T.R.
VAN YUZUNCU YIL UNIVERSITY
INSTITUTE OF NATURAL AND APPLIED SCIENCES
DEPARTMENT OF CHEMICAL ENGINEERING

MONO AND BIMETHALIC EFFECTS OF ACTIVATED CARBON SUPPORTED Pd-Ru CATALYSTS ON HYDROGEN PRODUCTION

M.Sc. THESIS

PREPARED BY: Rawezh Muhtasim MUSTAFA
SUPERVISOR: Assoc. Prof. Dr. Hilal ÇELİK KAZICI

VAN-2021

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ACCEPTANCE and APPROVAL PAGE

This thesis entitled “Mono and Bimethalic Effects of Activated Carbon Supported Pd-Ru Catalysts on Hydrogen Production” presented by Rawezh Muhtasim Mustafa under supervision of Assoc. Prof. Dr. Hilal ÇELİK KAZICI. in the department of chemical engineering has been accepted as a M. Sc. thesis according to Legislations of Graduate Higher Education on …..../...../..... with unanimity / majority of votes members of jury.

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THESIS STATEMENT

All information presented in the thesis obtained in the frame of ethical behavior and academic rules. In addition all kinds of information that does not belong to me have been cited appropriately in the thesis prepared by the thesis writing rules.

Rawezh Muhtasim MUSTAFA

ABSTRACT

MONO AND BIMETHALIC EFFECTS OF ACTIVATED CARBON SUPPORTED Pd-Ru CATALYSTS ON HYDROGEN PRODUCTION

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In this study, activated carbon (AC) supported palladium, ruthenium and cobalt nanoparticle (PdRu/AC@Co) catalysts were prepared by in situ reduction of sodium borohydride ($NaBH_4$) and characterized by various techniques such as scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDX), and X-ray PhotoelectronSpectroscopy (XPS). The PdRu/AC@Co catalyst is active in the hydrolysis of ammonia-borane (AB) even at low temperatures. Compared with mono- (Pd) and bi-metallic (PdRu) nanoparticles, this trimetallic (PdRu@Co) structure showed greatly increased catalytic activity for AB hydrolysis. In the experiment carried out at 25 ºC, 1 mmol AB and 50 mg PdRu / AC@Co catalyst, the hydrogen production rate (HG) was determined to be 9898.65 mL $min^{-1}g^{-1}$. The activation parameters (Ea, ΔH and ΔS) in the catalytic hydrolysis of AB were obtained 19.6 $kJmol^{-1}$, 17.12kJ/mol and -184.85 J/mol.K, respectively. In addition, the study showed that $Pd_{0.5}Ru_{0.5}$/AC@1%Co (Pd:Ru:Co atomic ratio=5:5&1%) showed the total turnover frequency (TOF) value of 312.8 h^{-1}.

Keywords: Activated carbon, Ammonia borane, Hydrogen, Hydrolysis, Palladium cobalt ruthenium nanoparticles.

ÖZET

HİDROJEN ÜRETİMİ ÜZERİNE AKTİF KARBON DESTEKLİ Pd-Ru KATALİZÖRLERİNİN MONO VE BİMETALİK ETKİLERİ

MUSTAFA, Rawezh Muhtasim
Yüksek Lisans Tezi, Kimya Mühendisliği Anabilim Dalı
Danışman: Doç. Prof. Dr. Hilal ÇELİK KAZICI
Haziran 2021, 73 Sayfa

Bu çalışmada, aktif karbon (AC) destekli paladyum, Ruthenium ve kobalt nanopartikül (PdRu / AC @ Co) katalizörleri sodyum borohidrürün ($NaBH_4$) in situ indirgenmesi ile hazırlanmış gibi çeşitli tekniklerle karakterize edilmiştir. , taramalı elektron mikroskobu (SEM) ve enerji dağılımlı X-ışını spektroskopisi (EDX), ve X-ışını Fotoelektron Spektroskopisi (XPS). PdRu / AC @ Co katalizörü, düşük sıcaklıklarda bile amonyak boranın (AB) hidrolizinde aktiftir. Mono- (Pd) ve bi-metalik (PdRu) nanopartiküller ile karşılaştırıldığında, bu trimetalik (PdRu @ Co) yapı, AB hidrolizi için büyük ölçüde artmış katalitik aktivite gösterdi. 25 ºC, 1 mmol AB ve 50 mg PdRu / AC @ Co katalizöründe yapılan deneyde hidrojen üretim hızı (HG) 9898.65 mL min-1g-1 olarak belirlendi. AB'nin katalitik hidrolizinde aktivasyon parametreleri (Ea, ΔH ve ΔS) sırasıyla 19.6 kJmol-1, 17.12kJ/mol ve -184.85 J/mol.K elde edildi. Ayrıca çalışma, Pd0.5Ru0.5/AC@1%Co'nun (Pd: Ru: Co atomic ratio = 5: 5 & 1%) 312,8 h-1 toplam devir frekansı (TOF) değerini gösterdiğini göstermiştir.

Anahtar kelimeler: Aktif karbon, Amonyak boran, Hidrojenö Hidroliz, Palladyum kobalt rutenyum nanopartiküller.

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2021

Rawezh Muhtasim MUSTAFA

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SYMBOLS AND ABBREVIATIONS

Some symbols and abbreviations used in this study are presented below, along with descriptions.

Symbols	Description
AB	Ammonia borane
AC	ActivatedCarbon
Co	Cobalt
Ea	Activation energy
g	Gram
H_2	Hydrogen
k	Rate constant
kJ/kg	Kilojoule per kilogram
mg	Milligram
min	Minute
mol	Mole
ml	Millilitre
mM	Millimolar
M	Molarity
µM	Micromolar
Na	Sodium
NaOH	Sodium hydroxide
Nm	Nanometre
OH	Hydroxide
Pd	Palladium
Pm	Picometre
rpm	Round per Minute
Ru	Ruthenium
ºC	Degree Celsius

ΔH^o	Enthalpy change
ΔS^o	Entropy change
%	Percent

Abbreviations	**Description**
EDX	Energy Dispersive X-Ray
HG	Hydrogen Production Rate
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscope
TOF	Turnover Frequency
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-ray powder diffraction
T_{cr}	Temerature Critical

1. INTRODUCTION

Since the beginning of time people have employed the use of firewood to cook and keep themselves warm before coal was discovered as a new source of fuel with a higher calorific value. Fossil fuel was formed through a natural process as a result of accumulation of carbon-based energy sources and has been progressively used to meet about 80% of the worlds energy request. Fossil fuel such as natural gas, coal and petroleum have been projected to decline due to increasing worldwide energy requirement. This means that most of the resources will have been overused and there will be shortage in the next few decades (Midilli et al., 2005).

Due to the growing concern of environmental problems of global warming there is a need to explore other sources of renewable energies like biomass energy, solar energy, wind power, and power technologies among others. Global warming is caused by the gas emitted through the combustion of fossil fuel and consequently leads to the rise in sea levels, putting the cities adjacent to the water bodies at a risk of flooding, hurricanes or even the forest fires (Thomas et al., 2004; Armaroli and Balzani, 2011).

These renewable sources of energy have also been saddled with problems low efficiency, discontinuity, relatively high costs, storage and transportation over long distances. During transportation or storage of this energy, it is believed that a quite an amount energy is lost in the process. To avoid energy loss, hydrogen has been identified as perfect carrier since it is widely available and can be obtained from a variety of sources such as electrolysis, photoelectrochemical water splitting biomass and nuclear (Ewan and Allen 2005; Armaroli and Balzani, 2011).

In his novel ‘The Mysterious Island’ authored by Jules Verne in 1874, the protagonist Cyrus Harding conceived an idea on how we could use hydrogen to obtain an everlasting energy. He believed that a day will come when water will now be used as a source of energy. The demand for hydrogen has increased through industrial application at the last two decades since the combination of molecular O_2 and H_2 in a fuel cell creat heat and electricity with water as a byproduct compared to the fossil fuel that produces CO_2 and other pollutants (Bavykin, 2008; Armaroli and Balzani, 2011; Schlapbach and Züttel, 2011).

Hydrogen has been for the most part used in the chemical and petrochemical industry as a feedstock through a process that produces ammonia and refined fuels by the hydrocracking and several other chemicals. H_2 can be employed to various uses like propellant for rockets and space shuttle besides being used for hydrogen powered vehicles and other cars (Armaroli and Balzani, 2011).

Storing hydrogen gas has proved to be an herculean task since it has a low density besides being highly flammable. This makes it very challenging for the storing technologies to ensure storage is cost effective, compact, safe and reliable (Züttel, 2003). The kinds of storage approaches that are currently in use involves compressing hydrogen gas, cryogenic liquid hydrogen and the chemical hydrogen storage (Züttel, 2003, Satyapal et al., 2007).

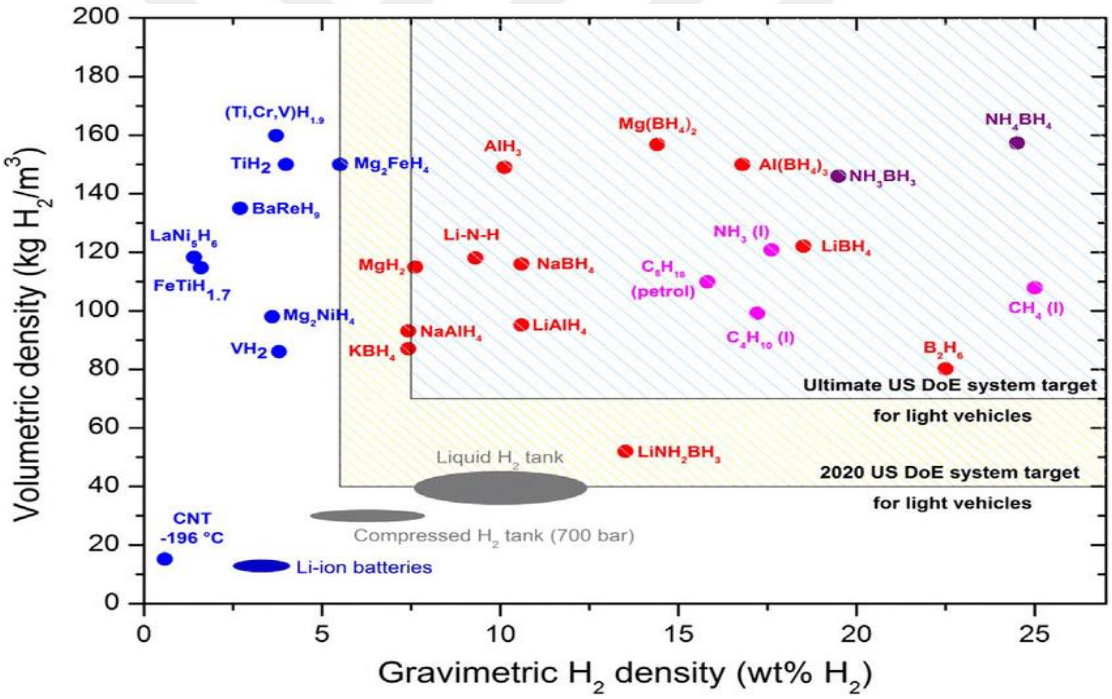

Figure 1.1. Diagram for hydrogen storage materials. Hydrogen volume density vs Hydrogen mass density.

The Chemical H_2 storage has been of attentiveness because of the high H_2 content containing compounds of the boron hydrides which was found to a (Solid state) of material of hydrogen storage due to its relatively great volumetric and also gravimetric H_2 density (Züttel, 2003; Züttel, 2004). (H_3NBH_3, AB) Ammonia borane has been given the special focus as a hydrogen storage material because it has a high hydrogen content of 19.6 wt. % stability and safety under fuel cell operating conditions (Marder, 2007; Stephens and Baker, 2007).

When ammonia is combined with a catalyst in the process of hydrolysis it releases borane in an exothermic reaction with enthalpy change of −156 kJ/mol at 25 °C (Schlesinger et al., 1953).

$$NH_3BH_3(aq)+H_2O(l) \xrightarrow{\text{Catalyst}} NH_4BO_2(aq)+3H_2(g) \quad (1.1)$$

Hydrolysis of AB has been tested with transition metals and their alloys as a catalyst in an effort to generate hydrogen. (Chandra and Xu, 2006; Kalidindi et al., 2008). The extensive studies that have been carried out seems to suggest that when a catalyst of appropriate metal is placed in a solution of various concentration it leads to a release of hydrogen gas with an H_2 to NH_3BH_3 mole ratio up to 3.0 matching 8.9 wt.% of the starting materials NH_3BH_3 and H_2O (Özkar, 2013).

The study also found that the catalytic activities of non -noble metallic catalysts of (Co, Cu, Fe, Ni) was supported on γ-Al_2O_3, SiO_2 and C in the process of generating hydrogen from hydrolysis of the AB with the highest activities being an observation of Co/Ac when Fe containing catalyst which gave no activity (Xu and Chandra, 2006). The generation of hydrogen gas was also faster in the presence of noble metals that were used as catalysts at a room temperature. Such catalysts were Pt, Rh and Ru (Chandra and Xu, 2006; Chandra and Xu., 2007). Moreover, the high reactivity of non-particles led to the tendency towards combination of nanoparticles which could be prevented through the use of stabilizers that have been reported for catalytic, steric and electro steric stabilization (Aiken and Finke, 1999).

2. LITERATURE REVIEW

2.1. Hydrogen

2.1.1. World energy crisis

The extensive use of carbon fuels has come with a host many problems such as emission of great amount of greenhouse gases together with other poisonous products that are known to cause global climate change and pollution (Armaroli and Balzani, 2011). The rapid reduction in fuel from fossils supplies has the ability to cause a sequence of systemic occurrences that will eventually plunge the planet into a crisis that can better be understood from the Figure below.

Despite the fact that fossil fuel has over the years has been an important source energy we have used to meet energy demand, they will not be used as a main source of energy in future because of increase in the world population that would outstrip the limited fossil fuel sources (Thomas et al., 2004; Midilli et al., 2005). The use of various types of fossil energy changed during the last 90 years. During the year 1925 most of the fuel that people used was contributed by coal while in recent years petroleum accounted for 45%, natural gas 25% and coal 30% of energy that got supplied.

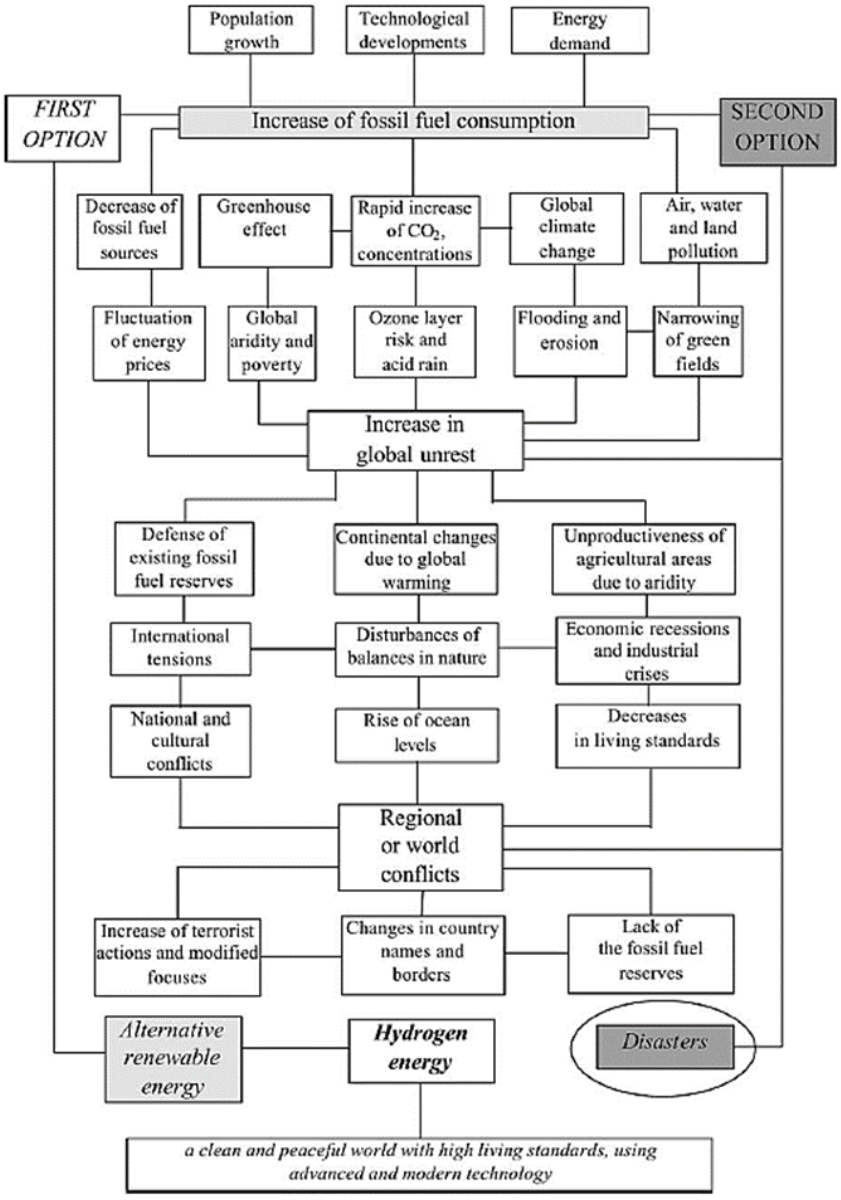

Figure 2.1. Global issues that could occur when fosill fuel is heavily used the resulting need for hydrogen energy solutions (Midilli et al., 2005).

Experts have also said that the available reserves for petroleum will be overused in less that less than 40 years, coal 250 years and natural gas will have been depleted in the next 60 years (Satyapal et al., 2007). Therefore, the cost of fossil fuel will increase due to shortage and we will be forced to look for other alternative sources of energy and we might perhaps consider solar hydrogen or wind related source.

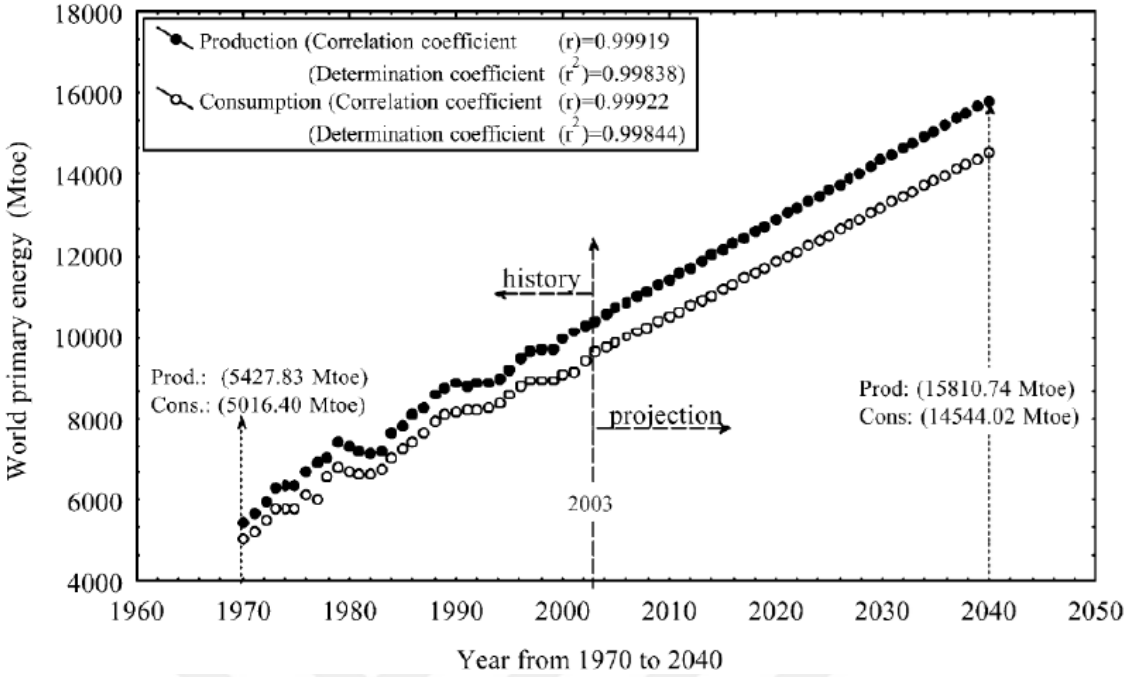

Figure 2.2. Changes in the global energy consumption and production consumption from 1971 to 2040.

2.1.2. Hydrogen property as a medium to carry energy

Hydrogen is projected to play a crucial role in shaping potential capacity, as it is predictable to substitute fossil fuels to several grade, in order to be the strongest automotive (energy carrier) (Schlapbach and Züttel, 2011). One of the attributes that makes hydrogen preferable is that it is not harmful and that it is often known to be a mass-based renewable energy carrier with high-specific energy and can be generated from different process. (Ewan and Allen, 2005).

There are several processes from which hydrogen can be produced such as through the use of solar and the use of renewable energy sources like steam reform of the natural gas or someother light HC, coal gasification and other heavy component. It can also be decomposition of water by electrolysis, both methods direct and indirect. Hydrogen can be processed for a prolonged period of time and can be used over a long period of time as opposed to electricity as seen below figure.

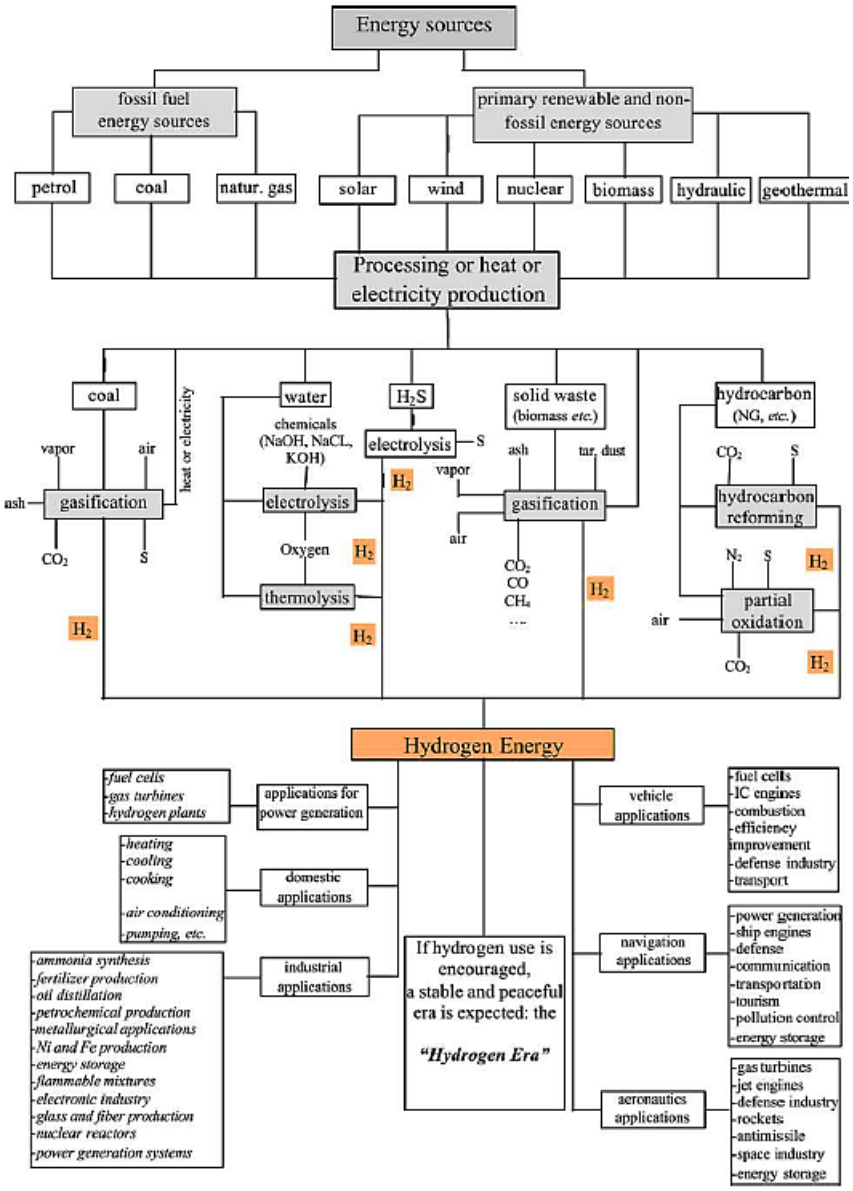

Figure 2.3. Techniques of production and kinds of the utilization of H_2. (Midilli et al., 2005).

Hydrogen has also raised safety concerns since it is extremely flammable when mixed with air. Its storage is also difficult because hydrogen can be liquefied at a very low temperatures.

Table 2.1. Hydrogen properties relative to other fuels (van den Berg & Areán 2008., Armaroli and Balzani 2011)

Properties	Hydrogen	Gasoline	Methanol	Methane	Propane	Ammonia
Boiling point [K]	20.3	350-400	337	112	231	240
Liquid density [kg m^{-3}]	71	702	797	425	507	771
Gas density [kg m^{-3}]	0.08	4.68	-	0.66	1.87	0.69
Lower heating value (Liquid) [MJ kg^{-1}]	120	44.4	20.1	50	46.4	18.6
Lower heating value (Liquid) [MJ kg^{-1}]	8960	31170	16020	21250	23520	14350
Lower flammability limit [vol,%in air]	4	1	7	7	2	15
Lower flaimability limit (at 0 ^{o}C , 1 atm) [vol,%in air]	75	6	36	15	10	28

2.1.3. Hydrogen storage

One of the properties of hydrogen is such that it is regenerative, environmentally friendly and largest heating efficiency per mass compared to many other chemical fuels. Hydrogen is not used as the main fuel for consumption because it is not an energy source, it only serves to carry energy. Because of its low and T_{cr} ,H_2 can be observed in gas state at normal Temperature.) (Züttel, 2004). For hydrogen to be used in stationary and mobile applications its storage would necessitate the use of gravimetric and volumetric density of the hydrogen.

Table 2.2. The six ways in which hydrogen can be stored (Züttel, 2004)

Storage Method	ρ_m [mass %][a]	ρ_v [kg H_2 m^{-3}]	T [^oC][c]	P [bar][d]
High Pressure gas cylinder	13	<40	RT[e]	800
Liquid hydrogen in cryogenic tanks	Size dependent	70.8	-252	1
Absorbed hydrogen	≈2	20	-80	100
Absorbed on interstitial sites in a host metal	≈2	150	RT	1
Complex compound	<18	150	>100	1
Metals and complexes together with water	<40	>150	RT	1

[a]Gravimetric density, [b]Volumetric density, [c]Operational temperature for storage method, and [d]Operational pressure for the storage method. [e]Room temperature (25C^o).

The final way in which hydrogen can be stored is by using a hydrogen rich substance with a great volumetric and gravimetric H_2 storage capacity (Himmelberger, 2010). There are also other forms under consideration that hydrogen can be stored such as Boron and Nitrogen compounds. Ammonia borane NH_3BH_3 is another example that can be used in the storing of hydrogen due to its more stability with various solvent for example water and methanol. Ammonia borane also have a high gravimetric H_2 content of 19.6% wt and with low molecular weight of 30.7 g mol -1 and a controllable release of H_2 (Staubitz et al., 2010; Yadav and Xu 2012).

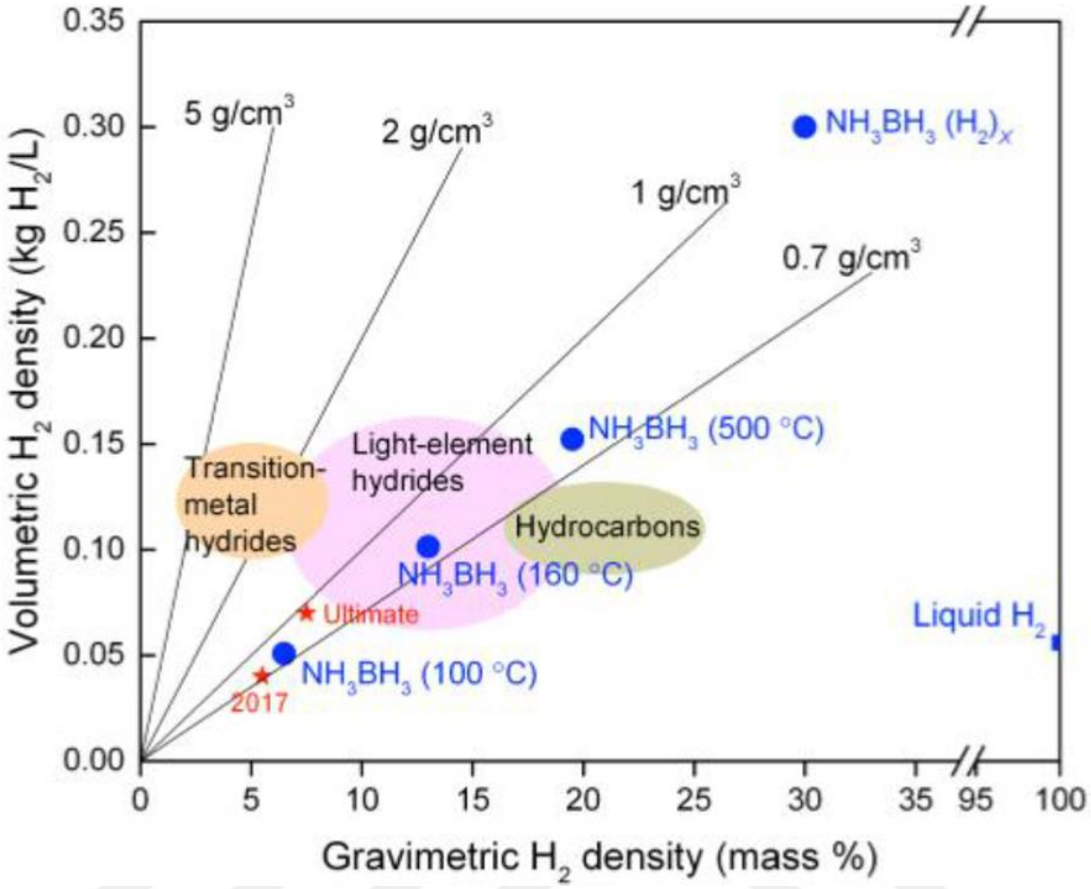

Figure 2.4. Relationship of the volumetric and gravimetric Hydrogen densities of various hydrogen storage (Lin and Mao, 2014).

Ammonia brane contains a high a hydrogen capacity than the ($LiBH_4$) (18wt%), N_2H_4 (12,6wt%) and Mg (BH_4)2 (13,7wt%) (Umegak et al., 2009; Moussa et al., 2013). Both B and N in the NH_3BH_3 can bond with a (H) atoms. The bonds of N-H and B-H tends to be protonic and hydridic that subsequently leads to H_2 gas being released (Lin and Mao 2014).

2.1.4. Storing of hydrogen in sodium borohydride material

Sodium borohydride ($NaBH_4$) is widely identified since it is largely used in organic chemistry as reducing agent and thus as a material for storing H_2 is credited with 60 years of history (Demirci et al., 2010). When hydrogen is stored in $NaBH_4$ it can be recovered through two ways that is by hydrolysis (Wee et al., 2006) or through thermolysis (Nakamori, 2008).

The investigations that have been carried out shows that hydrogen which had been produced through sodium borohydride hydrolysis is one of the most encouraging chemical hydrides for vehicles fuel cell apps. with a 10.8 wt. % gravimetric storage capacity (Züttel et al., 2007; Cakanyildirim and Gürü, 2008; Liu and Li, 2009). While $NaBH_4$ is stable, hydrogen gas is produced in (Eq.1) in the presence of catalyst hydrolysis reaction will happen after that can produce half of the H_2 from H_2O solvent (Amendola et al., 2000; Lee et al., 2002; Demirci, 2008). Therefore, this is a safer way to produce hydrogen for fuel cells.

$$NaBH_4(aq) + 2H_2O(l) \xrightarrow{\text{Catalyst}} NaBO_2(aq) + 4H_2(g) \quad (2.1)$$

In view of the fact that $NaBO_2$ is often dispersed in H_2O forming Na+ and $B(OH)_4^-$, the reaction can also be written as bellows;

$$NaBH_4(aq) + 4H_2O(l) \xrightarrow{\text{Catalyst}} Na^+(aq) + B(OH)_4^-(aq) + 4H_2(g) \quad (2.2)$$

Hydrogen that has been produced through a catalyzed reaction from (hydrolysis of alkaline) $NaBH_4$ sol. through Eq.1 has benefits (Padró and Lau, 2000) such as;

- $NaBH_4$ solutions have been non-flammable and air-stable for months.
- The production of H_2 can only occur in the attendance of an appropriate catalyst at normal temperature.
- Products from the reactions are also environmentally friendly.
- The rate at which H_2 is produced can be controlled.
- The efficiency of volumetric and gravimetric that stores H_2 is high.
- The products from the reaction can be recycled and H_2 can even be produced at a temperature of 0 ºC.

Those characterizations are unique among metal hydride systemthat produce H_2 after reacting with H_2O. To some point this hydrolysis will occur even without a catalyst if the sol. has a ($pH < 9$). Nevertheless, the sols. of $NaBH_4$ are usually preserved as an extremely alkaline solution by increasing NaOH so that maximize the shelf life of $NaBH_4$ solutions ,also avoid the sluggish development of H_2 gas. The key feature in

using that reaction for producing H_2 is the occurrence of H_2 gas production in alkaline $NaBH_4$ sols. pH > 14 only while the solutions are allowable to contact the specified heterogenous catalyst.

When catalyst is not used a strong alkaline $NaBH_4$ solutions would not produce a considerable amount of H_2. Because H_2 is produced when the specified catalyst is in contact with the $NaBH_4$ solution, it therefore ensures a quick, reliable and a manageable response to H_2 demand.in addition, the production of H_2 ends while catalyst is removed from the alkaline $NaBH_4$ sol. Since the hydrolysis process is highly exothermic there is energy needed to produce hydrogen.

When the temperatures are increased the hydrolysis process of $NaBH_4$ is also increased (Aiello et al., 1999). The reaction is even faster when an appropriate metal catalyst is used (Levy et al., 1960; Brown, 1962; Kaufman and Sen 1985) or acid (James and Wallbridge, 1970) is added into the solution. The byproducts of this hydrolysis reaction which is Sodium metaborate ($NaBO_2$) can dissolve in water. Moreover, sodium metaborate is environmentally friendly and can be used as a primary material in regenerating Sodium metaborate ($NaBO_2$).

Because the $NaBH_4$ is completely inorganic and there is no sulfur, it does not produce fuel cell poison like (S) (Sulphur) compounds, carbon monoxide CO, aromatics or soot through the hydrolysis process. The hydrolysis of Sodium metaborate can thus be viewed as safe, efficient and easily manageable process compared to when H_2 is generated from other methods (Padró and Lau, 2000). Since aqueous solution of $NaBH_4$ is difficult to ignite vehicle are much safer if they carry $NaBH_4$ solution compared to other fuels (Amendola et al., 2000).

The hydrogen that has been produced is then used in a fuel cell which is a device that has a capacity to produce electricity through the reaction of fuel and hydrogen in the presence of an electrolyte. (Vielstich et al., 2003). It is an electrochemical cell it has ability to convert chemical energy into electrical energy. Combination of O_2 and H_2 is the mean idea of hydrogen fuel cell as a result it can be got electricity and heat or energy. Different from engine, far from burning hydrogen or fuel, that can get much efficient and so clean.

Electrolyte channeled between anode and cathode and it has a stack to collect and obtain of the high power different from battery does not necessary for recharging. High efficiency of the device can make the society to use it. As mentioned before at the result no waste it has except water (which is very clean) by using this can avoid environment from pollutions individuals can use it in his car which is very clean to the climate.

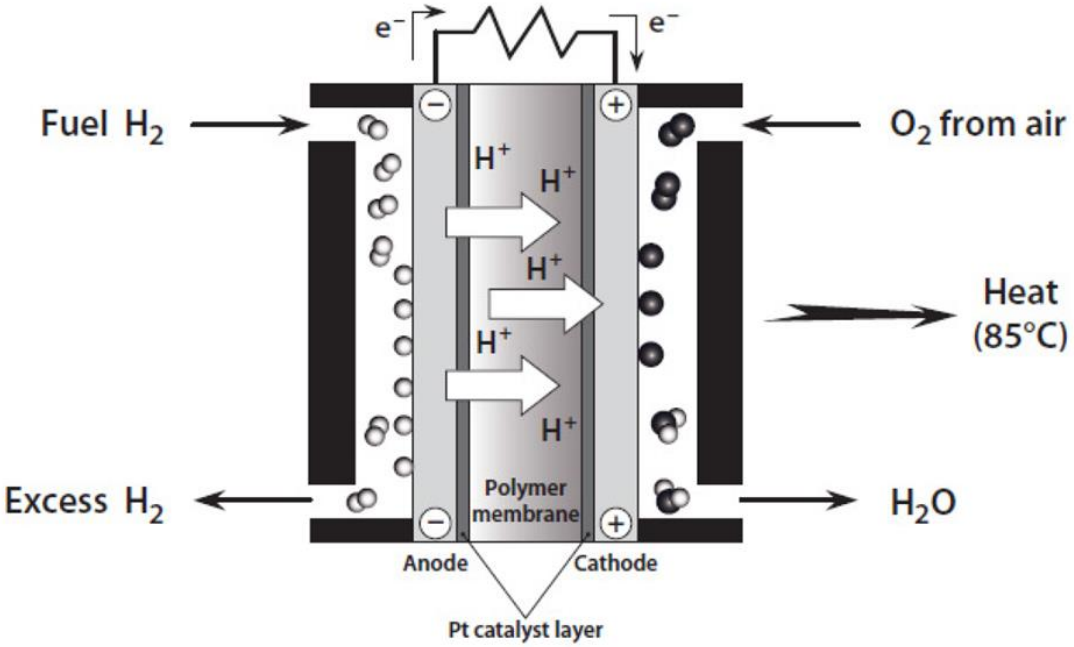

Figure 2.5. Proton exchange membrane (PEM) Proton exchange membrane, H_2 Fuel Cell.

2.1.5. Hydrogen release from ammonia borane

Some of properties of ammonia borane are such as colorless tetragonal crystal under favorable conditions.as well as It is a huge solubility in H_2 and other polar solvents (Lin and Mao, 2014). It also has the density of 0.74 g/cm3 and also the melting point between 110-125 ºC and this is because of variation of in its purity. It is worth noting that around 1950s, AB was fused first when boron- hydride based fuels that had a high energy for rockets and jets was being developed (Lu, 2010). The most critical

properties of AB are that it is environmentally friendly, non-toxic and can be used safely in any environmental situations.

Hydrogen will liberate from AB through (thermolysis) in both protonic solvent and solid state all of which will need to be catalyzed (Lu et al., 2014). Hydrogen that has been liberated from thermal hydrogenation of AB has been documented as an extraordinary activity (Karkamkar et al., 2007). High temperatures are needed to produce a higher volume of hydrogen in thermolysis. Yet high temperature allows side products like borazine to form. AB has to be stable for thermal decomposition to take place at high temperatures. The effects of temperatures in the process is that, when the temperature is reduced the amount of the undesirable products is therefore decreased and at the same time the amount of hydrogen also reduces.

That is, temperature is a concern due to the difficulties in regulating the reaction. Catalytic solvolysis, on the other hand, offers a more favorable route for the hydrogen production from AB. In specific catalytic hydrolysis is still the most important for the storage of hydrogen. Catalytic hydrolysis can be used to produce hydrogen from AB in the attendance of an appropriate catalysts (Jiang and Xu, 2011). The hydrolysis of AB happens at a considerable rate only at the existence of an possible catalyst to liberate three moles of H_2 per mole of ammonia borane (Lu et al., 2014; Akbayrak and Özkar, 2017) (Eq. 2.3).

$$NH_3BH_3\ (aq) + 2H_2O\ (l) \xrightarrow{\text{Catalyst}} NH_4{+}\ (aq) + BO_2{-}(aq) + 3H_2\ (g) \qquad (2.3)$$

The major concern with the use of nanoparticles of the transition metal as a catalyst is their ability to gather together as large particles and eventually into (bulk metal) that is a dynamic metal sink. (Rakap and Özkar, 2010) and organic metal frames (MOFs) (Yang et al., 2016).

Other materials that support Ruthenium nanoparticles include carboncous materials such as active carbon (Liang et al., 2012), carbon nanotube (Akba yrak and Özkar, 2012) . graphene (Du et al., 2015) or oxide supports such as titania TiO_2 (Mori et al., 2016), alumina Al_2O_3 (Rachiero et al., 2011), silica SiO_2 (Akbayrak et

al., 2014), ceria CeO_2 (Akbayrak et al., 2016) are very and great active catalyst in generating of H_2 from the hydrolysis of amonia borane.

However, more progress in the reuse of the Ru catalyst still has a problem. Magnetic regenerative catalysts have been of the highest importance in this regard, because the magnetic properties allow the isolation of the reaction solution from the filtration and centrifugation techniques (Akbayrak et al., 2014). Catalyst can be easily isolated and recycled by mixing magnetic nanoparticles with a catalytic active portion (Hudson et al., 2014). Cobalt, iron and nickel are also reusable and effective catalysts.

2.1.6. Catalysts experienced for the hydrolysis of ($NaBH_4$) sodium borohydride and (AB) ammonia borane

To date, there are also several catalysts used and examined in the process of NaBH4 and H3NBH3 hydrolysis. Just to mention but a few, examples include, ruthenium (Amendola et al., 2000), $Pt/LiCoO_2$ (Akbayrak et al., 2014), carbon supported platinum (Akbayrak et al., 2016), $PtRu/LiCoO_2$ (Akbayrak et al., 2014), Ru/IRA-400 (Hudson et al., 2014), nickel (Pinto et al., 2006), electrodeposited Co and Co-P (Cho and Kwon, 2007), $Co/\gamma\text{-}Al_2O_3$ (Ye et al., 2007), Co-B (Kim et al., 2007), Pt/Ac (Xu et al., 2007), nickel-cobalt-boride (Ingersoll et al., 2007), Co-Mn-B nanocomposite (Mitov et al., 2007), cobaltboron/ nickel foam (Dai et al., 2008), $Ru/LiCoO_2$ (Liu et al., 2008), cobalt-tungsten-boron/nickel foam (Dai et al., 2008), Co/Ac (Xu et al., 2008), electrolessly deposited Co-P (Eom et al., 2008), $Ru/\gamma\text{-}Al_2O_3$ (Hung et al., 2008), Co-B/MWCN (Huang et al., 2008), Ru-promoted sulphated zirconia (Demirci and Garin., 2008), Ni-Ru nanocomposite (Liu et al., 2009), fluorinated cobalt (Akdim et al., 2009), PtPd-carbon nanotubes (Pena-Alonso et al., 2007), aluminum chloride (Demirci et al., 2009), acetic acid (Akdim et al., 2009), Co-Cr-B (Fernandes et al., 2009), porous Fe-Co-B/Ni foam (Liang et al., 2010), Ru/Graphite (Liang et al., 2010), clay-supported Co-B (Tian et al., 2010), Catalyst Co-Ni-B (Patel et al., 2010), attapulgite CoB (Fernandes et al., 2009), Co-Cu-B (Ding et al., 2010), Pd/Ac(Patel et al., 2008), NixB (Hua et al., 2003), Co-powder (Liu and Suda., 2006), Ru/IR-120 (Hsueh et al., 2008), BMR07 (Ni based) (Zhang et al., 2007), Ru/Ac (Zhang et al., 2007), Ru-Pd-Pt (Hu et al., 2011), mono- and di-carboxylic acids (Kim et al., 2010), and

(Ni_3.6Co0.7Mn0.4Al0.3) 1.15 hydride electrodes (Santos et al., 2010) have been tested as catalysts.

For H3NBH3 hydrolysis: RuCl3, $PdCl_2$, as well as $CoCl_2$ (Ramachandran and Gagare, 2007), Non-noble γ-$A_{l2}O_3$, carbon, as well as SiO2-supported metals (Xu and Chandra., 2006), K_2PtCl6 (Mohajeri, 2007), Ni1-xPtx hollow spheres (Cheng et al., 2007), Ru/Ac (Basu et al., 2009), Catalysts with nanoparticles Rh(0), Ir(0), and Co(0) (Clark et al., 2007**)**, Cu@Cu_2O core shell catalysts (Kalidindi et al., 2008**)**, Ni-SiO_2 Hollow Nano-Sphere (Umegaki et al., 2009), Metals dependent on Pt- and Ni- (Yao et al., 2008), Fe(0) (Yan et al., 2008**)**, Fe-Ni magnetically recyclable alloy (Yan et al., 2009**)**, cobalt(0) (Yan et al., 2010**)**, Ni water/air-stable (Yan et al., 2009), Nanostructures of PtxNi1-x, (Yang et al., 2009), palladium(0) (Rakap and Özkar., 2010), A foam of cobalt-molybdenum-boron/nickel (Dai et al., 2010), hollow Co-B nanospindles (Tong et al., 2010), nanoparticle-assembled Co-B thin film (Patel et al., 2010), Au-Ni bimetallic nanoparticles found in the nanospheres of SiO2 (Jiang et al., 2010), Cu/Co_3O_4 (Yamada et al., 2010), Co-Ni-P/Pd-TiO22 electroless (Rakap et al., 2011), Pd-PVB-TiO_2 (Rakap et al., 2011), Co-SiO2 nanospheres have also been studied as catalysts (Umegaki et al., 2010). The use of small sizes and a highly scattered particles will allow the catalyst to sufficiently be in contact with the reactants for raising the reaction rate and decrease the amount of the catalyst used (Zhao et al., 2007). some metal (0) nanoclusters such as acetate-stabilized ruthenium (0) nanoclusters (Zahmakıran et al 2006), hydrogenphosphate- or polymer-stabilized nickel (0) (Metin et al., 2007), ruthenium (0) and palladium (0) (Metin et al., 2009) have in recent times been prepares and experimented in the hydrolysis process of $NaBH_4$ and H_3NBH_3 as a catalyst. The goal of such a research is usually to develop effective, recyclable and sustainable metal catalysts to additional progress the kinetic and thermodynamic characteristics of the sodium borohydride ($NaBH_4$) and ammonia borane (H_3NBH_3) hydrolysis reactions under relatively average conditions.

2.2. Nanoclusters Transition Metal (0)

2.2.1. Nanoclusters colloidal metal

Interest in nanochemistry has grown over the last decade (Kim 2008).

Nanoscience is technological advancement and analysis of macromolecular' atomic and molecular level, with a wavelength range of about 1 – 100 nanometers, to enhance a basic knowledge of nanoscale materials and procedures to build or utilize systems structures or devices that with unique functionalities due to their limited or intermediate sizes. The unique differentiating characteristics and features are generated on a crucial length scale usually below 100 nm (Gibson and Pula, 2009).

The word nanotechnology is used to describe scientist Richard Feynman's idea of nanomachine-based manufacturing plants to create sophisticated goods, including other nanomachines (Shi et al., 2010). Technology research reveals that this would be an incredibly efficient capability, capable of manufacturing massive goods with atomic accuracy, constructing them with advanced materials, cleanly and at cheaply (Fedlheim and Foss, 2001).

It is necessary to differentiate between contemporary nanoclusters and at least conventional colloids or nanoparticles (Cruz et al., 2013). Nanoclusters are monodispersed particles consisting of a transitional form of the substance around solids and molcules of approximately (1–10 nm) (10–100 Å) in dimension (Aiken and Finke, 1999). They are basically of great importance and this is because of their potential catalysis application in nano-based chemical sensors (Elghanian et al., 1997) as light producing diodes (Colvin et al., 1994) and in quantum machines (Glanz., 1995),

Nanoclusters have also shown that it can catalyze a number of reactions involving hydrogenation spanning hydrogenations (Lin and Finke, 1994); enantioselective hydrogenations (Bönnemann and Braun., 1996); hydrosilylations (Stein et al., 1999); hydropyrolysis and hydrogenolysis (Wilcoxon et al., 1994). There are properties and structure of nanoclusters that are so sensitive to their conformation and their size that might contribute to newer and exciting characteristics that have not yet been realized in the bulk material (Pool and Clusters, 1990).

These impacts can be much more evident when surface atoms are bound together (Marquardt et al., 1986). This results to various mechanical and electrical transport properties that explains the catalytic characteristics of nanocrystalline particles (Henglein, 1989).

2.3. Catalysis

2.3.1. Common principles of catalysis

The phrase "catalysis" was used for the first time by (Berzelius, 1836) the attempt on the catalytic disintegration of the hydrogen peroxide in (1836). Berzelius identified a brand new organization able to fostering a "catalytic touch" of chemical processes. He speculated that the function of such a product was to relax the bonds that held the atoms together in the reactive molecules. Therefore, he then used word "catalysis" which comes from two Greek words *kata'* meaning absolutely and *lein* to mean loosen.

In 1894 by Ostwald The contemporary concept of catalyst and its current definition was conceived. where he defined catalyst as a material which increase the chemical reaction rate while it remains chemically not changed while the reaction is finish. Since the catalysts are not changed during the chemical reaction each catalyst molecule will join in several successive cycles in that even the little quantity of the catalyst relative to the substrate is sufficient.

Historically Catalysis would be classified into 3 major types that is heterogeneous homogeneous, and bio catalysis.

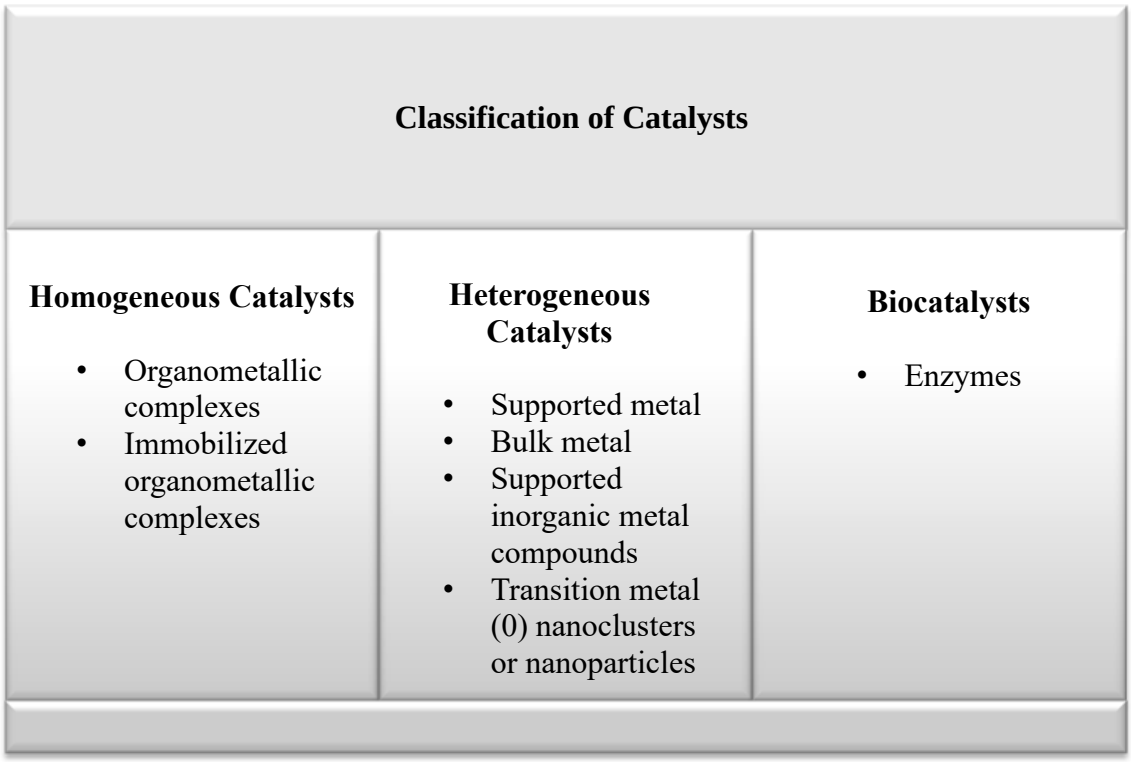

Figure 2.6. Catalysts classification (Rothenberg, 2008).

In such a (Homogeneous) the reactant and the Catalysis and their solution form a single phase. That form of Catalysis also could take place during the (Gas or Liquid) stage. During (1750), the initial catalyzed reaction was the oxidation of (SO_2) Sulphur dioxide in the existence of (NO) nitric oxide as a catalyst to form Sulphur trioxide (Farnetti et al., 2009). Heterogenous catalyst involves a framework in which catalysts and the reactants takes place in different stages. Additionally, the catalyst is usually in solid form while the reagents can be in gaseous or in liquid form.

The classic example of heterogenous catalysis to generate Sulphuric acid is the contact process through that (SO_2) reacts with O_2 to produce (SO_3) sulphur trioxide when a solid (V_2O_5) vanadium oxide is used as a catalyst. The major advantage that heterogenous catalyst have over the homogenous catalyst is that it is simple to remove the active catalyst from the reaction and recycle it in the subsequent run that provides a more continuous chemical reaction.

Comparatively the heterogenous catalyst is capable of working in an extreme condition of reactions than the homogenous one. Through heterogenous catalytic

reactions the reactants can be physically absorbed to the fluid stage to a catalyst through a weak Van der Waals forces or partial chemical bond. Well after forming an activated complex, the products from the reaction are pushed to the surface of the catalytic.

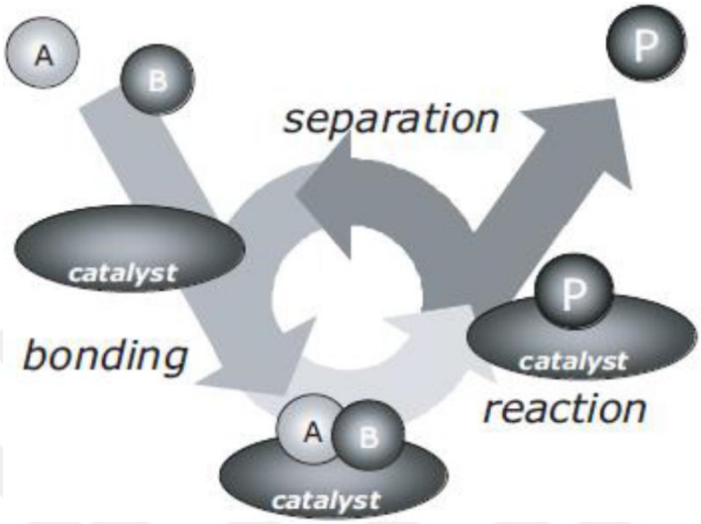

Figure 2.7. Heterogeneous catalysis mechanism (Chorkendorff and Niemantsverdriet, 2017).

In Catalytic reactions, the catalysts improve the response rate by providing an different mechanism which is very complex but energy-efficient. The activation energy (Ea) of a catalyzed reaction is less compare to the uncatalyzed reaction in consequence successful molecular collisions with poorer energies will exceed the new energy activation barrier, which greatly increases the response time. It should be remembered that the magnitude of the reaction is the same with all catalyzed and uncatalyzed reactions since the catalyst accelerates forward as well as reverse reactions to about the same degree. Therefore, the constant balance of the reaction is not disturbed. This implies that the catalyst has an effect on the kinetics of the reaction, and not on thermodynamics (Chorkendorff and Niemantsverdriet, 2017).

2.3.3. Properties of catalysts

2.3.3.1. Efficiency of catalytics

In such a catalyzed reaction catalyst must first be activated so as s to increase the rate of reaction. Regardless of various changes that the catalyst undergoes during the entire catalytic cycle, it still remains unchanged. Efficient catalysts can join several stages that can be called the number of turnovers. The (TON) turnover number is the cumulative number of reactive molecules that the catalyst transforms into commodity molecules (Hawkins, 2006).

$$\text{TON} = \frac{\text{volumetric rate of reaction number of centers}}{\text{volumes Lifetime of a catalyst}} \tag{2.4}$$

The (TOF) turnover frequency quantifies the particular activity of a catalytic per unit time.

$$\text{TOF} = \frac{\text{volumetric reaction number of centers}}{\text{volumes}} = \left(\frac{\text{Mole}}{\text{Volume.time}}\right)\left(\frac{\text{Volume}}{\text{mole}}\right) = \text{Time} - 1 \tag{2.5}$$

2.4. Literature Survey

Given the rapid decline of fossil-based capital and associated environmental concerns, in recent decades. Hydrogen is known to be a significant alternative to gasoline because it is a carbon-free energy carrier that has safe combustion properties. CO-free hydrogen has a high ability to be used as a fuel for PEM fuel cells. The evolution of better catalysts that reduce unnecessary side products and demonstrate strong behavior at low-temperature reforming reactions is still a problem in catalysis study.

A lifelong experiment with zeolite-contained cobalt (0) nanocluster catalyst in sodium borohydride hydrolysis was initiated with 2.0 mM zeolite-contained cobalt (0) nanoclusters in 50 mL aqueous sodium borohydride solution at 25 ^{o}C. They have a

gross turnover of 12000 over 75 h and a total TOF value of 250 mol H_2 (mol Co)-1 h-1. Rakap, Murat, man. July 2011. July 2011.

An extremely active and stable catalyst for hydrolytic dehydrogenation of (AB) was prepared by supporting monodisperse (Pd NPs) palladium nanoparticles with reduced graphene oxide (RGO) by a simple process. (Kılıc, 2012).

Amali et al. (2013) stated that the formation of metal-based nanostructured materials is essential for AB catalytic hydrolysis.

Aranishi et al. (2013) synthesized Fe0.3C0.7 doped carbon aerogel product catalysts using a chemical reduction process and used them in normal temperature AB hydrolysis. They stated that 40 percent by weight of the Fe0.3C0.7/Ac sample, particularly a high catalytic activity and long duration, had been prepared from prepared catalysts. The minimum hydrogen output rate was recorded at 298 K, 13,695 ml min-1 g-1 and the Ea was only 20,83 kJmol-1 (Aranishi et al., 2013).

Ultrafine copper nanoparticles (Cu NPs) in porous silica nanospheres ($Cu@SiO_2$) were making ready by using single-pot synthetic route in a reverse micelle framework defined by SEM, TEM, EDX, XRD, N_2 adsorption-desorption, CO-TPD, XPS, and ICP techniques. The analyzed result indicate that ultrafine Cu NPs with a diameter of around 2 nm are efficiently fixed in the middle of well-proportioned SiO_2 NPs with a diameter of around 25 nm. When we Compare it to commercial SiO_2 backed by Cu NPs, SiO_2, Cu NPs, free Cu NP and the $Cu@SiO_2$ synthesized core-shell nanospheres shows superior catalytic behavior for hydrolytic dehydrogenation of (AB, NH_3BH_3) and hydrazine borane (HB, $N_2H_4BH_3$) at normal temperature in friendly environment. The (TOF) for Amonia borane and hydrolysis of HB in the presence of the $Cu@SiO_2$ nanospheres was estimated at 3.24 and 7.58 mol H_2 (mol Cu min)21 accordingly. Zhujun Zhang, 2014.

Ru (0) nanostructure assisted by xonotlite nanowire (Ru(0)@X-NW) was made by ion exchanging of Ru_3+ ions with the Ca_2+ ions in xonotlite nanowire lattice preceded by sodium borohydride reduction in aqueous solution at ambient temperature. Ru(0)@X-NW has been characterized by a mixture of sophisticated analytical techniques.

The findings indicate which a very scattered Ru (0) nanoparticles of 4.4 ± 0.4 nm was produced on the surface of the xonotlite nanowire. Ru(0)@X-NW was found to exhibit a high catalytic activity in hydrogen production from hydrolytic dehydrogenation of AB with a TOF of up to 135 min−1 at 25.0 °C Serdar Akbayrak (2014).

In order to produce graphene-supported ruthenium (0) nanoparticles, the 1st graphene oxide was made from graphite using the adjusted Hummering process. Ru3+ ions was then mixed with graphene oxide. Eventually, AB used to reduce Ru (III) ions to ruthenium (0) nanoparticles backed by graphene. Ruthenium (0) nanoparticles have been distinguished by ICP-OES, XRD, SEM, SEM/EDX and TEM. Ruthenium (0) nanoparticles backed by graphene have been used to accelerate the hydrolysis of AB that releases 3 H_2 equivalents per ammonia borane mole. They were extremely active catalyst producing 200,000 hydrogen turnovers from AB hydrolysis at 25.0 °C with an initial turnover level of 150 min-1. Fatma as well as the Acar (2015).

Feng et al. (2017), nanoparticles (NPs) assisted by well-distributed, magnetically re-usable two-metal CoxNi1 (x = 0, 0.1, 0.3, 0.5, 0.7, 0.9, 1) graphene in situ using sodium borohydride methylamine. Of all CoNi/graphene catalysts examined, Co0.9Ni0.1/graphene NPs showed maximum catalytic activity for EU hydrolysis, while the turnover frequency was 16.4min-1. moreover, (Ea) value stated by synthesized Co0.9Ni0.1/graphene catalysts as 13.49 kJ/mol for catalytic dehydrogenation of AB. It was also stated that this catalyst demonstrated magnetic recyclability (Feng et al., 2017).

Qilu et al. (2016) synthesized Mo-reinforced transformed Ni nano-particles in graphene sheets by chemical reduction. To obtain hydrogen from the EU hydrolysis, the TOF value of these catalysts which do not include any noble metal was stated to be 66.7 min-1 (Qilu et al., 2016).

The (TOF) of rhodium (0) nanoparticles in H_2 production from AB methanolysis at 25.0 ± 0.5 degree celcious. The turnover frequency values, specified per rhodium contained within the catalyst as usually . Also the turnover frequency values adjusted for the number of Rh atoms on the surface of the nanoparticle, and the H_2 production rates for the AB methanolysis at varying initial rhodium concentrations at 25.0 ± 0.5 °C.The rhodium (0)/nanoSiO_2 extract with Rh load of 0.5 wt. percent rhodium produces

maximum catalytic performance with actual turnover frequency = 168 min-1. Derya Özhava (2018).

Ruthenium (0) nanoparticles backed by pure or silica-coated magnetite are made by infusion of Ru (III) ions on the support surface accompanied by their reduction with aqueous solution of sodium borohydride. The products are magnetically separated from the reaction solution and are distinguished with the mixture of developed analytical techniques comprising (ICP-OES, BET, XRD, SEM-EDS, TEM, XPS). This magnetically insolvable nanoparticles are used as the catalyst for the production of H_2 from ammonia boran hydrolysis at normal temperature. Ruthenium (0) nanoparticles is backed on naked magnetite and silica-coated magnetite which are extremely active catalyst gives TOF values of 29 and 127 min-1, respectively, in H_2 production from the hydrolysis of AB at 25 °C. Therefore, Silica coating of the magnetite surface leads to a major rise in the catalytic action of Ru (0) nanoparticles involving hydrogen production of ammonia borane hydrolysis. Ruthenium (0) nanoparticles, which are based on silica coated magnetite are also extremely reusable as they maintain their original catalytic activity well beyond the 5^{th} recycling of the hydrolysis in the H_2 generation. Sarıca Esra (2019).

3. MATERIAL AND METHOD

3.1. Material

3.1.1. Chemicals used

The chemicals used in the studies and the companies from which they are made available are given below.

- Potassium tetrachloropalladate (K_2PdCl_4) 99.99% - ALFA AESAR
- Ruthenium (III) ($RuCl_3.3H_2O$) 99.9% - SIGMA ALDRICH
- Cobalt (II) chloride ($CoCl_2.6H_2O$) 98% -SIGMA ALDRICH
- Ammonia borane (NH_3BH_3) 97% - SIGMA ALDRICH
- Sulfuric acid (H_2SO_4)97% –CHEM-LAB.

3.1.2. The experimental setup

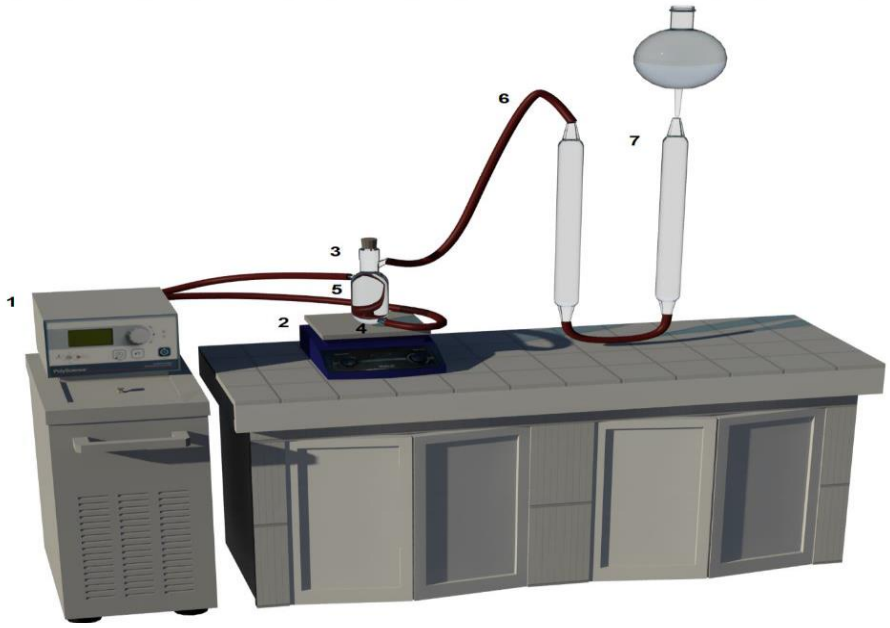

Figure 3.1. The experimental setup used in performing the catalytic hydrolysis of ammonia borane and measuring the hydrogen generation rate. 1: Water Bath Circulator, 2: Magnetic Stirrer, 3: Jacketed Schlenk Tube, 4: Water in, 5: Water out, 6: Plastic Hose, 7: Burette Filled with Water.

In this experiment hydrogen was generated from ammonia borane, a reaction system comprised primarily of two main components was developed. In the first segment, most of which are made of Pyrex glass, a heater-mixer plate, a water bath to maintain the reaction temperature stable, a 3-cock glass reactor with a volume of 50 mL, a pressure stabilizer liquid feeder with a volume of 25 mL, a back-cooler, a scrubber to provide cold water to the back-cooler, thermometers and fittings were used to ensure that the experiment is done in an environmentally friendly environment.

Throughout the second part, a 250 mL volume flask was used to store by-products like ammonia gas, a 100 mL volume gas burette device to quantify the hydrogen produced, and a 250 mL volume drop funnel to change the water level of the gas burette system. Until beginning the procedure, the gas burette device and the drop funnel were attached to the plastic hose. Water was pumped into the casting funnel and the water was loaded to the required leve in the gas burette method.

Ultrasonic baths: Ultrasonic baths used in the preparation of solutions and all other procedures (like washing) have been developed using a HUMAN ZeneerPower1 pure water unit. The resistance of this water is 18.3 M at.cm. Ultrasonic bath: homogeneous dispersion of particles and ultrasonic baths of the ISOLAB brand have been used in all other applications when preparing the catalyst.

Circulator: JSR/JSIB-11T Model Circulator was used to provide the rear cooler with cold and hot water.

3.1.3. Solutions used

In the tests, ammonia borane and sulfuric acid solution were used.

Ammonia borane solution: Ammonia borane has long been prepared and used in test. Ammonia borane solutions were prepared at 0.5, 1, 2 and 3 mmoles in use in the experiment.

Sulfuric acid solution: 5.32 mL of 97% sulphuric acid was applied to 200 mL of pure water and 0.1 N of H_2SO_4 solution was collected.

3.2. Experimental Studies

3.2.1. Preparation of the catalyst

The method of chemical reduction was used in preparing the catalysts in this analysis. Pd/AC, PdRu/AC and PdRuCo/AC catalysts were synthesized using K_2PdCl_4, Ruthenium (III) ($RuCl_3.3H_2O$) and $CoCl_26H_2O$ metal precursor salts with sodium borohydride ($NaBH_4$) reduction methods. Activated carbon (AC) has been used as a substitute.

Again, for Pd/AC catalyst, 0.0307 g K_2PdCl_4 was dispersed in 10 mL deionized water, followed by addition of 0.1 g activated carbon (AC) to this solution. This mixture was allowed to be mixed in the ultrasonic bath for 60 minutes and in the usual mixer for 60 minutes at room temperature. Therefore, by adding $NaBH_4$,10 times the amount of metal, the mixture was washed with deionized water then dried in a vacuum oven at 85 °C after the reduction had been done.

Similarly, Ru/AC and PdRu/AC @1 percent Co catalysts were dispersed in 0.0192 g ($RuCl_3.3H_2O$) and 0.022 g $CoCl_2.6H_2O$ metal salts in deionized water and reduced to $NaBH_4$. It was was cleaned with plenty of water then dried in a vacuum oven at 85°C.

Moreover, PdRu/AC catalyst was synthesized to examine the effect on the hydrolysis reaction of the addition of a second metal to the metal present in the medium. After dissolving the PdRu/AC catalyst, 0.0307 g K_2PdCl_4 and 0.0192 g $RuCl_3.3H_2O$ metal salts in 10 mL deionized water, 0.1 g activated carbon has been applied to the medium. After the product was kept in an ultrasonic bath and a standard mixer, $NaBH_4$ was applied to the medium and then after the reduction, refining, rinsing procedures were carried out.

Eventually PdRu/AC@ Co nano catalysts were synthesized by steadily changing the volume of Cobalt with PdRu constant atomic ratio (Pd0.5Ru0.5/AC@1 per cent Co, Pd0.5Ru0.5/AC@3 per cent Co, Pd0.5Ru0.5/AC@5 per cent Co, Pd0.5Ru0.5/AC@7 per cent Co, Pd0.5Ru0.5/AC@10 per cent Co) metal salts were introduced after dissolving in 10 mL distilled water. The resultant product was stirred at room

temperature for 2 hours and after 2 hours of mixing, the aqueous $NaBH_4$ solution was applied drop by drop and stirred for a further hour. At the end of the reduction, the catalytic converter was cleaned with much water, purified and dried in a vacuum oven at around 85 ^{0}C.

3.2.2. Characterization of the catalyst

XRD diffraction trends of the crystal structures of the compounds have been reported with a Rigaku X-ray diffractometer D/max-220/PC fitted with CuK5-007 radiation (40 kV, 20 mA). SEM and EDX analyzes investigated the morphology and structure of the substance collected. SEM images were captured in FEI ZEISS SIGMA 300 microscopes functioning at acceleration rates of 20 and 10 kV accordingly.
The Hitachi H-8000 transmission electron microscope (TEM) used at 200 kV is fitted with an energy-dispersing X-ray detector was being used to achieve a microscopy of regular micrographs to assess the morphology and scale of the samples prepared. The electron binding structures of Pd, Ru and Co on the catalytic surface were studied using the Specs-Flex electron spectrometer and X-ray photoelectron spectroscopy (XPS).

3.3. Hydrogen Production Test

The amount of hydrogen emitted was determined using a laboratory device using the water displacement process. Shortly, a solution having 3 mmol gas, equivalent to the highest potential hydrogen quantity below 1 mmol (30.8 mg) AB (25 °C, 0.908 atm pressure and below 80.7 mL, was then balanced in a thermostatic water bath, then a 50 mg catalyst, distributed in 5 mL of purified water in a reaction flask, and the reaction solution was stirred at 600 rpm. Hydrolysis of AB started right away. Results generated in repeated tests have been centrifuged and purified and cleaned various times with water.

3.4. Kinetics of the Hydrolysis of Ammonia Borane Catalyzed by PdRu/Ac@Co Nanoparticles Supported on Activated Carbon

To create the NH_3BH_3 catalytic hydrolysis speed rule using PdRu/Ac@Co nanoparticles based on activated carbon, three different sets of experiments were carried out in the same way as defined in the section. To find the catalytic behavior of PdRu/Ac@Co nanoparticles based on activated carbon in the hydrolysis of ammonia borane. In the first series of tests, hydrolysis reactions started with varying initial amounts of PdRu/Ac@Co (10, 30, 50, 100 mg) at room temperature (25.0 ± 0.1 °C) while initial concentrations of ammonia borane remained stable at 100 mM (30.8 mg = 1.00 mmol). The second group of test was conducted at room temperature (25.0 ± 0.1 °C) by keeping the original PdRu/Ac@Co stable at 50 mg and varying the NH_3BH_3 intensity. (50, 100, 200,300mM in size). Eventually, ammonia borane hydrolysis was conducted when it was mixed with PdRu/Ac@Co nanoparticles at consistent catalyst (50 mg) and substrate (100 mM) concentrations and at varying temperatures between 25 and 40 °C in order to achieve activation energy (Ea), enthalpy (ΔH) and entropy (ΔS).

3.5. Determination of AB Hydrolysis Activation Energy

According to the collision principle, the reaction happens when molecules with ample energy are collided to efficiently initiate the reaction and sever the bonds. The alternative route provided by the catalyst (PdRu/AC @Co) has a lower activation barrier than the reaction that did not have catalyst (Nautiyal et al., 2014).

$$\ln k = \ln A - (E_a/RT) \tag{3.1}$$

$$\ln(k/T) = \ln(K_B/h) + (\Delta S/R) - (\Delta H/R)(1/T) \tag{3.2}$$

Ea is activation energy, T the absolute temperature, K_B refers to Boltzmann constant, (1.381×10^{-23}J/K), while h is Planck constant, (6.626×10^{-34} J s), ΔH activation trap, ΔS denotes activation entropy and finally R is the ideal gas constant (8.314 J/K.mol).

4. RESULTS AND DISCUSSION

4.1. Charectarization of the PdRuCo/Ac Nanoparticles

The surface compositon and elemenatal states of the prepared catalyst (PdRuCo/Ac) was examined by x-ray photoelectron spectroscopy (Figure 4.1). As shown in survey scan XPS spectrum of PdRuCo/Ac(Figure 4.1a), the apperance of Pd, Co and Ru peaks indicating the succesfull deposition of each particles. Moreover, core-level spectra of Pd 3d (Figure 4.1b) can be deconvulated two peaks located at 335.4 eV (Pd $3d_{5/2}$) and 340.9 (Pd $3d_{5/2}$) indicating the presence of Pd (0). The core-level spectra of Ru 3p (Figure 4.1c) can be fitted two distinct peaks recorded at 462.4 eV (Ru $3p_{3/2}$) and 484.3 eV (Ru $3p_{1/2}$) showed the presence of Ru (0). In addition, the core-level spectra of Co 2p (Figure 4.1d) can be fitted two main peaks located at 780.4 eV (Co $2p_{3/2}$) and 796.1 eV (Co $2p_{1/2}$) with satellites peaks of Co (0) appeared at 785.4 for Co $2p_{3/2}$ and 803.7 eV for Co $2p_{1/2}$, respectively. The results indicated that deposition of the naoparticles on the activated carbon is reliable.

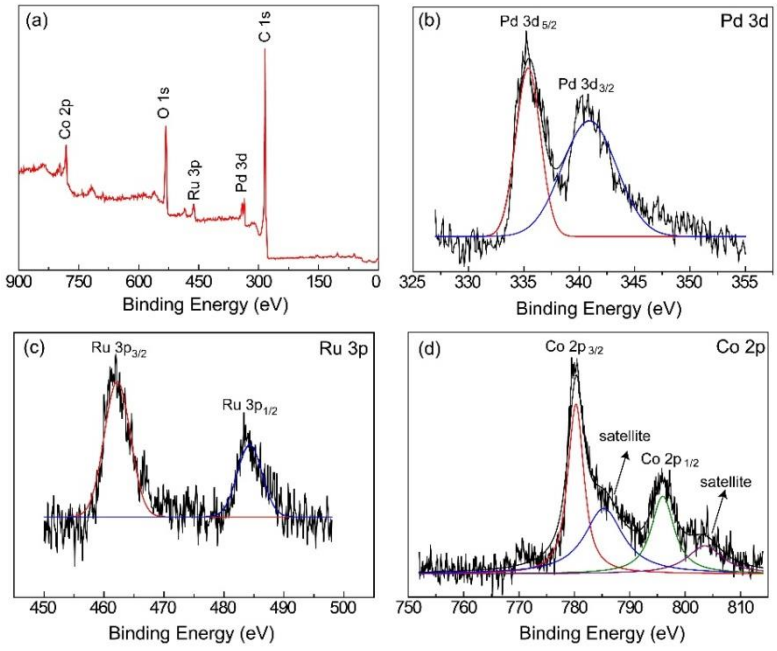

Figure 4.1a. XPS survey scan spectrum of PdRuCo/Ac and core-level XPS spectra for Pd 3d (b), Ru 3p (c) and Co 2p (d).

Surface morphology of the each catalyst was evaluated by scannimg electron microscopy (SEM) and corresponding SEM photomicrographs are shown in Figure 4.2. As presented, all nanoparticles distrubuted homogenously on activated carbon with some agglomeration. The agglomeration is most probably raised from due to high surface area/volume ratio of the particles. Moreover, as showed in the further stduies, the agglomeragation did not restrict the catalytic activity of the prepared catalyts.

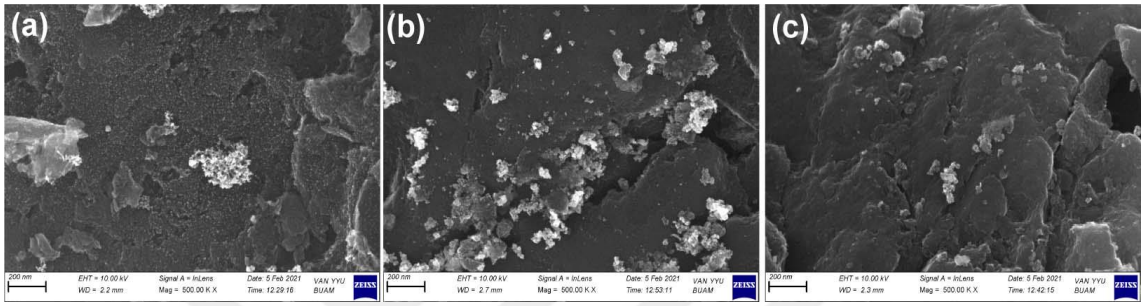

Figure 4. 2. SEM photomicrograps of (a) Pd/Ac, (b) PdRu/Ac and (c) PdRuCo/Ac.

SEM-EDX and elemenatal mapping analysis were also carried out for the best catalyst (PdRuCo/Ac) in the study. As shown in Figure 4.3, activated carbon was fully and homogenously coated with PdRuCo nanoparticles. Moreover, the specific peaks for Pd, Ru and Co were also detected and the peaks are well-match with the XPS results.

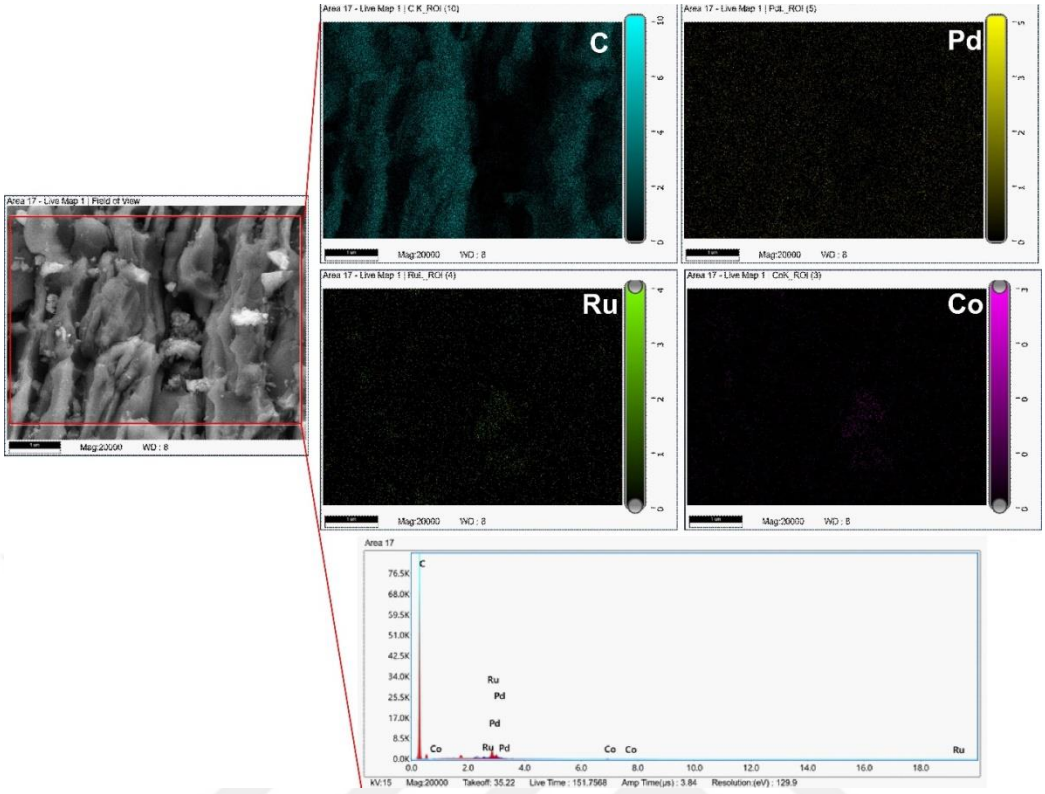

Figure 4.3. SEM photomicrograph, elemetal mapping and EDX spectrum for PdRuCo/Ac.

4.2. Comparison of Single, Double and Three Metal Activated Carbon Based Catalysts

The impact of single, twofold also triple metal catalysts based on Ammonia borane hydrolysis has been examined with Pd/Ac, PdRu/Ac then PdRuCo/Ac nanostructures. 50mg of catalyst was utilized within the hydrogenation containing 10ml of 1mmole Ammonia borane mixture. While Pd/Ac is catalyzed by PdRu/Ac and PdRuCo/Ac nanoparticles, the alter in volume of hydrogen versus time for Ammonia borane hydrogenation is seen in (Figure 4.4). Hydrogens were totally came out within 40 seconds when utilizing PdRuCo/AC catalyst come to the most noteworthy generation of hydrogen) of 9898.645 mL/min.g beneath the taking after conditions (1 mmole Ammonia borane, 50mg catalyst also 25^{o}C). The rate of hydrogen generation of Pd/Ac, single and two metal catalysts (7665.198mL/min.g and PdRu/Ac (9326.765 mL/min.g).

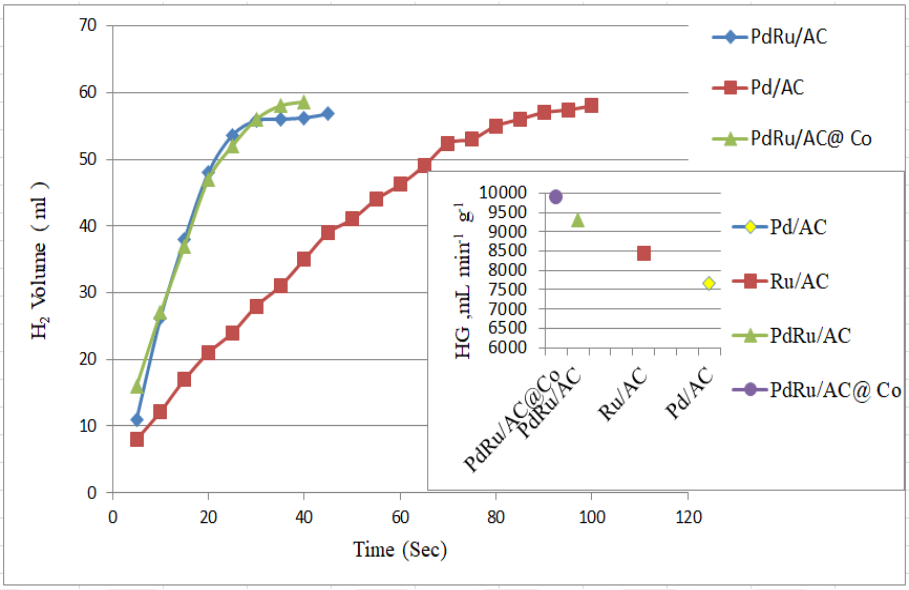

Figure 4.4. Effects of single, double and triple metal catalysts aided by Ac on AB hydrolysis (Condition of reaction: 1 mmol AB and 50 mg catalyst in 5 mL of pure water, 25 °C, 600 rpm).

4.3. Different Impact of Molar Rate

The impact of the catalysts' molar ratio significantly affects the AB's hydrolysis. The goal is to use catalysts to evaluate the dehydrogenation of AB in the liquid phase, having metal ratios Pd0.5Ru0.5/Ac, Pd0.9Ru0.1/Ac, Pd0.1Ru0.9/Ac, Pd0.7Ru0.3/Ac and Pd0.3Ru0.7/Ac. As observeb in the figure the highest hydrogen production rate was obtained by using (Pd0.5Ru0.5/Ac). Thus that molar ratio Pd0.5Ru0.5/Ac was used with adding Cobalt (Co) by using different Cobalt percent as follows (Pd0.5Ru0.5/Ac@1%Co, Pd0.5Ru0.5/Ac@3%Co, Pd0.5Ru0.5/Ac@5%Co, Pd0.5Ru0.5/Ac@7%Co, Pd0.5Ru0.5/Ac@10%Co) to know in which of them we can get highest hydrogen production rate, as shown in the figure (4.5b) the maximum hydrogen generation rate obtained by using (Pd0.5Ru0.5/Ac@1%Co). Hydrogen synthesis of metal nanoparticles of PdRu/Ac and PdRuCo/Ac has therefore been examined and the results can be seen below (Figure4.5a and Figure4.5b).

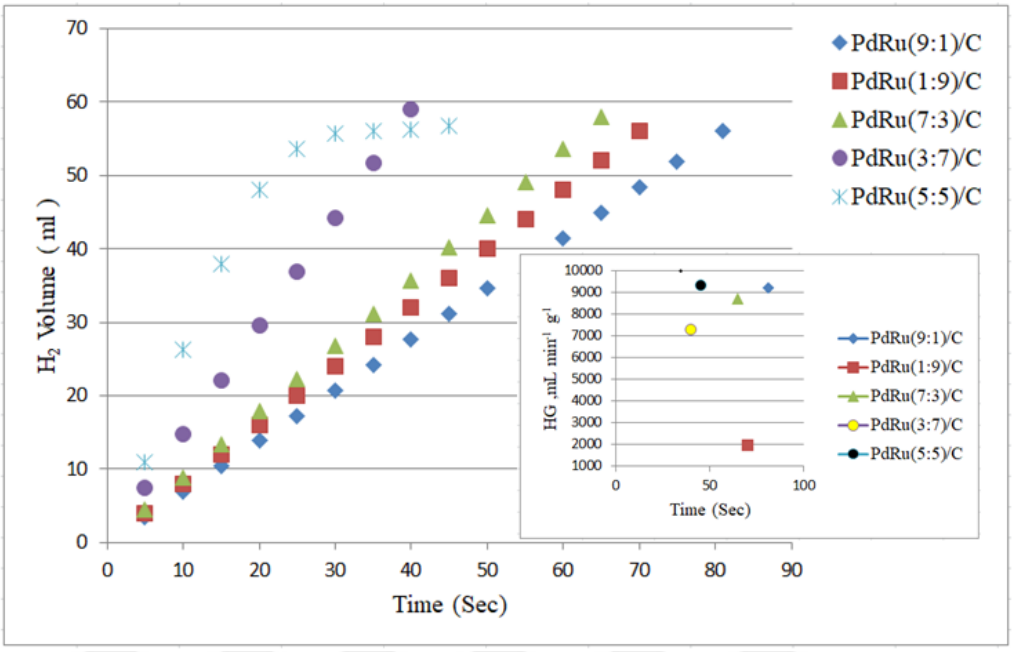

Figure 4.5a. Impact of the catalyst's atomic ratio on AB hydrolysis (Condition of reaction: 1 mmole AB and 50 mg catalyst with 5 ml deionized water, 25 ºC., 600 rpm).

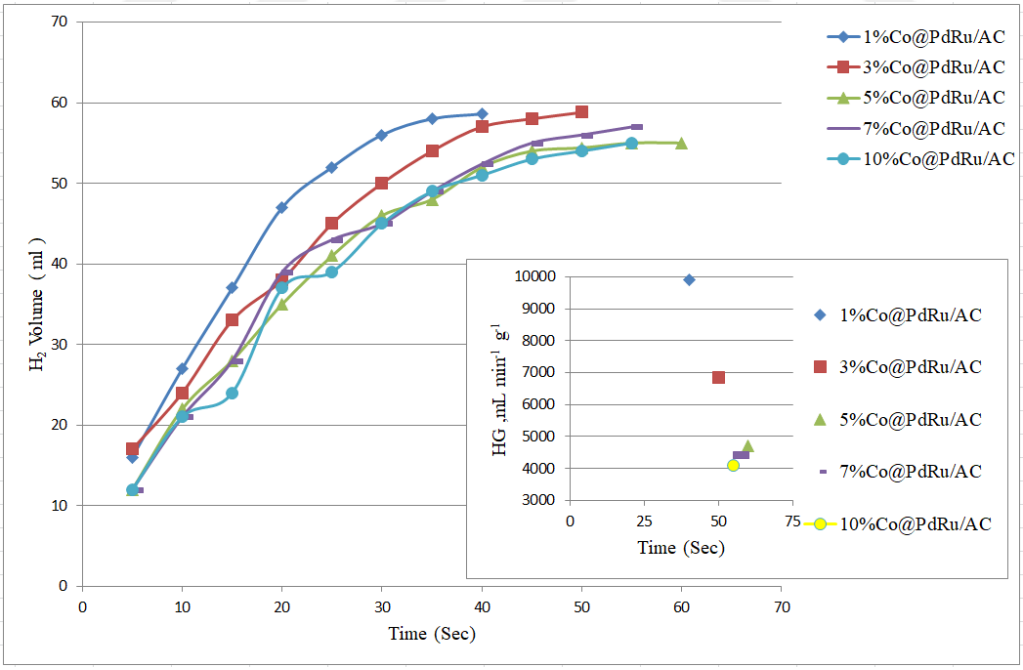

Figure 4.5b. Impact of various cobalt percentage catalysts on AB hydrolysis (Reaction condition: 1 mmole AB and 50 mg of catalysts with 5 ml deionized water, 25 ºC., 600 rpm).

4.4. Effect Amount of the Catalyst

So that to keep away from extra catalyst while looking at Generation of hydrogen proportions, their tests were inspected to assess the ideal catalyst stacking by changing the catalyst dose (PdRuCo/Ac) from 10 to 100 mg in 1% Ammonia borane arrangement by weight at 25°C.As can be seen from figure 4.6, as the quantity of catalyst rise the quantity of hydrogen substance per catalyst unit diminishes. Conceivable reason is that as the sum of catalyst increments, all dynamic catalyst surfaces are utilized at a steady Ammonia borane concentration. In this manner, since the hydrolysis carried out were in specific dynamic destinations of the catalyst, other dynamic locales are unworkable. The time to total the hydrolysis of Ammonia borane has reduced by increasing catalyst dose. The greatest hydrogen generation ratio was calculated as 9898.645 mL/min. g for 50mg PdRuCo/Ac catalyst.

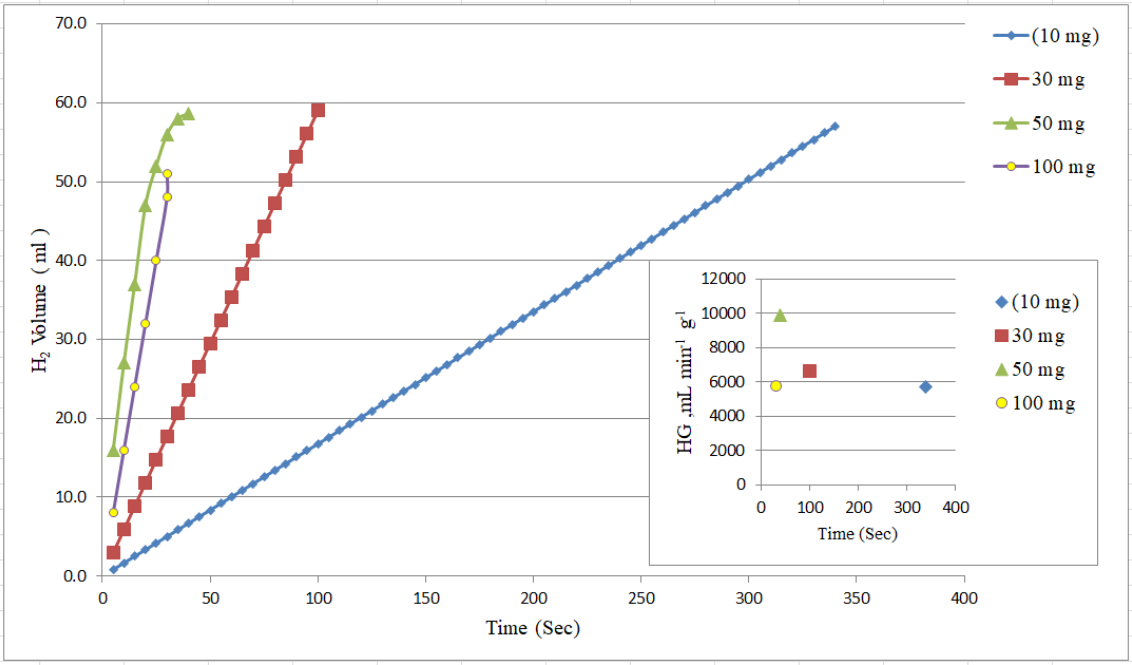

Figure 4.6. Effects of the amounts of catalyst on AB hydrolysis (Condition of reaction: 1 mmole AB in 5 mL of purified water, 25 °C, 600 rpm).

For each concentration of PdRuCo nanoparticles, the hydrogen production rate was determined from the slope calculated in the nearly linear portion of the graph.

Figure 4.7 shows the hydrogen production rate graph compared to the initial PdRuCo concentration, both on a logarithmic scale, giving a straight line with a slope of 1.02 showing that AB hydrolysis is first order according to PdRuCo concentration.

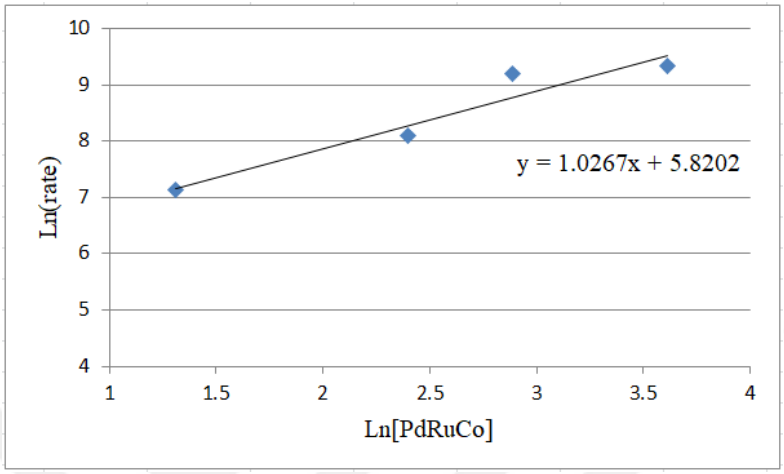

Figure 4.7. Hydrogen production rate graph against PdRuCo concentrations on the log scale for ammonia borane hydrolysis at various PdRuCo concentrations [PdRuCo] = 3.7, 11, 18, 37 mM, AB concentration = 1mmol=100mM at 25 °C.

4.5. The Effect of AB Concentrations on The Production of Hydrogen

With different initial AB concentrations, the effect of the AB concentration on the hydrogen production rate was examined (0.5, 3 mmole). Figure 4.8 displays a graph of H_2 volume against time for different ammonia borane concentrations. And viscosity of the solution rise with the beginning concentration ammonia borane. Hence, mass exchange of ammonia borane to the catalyst surface is restricted. Imore addition n expansion, an increment within the PH of concentrated solution encompasses a stabilizing impact driving to a diminish in hydrogen generation.The highest hydrogen generation ratio was gotten in 3mmole ammonia borane arrangement. In any case, in all tests the quantity of AB beginning solution was kept steady at 1 mmole, as a generally satisfactory esteem of hydrogen generation rate was accomplished in 1 mmole ammonia borane solution.

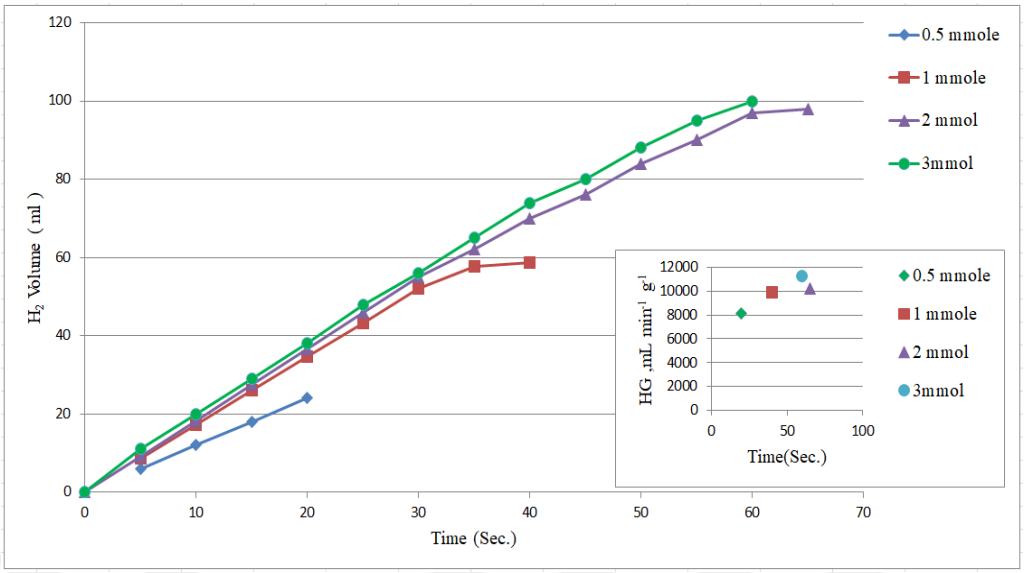

Figure 4.8. concentration of ammonia borane will affect the generationg of Hydrogen (condition of the reaction 50 mg catalyst, 25 °C, 600 rpm).

The line has a slope which fitted to the data of the experimental that appears in was so small illustratingthat the hydrolysis reaction will be considered as Zero order with respecting the concetrate of ammonia borane.

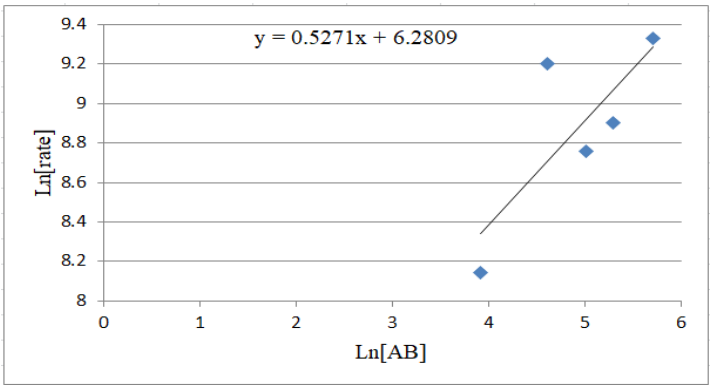

Figure 4.9. Hydrogen generation rate against AB concentrations on a log scale for hydrogenation of AB at different ammonia borane concentrations = 50, 100, 150,200,300 mM, catalyst qauantity PdRuCo = 50 mg at 25 degree Celsius °C.

Hence the Rate equation for Catalyzed hydrolysis of AB will be ;

$$-3[NH_3BH_3]/dt = d[H_2]/dt = k[\text{PdRuCo}] \qquad (4.1)$$

4.6. Hydrolysis Kinetics of PdRuCo/Ac Catalyst

The reaction rate was increased with an increase in the temperature of the reaction, as can be seen in Figure 4.10. The constant rate k value calculated from the linear parts of both the hydrogen volume graph against time were estimated at four different temperatures.

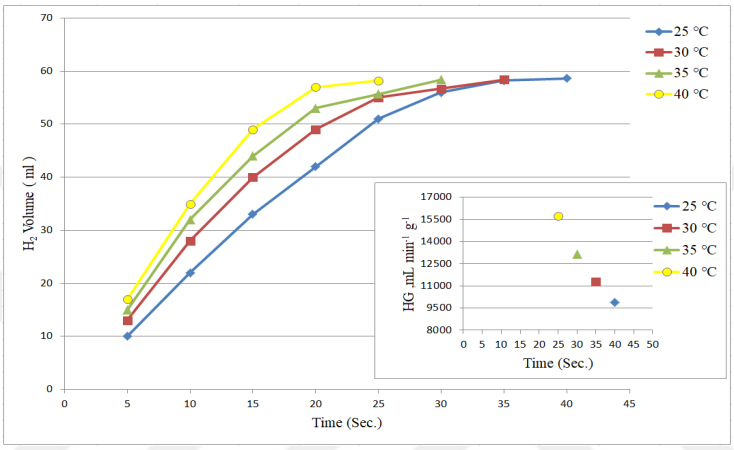

Figure 4.10. Graph of H_2 volume against time for the hydrolysis of AB in different temperatures, T = 25, 30, 35, 40 °C, the catalyst amount PdRuCo = 50 mg, the substrate concentration [AB] = 100 mM.

The value of the K constant rate was determined from the slope of the AB catalyzed hydrolysis rate of PdRuCo nanostructures. In Table 4.1, they are mentioned.

Table 4.1. Constants rates K for the hydrolysis AB catalyzed by PdRuCo nanostructures.

Temp. (°C)	Constant rates , k ($[NH_3BH_3].[molPdRuCo]^{-1}.s^{-1}$)
25	0.057216
30	0.059756
35	0.068086
40	0.083739

$$k = Ae^{-\frac{Ea}{RT}} \quad (4.2)$$

$$\ln k = \ln A - (Ea/\mathrm{RT}) \quad (4.3)$$

Temperature and K value were calculated by the Arrhenius Equation also Eyring equation to get the Enthalpy ,Energy also Entropy for the activation but at the begining shoul be used Arrhenius Equation for estimation.

$$k = Ae^{-\frac{Ea}{RT}} \quad (4.2)$$

There Ea and A are Constants properties of the reaction and Gas constant (R).but Ea is the ativation energy also A is exponetial factor (Lehninger et al., 2005).Taking the natural log. of "Eq 4.2.", showes "Eq 4.3." :

$$\ln k = \ln A - (Ea/\mathrm{RT}) \quad (4.3)$$

in addition Figure 4.11 gives the Arrhenius Graph, ln(k) against the corresponding (1/T) absolute temperature. The straight line slope shows Ea of 19.6 ± 1 kJ mol^{-1} for H2 production from the hydrolysis of ammonia borane catalyzed by PdRuCo nanostructures assisted on Ac.

Thus k is corresponded to the exponential of (1/T), unusual fluctuations in Temp. Will make greater deviations in the rate at lower Temp. anyhow any rising in the temp. Will decrease the standard deviation as seen in Figure 4.11.

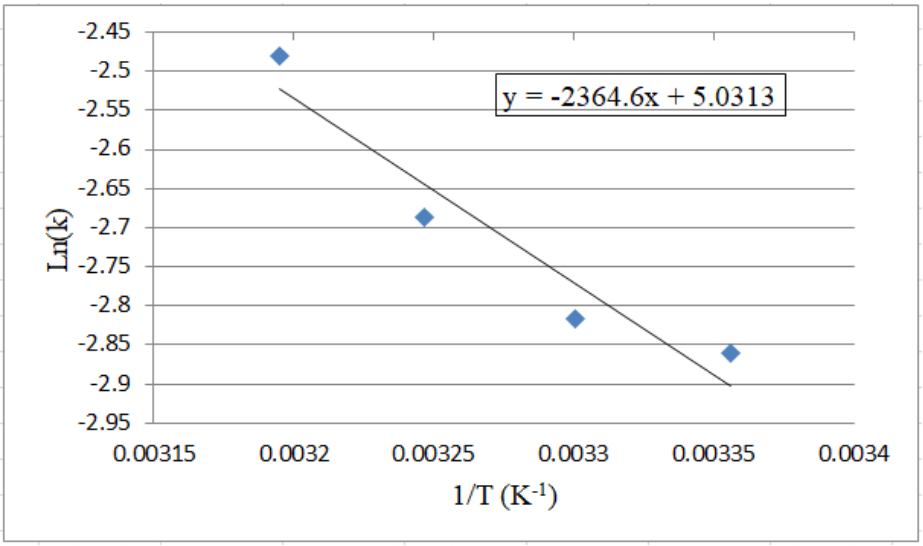

Figure 4.11. For the hydrolysis of AB catalysed by PdRu/Ac@Co nanostructures in the temperature range, the Arrhenius graph, lnk versus corresponding absolute temperature 1/T, is 25 – 40 degree Celsius °C.

$\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ was calculated from the Eyring equation, Equation 4.4, by plotting the graph of ln(k/T) versus (1/T),

$$Ln\left(\frac{K}{T}\right) = Ln\left(\frac{\mathrm{Kb}}{h}\right) + \frac{1}{T}\left(-\frac{\Delta \mathrm{H}\ddagger}{R}\right) + \frac{\Delta \mathrm{S}\ddagger}{R} \qquad (4.4)$$

The Eyring graph, ln(k/T) against corresponding absolute temperature (1/T), is shown in Figure 4.12. The straight line slope provides an activation enthalpy of 17.12 ± 1 kJ/mol and also the intercept provides an activation entropy of -184.8 ± 3 J/ mol.K. The low activation enthalpy value as well as the lage activation entropy negative value are representative of an associative process for catalyzed AB hydrolysis of PdRuCo nanostructures, consistent with the mechanism proposed in the literature for the hydrolysis of ammonia borane (D'Ulivo, 2011).

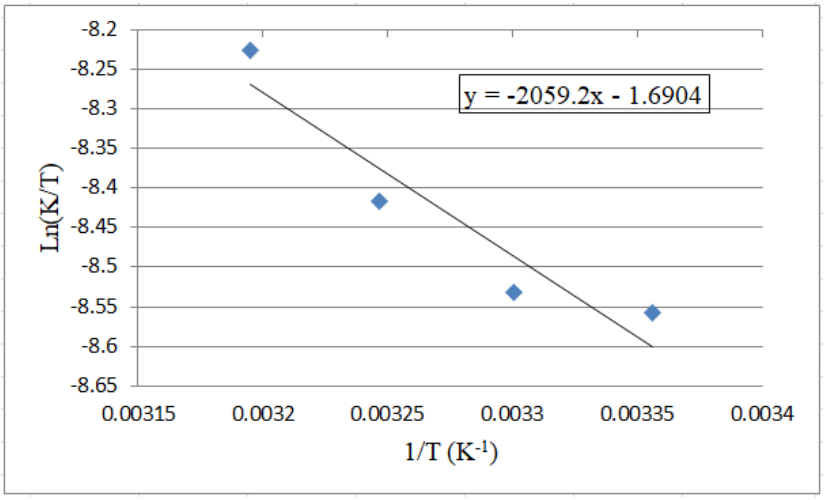

Figure 4.12. For the hydrolysis of AB catalyzed by PdRu/Ac@Co nanostructures in the range of temperature 25 - 40 degree Celsius , Erying graph, ln (k/T) against corresponding absolute temperature 1/T.

4.8. PdRuCo/Ac Reusability

The reusability of the (PdRuCo/Ac) catalyst in ammonia borane hydrolysis were tested by determining the amount of generation of hydrogen throughout the serial run of the experiment, as can be seen in Figure 4.13. therefore, for this reason, the test was initiated with a 20 mL aqueous nanostructures catalyst solution containing 30 mg PdRuCo/Ac with 30.8 mg ammonia borane (1 mmole= 100 mM) at 25 degree Celsius The catalyst were separated from the reaction solution through centrifugation after the release of stoichiometric hydrogen gas (3.0 mol H2/mol ammonia borane) and washed with 30 ml distilled water. In 5mL water with 30.8mg (1mmol=100 mM) of the ammonia borane, the separated catalyst was redispersed Hydrolysis were initiated and the release of hydrogen was registered at 25 ^{o}C. Throughout 6 experiments, this process was replicated and the results were evaluated as percentage of PdRuCo/Ac initial Ac's catalytic activity in the consecutive ammonia borane hydrolysis. The hydrogen generation value did not alter dramatically between the 1st and 2nd catalytic cycles. Throughout the catalytic cycles beginning from the first catalytic cycle, the explanation for the decrease in the generation of hydrogen value after the 2nd cycle was noticed to be the reason that the catalyst reduced its activity due to the catalyst surface closure.

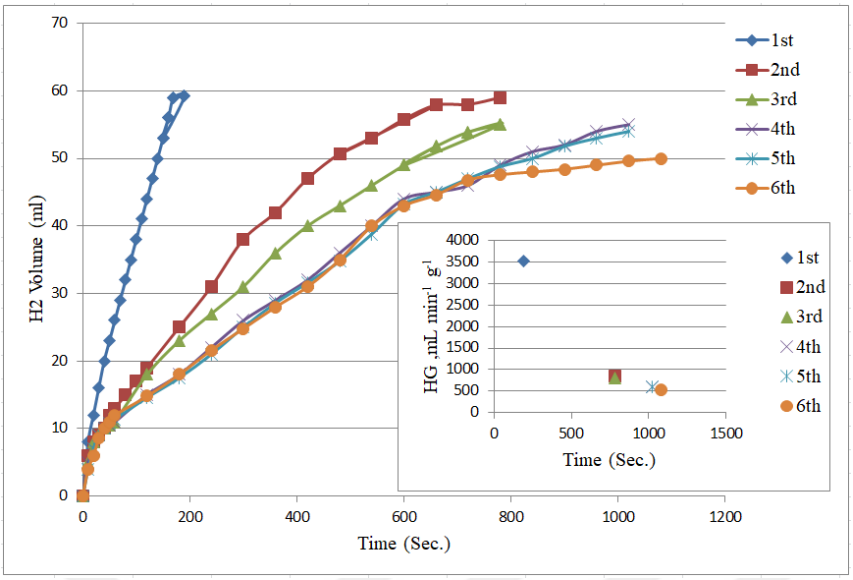

Figure 4.13. Catalytic hydrolysis re - usability of ammonia borane across PdRuCo/AC.

4.9. NaOH Concentration Effects

Fig.4.14 shows that the amount of hydrogen generation varies with distinct NaOH concentrations, i.e. 0 wt percent, 1 wt percent, 2 wt percent, and 3 wt percent, 4 wt percent, 5 wt percent, with 50 mg of PdRuCo/Ac complicated catalyst, on hydrogen output volume at 25 ^{o}C in 1 percent AB. To retain the stabiliser. Nonetheless, through our research, the concentration of NaOH substantially affects the production of hydrogen. The hydrogen production rate provides a high at the NaOH concentration of 0wt percent, that is without NaOH addition, and subsequently decreases with more increasing within NaOH concentration. The hydrogen production rate decreased significantly when the NaOH concentration rose to 1 percent. As NaOH increases, the rate production of hydrogen eventually decreases. The feasible explanation is that the hydroxyl ion is included in H_3NBH_3 hydrolysis. The hydrolytic compounds NH_4+BO_2.nH_2O and $NH_4B(OH)_4$ were deposited on the catalyst's surface at high NaOH concentrations, which further prevented the production of hydrogen. In another case, the catalyst surface was occupied by several OH- anions rather than BH_3- anions, thereby preventing further generation of hydrogen.

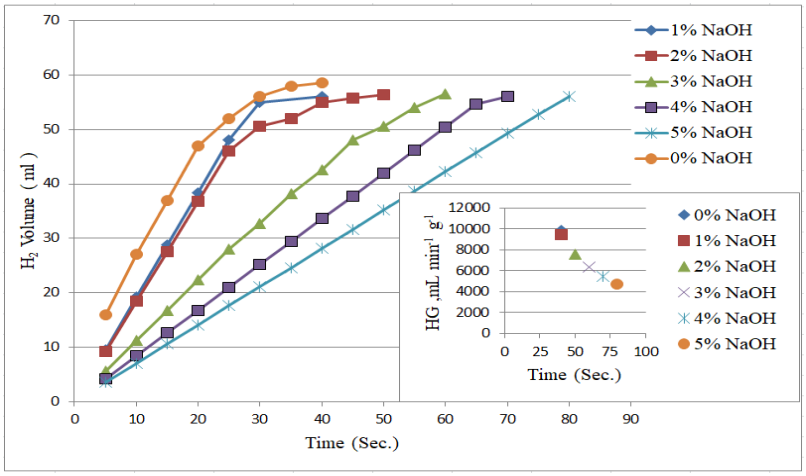

Figure 4.14. The impact of the concentration of NaOH on the rate of hydrogen production.

5. CONCLUSSION

The key results related to the producing with characterization of Pd0.5Ru0.5/Ac@1%Co nanostructures assisted on activated carbon as well as their catalytic activity throughout the generation of hydrogen achieved AB's hydrolysis can also be summed up as follows:

- Pd, Pd0.5Ru0.5/Ac also Pd0.5Ru0.5/Ac@1%Co using the chemical reduction method with sodium borohydride solution, nanostructures assisted by AC were prepared.
- PdRuCo nanostructures assisted by AC are really a highly effective catalyst in the production of hydrogen from AB hydrolysis, generating a highest HG value of 9898.645 ml/g.min at 25 ^{o}C related to activated carbon assisted Pd and PdRu catalysts. The catalytic behavior was observed while the hydrogen production was examined through PdRuCo/AC > PdRu/AC > Pd/AC.
- At ambient temperature, the resulting AC assisted PdRuCo nanostructures show high catalytic activity for the hydrolysis of AB with an original TOF of 312.8 h^{-1}.
- When the catalyst was examined for repeatability throughout the dehydrogenation of AB, the catalyst produced 3 mol of H_2 / mole of AB though in the sixth test.
- The findings of the kinetic analysis on the production of hydrogen through AB dehydrogenation showed that the hydrolysis reaction is 0.5th order and also the activation energy for the producing hydrogen catalyzed by Pd0.5Ru0.5/Ac@1%Co reaches 26.836 kJ/mol.

Pd0.5Ru0.5/Ac@1%Co has been observed to be an extremely effective and durable catalyst for the generation of hydrogen from AB dehydrogenation, taking into account the data obtained above. It can be deduced that the catalyst design and also the catalyst atomic ratios play a key role throughout the PdRuCo/Ac dehydrogenation of AB. In addition, at the optimum synthesis of K_2PdC_{l4}, $COCl_2.6H_2O$ and $RuCl_3$ as precursor salts, the catalyst addition amount at 50 mg with AB concentration 1 mmol, we therefore generated a non-precious transition metal of Co, Ru with intense impact

for dehydrogenation of AB. The good understanding of active places also the association of synthesis-composition-completion will show us the way to achieve greater activity also extra stability of PdRuCo/Ac chemical agent.

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EXTENDED TURKISH SUMMARY
(GENİŞLETİLMİŞ TÜRKÇE ÖZET)

HİDROJEN ÜRETİMİ ÜZERİNE AKTİF KARBON DESTEKLİ Pd-Ru KATALİZÖRLERİNİN MONO VE BİMETALİK ETKİLERİ

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Bu çalışmada, aktif karbon (AC) destekli paladyum, ruthenium ve kobalt nanopartikül (PdRu / AC @ Co) katalizörleri sodyum borohidrürün ($NaBH_4$) in situ indirgenmesi ile hazırlanmış gibi çeşitli tekniklerle karakterize edilmiştir. , taramalı elektron mikroskobu (SEM) ve enerji dağılımlı X-ışını spektroskopisi (EDX), ve X-ışını Fotoelektron Spektroskopisi (XPS). PdRu / AC @ Co katalizörü, düşük sıcaklıklarda bile amonyak boranın (AB) hidrolizinde aktiftir. Mono- (Pd) ve bi-metalik (PdRu) nanopartiküller ile karşılaştırıldığında, bu trimetalik (PdRu @ Co) yapı, AB hidrolizi için büyük ölçüde artmış katalitik aktivite gösterdi. 25 ºC, 1 mmol AB ve 50 mg PdRu / AC @ Co katalizöründe yapılan deneyde hidrojen üretim hızı (HG) 9898.65 mL min-1g-1 olarak belirlendi. AB'nin katalitik hidrolizinde aktivasyon parametreleri (Ea, ΔH ve ΔS) sırasıyla 19.6 kJ/mol 17.12kJmol-1 ve -184.85 J/mol.K elde edildi. Ayrıca çalışma, Pd0.5Ru0.5/AC@1%Co'nun (Pd: Ru: Co atomic ratio = 5: 5 & 1%) 312,8 h-1 toplam devir frekansı (TOF) değerini gösterdiğini göstermiştir.

Anahtar kelimeler: Aktif karbon, Amonyak boran, Hidrojenö Hidroliz, Palladyum kobalt rutenyum nanopartiküller.

1. GİRİŞ

Zamanın başlangıcından beri insanlar, kömürün daha yüksek kalori değerine sahip yeni bir yakıt kaynağı olarak keşfedilmesinden önce kendilerini sıcak tutmak ve pişirmek için yakacak odun kullandılar. Fosil yakıt, karbon bazlı enerji kaynaklarının birikmesi sonucunda doğal bir süreçle oluştu ve giderek dünyanın enerji talebinin yaklaşık% 80'ini karşılamak için kullanıldı. Doğal gaz, kömür ve petrol gibi fosil yakıtların dünya çapında artan enerji ihtiyacı nedeniyle azalacağı tahmin edilmektedir. Bu, kaynakların çoğunun aşırı kullanılacağı ve önümüzdeki birkaç on yıl içinde kıtlık olacağı anlamına gelir (Midilli et al., 2005).

Küresel ısınmanın çevre sorunlarıyla ilgili artan endişeler nedeniyle, diğerleri arasında biyokütle enerjisi, rüzgar enerjisi, güneş enerjisi ve güç teknolojileri gibi diğer yenilenebilir enerji kaynaklarını keşfetme ihtiyacı vardır. Küresel ısınma, fosil yakıtın yanmasıyla ortaya çıkan gazdan kaynaklanır ve sonuç olarak deniz seviyelerinde yükselmeye neden olarak su kütlelerine bitişik şehirleri sel, kasırgalar ve hatta orman yangınları riskiyle karşı karşıya bırakır(Thomas et al., 2004; Armaroli and Balzani, 2011).

Hidrojen, amonyak ve rafine yakıtları hidro-kırma ve diğer bazı kimyasallarla üreten bir süreç aracılığıyla, kimya ve petrokimya endüstrisinde hammadde olarak büyük ölçüde kullanılmıştır. Hidrojen, hidrojenle çalışan araçlar ve diğer arabalarda kullanılmasının yanı sıra roketler için itici gaz ve uzay mekiği gibi çeşitli kullanımlar için de kullanılabilir (Armaroli and Balzani, 2011).

Kimyasal hidrojen depolaması, nispeten yüksek hacimsel ve gravimetrik hidrojen yoğunluğu nedeniyle katı halde hidrojen depolama malzemesi olarak bulunan bor hidrür bileşiklerini içeren yüksek hidrojen içeriği nedeniyle ilgi çekmiştir (Züttel, 2003; Züttel, 2004). Amonyak boran (H_3NBH_3, AB), ağırlıkça 19.6'lık yüksek bir hidrojen içeriğine sahip olduğundan, hidrojen depolama malzemesi olarak özel bir odak noktası verilmiştir. Yakıt hücresi çalışma koşullarında% stabilite ve güvenlik (Marder., 2007; Stephens and Baker, 2007).

Hidroliz işleminde amonyak bir katalizör ile birleştirildiğinde, boranı, 25 ° C'de -156 kJ / mol'lük standart bir entalpi değişimi ile ekzotermik bir reaksiyonda serbest bırakır (Schlesinger ve diğerleri, 1953).

$$NH_3BH_3(aq)+H_2O(l) \xrightarrow{\text{Catalyst}} NH_4BO_2(aq)+3H_2(g) \quad (1.1)$$

Amonyak boranın hidrolizi, hidrojen üretme çabasıyla bir katalizör olarak geçiş metalleri ve bunların alaşımları ile test edilmiştir. (Chandra ve Xu., 2006; Kalidindi ve diğerleri, 2008). Yürütülen kapsamlı araştırmalar, uygun metalden oluşan bir katalizörün çeşitli konsantrasyonlarda bir çözelti içine yerleştirildiğinde, ağırlıkça% 8.9'a karşılık gelen 3.0'a kadar bir H_2: NH_3BH_3 mol oranına sahip bir hidrojen gazı salımına yol açtığını gösteriyor gibi görünmektedir başlangıç malzemeleri NH_3BH_3 ve H_2O (Özkar, 2013).

2. MATERYAL VE YÖNTEM

2.1. Materyal

2.1.1. Kullanılan Kimyasallar

Çalışmalarda kullanılan kimyasallar maddeler ve temin edildikleri firmalar aşağıda verilmiştir.

- Potasyum tetrakloropalladat (K_2PdCl_4) % 99.99 - ALFA AESAR
- Kobalt (II) klorür ($CoCl_2.6H_2O$) % 98 -SIGMA ALDRİCH
- Rutenyum (III) (RuCl3.3H2O)% 99,9 - SIGMA ALDRICH
- Amonyak boran % 97 - SIGMA ALDRICH
- Sülfürik asit % 97 –CHEM-LAB

2.2. Deneysel Çalışmalar

2.2.1. Katalizörün Hazırlanması

Bu analizde katalizörlerin hazırlanmasında kimyasal indirgeme yöntemi kullanılmıştır. Pd / AC, PdRu / AC ve PdRuCo / AC katalizörleri, sodyum borohidrit (NaBH4) indirgeme yöntemleri ile K2PdCl4, Ruthenium (III) ($RuCl_{3.3}H_2O$) ve $CoCl_{26}H_2O$ metal öncü tuzları kullanılarak sentezlendi. Destek bileşeni olarak aktif karbon (AC) kullanılmıştır.

Yine Pd / AC katalizörü için 0,0307 g K_2PdCl_4, 10 mL deiyonize su içinde çözündürüldü, ardından bu çözeltiye 0,1 g aktif karbon (AC) ilave edildi. Bu karışımın ultrasonik banyoda 60 dakika ve normal mikserde 60 dakika oda sıcaklığında karıştırılmasına izin verildi. Bu nedenle, metal miktarının 10 katı NaBH4 ilave edilerek karışım, deiyonize su ile yıkandı ve indirgeme yapıldıktan sonra 85 ° C'de vakumlu bir fırında kurutuldu.

Benzer şekilde Ru / AC ve PdRu / AC @ yüzde 1 Co katalizörleri, deiyonize su içinde 0.0192 g ($RuCl_{3.3}H_2O$) ve 0.022 g $CoCl_{2.6}H_2O$ metal tuzlarında çözündürüldü ve $NaBH_4$'e indirgendi. Bol su ile temizlendi ve 85 ° C'de vakumlu fırında kurutuldu.

Ayrıca, ortamda bulunan metale ikinci bir metalin eklenmesinin hidroliz reaksiyonu üzerindeki etkisini incelemek için PdRu / AC katalizörü sentezlendi. PdRu / AC katalizörü, 0.0307 g K_2PdCl_4 ve 0.0192 g $RuCl_3.{}_3H_2O$ metal tuzlarını 10 mL deiyonize suda çözdükten sonra, ortama 0.1 g aktif karbon uygulandı. Ürün ultrason banyosunda ve standart bir karıştırıcıda tutulduktan sonra ortama NaBH4 uygulandı ve ardından indirgeme, rafine etme, durulama işlemleri yapıldı.

Sonunda PdRu / AC @ Co nano katalizörleri, PdRu sabit atomik oranlı Kobalt miktarını sürekli değiştirerek sentezlendi. (Pd0.5Ru0.5/AC@1 % Co, Pd0.5Ru0.5 / AC @ 3% Co, Pd0.5Ru0.5 / AC @ 5% Co, Pd0.5Ru0.5 / AC @ 7% Co, Pd0.5Ru0.5/AC@10%Co) metal tuzları 10 mL distile suda çözüldükten sonra eklenmiştir. Nihai ürün, oda sıcaklığında 2 saat karıştırıldı ve 2 saat karıştırıldıktan sonra sulu NaBH4 çözeltisi, damla damla uygulandı ve bir saat daha karıştırıldı. İndirgeme işleminin sonunda, katalitik konvertör bol su ile temizlendi, saflaştırıldı ve yaklaşık 85 ºC'de vakumlu bir fırında kurutuldu.

2.3. Hidrojen Üretim Testi

Yayılan hidrojen miktarı, suyla yer değiştirme işlemi kullanılarak bir laboratuvar cihazı kullanılarak belirlendi. Kısaca, 1 mmol (30,8 mg) AB'nin (25 ° C, 0,908 atm basınç ve 80,7 mL'nin altında) en yüksek potansiyel hidrojen miktarına eşdeğer 3 mmol gaza sahip bir çözelti, daha sonra bir termostatik su banyosunda dengelendi, ardından 50 mg katalizör, bir reaksiyon şişesine 5 mL saflaştırılmış su içinde dağıtıldı ve reaksiyon çözeltisi 600 rpm'de karıştırıldı AB'nin hidrolizi hemen başladı. Tekrarlanan testlerde elde edilen sonuçlar santrifüjlendi ve su ile çeşitli zamanlarda saflaştırıldı ve temizlendi.

2.4. Katalizörün Karakterizasyonu

Bileşiklerin kristal yapılarının XRD kırınım eğilimleri, CuK5-007 radyasyonu (40 kV, 20 mA) ile donatılmış bir Rigaku X-ışını difraktometresi D / max-220 / PC ile bildirilmiştir. SEM ve EDX analizleri, toplanan maddenin morfolojisini ve yapısını araştırdı. SEM görüntüleri, buna göre 20 ve 10 kV hızlanma hızlarında çalışan FEI ZEISS SIGMA 300 mikroskoplarında

yakalandı.200 kV'de kullanılan Hitachi H-8000 transmisyon elektron mikroskobu (TEM), hazırlanan örneklerin morfolojisini ve ölçeğini değerlendirmek için düzenli mikrograflardan oluşan bir mikroskopi elde etmek için enerji dağıtıcı bir X-ışını dedektörü ile donatılmıştır. Katalitik yüzey üzerindeki Pd, Ru ve Co'nun elektron bağlama yapıları, Specs-Flex elektron spektrometresi ve X-ışını fotoelektron spektroskopisi (XPS) kullanılarak incelenmiştir.

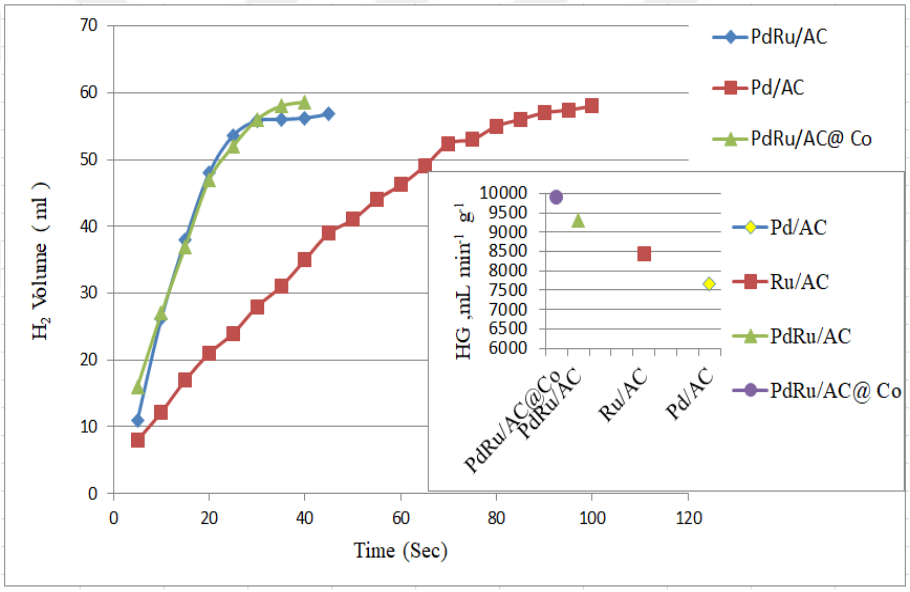
2.5. Aktif Karbonda Desteklenen PdRu / Ac @ Co Nanopartiküllerle Katalize Edilmiş Amonyak Boran Hidrolizinin Kinetiği

Aktif karbona dayalı PdRu / Ac @ Co nanopartikülleri kullanarak NH3BH3 katalitik hidroliz hız kuralını oluşturmak için, bölümde tanımlananla aynı şekilde üç farklı deney seti gerçekleştirildi. Amonyak boranın hidrolizinde aktif karbona dayalı PdRu / Ac @ Co nanopartiküllerinin katalitik davranışını bulmak. İlk test serisinde, hidroliz reaksiyonları, oda sıcaklığında (25.0 ± 0.1 °C) değişen başlangıç miktarlarında PdRu / Ac @ Co (10, 30, 50, 100 mg) ile başlarken, amonyak boranın başlangıç konsantrasyonları 100'de sabit kalmıştır. mM (30,8 mg = 1,00 mmol). İkinci test grubu, orijinal PdRu / Ac @ Co'nun 50 mg'da stabil tutulması ve NH_3BH_3 yoğunluğunun (50, 100, 150, 200 ve 300 mM) değiştirilmesiyle oda sıcaklığında (25.0 ± 0.1 ° C) gerçekleştirildi. Sonunda, amonyak boran hidrolizi, tutarlı katalizör (50 mg) ve substrat (100 mM) konsantrasyonlarında ve aktivasyon enerjisini (Ea), entalpi (ΔH) ve entropi (ΔS).

3. SONUÇLAR VE TARTIŞMA

3.1. Tek, Çift ve Üç Metal AC Bazlı Katalizörlerin Karşılaştırılması

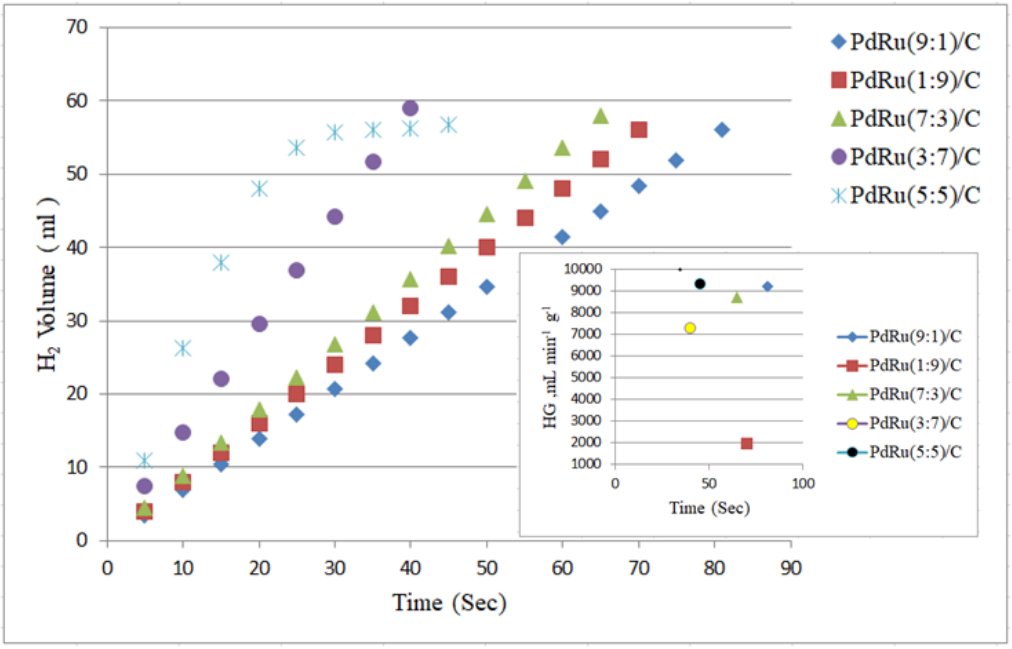
Tekli, çiftli ve üçlü metal bazlı katalizörlerin AB'nin hidrolizi üzerindeki etkisi Pd / Ac, PdRu / Ac ve PdRuCo / Ac nanopartiküller ile incelenmiştir. 10 ml 1 mmol AB çözeltisinin hidrolizinde 50 mg katalizör kullanıldı. Pd / Ac, PdRu / Ac ve PdRuCo / Ac nanopartiküller tarafından katalize edildiğinde, AB hidrolizi için hidrojen hacminin zamana karşı değişimi (şekil 3.1) 'de gösterilmektedir.



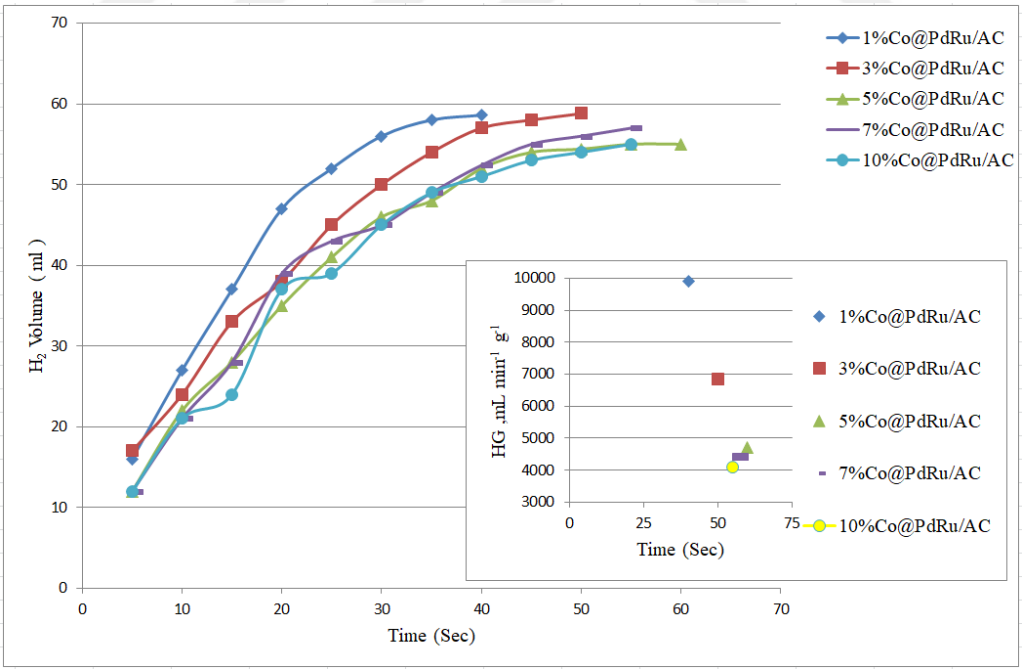
Şekil 3.1. Ac destekli tek, çift ve üçlü metal katalizörlerin AB'nin hidrolizi üzerindeki etkisi (Reaksiyon koşulu: 5 mL saf su içinde 1 mmol AB ve 50 mg katalizör, 25 °C, 600 rpm).

3.2. Farklı Molar Hız Etkisi

Katalizörlerin molar oranının etkisi, AB'nin hidrolizini büyük ölçüde etkiler. AB'nin sıvı fazdaki dehidrojenasyonunun farklı metal oranlarına sahip katalizörler kullanılarak belirlenmesi amaçlanmıştır.



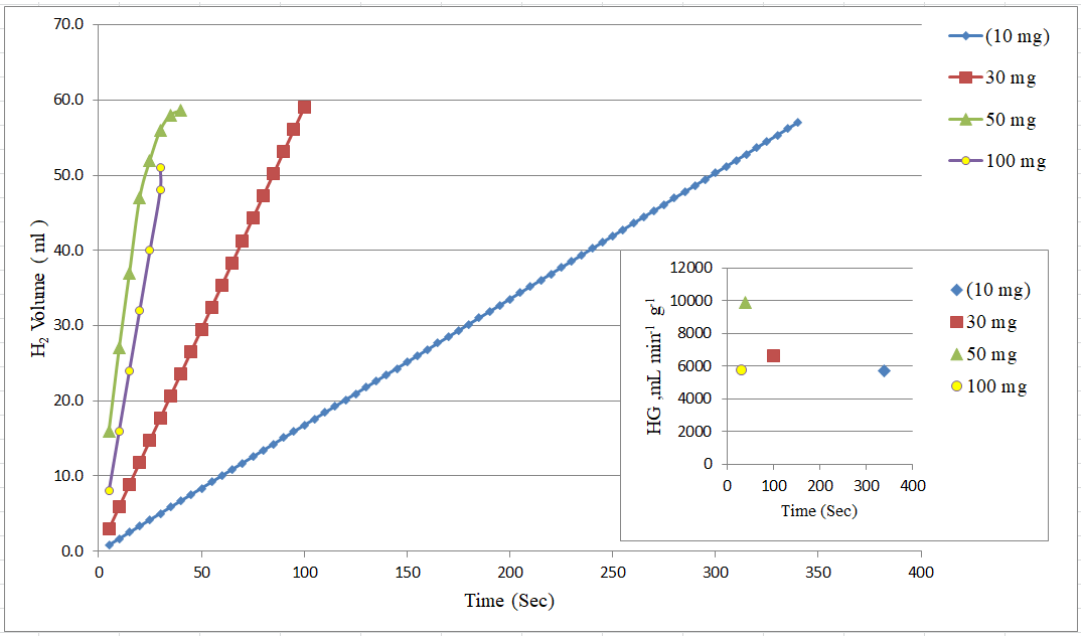
Şekil 3.2a. Katalizörün atomik oranının AB hidrolizi üzerindeki etkisi (Reaksiyon koşulu: 1 mmol AB ve 5 mL damıtılmış suda 50 mg katalizör, 25 ° C, 600 rpm).



Şekil 3.2b. Farklı kobalt yüzdesi kullanmanın AB hidrolizi üzerindeki etkisi (Reaksiyon koşulu: 1 mmol AB ve 5 mL damıtılmış suda 50 mg katalizör, 25 °C, 600 rpm).

3.3. Katalizörün Etki Miktarı

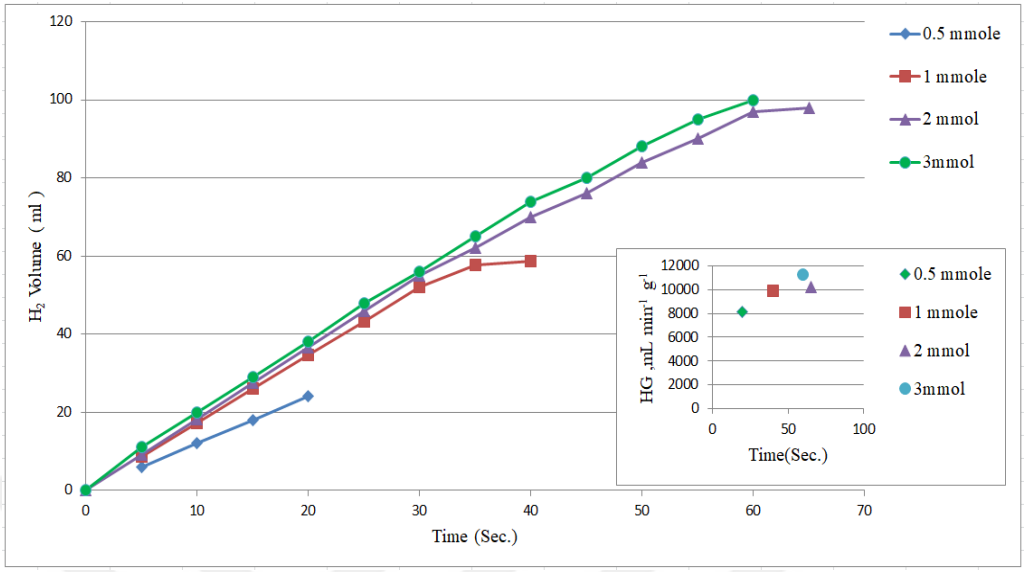
HG oranlarını incelerken fazla katalizörden kaçınmak için, 25ºC'de ağırlıkça% 1 AB çözeltisi içinde 10 ila 100 mg katalizör dozajını (PdRuCo / Ac) değiştirerek optimum katalizör yüklemesini değerlendirmek için deneyleri incelenmiştir.



Şekil 3.3. Katalizör miktarının AB hidrolizi üzerindeki etkisi (Reaksiyon koşulu: 5 mL distile su içinde 1 mmol AB, 25 ° C, 600 rpm).

3.4. AB Konsantrasyonunun Hidrojen Üretimine Etkisi

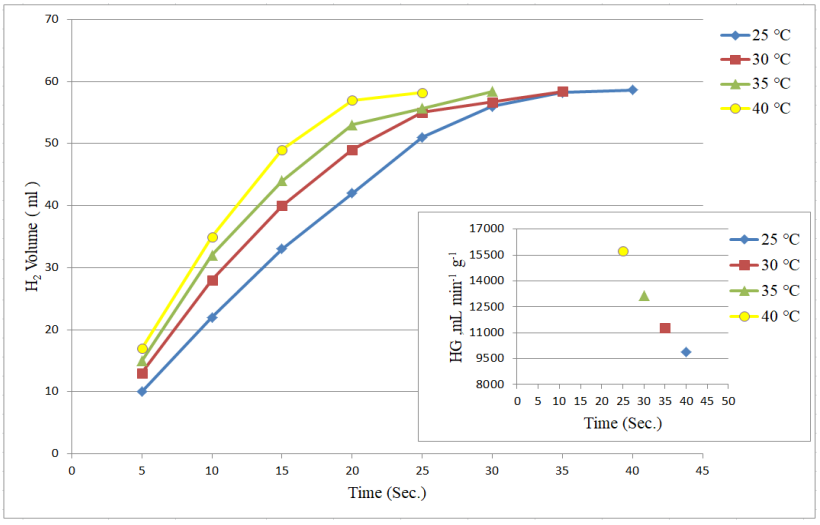
AB konsantrasyonunun hidrojen üretim hızı üzerindeki etkisi, çeşitli başlangıç AB konsantrasyonları (0.5, 3 mmol) ile araştırıldı. Çeşitli AB konsantrasyonları için zamana göre hidrojen hacmi grafiğini gösterir (şekil 3.4).



Şekil 3.4. AB konsantrasyonunun hidrojen üretimi üzerindeki etkisi (Reaksiyon koşulu: 50 mg katalizör, 25 °C, 600 rpm).

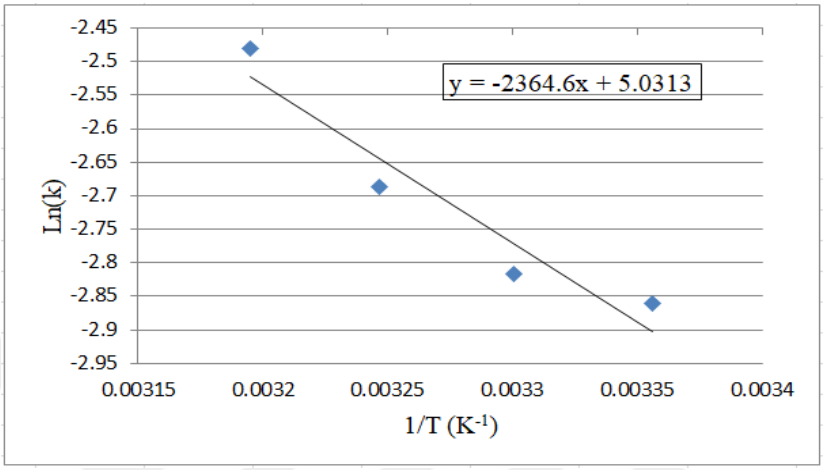
3.5. PdRuCo / Ac Katalizörünün Hidroliz Kinetiği

Şekil 3.5'de gösterildiği gibi, reaksiyon sıcaklığında bir artış ile reaksiyon hızı hızlandırılmıştır. Hidrojen hacmi grafiğinin doğrusal bölümlerinden zamana karşı farklı dört sıcaklıkta belirlenen hız sabiti k değerleri belirlendi.



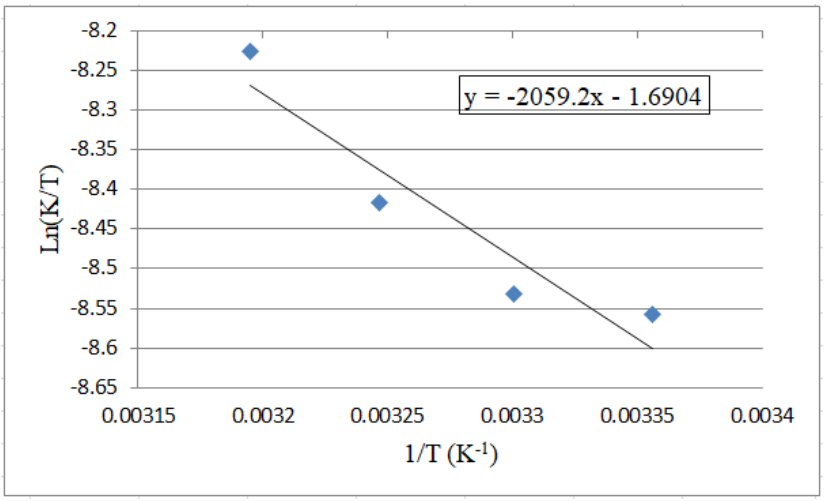
Şekil 3.5. Çeşitli sıcaklıklarda amonyak boranın hidrolizi için H2 hacmine karşı zaman grafiği, T = 25, 30, 35, 40 °C, katalizör miktarı PdRuCo = 50 mg, substrat konsantrasyonu [NH3BH3] = 100 Mm.

Ayrıca Şekil 3.6, Arrhenius grafiğini, ln (k) ile karşılıklı mutlak sıcaklığa (1 / T) karşı gösterir. Düz çizginin Slpoe'si, Ac üzerinde desteklenen PdRuCo nanopartikülleri tarafından katalize edilen AB'nin hidrolizinden hidrojen üretimi için 19.6 ± 1 kJ mol-1 aktivasyon enerjisi verir.



Şekil 3.6. Sıcaklık aralığında PdRu / Ac @ Co nanopartikülleri tarafından katalize edilen amonyak boranın hidrolizi için Arrhenius grafiği, lnk karşılıklı mutlak sıcaklık 1 / T'ye karşı 25 - 40 ° C'dir.

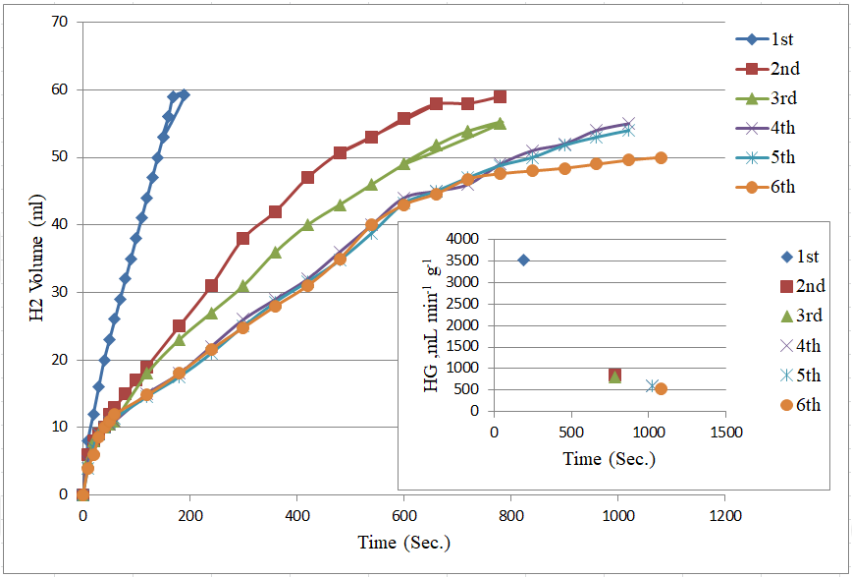
Şekil 3.7, karşılıklı mutlak sıcaklığa (1 / T) karşı göz halkası grafiğini, ln (k / T) gösterir. Düz çizginin eğimi, 17.12 ± 1 kJ mol-1'lik bir aktivasyon toplu ısısı verir ve kesişim, -184.8 ± 3 J (mol.K) -1 aktivasyon entropisini verir.



Şekil 3.7. 25 - 40 ° C sıcaklık aralığında PdRu / Ac @ Co nanopartikülleri tarafından katalize edilen amonyak boranın hidrolizi için Erying grafiği, ln (k / T) karşılıklı mutlak sıcaklık 1 / T'ye karşı.

3.7. PdRuCo / Ac'nin Yeniden Kullanılabilirliği

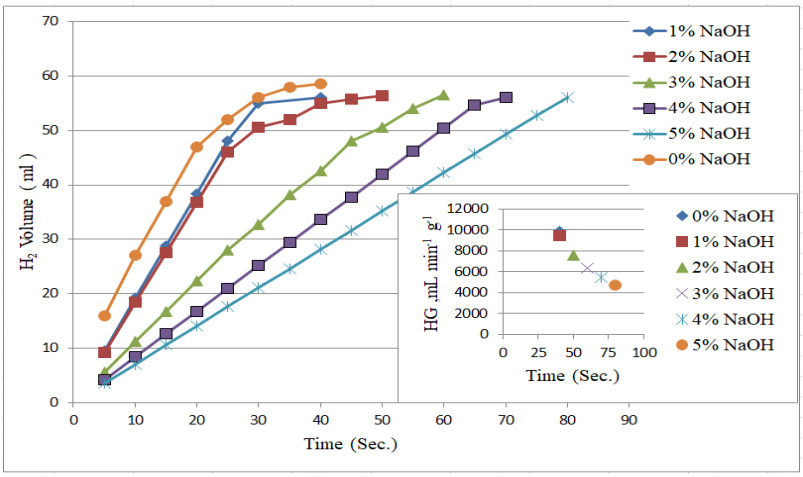
AB'nin hidrolizinde katalizörün (PdRuCo / Ac) yeniden kullanılabilirliği, (Şekil 3.8) 'de gösterildiği gibi deneyin ardışık çalışması sırasında hidrojen üretim hızı ölçülerek test edildi.



Şekil 3.8. AB'nin PdRuCo / AC üzerinden katalitik hidrolizinin yeniden kullanılabilirliği.

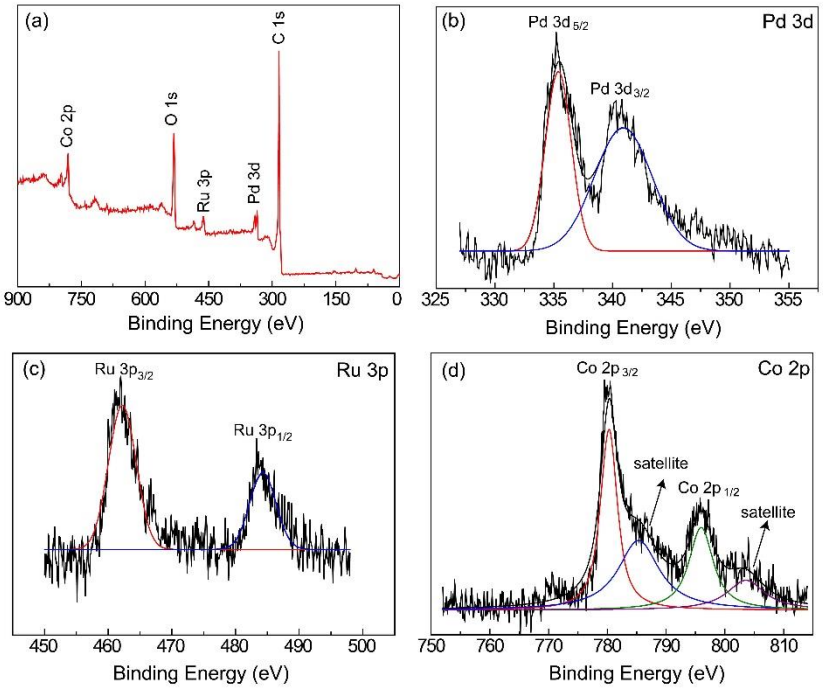
3.8. NaOH Konsantrasyonunun Etkisi

Şekil 3.9, hidrojen üretim hacminin farklı NaOH konsantrasyonu ile değiştiğini göstermektedir, yani 1'de 25 oC'de hidrojen üretim hacmine göre ağırlıkça% 0, ağırlıkça% 1, ağırlıkça% 2 ve ağırlıkça% 3, ağırlıkça% 4, ağırlıkça% 5 50 mg PdRuCo / Ac kompleks katalizörü ile% AB.



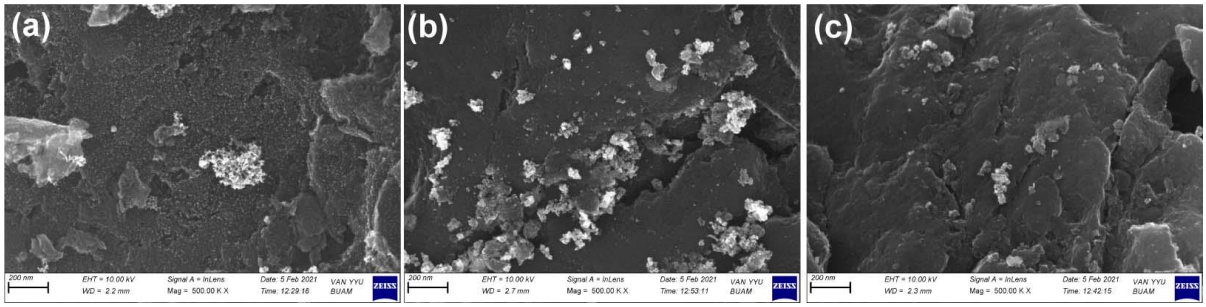
Şekil 3.9. NaOH konsantrasyonunun hidrojen üretim hızına etkisi.

Hazırlanan katalizörün (PdRuCo / C) yüzey bileşimi ve elemenatal durumları x-ışını fotoelektron spektroskopisi ile incelenmiştir (Şekil 12). PdRuCo / C anket taraması XPS spektrumunda gösterildiği gibi.



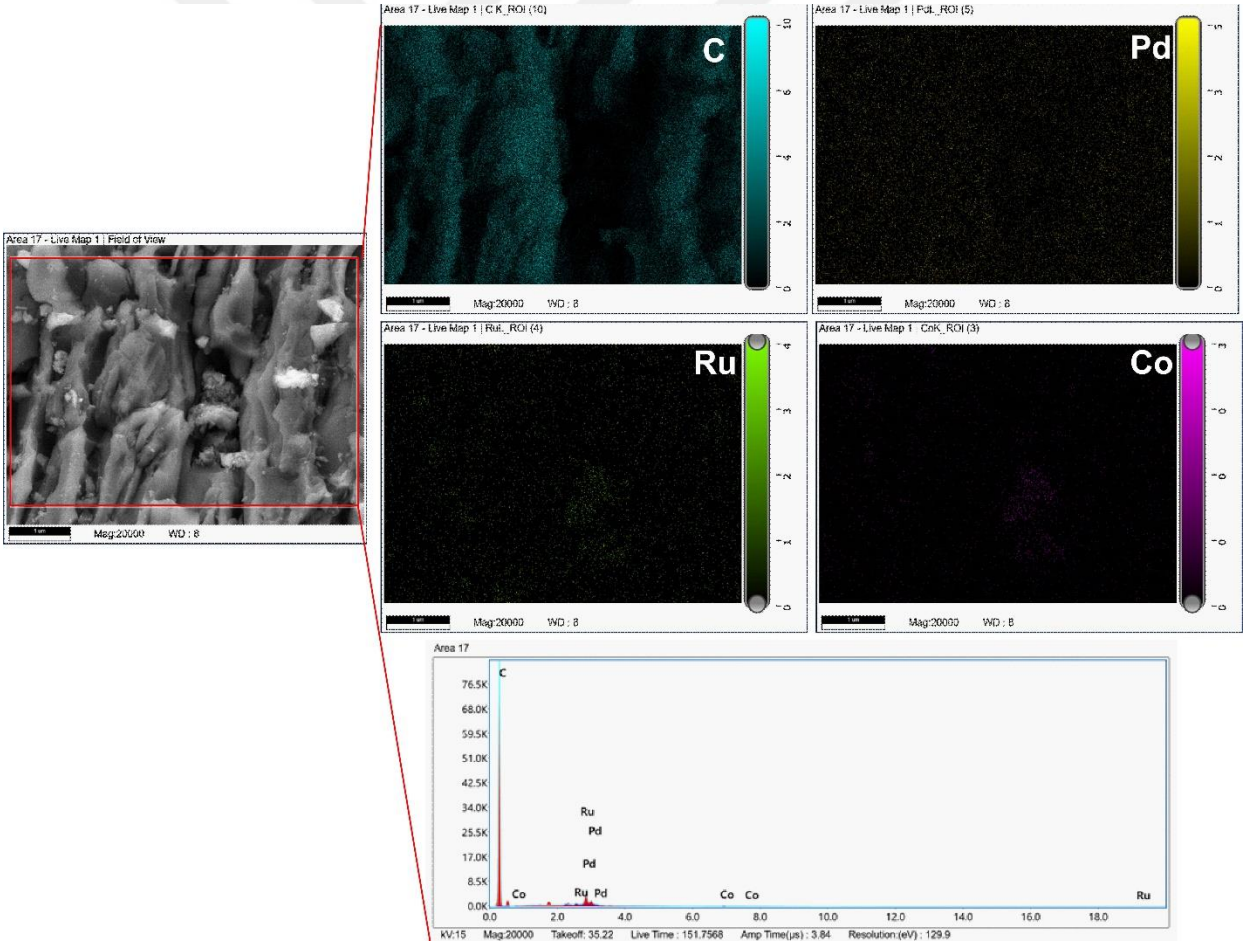
Şekil 3.10. (a) PdRuCo / C'nin XPS anket tarama spektrumu ve Pd 3d (b), Ru 3p (c) ve Co 2p (d) için çekirdek düzeyinde XPS spektrumları.

Her katalizörün yüzey morfolojisi, taramalı elektron mikroskobu (SEM) ile değerlendirildi ve karşılık gelen SEM fotomikrografları, Şekil 13'te gösterildi.



Şekil 3.11. (A) Pd / C, (b) PdRu / C ve (c) PdRuCo / C'nin SEM fotomikrografları.

Çalışmada en iyi katalizör (PdRuCo / C) için SEM-EDX ve elemenatal haritalama analizi de gerçekleştirildi. Şekil 14'te gösterildiği gibi.



Şekil 3.12. PdRuCo / C için SEM fotomikrografı, elemetal haritalama ve EDX spektrumu.

CURRICULUM VITAE

She finished secondary school in Zanko school and preparatory school in Koya school . In 2008, got acceptance in Chemical Engineering Department/ Koya University. In 2012, achieved B.Sc in Chemical Engineering with rank 1st out of 24 students. Since 2012, was employed as Demonstrator/Assistant Engineer at Koya University. in February, 2019 started his postgraduate study in the Department of Chemical Engineering, faculty of engineering of Van Yüzüncü Yıl University and finished master studying in Chemical Engineering Department in 2021.

UNIVERSITY OF VAN YUZUNCU YIL
THE INSTITUTE OF NATURAL AND APPLIED SCIENCES
THESIS ORIGINALITY REPORT

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Program: Chemical Engineering
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