of catalysts (Figure 9):

- Homogeneous catalyst
- Heterogeneous catalyst
- Biocatalyst

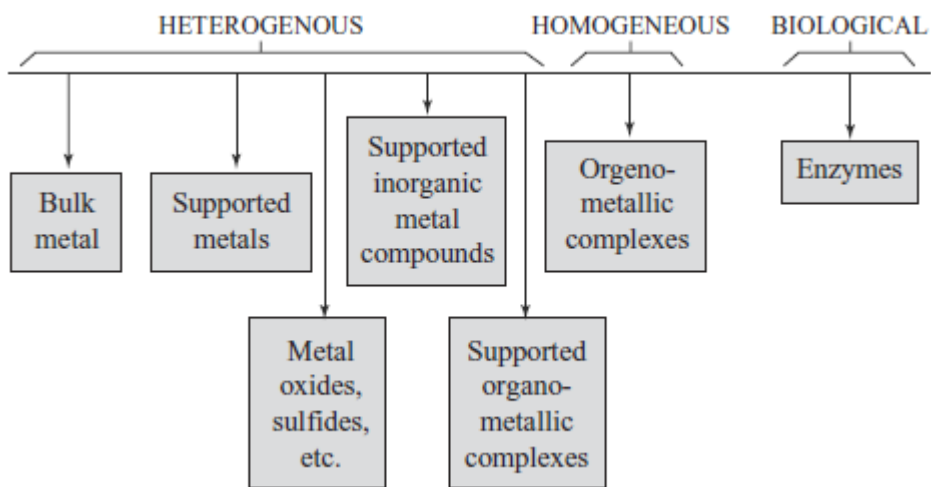


Figure 9. Classification of catalysts [80].

Homogeneous catalyst is the same phase with the reactants and products. It means that there is an uniform phase. Homogeneous catalysts are composed of well-defined chemical or coordination compounds. Mineral acids and transition metal compounds are the illustrations of homogeneous catalysts. On the other hand, heterogenous catalysts are generally solid phase and their phases are different from the reactants and products. Examples of heterogeneous catalysts contain amorphous or crystalline aluminosilicates for cracking petroleum fractions. The other type is the biocatalysts. This class consists of enzymes which are the protein molecules and enzymes are important for the life cycle. Therefore, these catalysts are special and valuable between homogeneous and heterogenous catalysts [78].

3.2. Nanoparticles: Transition Metal Nanoparticles as Catalysts

Nanoscience and nanotechnology have a rising trend in the recent centuries. A variety of applications, products, computers, nanomagnets, nanowires are the results of the nanometric catalysts [75]. Nanotechnology is the science which is interested in very small particles at the scale of one billionth of meter (Figure 10) [81].

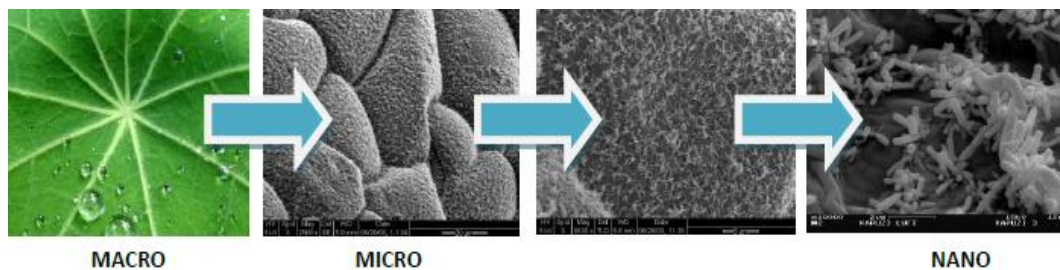


Figure 10. The images of macro, micro and nanoscales particles [82].

Nanoparticles, which are with sizes 1-25 nm, attract attention so much. NPs exhibit optical, magnetic, electrical, catalytic properties and mechanical flexibility [83] based on their sizes. These properties are not valid for bulk materials. They cannot

prefer because of their huge sizes [65]. In the nanoscale chart, NPs are between the bulk materials and molecular state and they demonstrate valuable properties (Figure 11) [75].

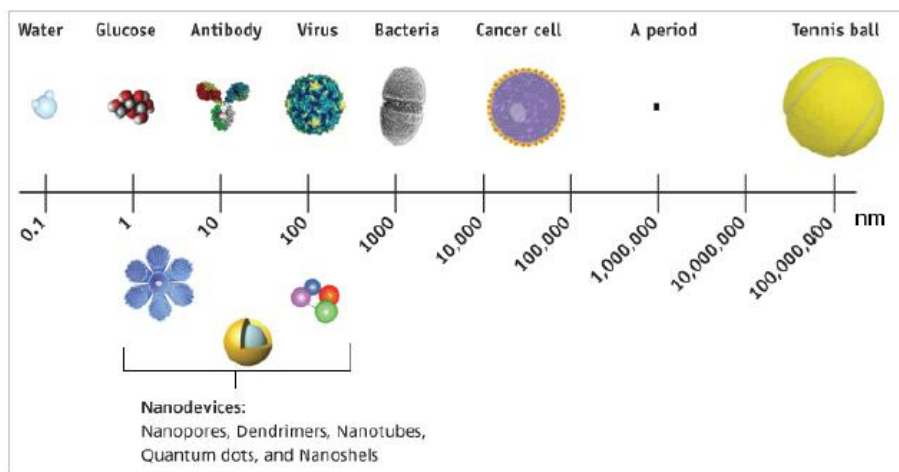


Figure 11. Schematic representation of the size of the particles [82].

A nanoparticle is a kind of substance which is composed of equal size particles [84]. When nanoparticles are used with transition metals, their physical and chemical properties become more attractive. Transition metal nanoparticles gain importance among the researchers because of the fact that they have interesting and novel chemical and physical properties. Due to their attractive properties, they are used in many applications, e.g. catalysts in many organic and inorganic reactions and electrocatalysts in fuel cells. Transition metal nanoparticles are so active compared to bulk counterparts. Since, activity is related to surface area and metals on the surface of nanoparticle increases the surface area. Accordingly, transition metal nanoparticles are preferred for many applications [85].

3.3. Synthesis of Metal Nanoparticles

In many applications, the purpose of the synthesis of transition metal nanoparticle is to obtain smaller size particle (1-10nm), clean surfaces, well-defined composition and narrow size distribution at the same time [86]. Therefore, two methods

are generally used: (i) breakdown method (ii) buildup method. In breakdown method, bulk material is splitted into small pieces by using mechanical grinding and mechanical milling (Figure 12). In this method, controlling the particle size at the nano level is very critical.

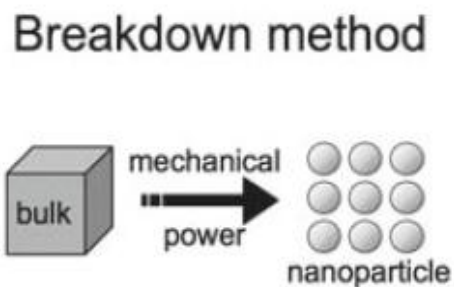


Figure 12. Breakdown method for synthesis of metal NPs

On the contrary, build up method is used for gathering the small pieces. This process is composed of two parts, chemical and physical processing (Figure 13) [87].

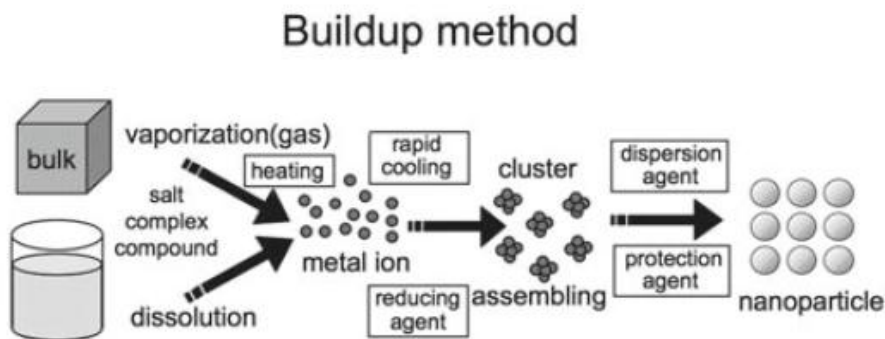


Figure 13. Build up method for synthesis of metal NPs

Apart from these, there are four different methods for synthesis of metal NPs [88]:

- Transition metal salt reduction
- Thermal decomposition and photochemical methods

- Ligand reduction and displacement from organometallics
- Metal vapor synthesis

3.4. Stabilization of Metal Nanoparticles

This phenomena is related to the surface which specifies the term ‘clean surface’ [89,90]. The small particles tend to generate large particles because of their free energy driving force. Therefore, they want to make bulk materials by agglomeration. Generally, to prevent agglomeration, stabilizing agents are used. They are adsorbed on the surface. Briefly, nanoparticles are stabilized against agglomeration. Three methods provide the stabilization of nanoparticles: namely, electrostatic stabilization, steric stabilization and electrosteric stabilization [75].

3.4.1. Electrostatic Stabilization

This type stabilization is known as DLVO theory and Derjugin, Landau, Verwey, and Overbeek develop the theory of electrostatic stabilization in 1940s. DLVO theory explains the stabilization of nanoparticles which is based on the balance between the Coulombic forces and Van der Waals forces [91]. There are anions and cations which come from starting material in the solution medium. The anions are adsorbed on the surface of metal nanoparticle and electrical double layer is formed to create a Coulombic repulsion effect. Agglomeration is prevented by this electrical layer (Figure 14) [92].

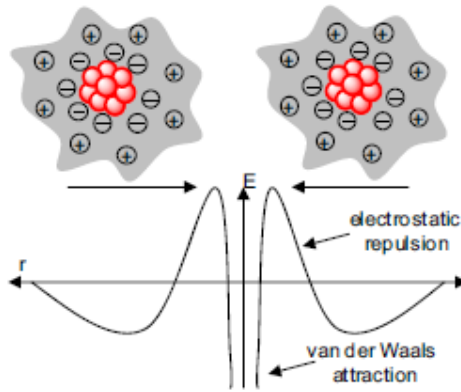


Figure 14. Electrostatic stabilization (DLVO theory).

3.4.2. Steric Stabilization

For stopping the agglomeration, polymers or surfactants are used in this stabilization system. These large molecules are adsorbed on the surface via chemical bonding or physisorption to form a protecting layer. Motion and conformations are restricted and because of this, while entropy is decreasing, free energy is increasing (Figure 15) [75].

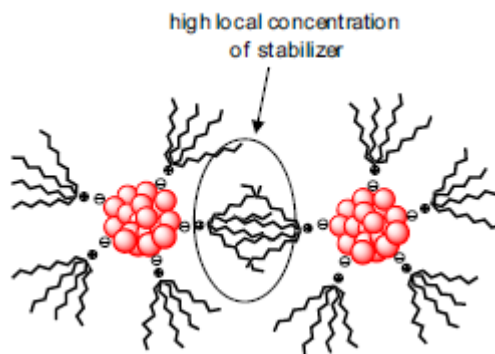


Figure 15. Steric stabilization

3.4.3 Electrosteric Stabilization

In order to obtain thermodynamically stable nanoparticles, the usage of combination of steric stabilization and electrostatic stabilization is suitable. In this process, large surfactants such as polymers, oligomers are used. These surfactants must be ionic. Electrical double layer and steric effect are formed using these ionic surfactants. These prevent agglomeration (Figure 16) [93].

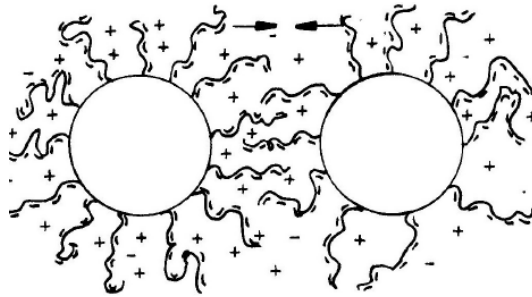


Figure 16. Electrosteric stabilization

3.5. Characterization of Metal Nanoparticles

Today's world, nanomaterials are very famous and one of the most studied area due to the properties of them: small size, large surface area, high surface energy and large proportion of surface atoms [94]. They are used in many important applications such as fuel cells and transport applications because of their properties. Therefore, most of the scientists are interested in nanomaterials. However, more detailed information is needed about nanomaterials and this is obtained by characterization techniques [95].

The most common techniques are given in Figure 17 [96]:

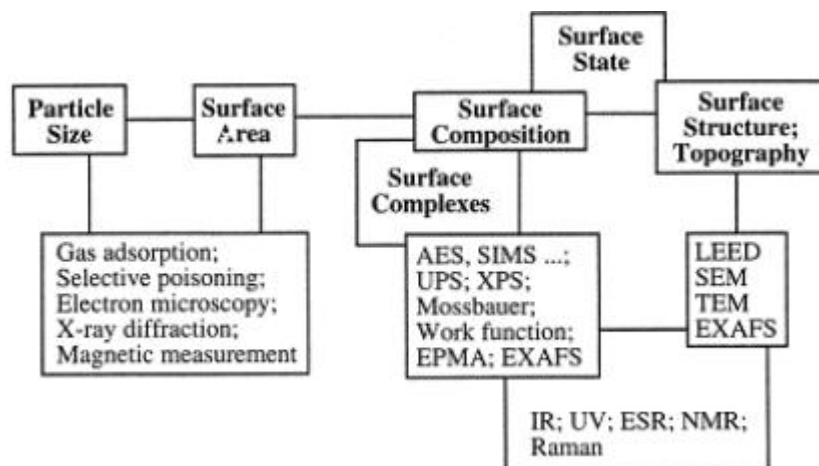


Figure 17. Common methods for characterization of nanomaterials

CHAPTER 4

EXPERIMENTAL

4.1. Materials

Nickel(II) 2-ethylhexanoate solution (78% wt) in 2-ethylhexanoic acid, sodium borohydride (99%), methanol (99%), tetrahydrofuran (99%), and ammonia borane (98%) were purchased from Sigma-Aldrich. Dihydrazine sulfate ($\text{N}_2\text{H}_4 \cdot 0.5\text{H}_2\text{SO}_4$) was purchased from Acros-Organics. Tetrahydrofuran and methanol were distilled over sodium/benzophenone and metallic magnesium, respectively and stored under argon. Distilled methanol was used in all methanolysis reactions under inert gas atmosphere unless otherwise specified. All glassware were cleaned with acetone, followed by copious rinsing with distilled water before drying in an oven at 120 °C.

4.2. Characterization of PVP Stabilized Nickel(0) Nanoparticles

The transmission electron microscope (TEM) image was obtained using a JEM-2010 (JEOL) TEM instrument operating at 120 kV. The samples used for the TEM experiments were collected from *in situ*-generated PVP-stabilized nickel(0) nanoparticles solution that was obtained at the end of the catalytic methanolysis of hydrazine-borane. The nanoparticle solution was centrifuged at 8000 rpm for 8 min. The separated nanoparticles were washed with ethanol to remove the excess PVP and other residuals. Then, the nanoclusters were redispersed in 5 mL acetone. One drop of the colloidal solution was deposited on carbon coated copper grid and evaporated under inert atmosphere. Samples were examined at magnifications between 150 and 600 K. The samples used for XPS analysis were harvested from *in-situ* generated PVP-stabilized nickel(0) nanoparticles solution at the end of the catalytic methanolysis of

hydrazine borane. The polymer-stabilized nanoparticles were separated by centrifugation at 8000 rpm for 8 min and dried under vacuum. XPS analysis was performed on a Physical Electronics 5800 spectrometer equipped with a hemispherical analyzer and using monochromatic Al K α radiation (1486.6 eV, the X-ray tube working at 15 kV, 350W and pass energy of 23.5 keV). UV-vis electronic absorption spectra of PVP-stabilized nickel(0) nanoparticles were recorded in methanol solution on Varian-Carry100 double beam instrument. NMR spectra were recorded on a Bruker Avance DPX 400 with an operating frequency of 128.15 MHz for ^{11}B . After the catalytic methanolysis of hydrazine borane or ammonia borane, a 0.1 mL aliquot of the reaction solution was transferred into a quartz NMR tube containing 0.5 mL d-chloroform with a glass pipette.

4.3. Synthesis and Characterization of Hydrazine Borane

Dihydrazine sulfate and sodium borohydride react with each other to form hydrazine borane ($\text{N}_2\text{H}_4\text{BH}_3$) in cyclic ethers such as tetrahydrofuran (THF) and identified according to literature procedure [97].

The melting point of hydrazine-borane: $\sim 60\text{ }^\circ\text{C}$; (DP-MS) $m/z = 46$ (45.87 calculated for $\text{N}_2\text{H}_4\text{BH}_3$); ^1H NMR (400.1 MHz, CD_2Cl_2) 5.1 ppm (t, 2, $\text{NH}_2\text{-NH}_2\text{-BH}_3$), 3.4 ppm (b, 2, $\text{H}_2\text{N-NH}_2\text{-BH}_3$), 1.2 ppm (t, 3, $\text{H}_2\text{N-NH}_2\text{-BH}_3$); ^{11}B NMR (128.2 MHz, H_2O) -20 ppm (q, BH_3); ATR-IR (selected, cm^{-1}) 3310 (s), 3200 (s), 2840 (m), 2650 (m), 2370 (m), 2214 (m), 1620 (s), 1588 (m), 1435 (w), 1332 (m), 1150 (s), 910 (m), 747 (w) in agreement with the literature values [97].

4.4. General Procedure for Generation of PVP stabilized Nickel(0) Nanoparticles During the Methanolysis of Ammonia-Borane and Hydrogen Generation Data Handling

The formation of PVP stabilized nickel(0) nanoparticles and the catalytic methanolysis of hydrazine-borane were performed in the same reaction flask. The

experimental set-up used to perform the catalytic reaction and measure the amount of hydrogen liberated during methanolysis reaction is given Figure 18. First of all, reaction flask, filled in N_2 , with a stir bar was evacuated to remove any trace of oxygen and water present. Reaction flask was connected to a graduated glass tube filled with water *via* bubbler containing 20.0 mL of methylcyclohexane in order to determine the volume of hydrogen gas evolving from methanolysis reaction. A jacketed reaction flask with a stir bar was placed on magnetic stirrer and reaction flask was connected to water circulator to keep temperature at 25.0 ± 0.1 °C.

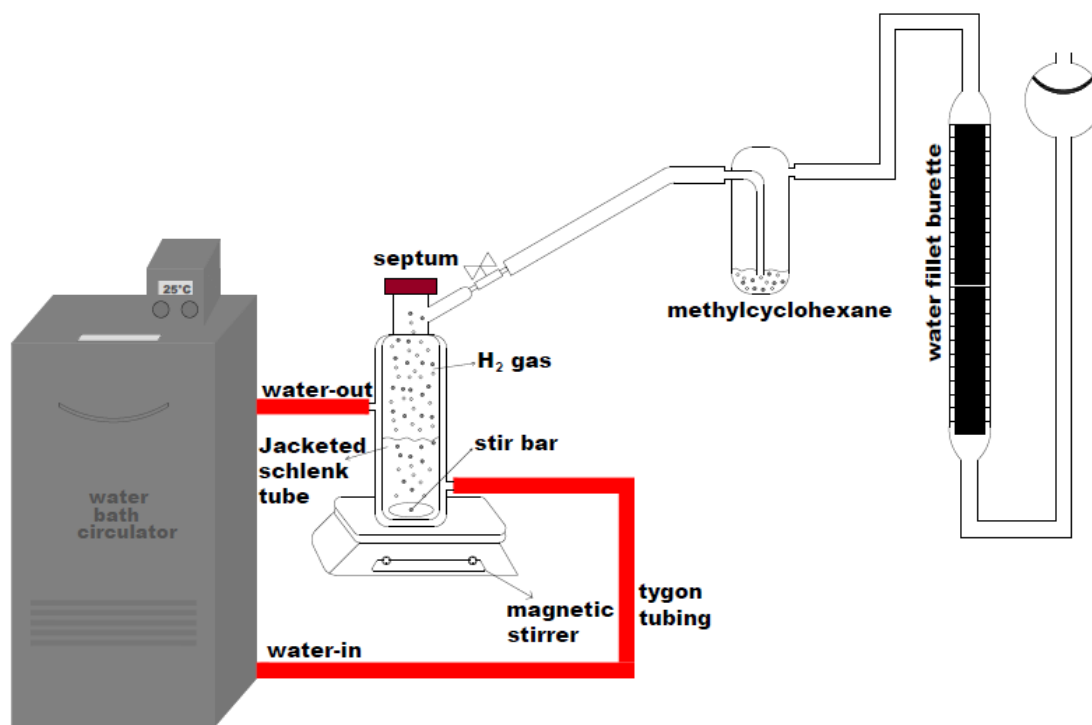


Figure 18. Experimental set-up used for performing the preparation of PVP-stabilized Ni(0) nanoparticles and methanolysis

A stock solution of 10 mM Ni²⁺ was prepared by transferring 0.115 mL (0.25 mmol Ni) nickel(II) 2-ethylhexanoate solution into 25 mL volumetric flask and diluted with methanol to 25 mL. The catalytic reaction solution with the desired concentration of nickel was prepared by taking certain aliquot from the stock solution and diluted by adding methanol. For instance, in order to prepare 1.0 mM Ni catalyst solution, 1.0 mL (0.010 mmol Ni), an aliquot of stock solution is transferred into the reaction flask containing 2.2 mg PVP (polymer to metal ratio of 2) and 6.0 mL methanol with a glass pipette. In a separate flask, 92 mg (1.8 mmol) HB is dissolved in 3.0 mL methanol while stirring under argon. Then, HB solution was added to the reaction flask *via* a gastight syringe, all at once, to launch the catalytic methanolysis of HB. After an induction time the color changes from pale green to dark brown indicating the formation of nickel(0) nanoparticles in methanol solution and a rapid hydrogen generation from the methanolysis of HB starts immediately. The volume of hydrogen evolved during catalytic methanolysis was recorded by measuring the displacement of water level in the glass tube at constant pressure. When no more hydrogen was liberated, experiment was stopped. An aliquot of the reaction solution was used for taking the ¹¹B NMR spectrum. In catalytic methanolysis of ammonia borane, the same procedure as described above was followed. However, at this time preformed PVP-stabilized nickel(0) nanoparticles was used as catalyst in the methanolysis of AB because AB is not able to reduce nickel(II) ions to nickel(0) nanoparticles. For this purpose, after the liberation of expected amount hydrogen from the methanolysis of 180 mM HB catalyzed by PVP-stabilized nickel(0) nanoparticles, 64 mg (2.0 mmol) AB was added to the reaction flask making 200 mM AB solution. Due to the use of preformed PVP-stabilized nickel(0) nanoparticles, rapid hydrogen generation started immediately without induction time after the addition of AB. The hydrogen generation from the methanolysis of AB was recorded by measuring the displacement of the water in glass tube at constant pressure. At the end of the methanolysis, an aliquot of the reaction solution is used to take the ¹¹B NMR spectrum.

4.5. Kinetics of Methanolysis of AB Catalyzed by PVP-stabilized nickel(0) nanoparticles

In order to determine the rate law of PVP stabilized nickel(0) nanoparticles catalyzed methanolysis of ammonia-borane, two different sets of experiment were performed.

In the first set of experiments, the catalytic methanolysis of AB was started with preformed PVP-stabilized nickel(0) nanoparticles catalyst in various metal concentrations (0.5, 1.0, 1.5, and 2.0 mM Ni) at 25.0 ± 0.1 °C.

In the second set of the experiments, catalyst concentration was kept constant at 1 mM Ni and [PVP]/[Ni] ratio constant at 2.0 at 25.0 ± 0.1 °C while AB concentrations were altered in the range of 100-500 mM.

4.6. Determination of Activation Parameters for PVP-stabilized nickel(0) nanoparticles Catalyzed Methanolysis of Ammonia-Borane

In order to determine activation parameters (E_a , ΔH , and ΔS) for the methanolysis of 200 mM ammonia-borane catalyzed by preformed PVP-stabilized nickel(0) nanoparticles was performed at various temperature in the range of 25-40 °C starting with catalyst concentration of 1 mM Ni and [PVP]/[Ni] ratio of 2.0. The values of observed rate constants k_{obs} for catalytic hydrolysis of NH_3BH_3 were determined for each temperature and utilized to calculate the activation energy by using Arrhenius plot; enthalpy and entropy of activation by using Eyring plot.

4.7. Catalytic Lifetime of PVP-stabilized Nickel(0) nanoparticles in the Methanolysis of Ammonia-Borane

The life time of the catalyst was measured by determining the total turnover number (TTON) in the methanolysis of ammonia-borane catalyzed by PVP-stabilized nickel(0) nanoparticles. For this purpose, lifetime experiment was initiated by adding 0.50 mL (5.0 micromole Ni) aliquot from stock solution of nickel(II) 2-ethylhexanoate

precursor by keeping [PVP]/[Ni] ratio of 2.0 and 500 mM ammonia-borane at 25 ± 0.5 °C. When expected amount of hydrogen evolved, a new batch of substrate (AB) was added to the reaction medium under nitrogen inert gas. Same procedure was applied until no more hydrogen liberation was observed.

4.8. Carbon Disulfide (CS₂) Poisoning in the Methanolysis of Hydrazine Borane Catalyzed by PVP-stabilized Nickel(0) Nanoparticles

In order to confirm heterogeneity of PVP-stabilized nickel(0) nanoparticles, catalyst poisoning experiment was performed by using carbon disulfide (CS₂) as poison. Firstly, a 2.0 mM stock solution of CS₂ was prepared in 10 mL methanol. Then, typical methanolysis reaction of hydrazine borane catalyzed by PVP-stabilized nickel(0) nanoparticles was initiated with 1.0 nickel(II) 2-ethylhexanoate and 180 mM hydrazine borane at 25 ± 0.5 °C. At the time when about 40% of hydrogen evolved, 1.0mL (2.0 micromole) CS₂ was added to reaction medium *via* syringe in order to poison catalyst and the reaction was followed for 30 minutes.

CHAPTER 5

RESULTS AND DISCUSSION

5.1. Preparation and Characterization of PVP-Stabilized Nickel(0) Nanoparticles

In-situ formation of nickel(0) nanoparticles from the reduction of nickel(II) ions in the presence of poly(*N*-vinyl-2-pyrrolidone) and concomitant hydrogen release from the methanolysis of hydrazine-borane were performed in the same medium.

In a typical experiment, first of all, nickel(II) 2-ethylhexanoate and PVP were stirred in methanol at 1000 rpm. After that hydrazine borane solution was injected to the reaction flask *via* a gastight syringe. In the reaction medium, reduction of Ni(II) ions to Ni(0) and hydrogen generation from methanolysis of hydrazine borane occur at the same time. The experiment was started with 180 mM hydrazine borane and 2.0 mM nickel(II) 2-ethylhexanoate plus 4.0 mM PVP in 10.0 mL methanol at 25.0 ± 0.5 °C. Both the reduction of nickel(0) nanoparticles from nickel(II) ions and hydrogen release from methanolysis of HB were followed by monitoring the volume of H₂ generated. Figure 19 depicts the plot of equivalent mole H₂ evolved per mole of hydrazine borane *versus* time for the catalytic methanolysis of hydrazine borane.

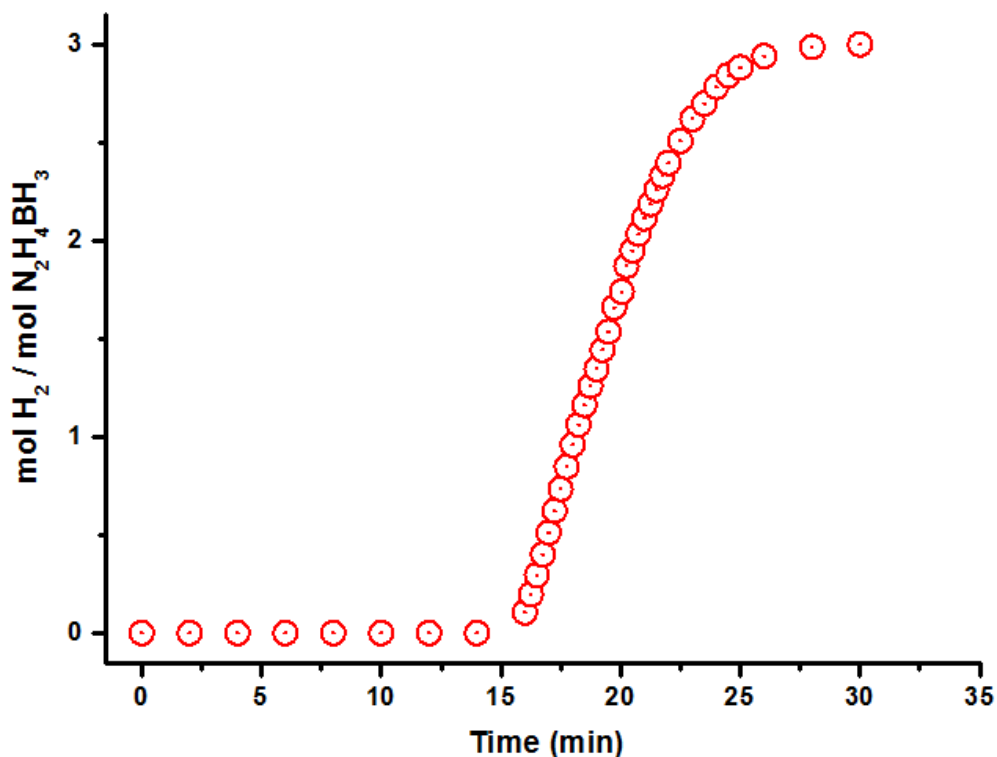


Figure 19. Plot of mole H₂ evolved per mole of hydrazine borane *versus* time for methanolysis of 180 mM HB starting with 2.0 mM nickel(II) 2-ethylhexanoate and 4.0 mM PVP in 10.0 mL methanol at 25.0 ± 0.5 °C

The color change showed the occurrence of reduction. At the beginning, the color of solution was pale green. The color of the solution changed from pale green to dark brown after a short induction time period (less than 15 minutes), and the hydrogen liberation continues linearly until the complete consumption of hydrazine borane (Figure 19). The reduction of nickel(II) ions to nickel(0) nanoparticles can also be followed in the UV-visible electronic absorption spectra. Figure 20 depicts the UV-visible absorption spectra of nickel(II) 2-ethylhexanoate solution in methanol, nickel(II) 2-ethylhexanoate in the presence of PVP before methanolysis and PVP-stabilized nickel(0) nanoparticles after methanolysis of hydrazine borane, all in 2.0 mM Ni solution.

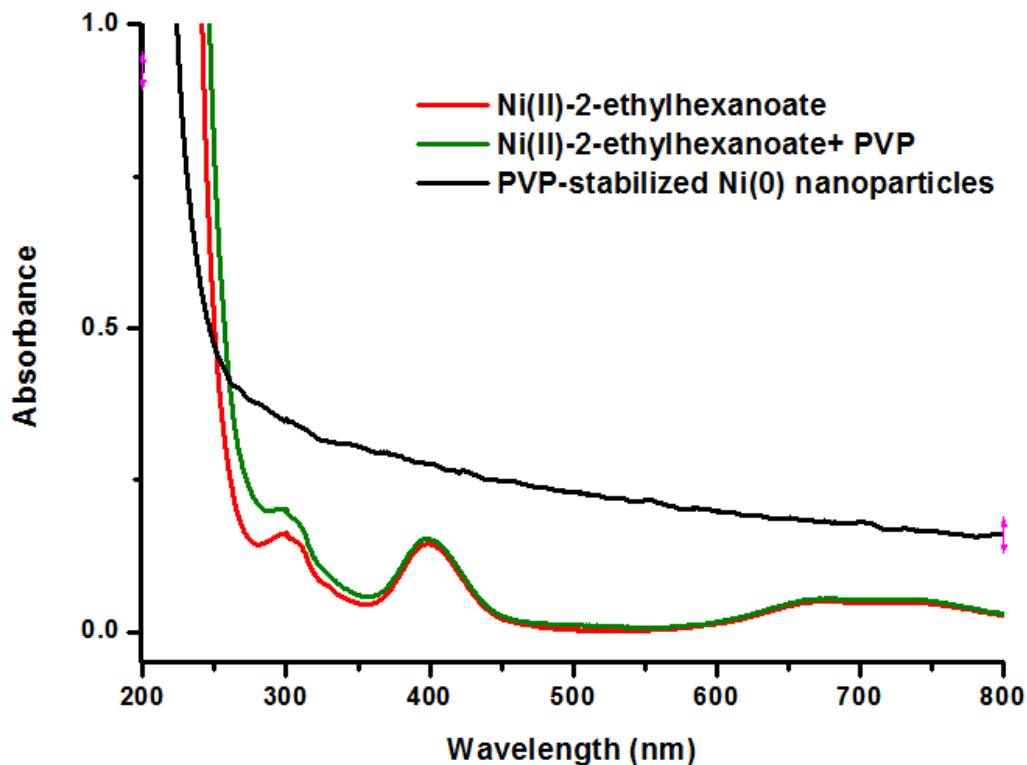


Figure 20. UV-visible absorption spectra of 2.0 mM pure nickel(II) 2-ethylhexanoate solution in methanol, 2.0 mM nickel(II) 2-ethylhexanoate in the presence of 4.0 mM PVP before methanolysis and PVP-stabilized nickel(0) nanoparticles after methanolysis of 180 mM hydrazine-borane with catalyst concentration at $[\text{Ni}] = 2.0 \text{ mM}$ plus 4.0 mM PVP.

The absorption bands at 301 and 400 plus a broad band spanning from 600 nm and 800 nm are observed in the UV-visible absorption spectra of nickel(II) 2-ethylhexanoate in the absence and presence of PVP stabilizer [98]. After reduction, these bands disappeared and one observed a typical Mie exponential decay for the PVP-stabilized nickel(0) nanoparticles [99]. This spectroscopic observation verifies that reduction of nickel(II) ions to nickel(0) nanoparticles is completed within 15 min.

The nickel(0) nanoparticles, formed *in-situ* from the reduction of nickel(II) ions during the methanolysis of hydrazine borane and stabilized by PVP, could be isolated from the reaction solution by centrifugation and characterized by ‘transmission electron microscopy’ (TEM) and ‘X-Ray photoelectron spectroscopy’ (XPS). The morphology and particle size of the PVP-stabilized nickel(0) nanoparticles were investigated using transmission electron microscopy (TEM). TEM images, shown in Figure 21 (a) and (b), show that PVP-stabilized Ni(0) nanoparticles are quite-dispersed. Histogram in Figure 21 (c) was constructed and exhibited that PVP-stabilized nanoparticles have average particle size of 3.0 ± 0.7 nm.

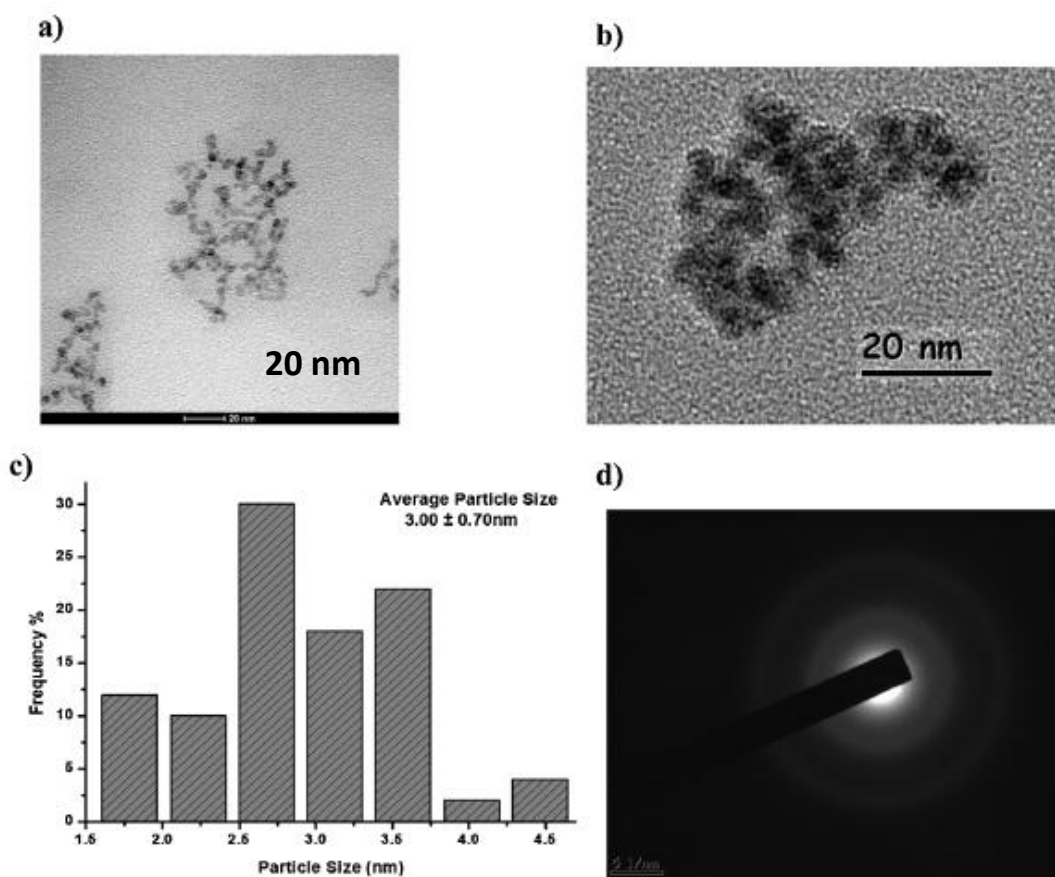


Figure 21. (a and b) TEM images of PVP stabilized nickel(0) nanoparticles in different magnifications with scale bar of 20 nm, (c) the particle size histogram constructed by measuring the nanoparticles from different TEM images, (d) SAED ring pattern for the PVP stabilized nickel(0) nanoparticles showing the existence of fcc nickel.

Selected-area electron diffraction (SAED) (Figure 21 (d)) shows the characteristic diffraction rings for Ni(0) metal. These diffraction rings show that Ni(0) metal is face centered cubic (fcc) structure [100].

X-ray photoelectron microscopy helps the determination of the oxidation state of nickel and the surface composition of PVP-stabilized nickel(0) nanoparticles. Figure 22 demonstrates X-ray photoelectron spectrum of PVP-stabilized nickel(0) nanoparticles that were obtained from the reduction of nickel(II) ions to nickel(0) nanoparticles after the methanolysis of HB. The survey-scan XPS spectrum of PVP-stabilized nickel(0) nanoparticles (Figure 22 (a)) indicates that nickel is the only element detected in the sample in addition to elements of PVP (C, N, and O). Two prominent bands at 854.5 and 872.1 eV can be attributed to Ni(0) $2p_{3/2}$ and Ni(0) $2p_{1/2}$, respectively [101]. The relative intensities of the $2p_{3/2}$ and $2p_{1/2}$ are about 1:2. The $2p_{3/2}$ and $2p_{1/2}$ binding energies are slightly shifted to the higher values due to the matrix effect [102,103] as well as quantum size effect [104] compared to the values of bulk nickel. It is observable that there are two additional lower intensity peaks at higher energy 858.6 and 874.1 eV, ascribable to Ni(II) $2p_{3/2}$ and Ni(II) $2p_{1/2}$ by comparing with the values of bulk nickel (852.3 and 869.7 eV), respectively [105].

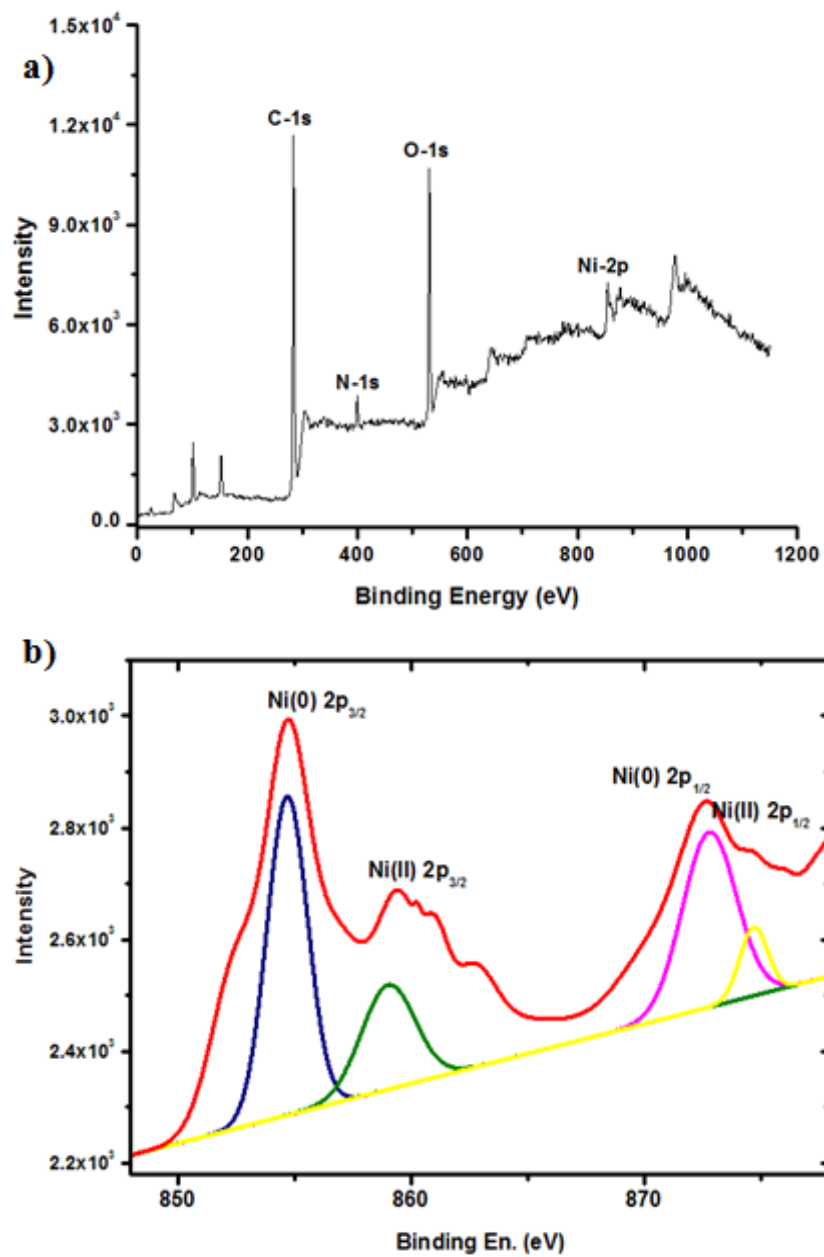


Figure 22. (a) X-ray photoelectron (XPS) survey scan of PVP-stabilized nickel(0) nanoparticles (b) XPS high resolution 3D spectra of PVP-stabilized nickel(0) nanoparticles for Ni 2p after the methanolysis of hydrazine borane.

5.2. Catalytic Activity of PVP-stabilized Nickel(0) Nanoparticles in the Methanolysis of Ammonia-Borane

PVP-stabilized nickel(0) nanoparticles, obtained in the methanolysis of hydrazine borane, are highly active catalyst in hydrogen liberation from methanolysis of ammonia borane, even in low concentration at room temperature.

5.2.1. Kinetics of Methanolysis of Hydrazine-Borane Catalyzed by PVP-Stabilized Nickel(0) Nanoparticles

The usage of stabilizer is necessary to obtain stable nickel(0) nanoparticles catalyst for the methanolysis of ammonia borane. If the stabilizer is not present in the reaction medium, nickel(0) nanoparticles tend to aggregate during the reaction. Before the kinetic studies of methanolysis reaction of ammonia borane in the presence of preformed catalyst, PVP-stabilized nickel(0) nanoparticles, optimization of the concentration of PVP in the methanolysis of hydrazine borane was performed regarding the activity and stability of nickel(0) nanoparticles. Therefore, methanolysis of hydrazine borane was started with nickel(II) 2-ethylhexanoate (1.0 mM), hydrazine borane (200 mM) and different concentrations of PVP corresponding to the ratio of $[PVP]/[Ni] = 0.5, 1.0, 1.5, 2.0$. When PVP is used in molar ratio of 0.5, 1.0 or 1.5, both hydrogen evolution and Ni(0) nanoparticles formation were observed. However, the stabilization of Ni(0) nanoparticles were not enough. There was precipitate of bulk metal in the reaction medium. On the other hand, when PVP was used in molar ratio 2.0, it was seen that nanoparticles are so stable and the precipitation was not observed during methanolysis reaction. In conclusion, $[PVP]/[Ni]$ ratio was decided as 2.0.

In the methanolysis of ammonia borane, isolated and characterized PVP-stabilized nickel(0) nanoparticles, obtained at the end of hydrogen generation from methanolysis of 200 mM hydrazine borane, were used as preformed catalyst. In this part, in order to determine the rate law for methanolysis reaction and also activation parameter of this reaction, kinetic studies were performed. The kinetics of the

methanolysis of ammonia borane was studied by changing catalyst concentration, substrate concentration and temperature. Firstly, different concentrations of PVP-stabilized nickel(0) nanoparticles were studied. Figure 23 demonstrates H₂ evolved from ammonia borane *versus* time for the methanolysis of 200 mM ammonia borane in the presence of PVP-stabilized nickel(0) nanoparticles which have different nickel concentrations (0.5, 1.0, 1.5, and 2.0mM) at 25.0 ± 0.1 °C. As soon as catalyst was put, the generation of H₂ started immediately without induction time because of the fact that a preformed catalyst is used in the methanolysis of ammonia borane. Hydrogen generation rate was determined by using the linear portion of each plot for the methanolysis reaction of ammonia borane which was performed with different catalyst concentrations in inset in Figure 23.

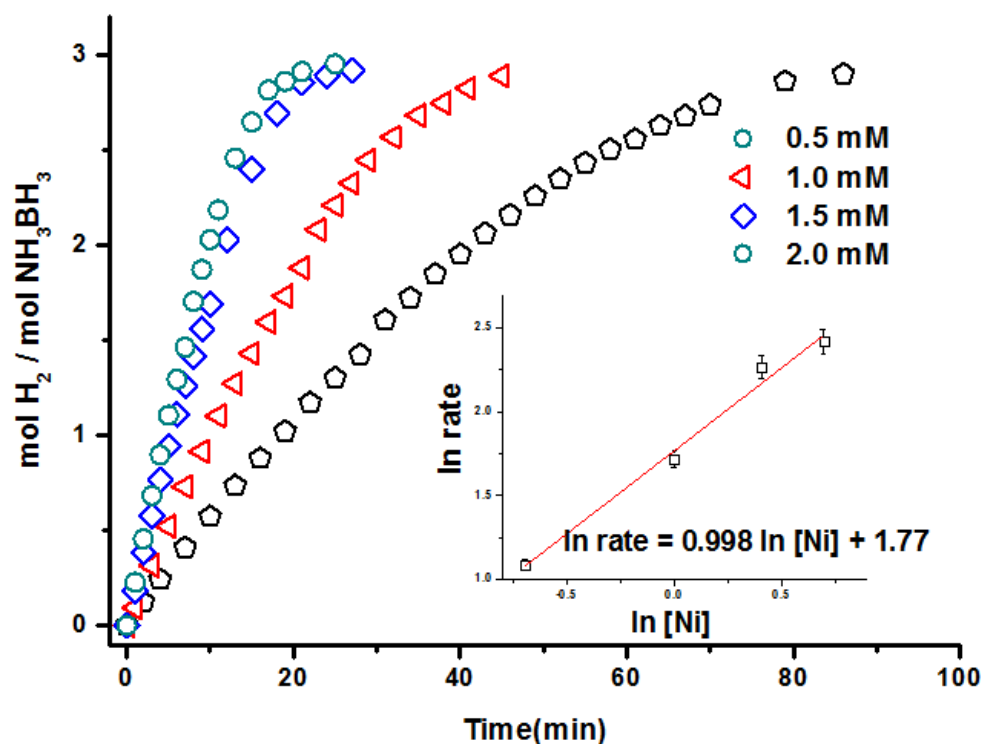


Figure 23. Plots of mol H₂ evolved per mol of ammonia-borane *versus* time for methanolysis of 10 mL of 200 mM ammonia-borane in different nickel concentrations ([Ni] = 0.5, 1.0, 1.5, and 2.0 mM) at 25.0 ± 0.5 °C. Inset: Plot of hydrogen generation rate *versus* the concentration of nickel (both in logarithmic scale.)

The inset in Figure 23 indicates the logarithmic form of hydrogen generation rate *versus* logarithmic scale of nickel concentration. This plot gives a straight line with a slope of 0.998 ≈ 1. This means that catalytic methanolysis of ammonia borane, which were catalyzed by preformed PVP-stabilized nickel(0) nanoparticles, is first order with respect to the catalyst concentration.

In the next part, different substrate (ammonia borane) concentrations were studied to see the effect of ammonia borane concentration on the generation rate of hydrogen. For this purpose, different initial concentrations of ammonia borane were

used in the range of 100, 200, 300 and 500 mM by keeping catalyst concentration constant at 1.0 mM Ni in the presence of [PVP]/[Ni] ratio of 2.0 in the catalytic methanolysis of ammonia borane. Figure 24 indicates H₂ evolved from ammonia borane *versus* time for the methanolysis of 1.0 mM PVP-stabilized nickel(0) nanoparticles as catalyst and substrate (ammonia borane) which has different concentrations (100, 200, 300, and 500 M) at 25.0 ± 0.1 °C.

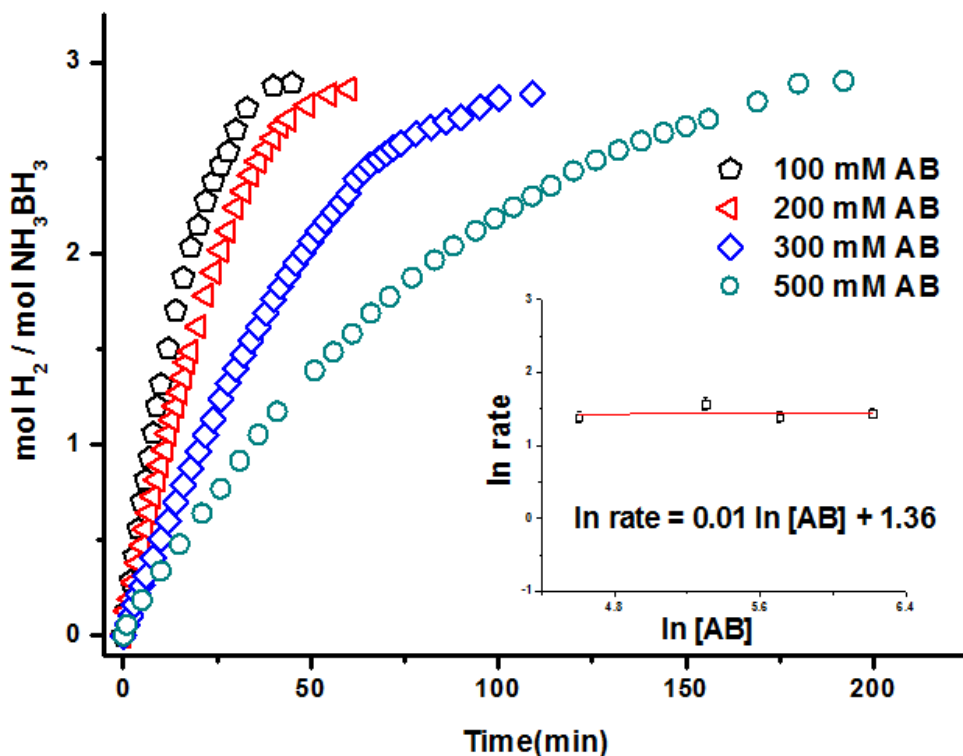


Figure 24. Plots of mol H₂ evolved per mol of ammonia-borane *versus* time for the methanolysis of ammonia-borane in different concentrations (100, 200, 300, 500 mM) starting with catalyst concentration of 1 mM nickel at 25 ± 0.5 °C. Inset: Plot of hydrogen generation rate *versus* substrate concentration (both in logarithmic scale.)

Hydrogen generation rate was determined by using the linear portion of each plot for each methanolysis reaction of ammonia borane and plotted versus initial concentration of ammonia borane, both in logarithmic scale (the inset in Figure 24). According to the

inset in Figure 24 slope of the given line is $0.01 \approx 0$. The methanolysis reaction order was found to be zero when the different substrate concentrations were used.

As a result of these, the rate law of catalytic methanolysis of AB in the presence of PVP-stabilized nickel(0) nanoparticles is found as given in Equation 13:

$$\frac{-3d[AB]}{dt} = \frac{d[H_2]}{dt} = k[Ni] \quad (13)$$

In order to determine activation parameter, while keeping the substrate (ammonia borane, 200 M) and catalyst (Ni, 1.0 mM) concentration constant, methanolysis reaction was performed at different temperatures in the range of 25-40 °C. The values of rate constants for methanolysis of ammonia borane were calculated from the linear part of each plot presented in Figure 25 and these values are employed for the construction of Arrhenius and Eyring plots to determine activation parameters.

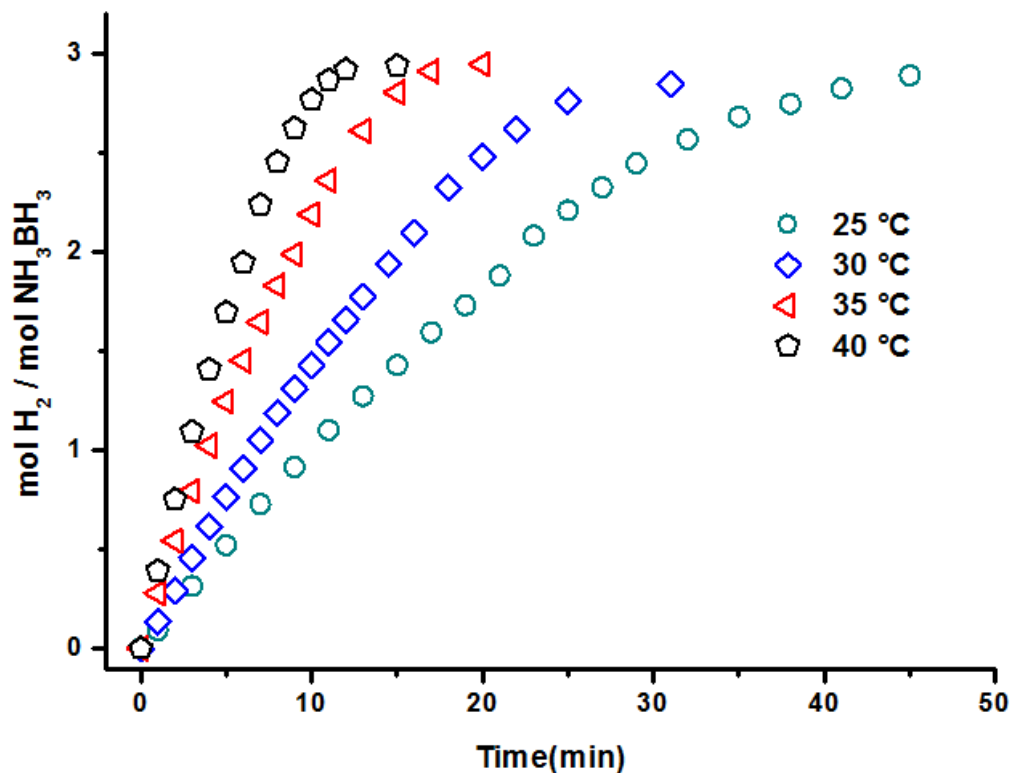


Figure 25. Plots of mol H₂ evolved per mol of ammonia-borane *versus* time for the catalytic methanolysis of ammonia-borane ([AB] = 200 mM in 10.0 mL methanol) starting with nickel concentration of 1.0 mM at different temperatures 25, 30, 35, and 40 °C.

- Arrhenius plot shows the dependence of rate constant to derive activation energy.
- Eyring equation depicts the dependence of rate constant to derive the activation enthalpy and the activation entropy [106].

The values of rate constants 'k' of the catalytic methanolysis of ammonia borane by using preformed PVP-stabilized nickel(0) nanoparticles as catalyst were obtained from the Arrhenius plot (Figure 26).

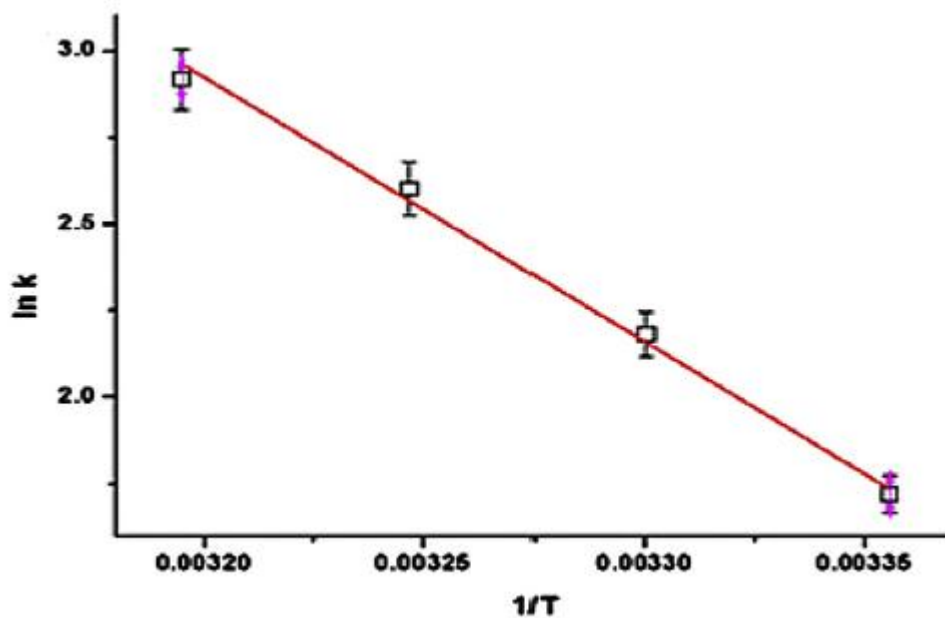


Figure 26. Arrhenius plot (lnk versus the reciprocal absolute temperature 1/T (K⁻¹) for the catalytic methanolysis of AB catalyzed by PVP-stabilized nickel(0) nanoparticles.

First of all, the most common method of determining the activation energy (E_a) is by using Arrhenius equation (Equation 14):

$$k = A \cdot e^{(-E_a/R)} \quad (14)$$

R is the gas constant and T is the temperature in terms of Kelvin. E_a is the activation energy and A is the pre exponential factor and these constants are characteristics of reactions [90].

To calculate activation energy, natural logarithm of Arrhenius equation is found and according to this, Arrhenius graph is plotted.

$$\ln k = \ln A - (E_a/RT) \quad (15)$$

The slope of Arrhenius plot (Figure 26) was used to determine the activation energy (E_a) of the catalytic methanolysis of AB catalyzed by PVP-stabilized nickel(0) nanoparticles. The slope is $[-E_a/R]$ and by using this, E_a was found $62 \pm 2\text{kJ}\cdot\text{mol}^{-1}$.

Secondly, Eyring equation (equation 16) was used to calculate enthalpy of activation (ΔH) and entropy of activation (ΔS).

$$\ln(k/T) = (1/T)(-\Delta H/R) + \ln(k_b/h) + (\Delta S/R) \quad (16)$$

R is gas constant, k_b is Boltzmann's constant and h is Planck's constant.

To calculate these, by using Eyring equation, $\ln(k/T)$ versus $(1/T)$ was plotted (Figure 27).

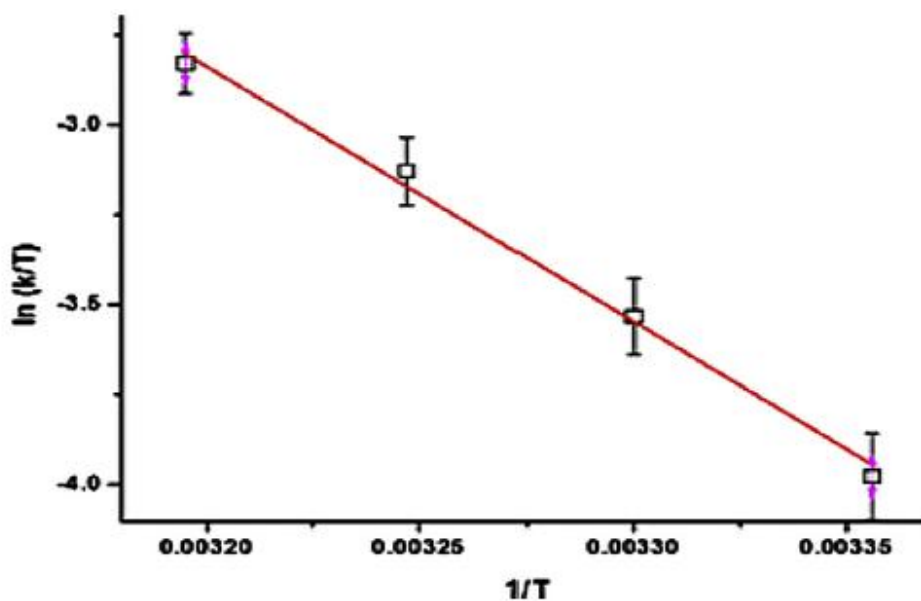


Figure 27. Eyring plot ($\ln(k/T)$ versus $1/T$) for catalytic methanolysis of AB catalyzed by PVP-stabilized nickel(0) nanoparticles.

The slope of the graph is $(-\Delta H/R)$ and from slope, ΔH was calculated as 60 ± 2 kJ/mol. Besides this, from intercept, ΔS was calculated as -30 ± 2 J/K.mol.

5.2.2. The Catalytic Lifetime of PVP-Stabilized Nickel(0) Nanoparticles in the Methanolysis of Ammonia-Borane

In this part, catalyst lifetime experiment was performed. The lifetime of the catalyst, which means the activity of catalyst, is determined by turnover number. The term of turnover number (TON) can be defined as the number of catalytic cycles for a given process. This is represented as moles of product per moles of catalyst. In order to determine turnover number, hydrogen generation from ammonia borane was studied in the methanol. The catalytic lifetime experiment for the preformed PVP-stabilized nickel(0) nanoparticles in the methanolysis of ammonia borane was studied by initiating with catalyst concentration of 0.5 mM nickel in 10.0 mL methanol and 500 mM ammonia borane at 25 ± 0.5 °C. After the consumption of substrate, a new batch of ammonia borane was added to reaction flask. This procedure was followed until no more hydrogen evolved, and catalyst deactivated. The preformed PVP-stabilized nickel(0) nanoparticles provide 5300 turnovers over 52 hours in the methanolysis of ammonia borane at 25 ± 0.5 °C. According to this experiment, catalyst, PVP-stabilized nickel(0) nanoparticles, is long-lived in the methanolysis reaction of ammonia borane (Figure 28).

The turnover frequency (TOF) for hydrogen generation from methanolysis of ammonia borane (200 mM) catalyzed by preformed PVP-stabilized nickel(0) nanoparticles (1.0 mM Ni) at 25 ± 0.5 °C was found from the linear part of plot in Figure 28. The TOF value of preformed PVP-stabilized nickel(0) nanoparticles was calculated to be 12.1 min^{-1} (mol H₂/mol Ni min). It is noteworthy that preformed PVP-stabilized nickel(0) nanoparticles ensure the highest TOF value ever reported for the methanolysis of ammonia borane using nickel catalysts such as NiCl₂ (TOF = 2.9 min^{-1}) [26], Ni-Ni₃B (TOF = 5.0 min^{-1}) [30], Co-Ni-B (TOF = 10.0 min^{-1}) [30]. The high

activity of preformed PVP-stabilized nickel(0) nanoparticles can be attributed to good stabilization of nickel(0) nanoparticles by poly(*N*-vinyl-2-pyrrolidone) and the smaller particles size of nickel(0) nanoparticles found to be 3.0 ± 0.7 nm.

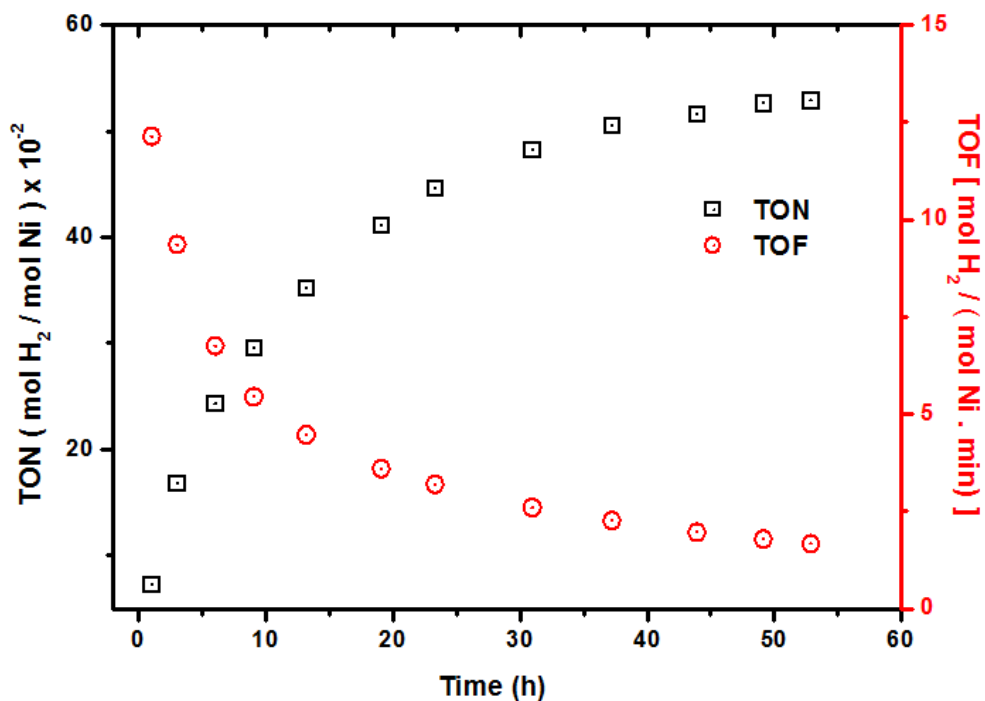


Figure 28. Plot of total turnover number (TTO) versus time for the methanolysis of ammonia-borane (NH_3BH_3) with a 10 mL solution of 0.5 mM nickel(0) nanoparticles and 500 mM (for each run) NH_3BH_3 at 25.0 ± 0.1 °C.

5.2.3. Carbon Disulfide (CS_2) Poisoning of PVP-Stabilized Nickel(0) Nanoparticles and Its Monitoring in the Catalytic Methanolysis of HB as Heterogeneity Test

There are different kinds of experiment to distinguish homogeneous catalyst from heterogeneous catalyst. Among them, poisoning experiments are commonly used and these experiments are performed by using some chemicals like S-based (CS_2 , RSH , PhSH , H_2S , thiophene etc.), N-based (pyridine, H_3N), P-based (PR_3), C-based (CO), O-

based (OH^- , RO^-) or other element based poison like mercury etc. [107,108, 109, 110]. The most common and studied poisons are sulfur-based chemicals. Among S-based poisons, CS_2 is most favorite poison [111]. In this study, in order to see whether catalyst is heterogeneous or homogenous, poisoning test was performed by using carbon disulfide, CS_2 . Chemicals, using as poison, affects the catalytic activity of catalyst by changing chemical and physical properties. That is adsorbed on the active site of catalyst and catalyst is blocked towards substrate [112, 113].

In our poisoning experiment, after the liberation of 40% hydrogen from methanolysis of hydrazine borane (200 mM) catalyzed by 1.0 mM Ni, 0.2 equivalent CS_2 per mol of catalyst was injected to reaction flask, all at once; hereby, the activity of PVP-stabilized nickel(0) nanoparticles was hindered and hydrogen generation from methanolysis of HB stopped (Figure 29). As seen from the plot, when the carbon disulfide was added to the reaction medium at nearly 40% conversion, hydrogen generation stopped suddenly. This is the direct prove for the heterogeneity of PVP-stabilized nickel(0) nanoparticles in the methanolysis reaction of ammonia borane.

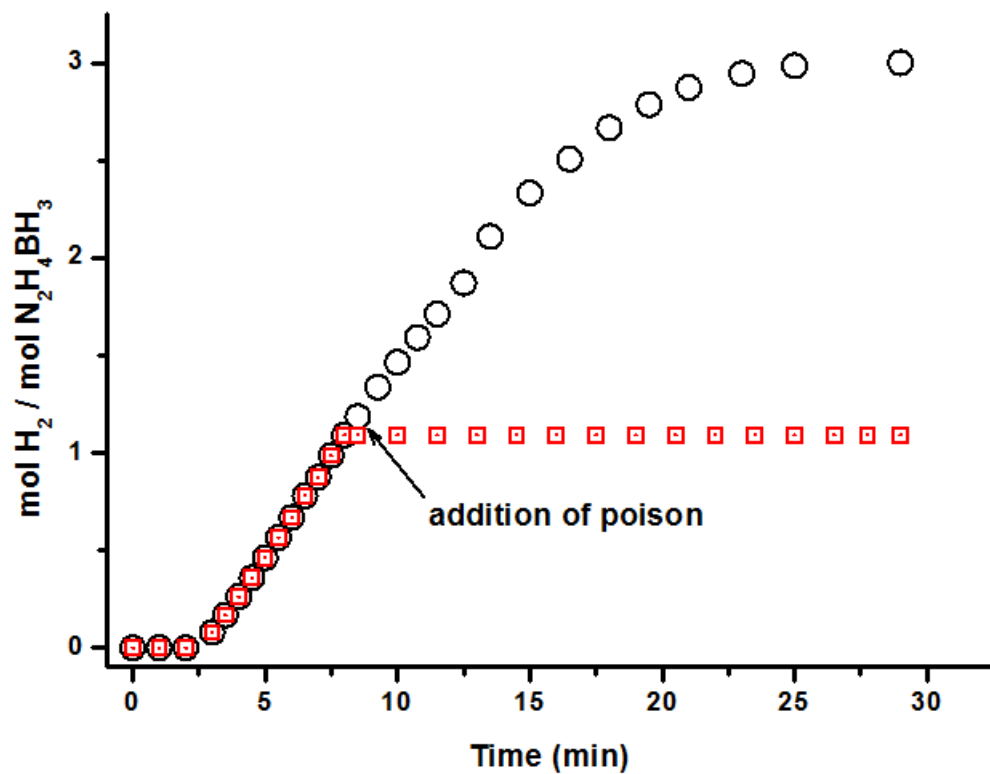


Figure 29. Plot of mol H₂ evolved per mol of hydrazine-borane *versus* time for the methanolysis of 200 mM hydrazine-borane catalyzed by PVP-stabilized nickel(0) nanoparticles (1.0 mM Ni) with and without addition of 0.2 equiv. CS₂ at 25.0 ± 0.5 °C

CHAPTER 6

CONCLUSIONS

In conclusion, main findings of this study about preparation and characterization of PVP-stabilized Ni(0) nanoparticles and its catalytic activity in hydrogen generation from catalytic methanolysis of ammonia-borane can be summarized as follows;

- PVP-stabilized nickel(0) nanoparticles were prepared *in-situ* by reduction of nickel(II) 2-ethylhexanoate during the catalytic methanolysis of hydrazine borane in the presence of PVP as stabilizer. They can be isolated by centrifugation from the reaction solution in the form of powder.
- PVP-stabilized nickel(0) nanoparticles were characterized using UV-vis spectroscopy, TEM and XPS techniques. The results reveal the formation of nearly monodispersed nickel(0) of 3.0 ± 0.7 nm particle size stabilized by water soluble PVP polymer.
- Catalytic activity of transition metal nanoparticles depends on the surface and particle size. When the particles size decreases, catalytic activity increases. These well-dispersed PVP-stabilized nickel(0) nanoparticles were found to be quite active in the methanolysis of AB providing the release of 3.0 equivalent H₂ gas.
- The turnover frequency for the methanolysis of AB catalyzed by PVP-stabilized nickel(0) nanoparticles was determined to be 12.1 min^{-1} , which is greater than the values reported in literature [NiCl₂] (TOF = 2.9 min^{-1}) [12], Ni-Ni₃B (TOF = 5.0 min^{-1}) [16], Co-Ni-B (TOF = 10.0 min^{-1}) [16] for the same reaction using different nickel catalysts at 25.0 ± 0.5 °C.

- PVP-stabilized nickel(0) nanoparticles provide 5300 turnovers in the methanolysis of ammonia borane over 52 h before deactivation at room temperature.
- The results of kinetic study show that methanolysis reaction of AB is first order in nickel concentration and zero order in substrate concentration.
- The temperature dependent rate constant data enable us to calculate the activation parameters of the catalytic methanolysis of ammonia-borane catalyzed by PVP-stabilized nickel(0) nanoparticles: Activation energy $E_a = 62 \pm 2 \text{ kJ.mol}^{-1}$, activation enthalpy, $\Delta H = 60 \pm 2 \text{ kJ/mol}$. entropy of activation, $\Delta S = -30 \pm 2 \text{ J/K.mol}$.
- Performing carbon disulfide poisoning experiments showed that PVP-stabilized nickel(0) nanoparticles are kinetically competent catalyst and the catalytic methanolysis of AB is heterogeneous.

High catalytic activity, stability, easy preparation, and low cost make PVP-stabilized nickel(0) nanoparticles a promising catalyst for the portable hydrogen generation systems based on the methanolysis of ammonia borane.

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