DESIGN OF PROTOTYPE REACTOR FOR HYDROGEN PRODUCTION FROM SODIUM BOROHYDRIDE

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ABSTRACT

DESIGN OF PROTOTYPE REACTOR FOR HYDROGEN PRODUCTION FROM SODIUM BOROHYDRIDE

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Sodium borohydride ($NaBH_4$) offers a simple and safe technology for storage and on demand production of hydrogen being a promising and a feasible method for fuel cell applications.

The objectives of the present study are to emphasize the role of sodium borohydride as a part of future hydrogen energy system, to investigate the kinetics of the catalytic hydrolysis reaction of $NaBH_4$ in a batch and flow system with respect to temperature, concentration, catalyst and flow rate for flow reactor by proposing a kinetic model and finally based on kinetic analysis, to design a prototype reactor to meet the hydrogen requirement for a 100W PEM fuel cell and operate it in steady state conditions.

To express hydrolysis reaction by a kinetic model, series of batch experiments was performed in a glass flask (30mL) where the following parameters were systematically changed: the solution temperature varied as 20, 30 and 50°C, the $NaBH_4$ concentration changed as 0.17, 0.23 and 0.3M, NaOH concentration varied as 0.27, 1.32 and 2.85M and catalyst amount was changed as 0.048, 0.07 and 0.1g

Pt/C (ETEK®). In the kinetic model catalyst effect proposed within the rate constant. The kinetic model was purposed as:

$$r'_{H_2} = 13.4\times10^{6}\times e^{-\frac{46.0}{RT}}\times\frac{C^{0.26}_{NaBH_4}}{C^{0.31}_{NaOH}} \qquad \frac{mol}{\min g_{cat}} \text{ with } \mathrm{R}^2 = 0.986$$

For flow reactor system, in a differential glass reactor (5mL) concentration, catalyst amount, catalyst type and flow rate was systematically analyzed at a constant temperature. For Pt/C catalyst the purposed model was:

$$r_{H_2}{}' = 0.163\frac{C^{1.1}_{NaBH_4}}{C^{0.22}_{NaOH}} \quad \frac{\mathrm{mol}}{\min \mathrm{g_{cat}}} \quad \text{when } \nu\text{=1mL/min at } 25^{0}\mathrm{C} \quad R^2 = 0.98$$

Also, for intrazeolite Co(0) nanoclusters, as a result of controlled experiments, the rate expression was found as:

$$r_{H_2} = 2.4\times10^{-3}\times C^{0.29}_{NaBH_4}C^{0.34}_{NaOH}\,\frac{mol}{\min g_{cat}}$$

Based on these data prototype reactor (recycle) with internal volume of 122cm^3 and storage volume of 1336 cm^3 was designed, manufactured from Delrin® and operated.

Keywords: Sodium Borohydride, Hydrolysis, Hydrogen Generation, *Pt/C*, Co(0) Nanoclusters, Catalyst

ÖZ

SODYUM BORHİDRÜRDEN HİDROJEN ÜRETİMİ İÇİN PROTOTİP BİR REAKTÖR GELİŞTİRİLMESİ

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Eylül 2011, 103 sayfa

Sodyum borhidrür ($NaBH_4$) basit ve güvenilir bir depolama ve istenildiğinde hidrojen üretme teknolojisini sunması açısından yakıt pili uygulamaları için umut vaat edicidir.

Bu çalışmanın amacı sodyum borhidrürün gelecek hidrojen enerjisi ekonomisindeki yerini vurgulamak, katalitik hidroliz tepkimesini kesikli ve sürekli reaktörlerde, $NaBH_4$ ve NaOH konstantrasyonu, sıcaklık, katalizör ve besleme hızı açısından etkilerini kinetik model ile açıklamak ve son olarak bu kinetik deneylere dayanarak 100W gücünde yakıt pilinin hidrojen ihtiyacını karşılayabilecek bir prototip reaktör tasarımı yapmak ve kararlı durumda çalıştırmaktır.

Hidroliz tepkimesini kinetik model ile açıklayabilmek için kesikli sistemde gerçekleştirilen deneylerde 30mL hacminde cam şişeden bir reaktör kullanılmış olup şu parametreler sistematik olarak değiştirilmiştir: çözelti sıcaklığı; 20, 30 ve 50°C, $NaBH_4$ konsantrasyonu; 0.17, 0.23 ve 0.3M, NaOH konsantrasyonu; 0.27, 1.32 ve 2.85M ve son olarak katalizör miktarı; 0.048, 0.07 and 0.1g Pt/C (ETEK®). Bu deneyler sonucunda ulaşılan kinetic model aşağıdadır:

$$r'_{H_2} = 13.4\times10^{6}\times e^{-\frac{46.0}{RT}}\times\frac{C_{NaBH_4}^{0.26}}{C_{NaOH}^{0.31}} \qquad \frac{mol}{dak.g_{kat}} \quad \mathrm{R}^2 = 0.986$$

Sürekli sistemde yapılan deneyler sırasında 5mL diferansiyel cam reaktör kullanılmış olup konsantrasyon, katalizör miktarı ve cinsi, ve besleme hızı parametreleri sabit sıcaklıkta incelenmiştir. Pt/C katalizörü ile yapılan deneyler için önerilen model:

$$r_{H_2}{}' = 0.163\frac{C_{NaBH_4}^{1.1}}{C_{NaOH}^{0.22}} \quad \frac{\mathrm{mol}}{\mathrm{dak.g_{kat}}} \qquad \nu\mathrm{=1mL/dak} \quad \mathrm{T=25^0C} \quad R^2 = 0.98$$

Intrazeolit Co(0) nanokümeleri ile kontrollü deneyler sonucunda elde model ise aşağıdadır:

$$r_{H_2} = 2.4\times10^{-3}\times C_{NaBH_4}^{0.29}C_{NaOH}^{0.34}\,\frac{mol}{dak.g_{kat}}$$

Bu verilere dayanarak geri dönüşüm prensibi ile çalışan prototip reaktör iç hacmi 122cm^3 ve depo hacmi 1336 cm^3 olarak tasarlanmış, Delrin®'den imal edilmiş ve başarıyla işletime alınmıştır.

Anahtar Kelimeler: Sodyum Bor Hidrit, Hidroliz, Hidrojen Üretimi, *Pt/C,* Co(0) Nanokümeleri, Katalizör

To My Family

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HHV: Higher heating value
LHV: Lower heating value
K_M: Michaelis constant
Ka: Adsorption constant
$r'_{i:}$ Rate of species i generated or consumed (mol/min.g_{cat})
N_i: Total moles of species i (mol)
k: Reaction rate constant
Ea: Activation Energy (kJ/molK)
A: Pre-exponential factor
C_i: Concentration of species I (mol/L)
T: Temperature (K)
F_i: Molar flow rate of species i (mol/min)
W: Catalyst weight (g)
υ: Volumetric flow rate of solution (L/min)
wt%: Weight percent

Greek Letters:

η : Hydrogen generation efficiency (%)

η_{eff}: Effectiveness factor

CHAPTER 1

INTRODUCTION

The hydrogen economy is promoted as the next generation energy system after the petroleum era with the hydrogen as the energy carrier. The main idea behind the hydrogen economy is to replace fossil fuels on which the world currently depends on with hydrogen in order to obtain sustainable, secure, environmental friendly energy source by taking advantage of high energy content of hydrogen.

Hydrogen being lightest and the most abundant element on the world, it does not found on its molecular form. Therefore, it should be produced from another source before it can be used to carry energy. This is the main difference between hydrogen and fossil fuels. There are three major routes for the production of hydrogen in future considered as; (Mcdowell and Eames, 2007)

- Nuclear power plants, either electrically or direct thermal or chemical processes in high temperature reactors.
- Fossil fuel plants, coal gasification and natural gas reforming with carbon dioxide sequestrating.
- Renewable sources, wind, hydropower and biological hydrogen production routes.

Hydrogen is the ideal fuel for the fuel cells for electricity generation. It has the highest higher heating value (HHV) of 141.9 MJ/kg quantified as energy density on a mass basis of all chemical fuels. Higher heating value corresponds to the total amount of heat released during complete combustion of unit quantity of fuel including the heat release during phase change of water. On the other hand lower heating value (LHV) is obtained by subtracting the latent heat of vaporization of water vapor formed by combustion. Table 1.1 shows the comparison of higher heating values and lower heating values of some selected chemical fuels (Lo, 2006).

Table 1-1 Higher and lower heating values of chemical fuels (Lo,2006)

Fuel	HHV(MJ/kg)	LHV(MJ/kg)
Coal	34.1	33.1
Methane	55.5	50.1
Natural gas	42.5	38.1
Propane	48.9	45.8
Gasoline	46.7	42.5
Diesel	45.9	43.0
Hydrogen	141.9	120.1

Another important reason why hydrogen is being considered in future economy is its environmental benefit. Hydrogen, being a non-toxic and non-poisonous element, its release to the atmosphere does not cause environmental or water pollution. Therefore, it is considered to be clean and sustainable. Moreover, since it is odorless, colorless and tasteless, it is not detectable by human senses. So, like natural gas, hydrogen is a fuel that must be handled appropriately. On the other hand, storing hydrogen is the most challenging issue since hydrogen is the lightest and smallest element in the universe with a rapid diffusivity. In other words, when it is released, it dilutes quickly into a non-flammable concentration. (Momirlan and Vezioglu, 2005)

Hydrogen has the potential to become the most important component of sustainable future energy system. Figure 1.1 shows the vision of “hydrogen economy”. The use of hydrogen enables us the use of diverse arrays of renewable sources such as sunlight, wind power, biomass and hydroelectric power. In the first route, the electricity generated from these clean energy sources can be directly supplied to the community for their daily needs. In the second route, some portion of this produced electricity can be used in electrolysers for the production of hydrogen. It is important to note that hydrogen as a molecule can be stored or transported to where it is needed. Produced hydrogen can be used in fuel cells with air to produce more electrical energy for utilization in transportation, residential or industrial applications. Fuel cells are promising devices as a source of heat and electricity. The only other product coming from the fuel cell is the water vapor that can be used in cogeneration purposes by completing the cycle of hydrogen. (Lo, 2006)

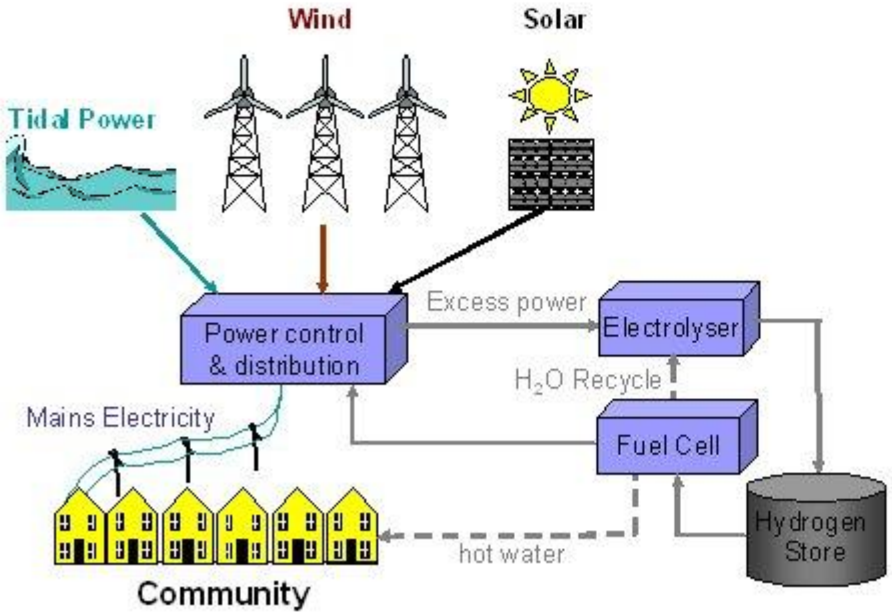


Figure 1-1 Conceptual vision of “hydrogen economy” in the near future (University of St. Andrews News, 2008)

There are several technical barriers in front of the hydrogen infrastructure that must be addressed before commercialization. One of the most challenging issues is the hydrogen storage. Developing safe, reliable, compact and cost effective hydrogen storage systems is crucial for fully understanding of the potential of energy system based on hydrogen as an energy carrier and to compete with currently existing technologies.

Hydrogen can be stored physically or chemically in several methods:

a) Physical storage as compressed gas in high pressure gas tanks

b) Physical storage as liquefied hydrogen (at -253°C) in insulated tanks

c) Chemical storage on metal and complex hydrides

d) Chemical storage on chemical hydrides

Each storage method has its own unique advantages and disadvantages. Among them chemical hydrides offer a possible solution of hydrogen supply problems. Sodium borohydride ($NaBH_4$) as a chemical hydride, draws much of the research interest due to its large theoretical hydrogen content of 10.9 wt.%. $NaBH_4$ and it is stable and easy to handle compared with other chemical hydride. (Kojima et al., 2004)

The present thesis will focus on hydrolysis of sodium borohydride ($NaBH_4$) for hydrogen generation. The objectives of this study are;

i. To emphasize the role of sodium borohydride as a part of future hydrogen energy system.
ii. To investigate the kinetics of the hydrolysis reaction of $NaBH_4$ with respect to temperature, concentration and catalyst and to propose a kinetic model.
iii. Perform hydrolysis reaction experiments in a batch reactor and a flow reactor in order to determine the type of prototype reactor.
iv. To design a prototype reactor to meet the hydrogen requirement for a 100W PEM fuel cell and operate it in steady state conditions.

In the following chapter; (Chapter 2) detailed literature survey about hydrogen storage and supply alternatives, their advantages and disadvantages are given. Also, sodium borohydride, its history, advantages, applications and role in hydrogen economy are explained comprehensively with recent literature studies.

In Chapter 3; methodologies of kinetic experiments are mentioned in detail including the batch and flow experiments and related experimental setups. The experimental results are given in Chapter 4. Chapter 4 covers the results and discussions of batch and flow reactors and rate model. Moreover, the design and operation of prototype reactor are explained in this chapter.

As a final chapter, conclusions and further recommendations are stated in Chapter 5. The thesis is completed with references and appendices sections that provide additional data.

CHAPTER 2

LITERATURE SURVEY

For the last two century, the world relies heavily upon fossil fuels, which are coal, oil, and natural gas. However, there are mainly three drawbacks of fossil fuels. Firstly, their sources are limited and will be depleted soon. Secondly, some reserves are becoming increasingly concentrated in regions of the world which results political and economic instability. The last drawback is the consumption of fossil fuels seriously pollutes the environment and causes global warming, ozone layer depletion, climate changes, rising sea levels, and agricultural land damage. In spite of the drawbacks associated with the fossil fuels, the ease of storage and transportation at a designated location make them very advantageous when compared with other renewable energy sources. Due to the drawbacks of fossil fuels, researches have been concentrated on alternative renewable energy sources. One of the most important and promising candidate is hydrogen. Since hydrogen can be stored, transported, and converted easily to other energy forms, there has been intense scientific, industrial, and governmental interest in the development of hydrogen based energy production technology (Şengül, 2007).

Hydrogen is envisaged as a future energy carrier for sustainable energy system to be the solution of numerous problems that our world currently facing such as green house gas emissions and water pollution. However, regarding the hydrogen and fuel cells, there are four main obstacles in front of the transition to hydrogen economy.

These can be listed as:

1. Hydrogen production: As mentioned before, hydrogen cannot found on its molecular form. Therefore, it must be produced from another source. An efficient and environmental friendly way to produce hydrogen must be addressed.
2. Distribution of hydrogen and public acceptance: These is no current infrastructure for hydrogen supply to customers hence it needs to be built. Also, people must be convinced to use hydrogen in fuel cell cars and accept the hydrogen.
3. High cost of fuel cells: The major contribution to the cost comes from that of the platinum catalyst. Within the years, the cost of the fuel cell system is towards decreasing. The fuel cell system cost was 275$/kW in 2002 and decreased to 110$/kW by the year 2006. It became 73$/kW in 2008. The 2015 target is to have $30/kW system.
4. Hydrogen storage: One of the most important challenges behind hydrogen infrastructure is hydrogen storage. It is necessary to purpose an efficient, low weight, high gravimetric and volumetric capacity method to storage hydrogen in order to be used in fuel cells. (Diwan, 2009).

In this chapter, starting from the commercial methods, studies in literature related with hydrogen storage are summarized, emphasizing chemical hydrides and sodium borohydride. Furthermore, recent literature studies about the use and hydrolysis reaction of sodium borohydride are evaluated.

2.1 Hydrogen Storage Methods

Hydrogen can be stored physically or chemically in several methods such as compressed gas in high pressure gas tanks, liquefied hydrogen in insulated tanks, adsorption on carbon nanotubes and metal, complex and chemical hydrides. Each storage method has its own unique advantages and disadvantages.

2.1.1 Compressed Hydrogen

Currently, most of the prototype vehicles that operates using fuel cells used hydrogen stored in high pressure tanks. Hydrogen is supplied from the compressed gas tanks with appropriate control units and it is fed to the fuel cell on demand. The gravimetric energy density of hydrogen (33.3 $\mathrm{kWhkg^{-1}}$) is approximately three times of gasoline (12.7 $\mathrm{kWh\ kg^{-1}}$). However the low volumetric energy density of hydrogen (0.77 $\mathrm{kWh\ l^{-1}}$ at 35 MPa and 300 K) in comparison with gasoline (8.76 $\mathrm{kWh\ l^{-1}}$) is the reason for increased package volume required for hydrogen storage system compared with conventional gasoline/diesel fuel systems. Therefore the main drawback of conventional compressed hydrogen tanks are increased volumes for needed hydrogen amounts (Stolten, 2010).

The main component, the hydrogen storage cylinder is designed to have optimum weight and functionality. Accordingly, strong, lightweight, filament-wound, carbon-fiber tanks are used to safely contain hydrogen at pressures up to 10,000 psi (680 atm). However, the use of carbon-fiber tanks increases the cost dramatically. The filling pressure and temperature are limited to 87.5 MPa (864 atm) and 85 °C according to the national regulations. Even at such high pressures, the best achievable energy density of 39 grams per liter (4.4 MJ/L) is about 14 percent of the energy content of gasoline (31.6 MJ/L) for a given volume. Considering the weight of the entire system, the high pressure tanks contain 3.5 to 4.5 percent of hydrogen by weight. Due to its bulk volume and weight, compressed tanks are limited in portable devices. Buses and other large vehicles have the physical size to accommodate the space that compressed tanks require, but it would be difficult to do so in cars and other smaller portable devices. They also have a physical danger as hydrogen is a combustible and explosive gas under high pressure. In addition, being a low molecular weight gas, leakage problems could occur. Finally, certain extra measures must be taken in refueling as hydrogen is in the gaseous state and must be pressurized which is not as simple and convenient as pouring a liquid fuel into a storage tank. This would also require a substantial hydrogen refueling infrastructure (Stolten, 2010 , Bartkus, 2011).

2.1.2 Liquid Hydrogen

Another widespread method for hydrogen storage is liquefied hydrogen. Liquefied hydrogen packs the most hydrogen for a given volume of any existing option. Also it is favorable than compressed tanks as its density at low pressure is nearly double of the compressed tanks storage method (at atmospheric pressure, 0.1 MPa, liquefied hydrogen has a density of 70.9 g/l which is 1.8 times the approximately 40 g/L of compressed hydrogen at 70 MPa and 288 K.) so they do not need transportation at high pressure tanks. However, even as a liquid its density is not very high so the hydrogen molecules are still widely spaced. Compared to the density of water, 70.8 g/liter is a small fraction of the nearly 1000 g/liter of water. This low density is unfortunate as this equates into an energy density (8.4 MJ/L) of only about 27 percent of gasoline. The weight density of liquid hydrogen systems depends largely on the containment and insulation equipment used. (Stolten 2010, Bartkus, 2011).

Liquid hydrogen is stored at 0.6 MPa, 20 K therefore considerable insulation and ancillary equipment are necessary to maintain the cryogenic low temperatures. As a result, the liquid hydrogen containers are rather complicated. Basically they should be double walled tanks and between two walls, thermal insulation material in vacuum should be used. Tanks should resist hydrogen permeation and generally they are made of stainless steel or an aluminum alloy. Aluminum alloys are favorable because of their low specific weight, high modulus and strength and high thermal expansion coefficient. A major concern of liquid hydrogen is boil-off. As a liquid cooled to and stored near its boiling temperature, any amount of heat transfer to the system will evaporate some of the liquid hydrogen. Any boil-off will result in a net loss in overall system efficiency as work was needed to liquefy the gas, and even greater loss occurs if this boiled-off gas is vented to the atmosphere if not recovered. Therefore the heat entry should be reduced by several layers of insulation. Common insulation material is aluminized polymer foils separated by glass fiber. As a final drawback, liquefying hydrogen takes considerably more energy than compressing it to high pressures which reduces the overall energy efficiency of the cryogenic cooling process. The theoretical work needed for hydrogen liquefaction (Joule Thomson cycle) from room temperature is 3.23 $kWh.kg^{-1}$. However, the actual work required has a range from 11.1 $kWh.kg^{-1}$ to 27.8 $kWh.kg^{-1}$. These valued represents 33.31 % of LHV of hydrogen which drives up the cost of the hydrogen fuel (Stolten 2010, Bartkus, 2011).

2.1.3 Adsorption Technologies

A promising possibility to store hydrogen is cryosorption of hydrogen molecules on lightweight nanoporous materials possessing large internal surfaces. Adsorption occurs when two non polar atoms or molecules approach together and a non-dispersive attraction called van der Waals is formed. If a molecule is approaching to the surface of a material it will remain at certain distance at which attractive and repulsive forces are equal to each other. The remaining of molecule at certain distance is called physisorption. The free particle is called adsorptive and the material is called adsorbent. The adsorptivity at certain surface area is a function of temperature, pressure and the material characteristics. The physisorption process of hydrogen is fast and fully reversible. As the boiling point of hydrogen is low, between 77 K and room temperature monolayer adsorption of hydrogen is formed. Therefore at low pressures the amount of hydrogen adsorbed depends on the applied pressure however it reaches saturation for higher pressures therefore greater amounts of hydrogen can only be adsorbed on materials having higher surface areas. Some materials which were produced by nano-scale engineering have yielded more than 5,000 square meters of surface area per gram of material (Satyapal et al. 2007). Activated carbons and nanostructered materials such as carbon nanotubes, zeolites, organic polymers, metal-organic frameworks could be used for the adsorption of hydrogen (Stolten, 2010). Carbon-based materials are attractive because of their light weight, low cost production, re-absorption capability, and for the ability to make several forms of nano-structures. Various levels of success have been achieved with hydrogen adsorption on carbon nano-structures.

Hirscher *et al.*, (2001) and Dillon *et al.*, (2001) have reported adsorptions of only 1 to 2 wt% hydrogen are possible with single walled carbon nanotubes. Browning *et al.*, (2002) studied on nano-fibers and reported 6.5 wt% adsorption of hydrogen. Nikitin *et al.*, (2008) have been able to successfully show that over 7 wt% hydrogen can be absorbed by single walled nano-tubes. Nanostructures operate under various different temperatures and pressures. This area of research is still heavily investigated (Bartkus, 2011).

2.1.4 Metal Hydrides

Metal hydrides are an attractive method for hydrogen storage. Various metallic elements form metallic hydrides which are thermodynamically stable. The reaction between a metal M and hydrogen is expressed in Equation (2.1).

$$M + H_2 \leftrightarrow MH_2 + \ Heat\ of\ Hydride\ Formation \tag{2.1}$$

Metal hydrides are formed by different bonding structures. Alkali metals forms ionic hydrides in which hydrogen has a negative charged such as NaH and ionic hydrides are too stable to release hydrogen at PEM fuel cell operating conditions. Alkali earth metals like magnesium form hydrides by both ionic and covalent bonding. Transition metals form interstitial hydrides in which hydrogen occupies the interstitial sites. As transition metals except vanadium cannot react with hydrogen reversibly, metal alloys are used for storage purposes. In addition to those base metals like aluminum could also form metal hydrides (Stolten, 2010).

The reactions between the metal and hydrogen gas is a heterogeneous solid-gas phase reaction. Hydrogen gas found in the surface of the metal, firstly absorbed on the surface and decomposed to its atoms. The hydrogen atoms diffuse into the metal bulk and form a metal hydride. The metal hydride is usually a fine powder and the surface of the metal plays an important role in the reaction kinetics. Hydride formation is usually endothermic. Therefore heat should be removed for hydrogenation and be introduced for dehydrogenation. They show rapid reaction rates, long cycle life, recyclability and significant volume density of hydrogen. Certain metals, in particular alloys of titanium, manganese, nickel, iron and chromium can react with hydrogen to form a metal hydride. Some examples of these metallic compounds are TiFe, $ZrMn_2$, $LaNi_5$, and Mg_2Ni. A metal hydride results when hydrogen is supplied to the metal alloy and adsorbed at elevated pressures. When the pressure is reduced, the hydrogen is desorbed. Therefore the reaction is reversible. Several charge and discharge cycles can be completed. Metal hydrides are inherently stable, and therefore do not require any extra energy for storage, but elevated temperatures are required for hydrogen desorption. The large weight of the system is a main drawback of metal hydrides for portable applications. Researchers have been able to attain about 2 wt% hydrogen for the total material weight associated with metal hydrides operating around 100°C (Stolten, 2010, Bartkus, 2011)

2.1.5 Chemical Hydrides

Complex chemical hydrides (particularly borohydrides) could also be employed as hydrogen sources for portable PEMFC. They generally exhibit greater gravimetric energy densities than most hydrogen storage methods. Their gravimetric hydrogen density exceeds that of transition metal hydrides. Although in metal hydrides, hydrogen atoms occupy the interstitial states of the metal host lattice, in complex borohydrides BH_4^- ions are ionically bound to metal cation. In contrast to the interstitial hydrides, desorption of hydrogen in chemical hydrides occurs through a chemical reaction with another substance such as water and most chemical hydrides are stable. As a result, these materials could store an important amount of hydrogen during long periods without usage. The main drawback to these chemicals is that the hydrogen producing reaction is not fully reversible and therefore these materials cannot be easily recycled. The byproduct of the reaction must be regenerated into the original chemical hydride with industrial processing. Extensive research has been done on various chemical hydrides which include lithium hydride (LiH), sodium hydride (NaH), calcium hydride (CaH_2), lithium borohydride ($LiBH_4$) and sodium borohydride ($NaBH_4$). Table 2.1 shows the various chemical hydrides and their physical properties with respect to hydrogen storage capacities.

Table 2-1 Hydrogen storage capacities of some selected chemical hydrides (Bartkus, 2011)

Name	Formula	Wt% Hydrogen	Density (kg/L)	Mass to store 1 kg of H_2 (kg)	Vol to store 1 kg of H_2 (L)
Lithium hydride	LiH	14.5	0.82	6.9	8.4
Sodium hydride	NaH	4.2	0.92	23.8	25.9
Calcium hydride	CaH_2	4.8	1.9	20.8	11.0
Lithium borohydride	$LiBH_4$	18.5	0.67	5.4	8.1
Sodium borohydride	$NaBH_4$	10.7	1.07	9.3	8.7

Among the chemical hydrides, sodium borohydride has received much attention as a hydrogen carrier. The gravimetric density and volumetric density are attractive, and the chemical reaction between $NaBH_4$ and water is spontaneous, but relatively stable. The solution is highly controllable. Hydrogen production can be accelerated with the aid of a catalyst and can be stopped by adding an alkaline compound that makes solution basic. Moreover, $NaBH_4$ is safe to work with. Because of the strong interest and high potential, this work focuses on the chemical hydride sodium borohydride and its hydrogen production and storage for fuel cell use. (Bartkus, 2011). Figure 2.1 shows a summary of hydrogen storage methods.

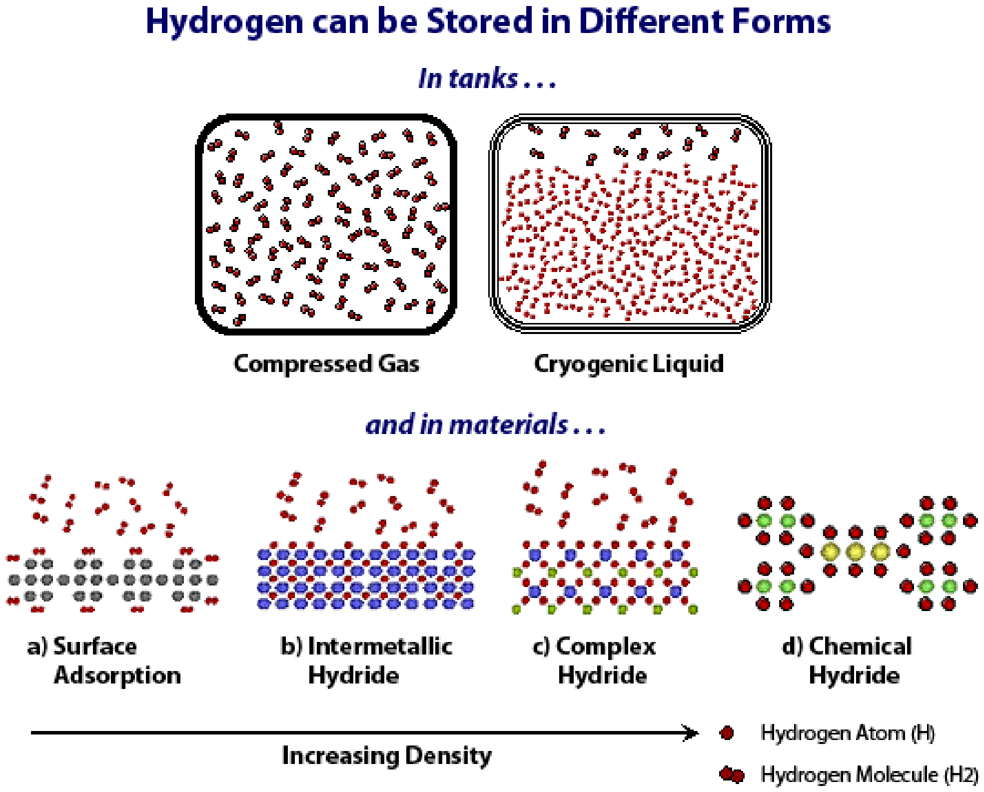


Figure 2-1 The molecular structure of hydrogen stored in different storage methods (US DOE, 2008)

The DOE had set a gravimetric storage target for on-board hydrogen storage (for the entire system, not just the material) of 6 wt.% by 2010 and 9 wt.% by 2015. The volumetric targets were 45 g L^{-1} by 2010 and 81 g L^{-1} by 2015. These targets were revised to 4.5 wt.% (28 g L^{-1}) by 2010 and 5.5 wt.% (40 g L^{-1}) by 2015 recently for light duty vehicles. Figure 2.6 shows the current status of hydrogen storage options.

None of these methods seems attractive to meet 2015 targets set by DOE. However, different than liquid hydrogen method, chemical hydrides as hydrogen storage materials are most convenient method that can be easily developed. In other words, finding efficient way to utilize chemical hydrides, the capacity of hydrogen storage can be increased and cost can be reduced

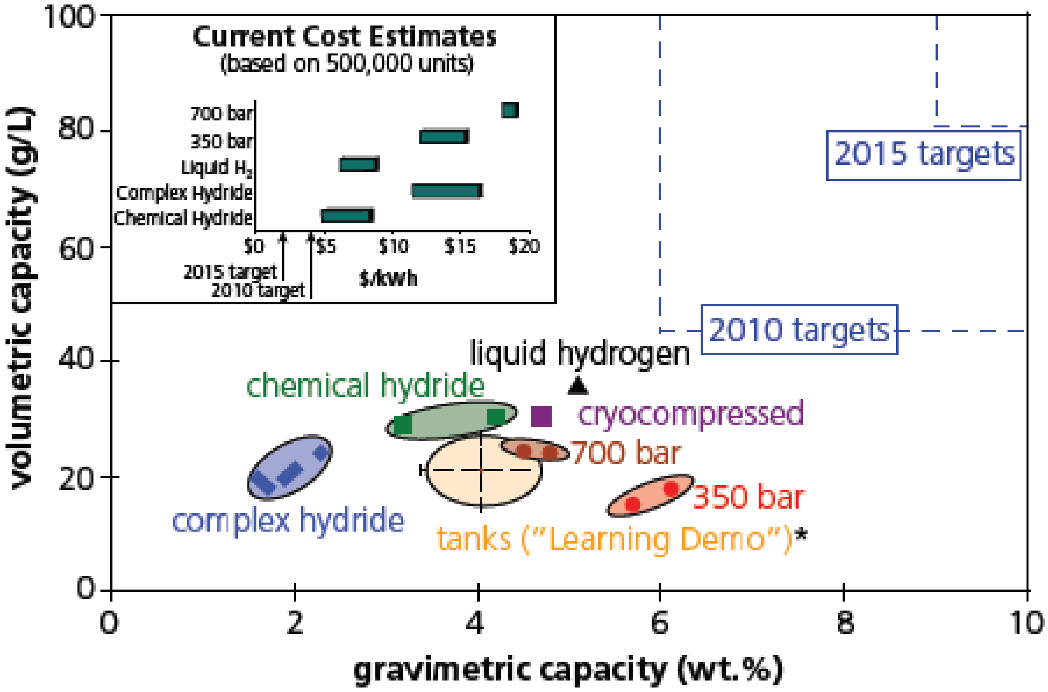


Figure 2-2 Current status of hydrogen storage methods (Basu, 2010)

2.2 Hydrolysis of Sodium Borohydride

Sodium borohydride ($NaBH_4$) has found wide range of use as a powerful reducing agent in pharmaceutical synthesizing, wastewater processing and paper blenching (Amendola et al., 2000). Moreover, its use as a hydrogen gas generator was first investigated by Schlesinger et al. (1953). They found that aqueous alkaline solutions of sodium borohydride in contact with selected catalysts generates hydrogen (H_2) and water soluble sodium metaborate ($NaBO_2$) via hydrolysis reaction shown in Equation (2.2):

$$NaBH_4 + 2H_2O \xrightarrow{catalyst} 4H_2 + NaBO_2 + heat \qquad (2.2)$$

This reaction can also occur without catalyst if the pH of the solution is below 9. This is called self-hydrolysis of sodium borohydride. The initial rate of hydrogen generation decreases by the increase in the pH of the solution due to the formation of strongly basic sodium metaborate ion as in Equation (2.3):

$$BH_4^- + H_2O \longrightarrow 4H_2 + BO_2^- \qquad (2.3)$$

Thus, initial rate decrease can be prevented by dissolving sodium borohydride in alkaline water rather than pure water (Schlesinger et al., 1953). This procedure also enables control of reaction rate, easy handling and storing sodium borohydride in aqueous solution with the increase in the shelf-life.

Zhang at his coworkers (2006) performed calorimetric analysis and determine the standard enthalpy change of reaction at 298K is -212.1 kJ/mol. Kojima et al. () determined the temperature dependent solubilities of $NaBH_4$ and $NaBO_2$ given in Equation 2.4 and Equation 2.5 respectively.

$$\text{Solubility of NaBH}_4\text{(g/100gwater)} = -261 + 1.05 \times T \qquad (2.4)$$

$$\text{Solubility of NaBO}_2\text{(g/100gwater)} = -245 + 0.915 \times T \qquad (2.5)$$

In equations 2.4 and 2.5, the temperature, T, was given in terms of Kelvin.

Sodium borohydride has received a lot of recent interest due to the work of a company called Millenium Cell. Millenium Cell developed a powerful catalyst that enables rapid hydrolysis of sodium borohydride. This system aims the use of sodium borohydride in fuel cell applications and is called the Hydrogen on Demand System™ (shown in Figure 2.7) with the demand term standing for controlling the reaction by insertion or removal of the catalyst from a base stabilized sodium borohydride solution. (Walter, 2007)

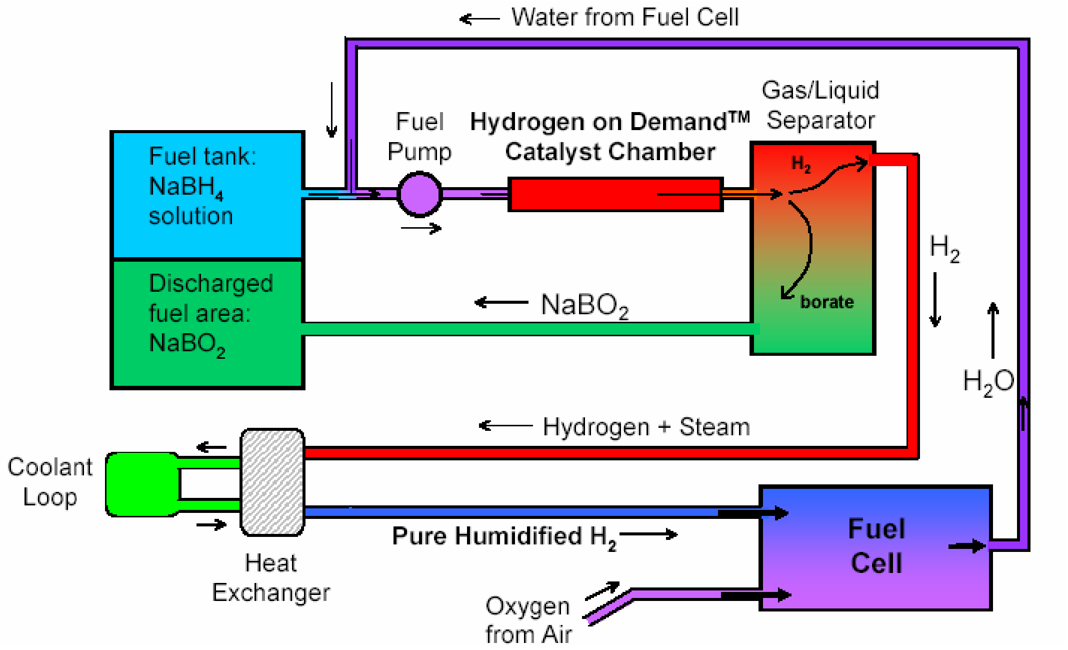


Figure 2-3 Hydrogen On Demand^{TM} system developed by Millennium Cell (Walter, 2007)

The hydrolysis reaction of sodium borohydride can be accelerated with the help of catalyst. Catalytic generation of hydrogen from $NaBH_4$ solutions has several advantages listed below: (Amendola et al. 2000)

1. $NaBH_4$ solutions are non-flammable and not toxic.
2. $NaBH_4$ solutions are stable in air for months.
3. H_2 generation only occurs in the presence of selected catalysts.

But this reaction can occur to some extent even without a catalyst if the solution pH is less than 9. However, to increase the shelf life of $NaBH_4$ solutions and to suppress the self hydrolysis of it, $NaBH_4$ solutions are typically maintained as a strongly alkaline solution by adding NaOH. According to the reactor type and amount of reactants, NaOH can be added in various amounts but generally in the range of 5-15 wt% of reactants. It must be noted that the excess amount of NaOH decreases the hydrogen yield. Mostly NaOH in the amount of 3-5% of reactant is thought to be sufficient to control hydrogen release. (Çakanyıldırım, 2008)

4. The only other product in the gas stream is water vapor.

The presence of water vapor is beneficial for use in PEM fuel cells where the water vapor can be used to humidify the PEM membrane. The H_2 gas generated is sufficiently pure and it can be used directly in PEM fuel cells without further cleanup.

Not only as a product but also as a reactant amount of water amount is an important parameter because approximately 95% of the reactant mass is occupied by water. As fuel cell applications needs low weight hydrogen devices, water content must be decreased as possible.

5. Reaction products are environmentally safe.

Since reaction (2.1) is totally inorganic and does not contain sulfur, it produces virtually no fuel cell poisons such as sulfur compounds, CO, soot, or aromatics. The reaction product sodium metaborate, $NaBO_2$, is water soluble and commonly found in laundry detergents and not environmental hazardous.

6. H_2 generation rates are easily controlled.

The heat generated by reaction Eq. (2.1), 75 kJ/mole H_2 formed, is considerably less than the typical > 125 kJ/mole H2, produced by reacting other chemical hydrides with water. This promises a safer, more controllable reaction. (Çakanyıldırım, 2008)

Moreover, to generate H_2, $NaBH_4$ solution is allowed to contact catalyst either by dipping catalyst into a $NaBH_4$ solution or injecting $NaBH_4$ solution on catalyst. This ensures fast response to H_2 demand, i.e., H_2 is generated only when $NaBH_4$ solution contacts with catalyst. When H_2 is no longer needed, $NaBH_4$ solution is removed from catalyst and H_2 production ceases.

7. Volumetric and gravimetric H_2 storage efficiencies are high.
8. The reaction products can be recycled.
9. H_2 can be generated even at $0^{o}C$.

Also hydrogen could be generated at temperatures below $0^{o}C$ if water-methanol or water-ethylene glycol mixtures were used.

2.3 Recent Literature Studies on Catalytic Hydrolysis of Sodium Borohydride

One of the most important feature of using sodium borohydride as hydrogen generator is to control hydrogen supply on demand. (Bartkus, 2011) High hydrogen generation rates with great control can be accomplished by the help of catalyst. A great deal of worked has been performed on catalytic hydrolysis of $NaBH_4$. Various types of catalysts have been found a use in catalyzing and controlling hydrolysis reaction ranging from precious metals like platinum (Pt) (Bai et al, 2006, Xu et al., 2007) and palladium (Pd) (Patel et al., 2008) to more common materials such as ruthenium (Ru) (Amendola et al, 2000, Shang et al., 2008), nickel (Ni) (Pinto et al., 2006), cobalt (Co), Ni-B, Ni-Co, Co-B (Dai et al., 2008), Co-P-B (Patel et al., 2009) and Ni-Co-B (Fernandes et al., 2009).

Catalytic hydrolysis reaction of $NaBH_4$ involves solid-phase dissolution, liquid-phase transfer of the reactant and byproduct, and the reaction occurring at the catalyst surface. Thus, catalytic hydrolysis is gas-liquid-solid multiphase reaction. Better mechanistic understanding of the hydrolysis kinetics of $NaBH_4$ with the presence of catalysts is clearly of significance for hydrogen generator design and the selection of process conditions to pursue optimal system performance. Nevertheless, despite extensive efforts, the study of catalytic hydrolysis kinetics lacks progress. Even the hydrolysis reaction order with respect to $NaBH_4$ concentration is still a subject of great controversy. (Dai et al., 2008)

Many literature reports that the hydrogen generation follows zero order kinetics with respect to $NaBH_4$ concentration. Özkar et al. (2006) and Guella et al. (2007) claims that hydrogen generation reaction follows zero order kinetics with respect to $NaBH_4$ concentration with their experiments performed with Ru nanoclusters and Pt/C catalyst, respectively. On the other hand, Penoa-Alonso et al. (2007) and Shang et al. (2006), suggested first-order kinetics with the presence of Pt-Pd/CNT and Ru/C catalysts. Additionally, recent studies using noble or non-noble metals as catalyst claimed fractional or even negative order reaction kinetics with respect to $NaBH_4$ concentration. (Jeong et al., 2005, Mitov et al. 2007)

Dai et al. (2008) applied Michaelis-Menten (M-M) model analysis for hydrolysis kinetics of $NaBH_4$ over Co-B catalyst. They synthesized Co-B catalyst in air by using chemical reaction method. Reaction is suggested to proceed according to the scheme shown in Figure 2.4. The important assumption behind M-M model is that the overall reaction is composed of two elementary steps; first the reactant BH_4^- comes in contact with catalyst M (Co-B), where an intermediate complex MBH_4 is produced with the rate constant of k_1. This intermediate complex may reversibly dissociate to M and BH_4^- with rate constant shown as k_{-1}. Second, the complex decomposes with the reaction of water to produce reaction products and regenerated catalyst, M, with the rate constant of k_2.

$$BH_4^- + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\text{int}\,ermediate}{MBH_4} \xrightarrow[4H_2O]{k_2} B(OH)_4^- + M + 4H_2$$

Figure 2-4 The scheme of the progress of hydrolysis reaction according to M-M method

In the steady state, the formation and breakdown of the intermediate complex are equal. The concentration of MBH_4 chance with time can be represented in the following Equation 2.6:

$$\frac{\mathrm{d}[\mathrm{MBH_4}]}{\mathrm{d}t} = k_1[\mathrm{BH_4^-}][\mathrm{M}] - k_{-1}[\mathrm{MBH_4}] - k_2[\mathrm{MBH_4}] = 0 \tag{2.6}$$

By rearranging Equation (2.6),

$$[\mathrm{MBH_4}] = \frac{k_1[\mathrm{BH_4^-}][\mathrm{M}]}{k_{-1} + k_2} = \frac{[\mathrm{BH_4^-}][\mathrm{M}]}{K_\mathrm{M}} \tag{2.7}$$

Where K_M called the Michaelis constant, is defined as:

$$K_\mathrm{M} = \frac{k_{-1} + k_2}{k_1} \tag{2.8}$$

The concentration of unoccupied metal sites [M] is equal to the total metal site concentration $[M_0]$ minus the concentration of the metal borohydride complex $[MBH_4]$. Then, by substituting [M] into the Equation (2.7) and arranging the rate equation accordingly, they obtained rate expression as:

$$r = \frac{k_2[\mathrm{M_0}][\mathrm{NaBH_4}]}{K_\mathrm{M} + [\mathrm{NaBH_4}]} \tag{2.9}$$

They performed experimental analysis to determine the constants in the rate expression. They first concluded that reaction is zero order with respect to the $NaBH_4$ concentration and for the solutions containing 0.5M NaOH and 5mg Co-B catalyst the rate can be expressed by the following equations:

$$V_{H_2} = 20.7t \quad (\text{when } [\text{NaBH}_4] \geq 0.4\text{M}) \tag{2.10}$$

$$V_{H_2} = 994(1 - e^{-0.0027t/V_{sol}}) \quad (\text{when } [\text{NaBH}_4] \leq 0.4\text{M}) \tag{2.11}$$

where, V_{sol} denotes the volume of the fuel solution in terms of dm^3 and t is the reaction time in minutes.

Shang et al. (2008) investigated the effect of temperature and concentrations of $NaBH_4$, $NaBO_2$ and NaOH on the hydrogen generation rate of hydrolysis over carbon supported Ru catalyst. They used commercial catalyst purchased from Johnson Matthey. They found that reaction is zero order with respect to $NaBH_4$ concentration. They observed that the rate decreases with the increase in NaOH concentration sue to the competitive adsorption of NaOH on the catalyst surface. The rate expression is suggested in the form as:

$$\mathrm{r}_{\mathrm{H}_2} = \frac{2.03 \times 10^{12} e^{-7756.3/T}}{1 + 1.31[OH^-]^{0.3}} \tag{2.12}$$

In the Equation (2.12) the hydrogen generation rate was expressed in terms of $cm^3H_2s^{-1}gcat$, NaOH concentration is defined in terms of $molkg^{-1}$ and reaction temperature unit is K.

Hung et al. (2008) investigated hydrolysis kinetics over Ru/γ -Al_2O_3. The catalyst was prepared by the impregnation-reduction method. They tried different models in order to be able to predict the kinetics such as zero-order, first order and Langmuir-Hinshelwood model.

For zero-order model the hydrogen generation rate isindependentfrom any concentration change. The rate can be expressed as:

$$\frac{\mathrm{d}C_{\mathrm{NaBH_4}}}{\mathrm{dt}} = -r_{\mathrm{NaBH_4}} = -k(T) \tag{2.13}$$

Integrating the Equation (2.13) gives:

$$\left(C_{NaBH_{4,0}} - C_{NaBH_4}\right) = kt \tag{2.14}$$

For the first-order kinetics with respect to $NaBH_4$ concentration the integrated rate equation can be written as:

$$\ln\left(\frac{C_{NaBH_{4,0}}}{C_{NaBH_4}}\right) = kt \tag{2.15}$$

Finally for Langmuir-Hinshelwood model following rate expression is considered:

$$\frac{dC_{NaBH_4}}{dt} = -r_{NaBH_4} = -k\frac{K_a C_{NaBH_4}}{1 + K_a C_{NaBH_4}} \tag{2.16}$$

where K_a is the adsorption constant. Integration of Equation (2.16) gives:

$$\frac{1}{K_a}\ln\left(\frac{C_{NaBH_{4,0}}}{C_{NaBH_4}}\right) + \left(C_{NaBH_{4,0}} - C_{NaBH_4}\right) = kt \tag{2.17}$$

At the end of kinetic experiments they concluded that zero-order model can only be applied to low conversions which is less than 50% whereas, the first-order model gives better results for temperatures up to 30°C. On the other hand, Langmuir-Hinshelwood mechanism is much more applicable for the determination of the kinetics of hydrolysis reaction of $NaBH_4$.

Rakap and Özkar (2009) synthesized a new catalyst for the hydrolysis reaction, which is intrazeolite Co(0) nanoclusters. The catalyst was prepared by ion-exchange of Co^{2+} ions with the extra framework Na^+ ions in the zeolite-Y followed by the reduction of Co^{2+} ions in the super cages of zeolite-Y with sodium borohydride at room temperature. The catalytic lifetime of intrazeolite cobalt(0) nanoclusters in the hydrolysis of sodium borohydride in both aqueous and basic media was determined by measuring the total turnover number (TTO). Intrazeolite cobalt(0) nanoclusters provide 36,000 turnovers and a turnover frequency up to 880 mol H_2 (mol Co)$^{-1}$ h^{-1} in the hydrolysis of $NaBH_4$ solution in the presence of 10 wt.% NaOH at room temperature.

The crystal morphology of the catalyst was investigated by scanning electron microscopy (SEM) and high resolution transmission electron microscopy (HRTEM). Figure 2.5 shows these images of intrazeolite Co(0) nanoclusters.

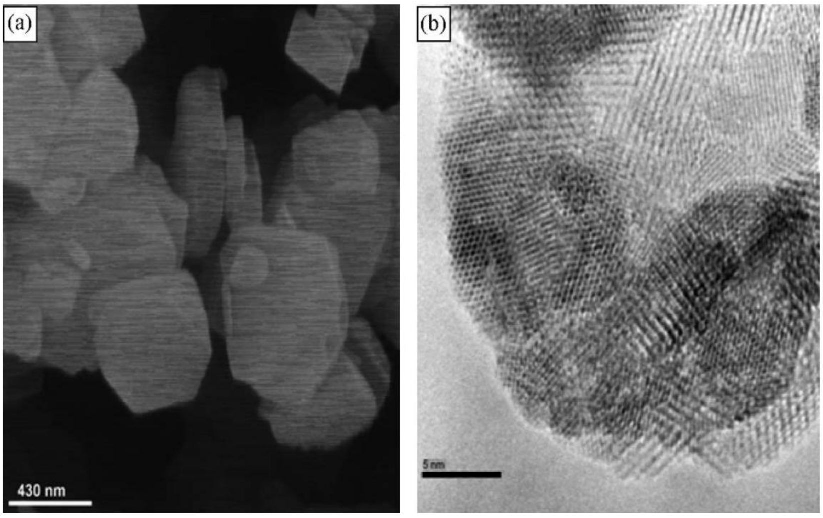


Figure 2-5 (a) SEM image (b) high resolution TEM micrograph of intrazolite Co(0) nanoclusters after complete hydrolysis of sodium borohydride (Rakap and Özkar, 2009)

The hexagonal structure of zeolite-Y can be seen in Figure 2.5 (a). Figure 2.5(b) shows uniform distribution of cobalt in highly ordered cages of zeolite-Y.
Rakap and Özkar (2009) also conducted a kinetic study, which shows that the catalytic hydrolysis of $NaBH_4$ is first order with respect to cobalt concentration and zero order with respect to $NaBH_4$ concentration.

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

Anhydrous and high purity (99.9%+) sodium borohydride ($NaBH_4$) is provided from MERK® in powder form. Sodium hydroxide as stabilizer is obtained from Sigma Aldrich. Finally, de-ionized water is used in hydrolysis experiments.

3.2 Batch Reactor

3.2.1 Catalyst

The commercial 20% HP Pt on Vulcan XC-72 (ETEK®) catalyst in powder form is used in experiments in a batch system.

3.2.2 Experimental setup and procedure for batch system

The experimental set up for hydrogen generation from sodium borohydride in a batch reactor is illustrated in Figure 3.1.

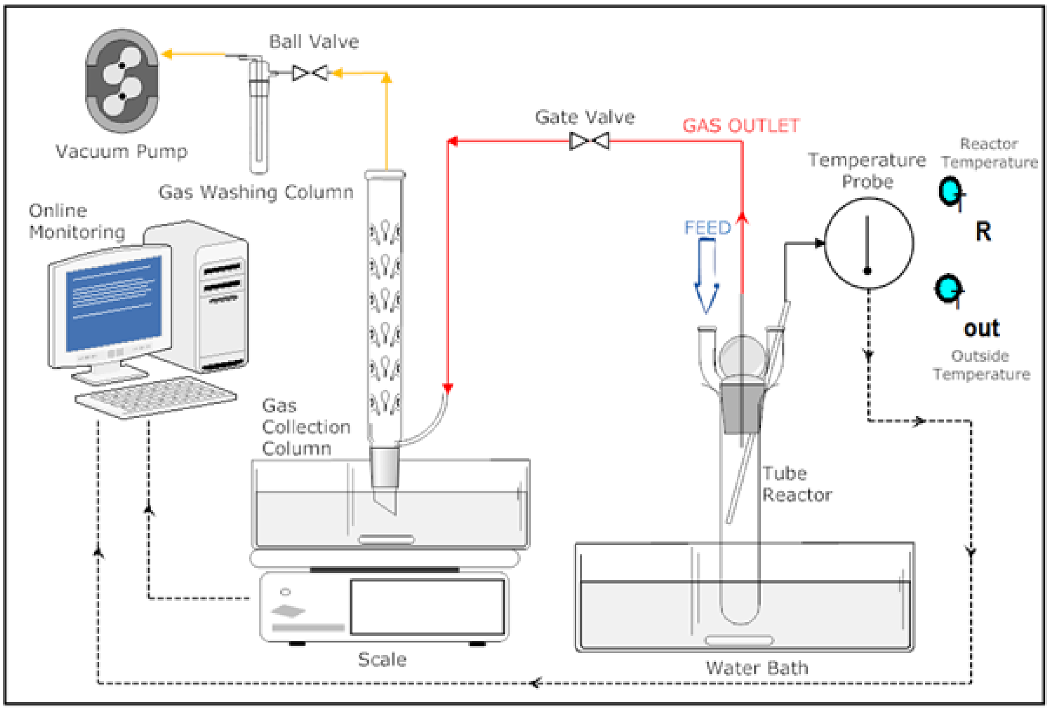


Figure 3-1 The experimental setup for hydrogen generation from $NaBH_4$ solution in a batch reactor

The hydrogen generating batch reactor is 30 mL three neck tube reactor that is kept in a constant temperature water bath. From one neck, $NaBH_4$ solution is introduced, from the other neck; temperature is measured and recorded online with thermocouple. The generated gas during the reaction is collected in a water displacement column. A scale is placed under the column in order to determine the amount of water displaced. The scale is also connected to a computer for online recording of weight. From the displacement of water, the generated amount of hydrogen is calculated. A sample calculation is given in Appendix A.1.

Before the experiments, water displacement column is filled with water by a vacuum pump. In order to prevent the water leakage to the pump, there is a gas washing column to collect the incoming water. The commercial catalyst that is 20% HP Pt on Vulcan XC-72 (ETEK®) is placed into the reactor. Deionized water (1-2mL) is added on the catalyst. Since, $NaBH_4$ spontaneously reacts with water, to prevent self-hydrolysis, solution is prepared on sodium hydroxide (NaOH) medium. The solution is heated till the reaction temperature. When the solution is poured into the reactor, hydrogen generation is started. The generated gas enters to the water displacement column from the bottom. The change in the scale is measured every 0.2s and temperature of the reactor and the ambient temperature are recorded at every 0.2s.

The effect of $NaBH_4$ and NaOH concentrations, catalyst amount and temperature are analyzed during the batch reactor experiments. Figure 3.2 shows the picture of the experimental setup.

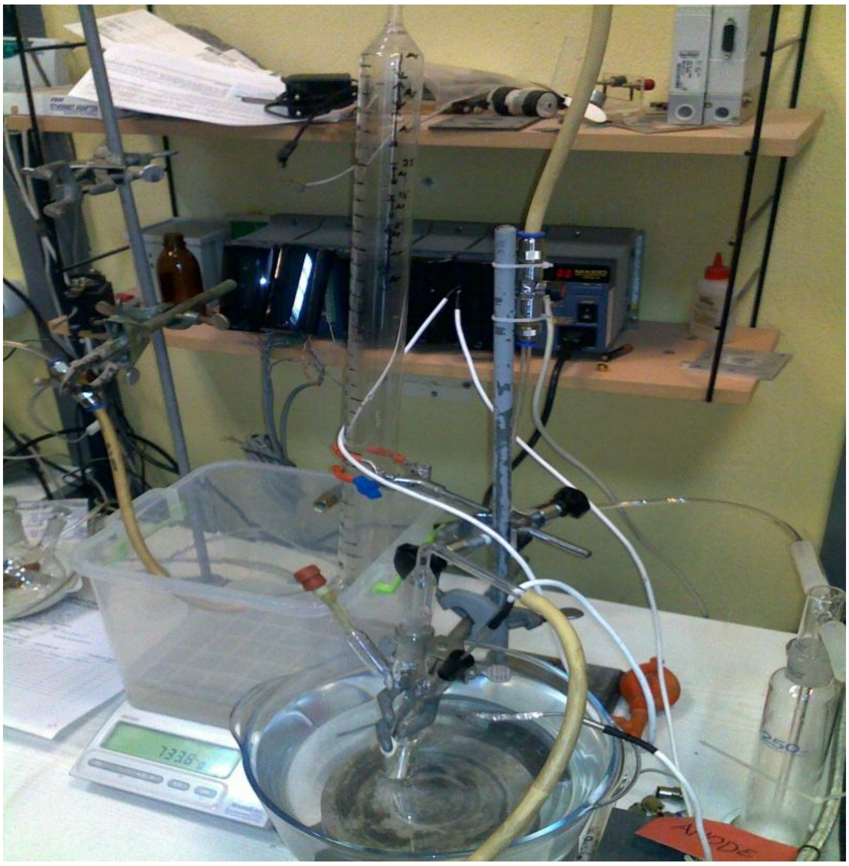


Figure 3-2 Picture of batch hydrogen generating system

3.3 Flow Reactor

3.3.1 Catalyst

Two different catalysts are used in the hydrolysis reaction in a flow reactor: Commercial 20% Pt/C on Vulcan (ETEK®) and intrazeolite Co(0) nanoclusters that are developed by the research group of Prof. Dr. Saim Özkar in Middle East Technical University.

The commercial 20% HP Pt on Vulcan XC-72 (ETEK®) catalyst is placed in the reactor following two methods; either placing it in a powder form in order to allow turbulence in the reactor or placing after coated it on a carbon cloth by using ultrasonic spray (SONO-TEK EXACTA COAT). In order to coat Pt/C catalyst on to the carbon cloth, 30 % of Nafion solution in dry basis is prepared and after the desired amount of catalyst is added to the solution, they are allowed to mix in an ultrasonic stirrer for 30 minutes. Then, it is coated on carbon cloth using ultrasonic spray in order to have evenly distributed catalyst on the surface of carbon cloth as a thin layer.

Intrazeolite Co(0) nanoclusters are used in powder form as they synthesized. Table 3.1 illustrates some properties of Co(0) catalyst.

Table 3-1 Properties of the catalysts used in experiments

Catalyst	**Surface Area(m^2/g)**	**Volume of micropores (cm^3/g)**	**Loading**	**Particle Size**
Intrazeolite Co(0) nanoclusters	652	0.294	0.85%	1-2nm
Pt/C (ETEK)	250	-	20%	2.6nm

3.3.2 Experimental setup and procedure for flow system

Figure 3.3 and Figure 3.4 (a), (b) shows the schematic of the hydrogen generation from sodium borohydride system and picture of flow system respectively.

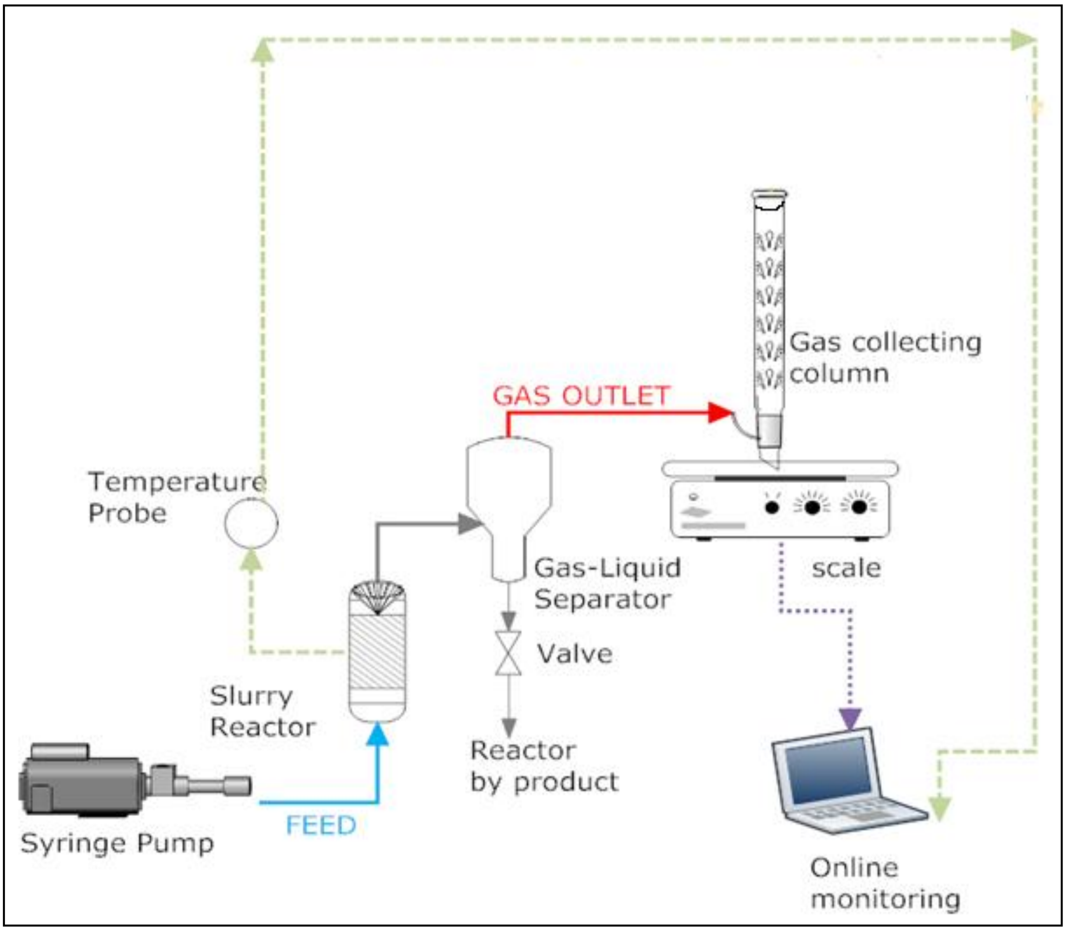
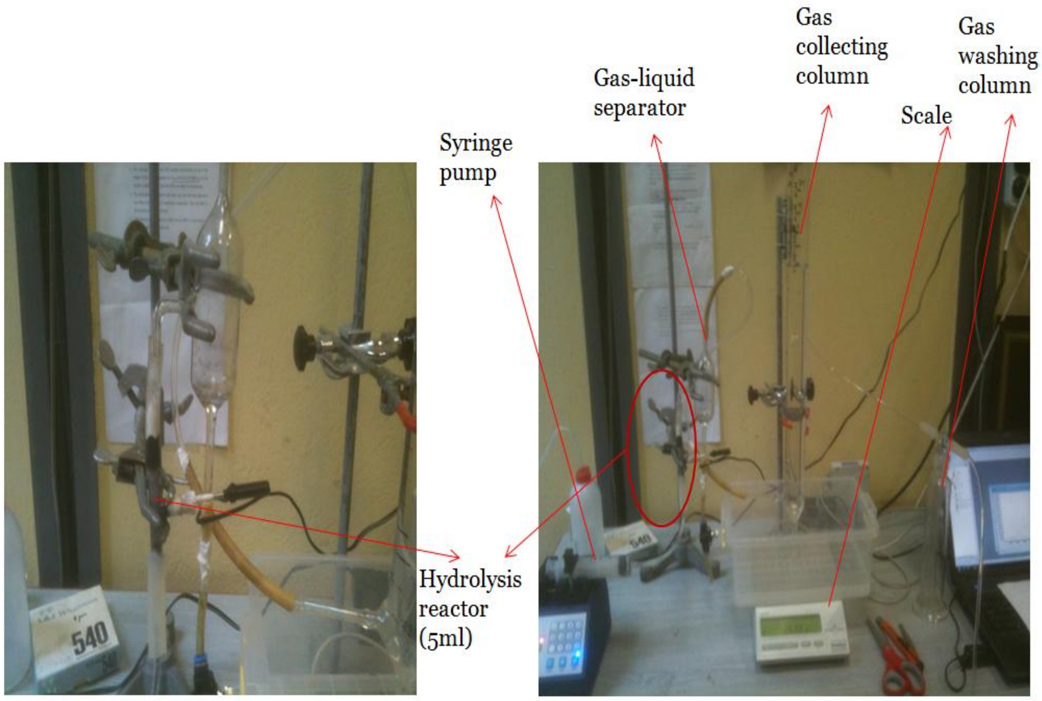


Figure 3-3 The flow sheet of the continuous system



(a) (b)

Figure 3-4 (a) Picture of flow reactor, (b) Picture of flow system used in controlled experiments

Catalyst (either Pt/C or intrazeolite Co(0) nanoclusters) is placed in a differential reactor (5mL) having inner diameter of 8mm. Sodium borohydride solution (containing $NaBH_4$ and NaOH) is pumped to the reactor by a syringe pump (Goldman Ar-01). The effluent is sent to a gas-liquid separator. The hydrogen gas evolved is measured by water-gas displacement method through a graduated cylinder located into a water bath placed on a scale (Mettle Toledo). A scale is connected to a PC computer by RS232 cable for online measuring.

The effect of $NaBH_4$ and NaOH concentrations, catalyst type and amount and the flow rate are analyzed in a flow system. The details of the experimental procedure of this analysis will be discussed in Section 3.5.

3.4 Prototype Reactor

Based on the kinetic experiments carried out in a batch and flow reactor, prototype reactor for hydrogen supply to 100W PEM fuel cell was designed. Reactor was manufactured from Delrin® and specifications were listed in Table 3.2. Figure 3.5 and Figure 3.6 shows the picture of the prototype reactor and flow sheet of the prototype system respectively.

Table 3-2 Specifications of prototype reactor

	Storage	**Prototype Reactor**
Internal Diameter	94 mm	33 mm
External Diameter	100 mm	37 mm
Length	210 mm	142 mm
Internal Volume	1336cm^3	122 cm^3
Mass of System (Empty)	1200 g	
Mass of System (Full)	1900 g	
Material of construction	Delrin	

Figure 3-5 Picture of the designed prototype reactor

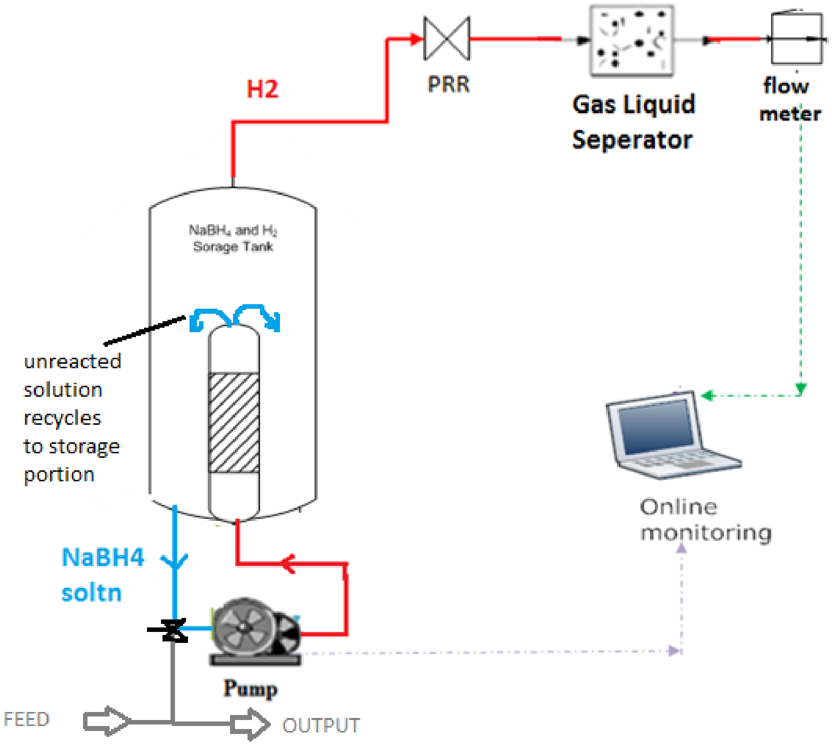


Figure 3-6 Flow sheet of the prototype sodium borohydride reactor

Before the start-up, the desired amount of catalyst that is commercial Pt/C (ETEK®) is placed in the reactor as coated on a carbon cloth in order to minimize catalyst lost during the hydrolysis reaction. Then, the solution prepared at the desired concentration of sodium borohydride and sodium hydroxide, is fed to the storage portion with the help of liquid pump. (Hardgreves) After, solution fills the storage, the pump is started to supply the solution into the reactor. The generated hydrogen is fed to the flow meter (Agilent ADM 3000) and recorded online at every 0.5 seconds. The pump flow rate is controlled by the control unit designed by Serdar Erkan (2011). Also the temperature of the liquid in the storage is recorded online. Figure 3.7 shows the picture of the prototype system that is designed and constructed. The details of the operation of prototype system will be discussed in Section 3.5.

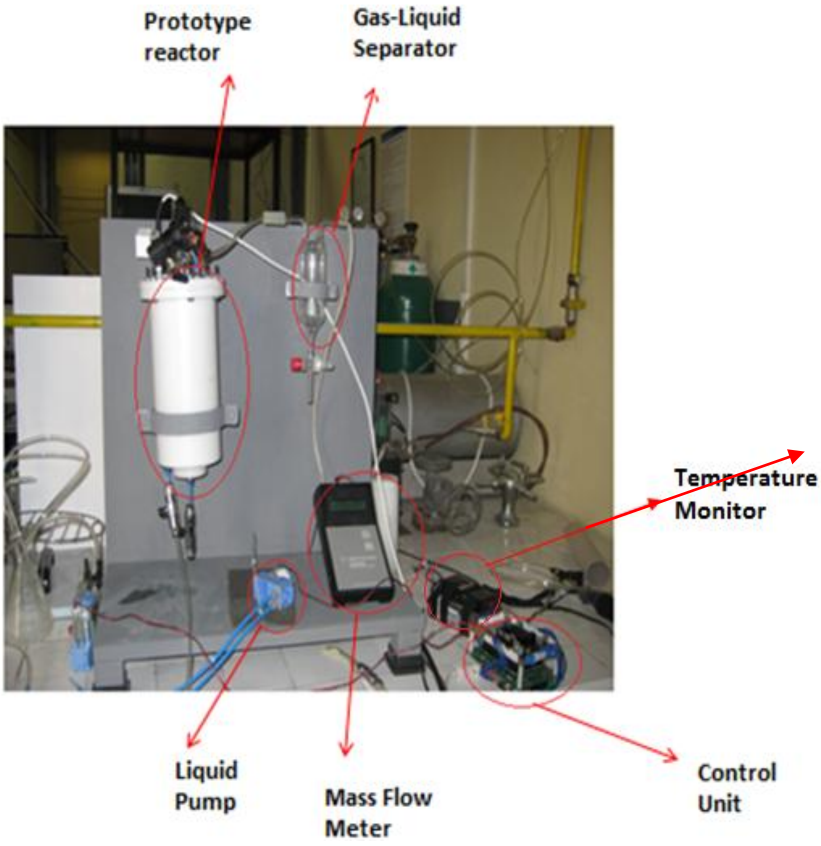


Figure 3-7 Picture of prototype system

3.5 Scope of the kinetic experiments

In kinetic experiments, the parameters are selected by considering the physical limitation of gas collecting column. In other words, the maximum amount of hydrogen generated is fixed by the volume of gas collecting column. Therefore, parameters are analyzed in our measurable quantities.

3.5.1 Batch reactor experiments

3.5.1.1 Effect of $NaBH_4$ concentration

To analyze the hydrogen generation rate and amount change with respect to $NaBH_4$ concentration change, three sets of material is prepared. In these sets, the only parameter that changed is $NaBH_4$ amount, others are kept as constant. 14mL of solutions are prepared with $NaBH_4$ concentrations of 0.17M, 0.23M and 0.3M while keeping constant NaOH concentration and catalyst amount of 0.27M and 0.048g Pt/C respectively. Figure 3.8 shows the compositions of three sets that were prepared. These three experiments are carried out at constant temperature of 20 °C. The pressure of system is 0.94 atm.

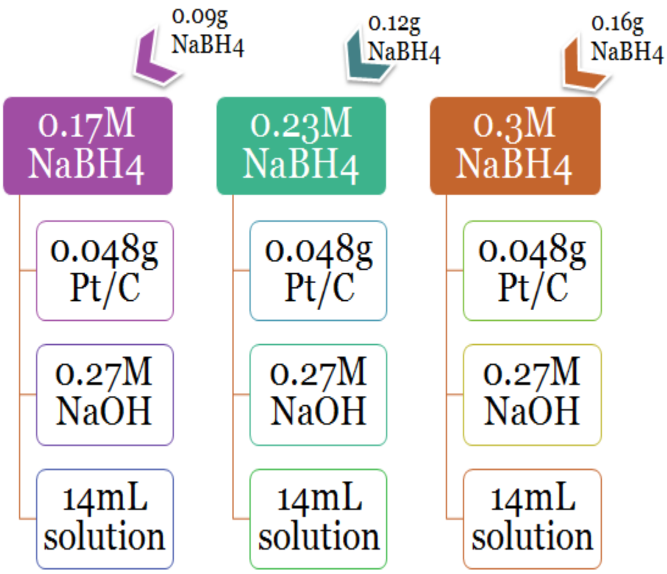


Figure 3-8 The composition of experiments for $NaBH_4$ effect

3.5.1.2 Effect of NaOH concentration

As mentioned in previous chapters, the solutions of $NaBH_4$ are prepared in NaOH in order to prevent self hydrolysis of sodium borohydride. To investigate the effect of NaOH concentration, three sets of experiments are performed that has 1wt% NaOH (0.27M), 5wt% NaOH (1.32M) and 10wt% NaOH (2.85M). The initial $NaBH_4$ concentration is 0.27M in a feed solution of 14mL. These three experiments are carried out at constant temperature of 20 °C. The pressure of system is 0.94 atm.

3.5.1.3 Effect of catalyst amount

To analyze how the hydrogen generation rate is affected from the catalyst amount change, three sets are prepared with initial $NaBH_4$ and NaOH concentrations of 0.23 and 0.27M respectively. 0.048, 0.07 and 0.1g Pt/C is placed in these three sets and experiments are carried out at 20°C and 0.94 atm pressure.

3.5.1.4 Effect of temperature

Again three sets of experiment with same amounts of NaOH, $NaBH_4$ and catalyst but have different temperatures of 20°C, 30°C and 50°C. These temperatures are chosen because they are operation temperatures of fuel cells. Figure 3.11 shows the composition of three sets.

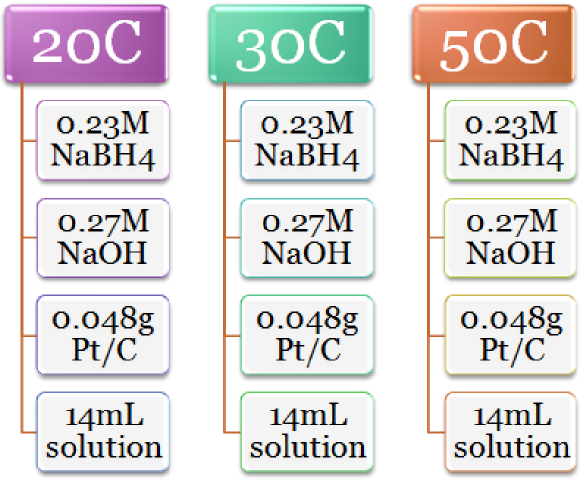


Figure 3-9 Experimental sets for temperature effect

3.5.2 Flow reactor experiments

3.5.2.1 Experiments conducted with commercial Pt/C catalyst

For the experiments carried out in a flow reactor with commercial Pt/C catalyst, first the effect of catalyst placement into the reactor is considered. Commercial Pt/C catalyst is placed in the reactor as coated on a carbon cloth or as a powder form. During the experiments 20 mL of aqueous solution containing 1 wt. % $NaBH_4$ and 0.3 wt. % NaOH are pumped into the reactor containing 0.015g Pt/C with a flow rate of 1 $mL \cdot min^{-1}$.

Then, the effect of $NaBH_4$ concentration was discussed. These experiments are carried out at a constant NaOH concentration as 0.3wt%, temperature of 20°C, with a feed rate of 1 $mL \cdot min^{-1}$ and using 0.015g powder form Pt/C by varying the $NaBH_4$ concentration as 0.5, 1, 1.5, 2, 3 and 3.6 wt.%.

Next, the effect of NaOH concentration was examined. For these experiments initial NaOH concentration is changed as 0, 0.3, 0.5 and 1 wt.% while the initial

$NaBH_4$ concentration is 1wt%, catalyst weight of 0.015g, temperature of 20°C at a feed rate of 1 $mL \cdot min^{-1}$.

Finally, to investigate the effect of feed flow rate to the hydrogen generation rate three sets of experiments are conducted with 0.015g powder form of Pt/C catalyst and feeding 0.3wt% NaOH and 1wt% $NaBH_4$ with a flow rate of 0.1, 0.5 and 1mL/min.

All experimental data and sample calculations are given in Appendix B.1.

3.5.2.2 Experiments conducted with intrazeolite Co(0) nanoclusters

$NaBH_4$ concentration is changed as 88.1, 264.57 and 440.57mM while keeping constant feed flow rate of 1mL/min and NaOH concentration of 83.3mM. 0.21g in powder form catalyst is used during the experiments.

Then, initial NaOH concentration is changed as 83.3, 166.7 and 250mM. During the experiments the initial $NaBH_4$ concentration is 264.57mM and feed flow rate is 1mL/min.

The 1, 2 and 3 mL/min feed solution flow rate is tested with 264.57mM $NaBH_4$ and 83.3mM NaOH.

All experimental data and sample calculations are given in Appendix B.2.

3.5.3 Prototype performance experiments

In order to check the performance of the designed prototype reactor 3 runs are made with different $NaBH_4$ concentrations and operation modes.

3.5.3.1 Run 1

In the first run 730 mL of 1wt% $NaBH_4$ and 0.5wt% NaOH solution circulated at a flow rate of 3mL/s is used. 1g of Pt/C ETEK® catalyst is placed in the reactor as coated on a carbon cloth. After the storage was filled with the 730 mL of solution in 15 minutes, pump is stated and this initiates the hydrolysis reaction. The reactor is allowed to operate 60 min and after 60 min, the pump is stopped. Then, it is started circulating again by the same parameters. Next, the performance is checked.

3.5.3.2 Run 2

In the second run, 710mL of 3wt% $NaBH_4$ and 0.5wt% NaOH solution circulated at a flow rate of 3mL/s. 1g of Pt/C ETEK® catalyst is placed in the reactor as coated on a carbon cloth. Again it is allowed to operate 60 min and after 60 minutes, the pump is stopped. Then, again started circulating by the same parameters and performance is checked and compared with run 1. Between the circulation steps, the solution remaining in the reactor is fed to the storage part in order to prevent hydrogen loss.

3.5.3.3 Run 3

In the third run, 700 mL of 5wt% $NaBH_4$ and 0.5wt% NaOH solution recycled with a flow rate of 3mL/s. 1g of Pt/C ETEK® catalyst is placed in the reactor as coated on a carbon cloth. Different than previous runs, the reactor is operated until the hydrogen generation stops.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Kinetic Analysis of Hydrolysis of Sodium Borohydride on a Batch System

There were mainly four parameters that were affecting the hydrogen generation rate such that $NaBH_4$ concentration, catalyst amount, NaOH concentration and the reaction temperature in a batch system. To investigate the order of magnitude of their effects the controlled experiments were carried out. The experimental setup was illustrated in Figure 3.2. The effect of $NaBO_2$ was not considered in this work.

4.1.1 The effect of $NaBH_4$ concentration on H_2 generation rate

Figure 4.1 shows the effect of $NaBH_4$ concentration on the hydrogen generation. The amount of H_2 generated was calculated from Peng-Robinson Equation of State. A sample calculation is shown in Appendix A.1. Also, the raw data of is tabulated in Table A.1 and a graph in terms of milliliters of H_2 produced was shown in the Appendix A in Figure A.1.

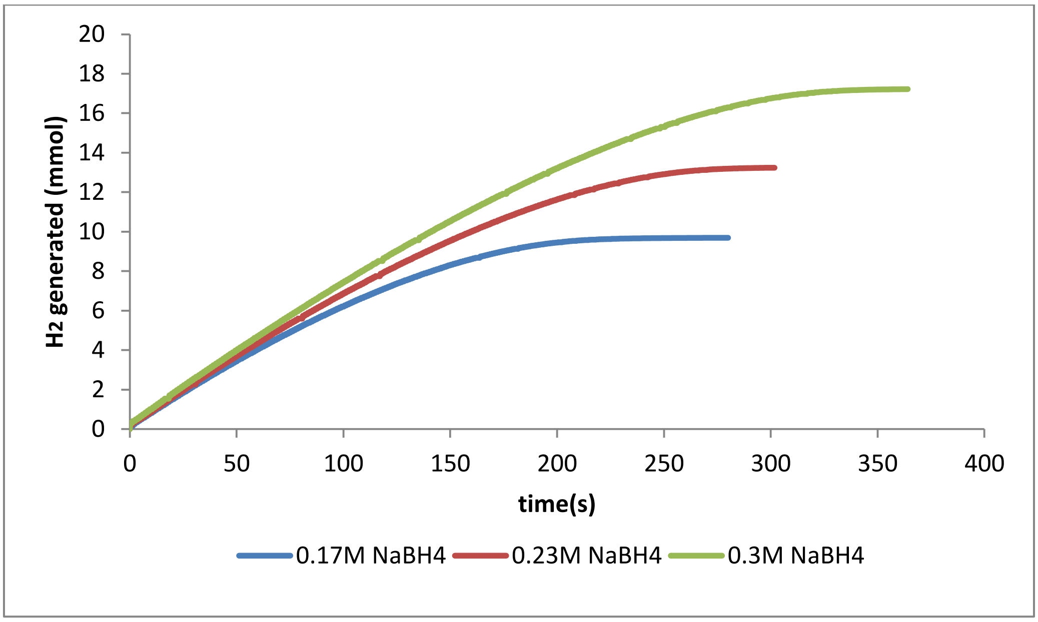


Figure 4-1 The effect of initial $NaBH_4$ concentration on H_2 generation rate

The hydrogen generation rate is calculated from the slope of the line best fitted to the cumulative H_2 generated (mmol) versus time (min). Figure 4.2 shows this linear fit.

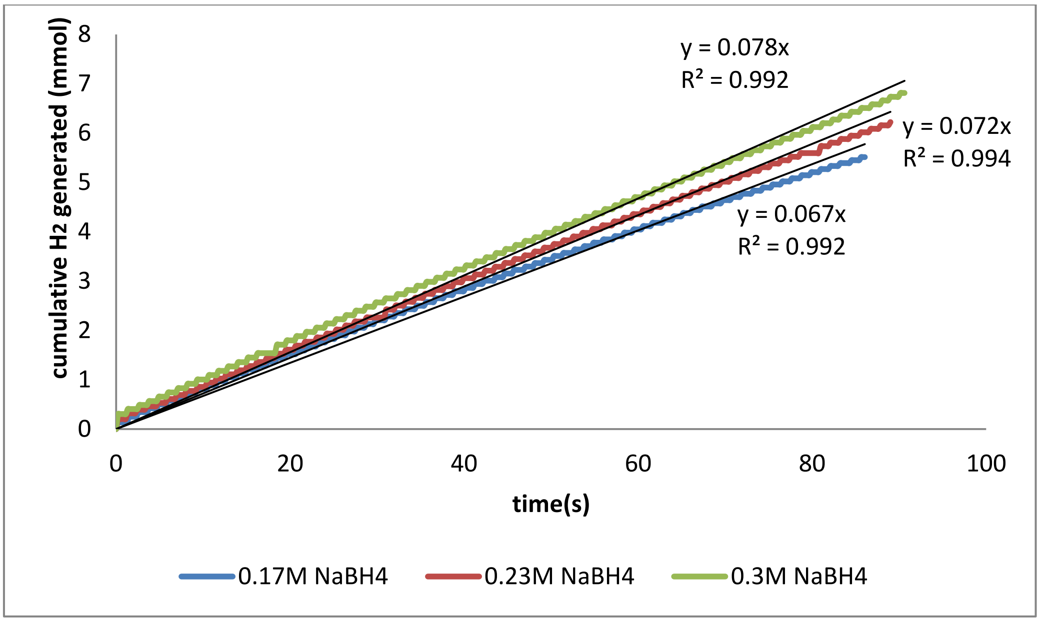


Figure 4-2 Best fitting line to the H_2 generated versus time data

Sample calculations for hydrogen generation rate are also shown in the Appendix A.2. The H_2 generated rates are calculated as 83.88, 90.25 and 97.50 mmol/min.g_{cat} for 0.17M, 0.23M and 0.3M $NaBH_4$ concentrations respectively.

According to the Figure 4.1, as $NaBH_4$ concentration increases, the maximum amount of H_2 generated increases. Also, the hydrogen generation rate shows a little increase. Therefore, the hydrogen generation rate is dependent on concentration of sodium borohydride.

Figure 4.3 shows the temperature profile during the three controlled experiments. The temperature of the reactor is successfully kept constant at desired temperature of 20±1°C. The deviations are acceptable since the reaction is highly exothermic and 0.5-1°C is assumed that had no effect on the reaction rate.

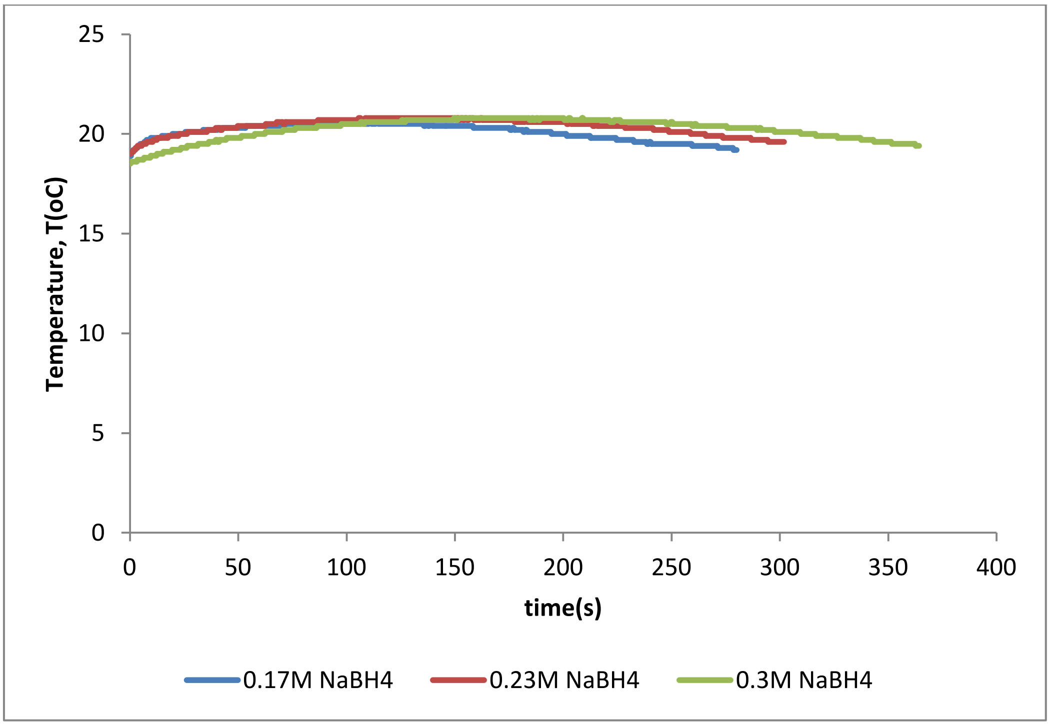


Figure 4-3 Temperature change in the reactor during the experiments with respect to time

4.1.2 The effect of NaOH concentration on H_2 generation rate

Figure 4.4 shows the effect of initial NaOH concentration on the cumulative hydrogen generated.

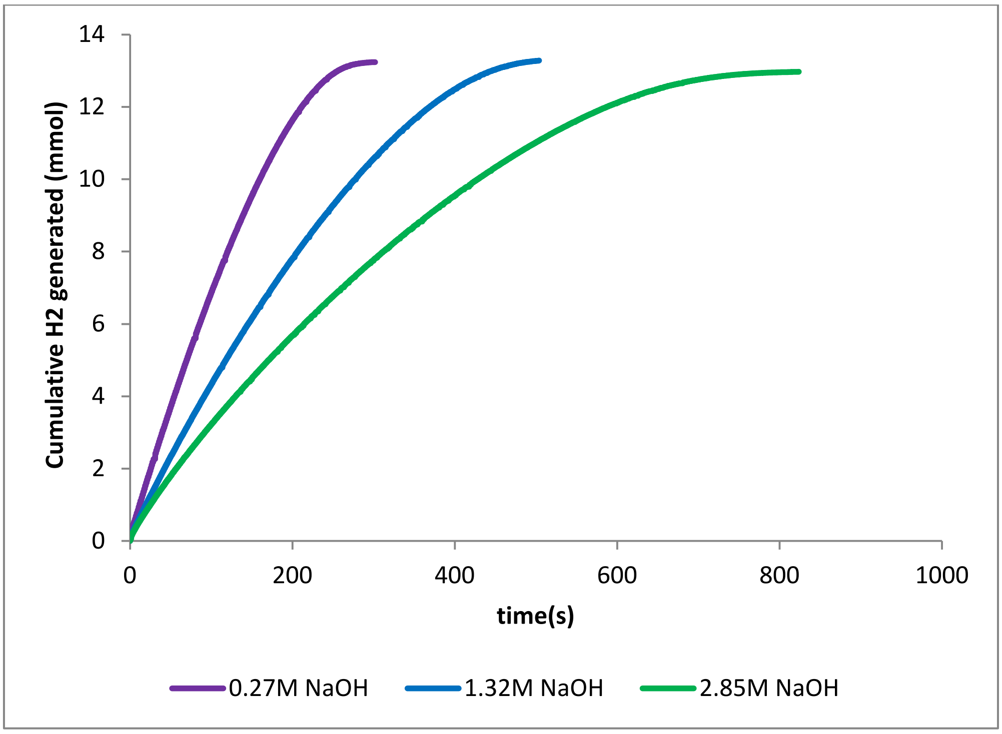


Figure 4-4 The cumulative H_2 generation for different NaOH concentrations

The hydrogen generation rates are calculated from the slope of the best fitting line as shown Figure 4.5.

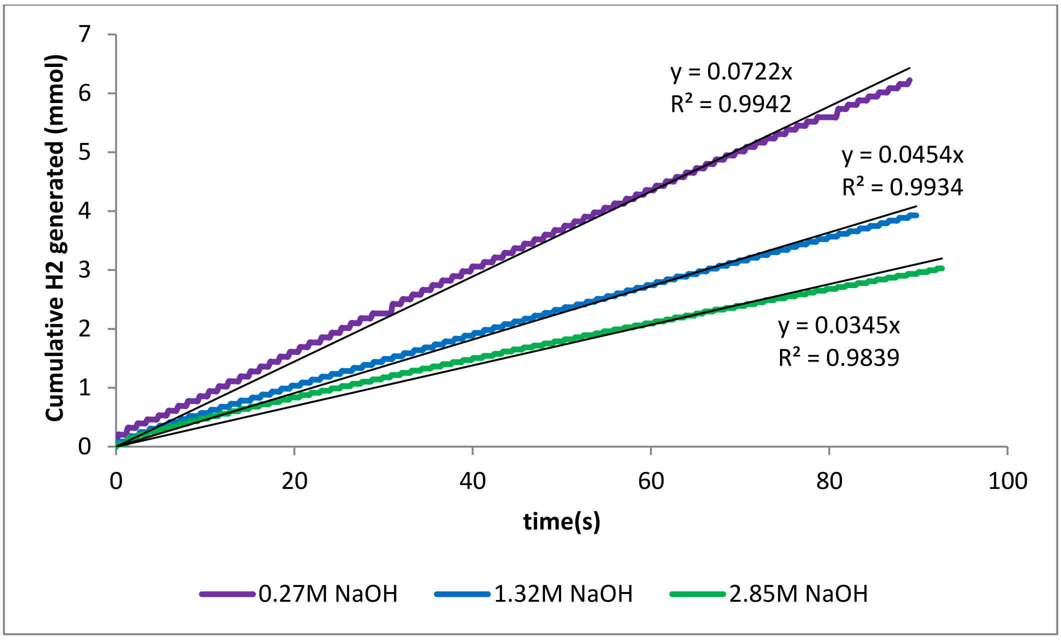


Figure 4-5 Linear fit to the cumulative hydrogen generated versus time data for different NaOH concentrations

For NaOH concentrations of 0.27M, 1.32M and 2.85M NaOH, the H_2 generation rates are calculated as 90.25, 56.75 and 43.13 mmol/min.g_{cat} respectively. The sample calculation is shown in Appendix A.2.

From the Figure 4.4, it can be seen that the maximum amount of hydrogen produced is same within 3 cases as expected since the $NaBH_4$ amount does not changed. Also, as NaOH concentration increases the H_2 generation rate decreases accordingly. So, it is concluded that for high production rates the NaOH concentration should be optimized. It is noted that temperature is kept constant at 20°C during all experiments.

4.1.3 The effect of catalyst amount on H_2 generation rate

Figure 4.6 shows the effect of catalyst on the hydrogen generation rate.

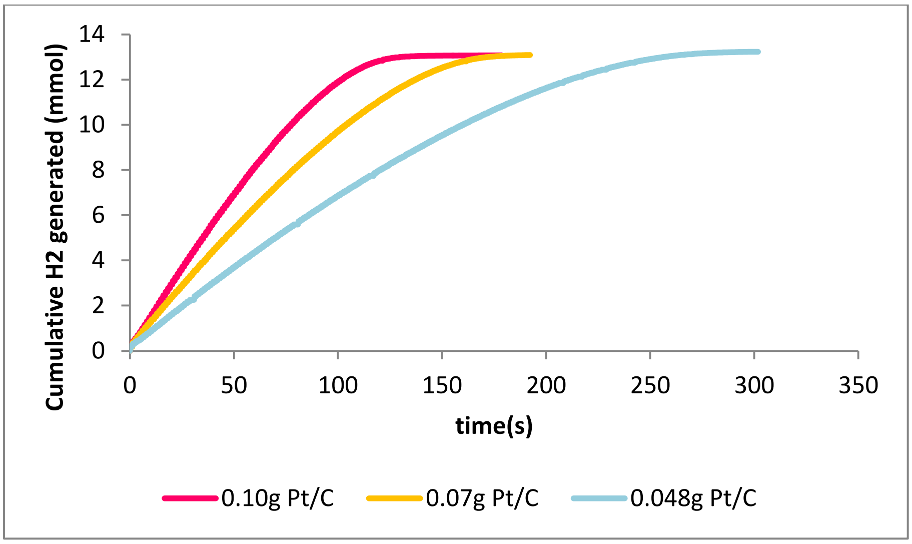


Figure 4-6 The cumulative hydrogen generated versus time for different amounts of catalyst

As expected it is seen that the hydrogen production rate increases with increase of catalyst whereas the maximum amount of hydrogen produced does not change.The hydrogen generation rates are calculated from the slope of the linear fit shown in Figure 4.7.

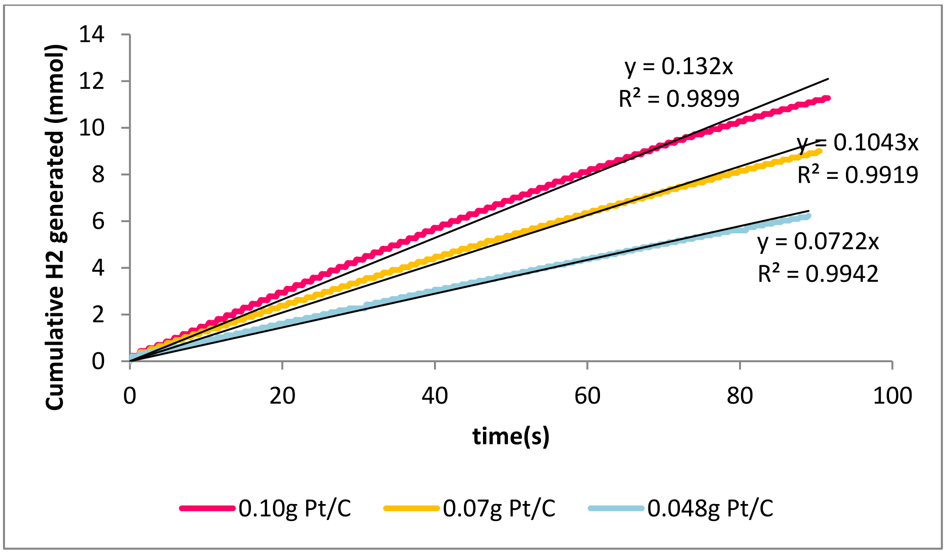


Figure 4-7 Best fitting line for H_2 generation rate calculation for different catalyst amounts

The H_2 production rates are calculated as 79.2, 89.4 and 90.25 mmol/min.g_{cat} for 0.1g, 0.07g and 0.048g Pt/C catalyst respectively. Sample calculation is shown Appendix A.2.

Figure 4.8 indicates the temperature profile for these three cases whereas the room temperature is 17°C. As can be seen from Figure 4.6 reaction temperature is kept constant at 20 °C.

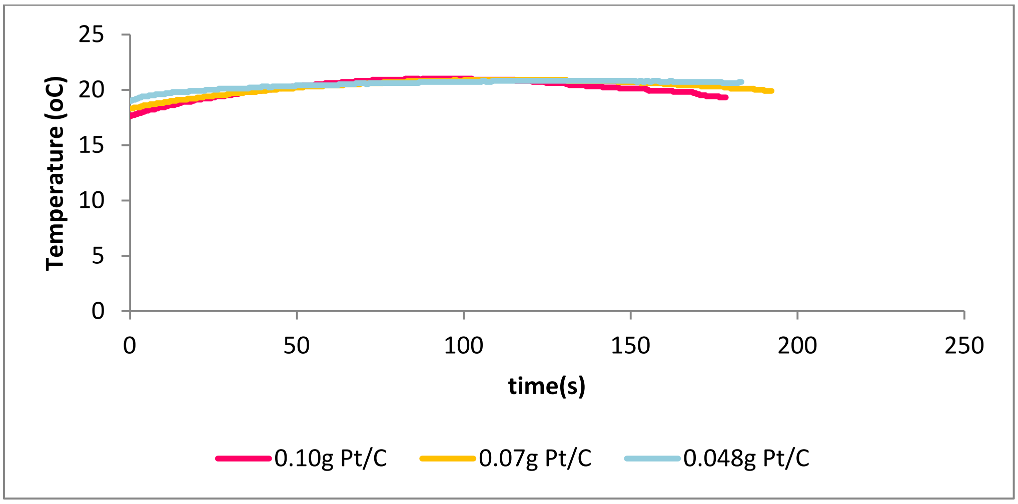


Figure 4-8 Temperature profile in the reactor during the hydrolysis reaction

4.1.4 The effect of temperature on H_2 generation rate

The raw data for cumulative H_2 generation (mL) versus time is shown in Appendix A.2 in Figure A.5. The raw data is converted into mmoles of H_2 using Peng-Robinson Equation of State. Figure 4.7 shows the cumulative H_2 generated (mmole) versus time for different reaction temperatures.

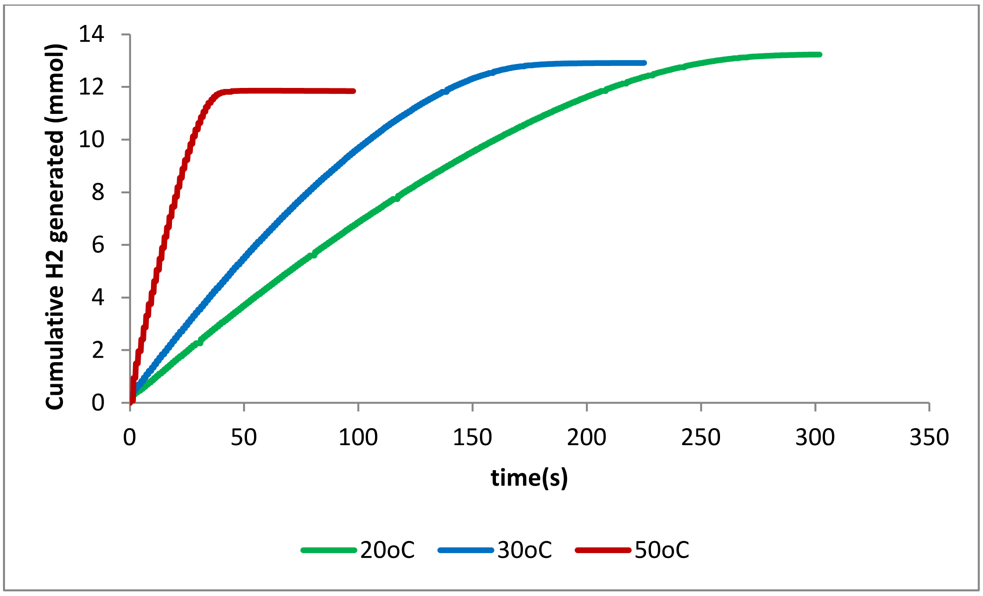


Figure 4-9 Effect of temperature on H_2 generation

The H_2 generation rate is calculated from the slope of the best fitting line to the cumulative H_2 production versus time data shown in Figure 4.10.

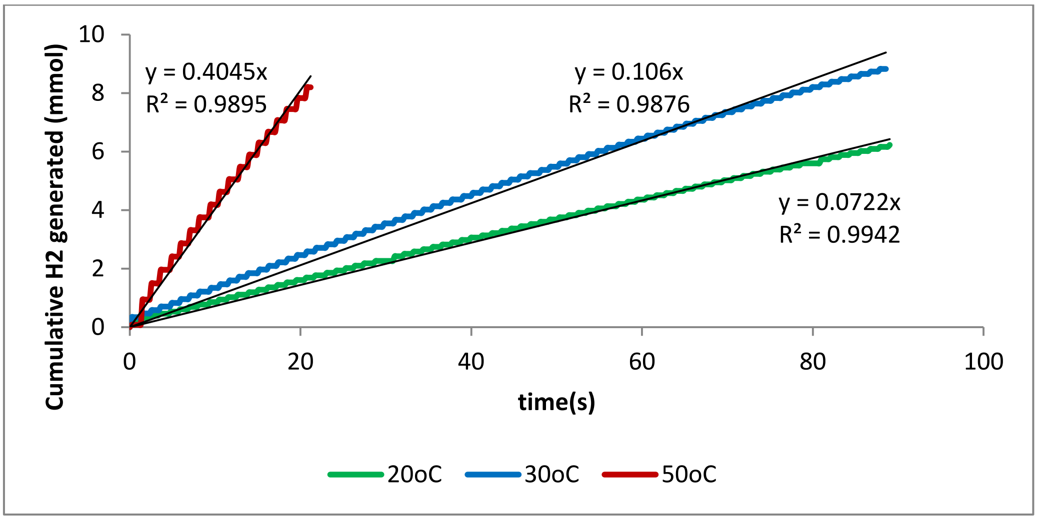


Figure 4-10 Linear fit to the cumulative H_2 production versus time data

The increase in the temperature of the reactor increases the rate dramatically. For 50 °C, the hydrogen generation rate is found as 505.63 mmol/min.g_{cat} whereas for 30 °C, rate is determined as 132.5 mmol/min.g_{cat}. Figure 4.11 shows the temperature of the reactor during the reactions.

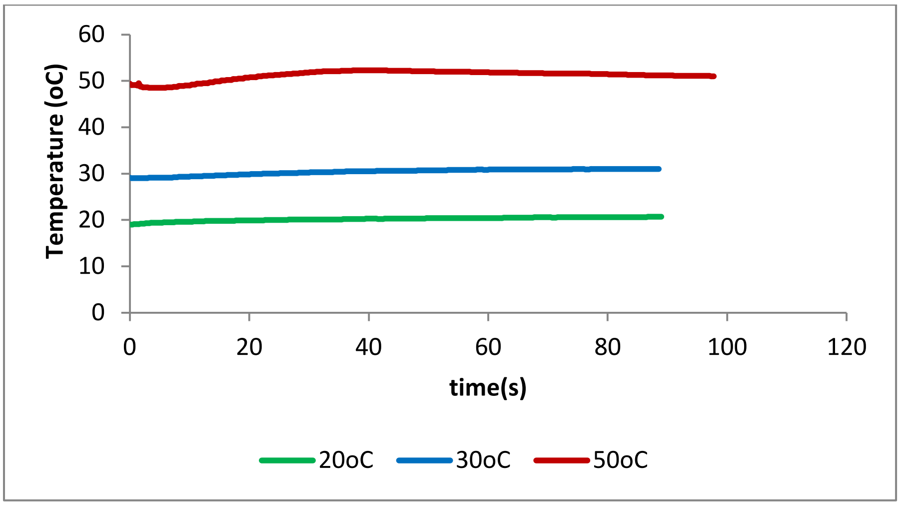


Figure 4-11 Temperature change in the reactor with respect to time

4.1.5 Determination of kinetic model

Before determination of the kinetic model, the reproducibility of experiments were checked. The experiments were found to be reproducible. This verification is shown in the Appendix section.

4.1.5.1 Assumptions and considerations

1. Evaporation from the water tank was negligible.
2. The diffusion of H_2 from the gas collecting column was negligible.

3. The solubility of H_2 in water was negligible.
4. The tube reactor was well mixed.
5. The pressure of the system was constant.
6. Temperature of the system was kept constant during the hydrolysis reaction.

The hydrolysis reaction is considered as in the following Equation 4.1:

$$NaBH_4(aq) + 2H_2O(l) \xrightarrow{catalyst} NaBO_2(aq) + 4H_2(g) \tag{4.1}$$

From the reaction stoichiometry the relationship between the rate expressions can be written as shown in the Equation 4.2.

$$-r_{NaBH_4} = r_{NaBO_2} = \frac{-r_{H_2O}}{2} = \frac{r_{H_2}}{4} \tag{4.2}$$

Therefore,

$$-r_{NaBH_4} = \frac{r_{H_2}}{4} \tag{4.3}$$

The batch reactor design equation was expressed in the following Equation 4.4.

$$\frac{d(N_{H_2})}{d(t)} = r_{H_2} \tag{4.4}$$

After the controlled experiments, it is found that the reaction rate depends on concentration of $NaBH_4$ and NaOH and temperature. The proposed model is shown in Equation 4.5.

$$r'_{H_2} = f(T, C_{NaOH}, C_{NaBH_4}) \tag{4.5}$$

The reaction rate in terms of hydrogen is expressed by using power law that is shown in Equation 4.6. It must be noted that the catalyst effect is included in the rate constant k in the Equation 4.6.

$$r'_{H_2} = kC^{\alpha}_{NaBH_4}C^{\beta}_{NaOH} \tag{4.6}$$

where,

$$k = Ae^{-Ea/RT} \tag{4.7}$$

For the first set of experiments, where only initial NaBH4 concentration is changed while other parameters are constant, the rate law in Equation 4.6 reduces to Equation 4.8. The stoichiometric relation shown in Equation 4.3 is also inserted into Equation 4.8.

$$-r'_{NaBH_4} = k'C^{\alpha}_{NaBH_4} \tag{4.8}$$

Where,

$$k' = \frac{k}{4}C^{\beta}_{NaOH} \tag{4.9}$$

By taking natural logarithm of both sides of the Equation 4.8:

$$\ln(-r'_{NaBH_4}) = \alpha InC_{NaBH_4} + Ink' \tag{4.10}$$

So the slope of the graph of InC_{NaBH_4} versus $-\ln r'_{NaBH_4}$ gives the value of α whereas the y-axis intersection point gives the Ink' value. Figure 4.12 gives this relation.

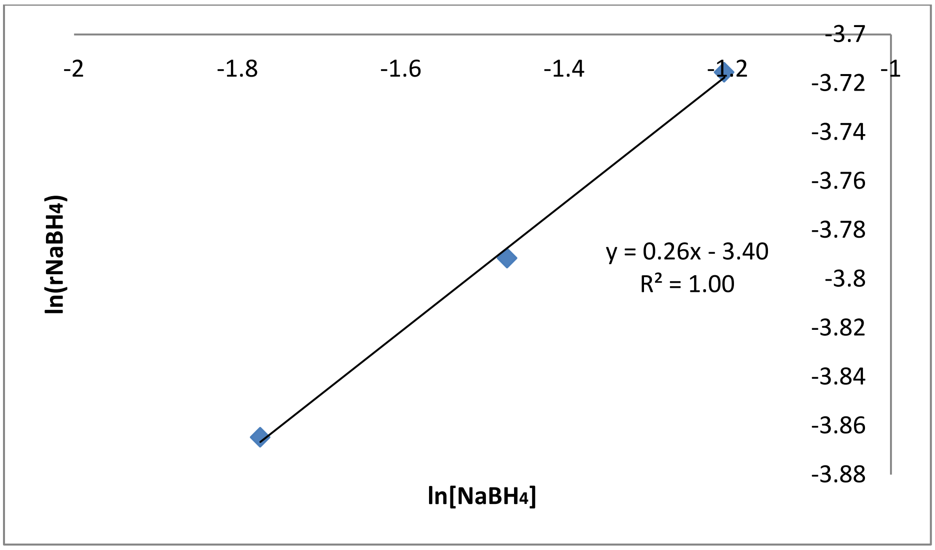


Figure 4-12 The ln(rNaBH$_4$) versus ln[NaBH$_4$] graph

From Figure 4.12 the α value was determined as 0.26 and k' was 33.38×10^{-3}.

$$k^{'} = k^{''} C_{NaOH}^{\beta} \tag{4.11}$$

For the next set of experiments, where the initial NaOH concentration is changed, the same methodology as for NaBH$_4$ is followed in order to determine the β. For constant initial NaBH$_4$ concentration and temperature Equation 4.6 reduces to Equation 4.12.

$$-r_{NaBH_4}^{'} = k^{'''} \times C_{NaOH}^{\beta} \tag{4.12}$$

Where,

$$k^{'''} = \frac{k}{4} C_{NaBH_4}^{\alpha} \tag{4.13}$$

Natural logarithm of both sides of Equation 4.12 is taken to get Equation 4.14.

$$\ln(-r_{NaBH_4}^{'}) = \beta \ln(C_{NaOH}) + \ln k^{'''} \tag{4.14}$$

The β value is determined from Figure 4.13, which gives the ln(-r'_{NaBH_4}) versus ln[NaOH] graph.

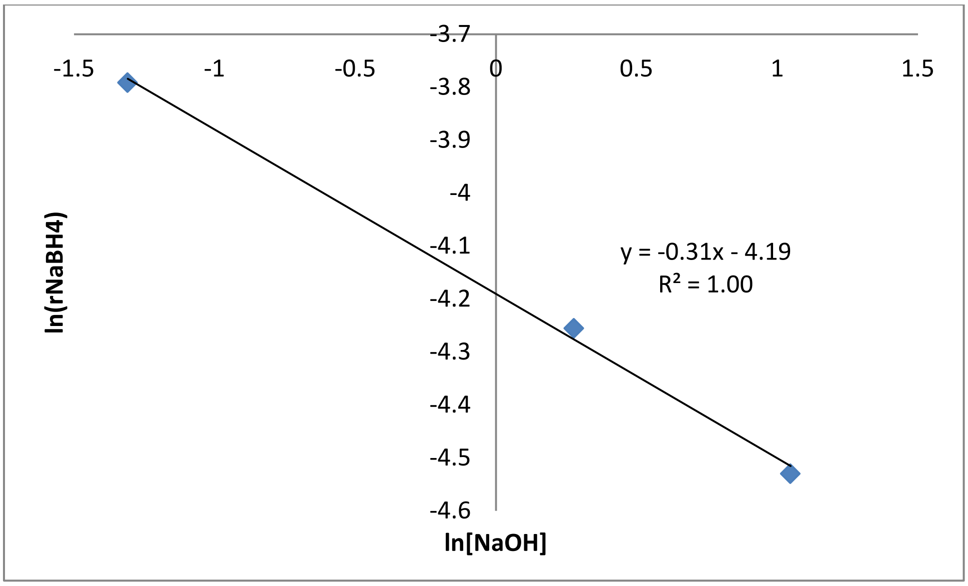


Figure 4-13 In(r_{NaBH4}) versus ln[NaOH] graph

From the Figure 4.13, β value is determined from the slope of the best fitting line as -0.31.

After finding β, from Equation 4.9, k value is determined as 88.97×10^{-3} $mol^{1.05}/L^{0.05}.min.g_{cat}$ by inserting the value of the constant concentration of NaOH, which was 0.27M.

So for constant temperature at 20°C and constant catalyst weight that is 0.048g Pt/C the rate expression is found as shown in Equation 4.15.

$$r'_{H_2} = 88.97\times 10^{-3}\times\frac{C_{NaBH_4}^{0.26}}{C_{NaOH}^{0.31}}\quad\frac{mol}{\min g_{cat}}\qquad \text{for } 20^{0}\text{C with } R^2 = 0.98 \qquad (4.15)$$

For the temperature analysis, by taking the natural logarithm of both sides of the Equation 4.7 Equation 4.16 is obtained.

$$\ln(k) = \ln A - \frac{E_a}{R}\frac{1}{T} \tag{4.16}$$

In order draw Arrhenius plot, k values at different temperatures are calculated using the model Equation 4.15.

For 20°C, k_1 is found as 88.97×10^{-3} $\text{mol}^{1.05}/\text{L}^{0.05}$.min.gcat

For 30°C, the hydrogen generation rate is found to be 132.5×10^{-3} mol/ming$_{cat}$. So, substituting the constant parameters in Equation 4.15 gives:

$$132.5\times10^{-3} = k_2(0.23)^{0.26}(0.27)^{-0.31} \tag{4.17}$$

$$k_2 = 0.130\ \text{mol}^{1.05}/\text{L}^{0.05}\text{min.g}_{\text{cat}} \tag{4.18}$$

For 50°C, the hydrogen generation rate is found to be 505.63×10^{-3} mol/min. So, substituting the constant parameters in Equation 4.15 gives:

$$505.63\times10^{-3} = k_3(0.23)^{0.26}(0.27)^{-0.31} \tag{4.19}$$

$$k_3 = 0.494 \quad \text{mol}^{1.05}/\text{L}^{0.05}.\text{min.g}_{\text{cat}} \tag{4.20}$$

From these calculations Arrhenius plot is drawn and shown in Figure 4.14.

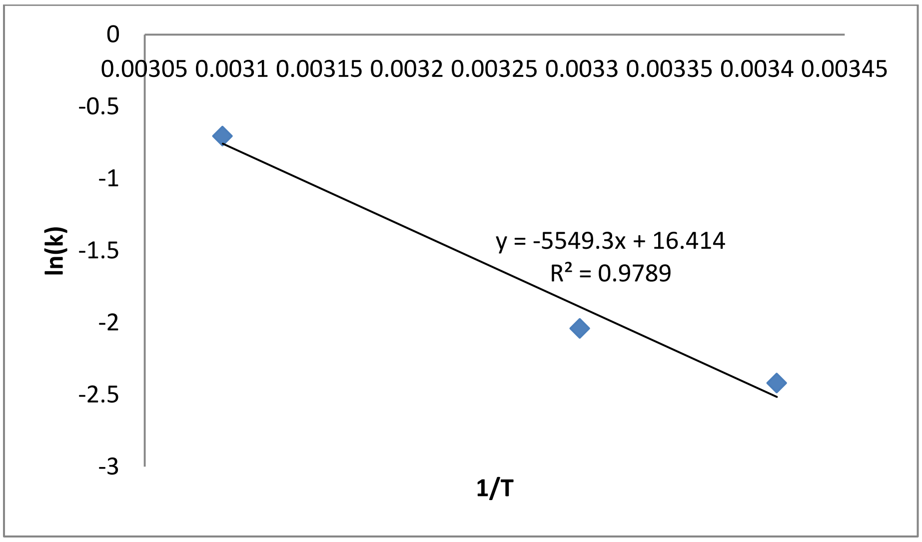


Figure 4-14 Arrhenius plot

The slope of the Figure 4.14 gives –E_a/R, where R is the gas constant, which is 8.314×10^{-3} kJ/mol.K and the intercept gives the ln(A), where A is the pre-exponential factor.

From Figure 4.14, the pre-exponential factor and activation energy were found as: 13.4×10^{6} mol/Lmin and 46.0±1 kJ/mol respectively.

So, the rate expression takes the form:

$$r'_{H_2} = 13.4\times10^{6}\times e^{-\frac{46.0}{RT}}\times\frac{C_{NaBH_4}^{0.26}}{C_{NaOH}^{0.31}} \qquad \frac{mol}{\min g_{cat}} \text{ with } \mathrm{R}^2 = 0.986 \tag{4.21}$$

Table 4.1 summarizes the results of batch reactor experiments.

Table 4-1 Results of kinetic experiments in a batch reactor

$NaBH_4$ Concentration (M)	NaOH Concentration (M)	Temperature (°C)	Catalyst Amount (g)	H_2 generation rate (mmol/min.g_{cat})
0.17	0.27	20	0.048	83.88
0.23	0.27	20	0.048	90.25
0.30	0.27	20	0.048	97.50
0.23	1.32	20	0.048	56.75
0.23	2.85	20	0.048	43.13
0.23	0.27	20	0.07	89.4
0.23	0.27	20	0.1	79.2
0.23	0.27	30	0.048	132.50
0.23	0.27	50	0.048	505.63

4.2 Kinetic Analysis of Hydrolysis of Sodium Borohydride in a Flow System

There were mainly four parameters tested in a flow system. These were $NaBH_4$ concentration, catalyst amount, NaOH concentration and the flow rate of solution in a flow system. The experimental setup for flow reactor controlled experiments was illustrated in Figure 3.5. Experimental data (cumulative volume of H_2 generated versus time) and a sample calculation for the H_2 production rate (mmol/min.g_{cat}) are given in Appendix B. The results are given below.

4.2.1 Results of the experiments carried out with Pt/C (ETEK®) catalyst in a flow reactor

4.2.1.1 Effect of catalyst placement

Figure 4.15 shows the effect of catalyst placement (either coated on carbon cloth or using as powder form) on the cumulative hydrogen generation.

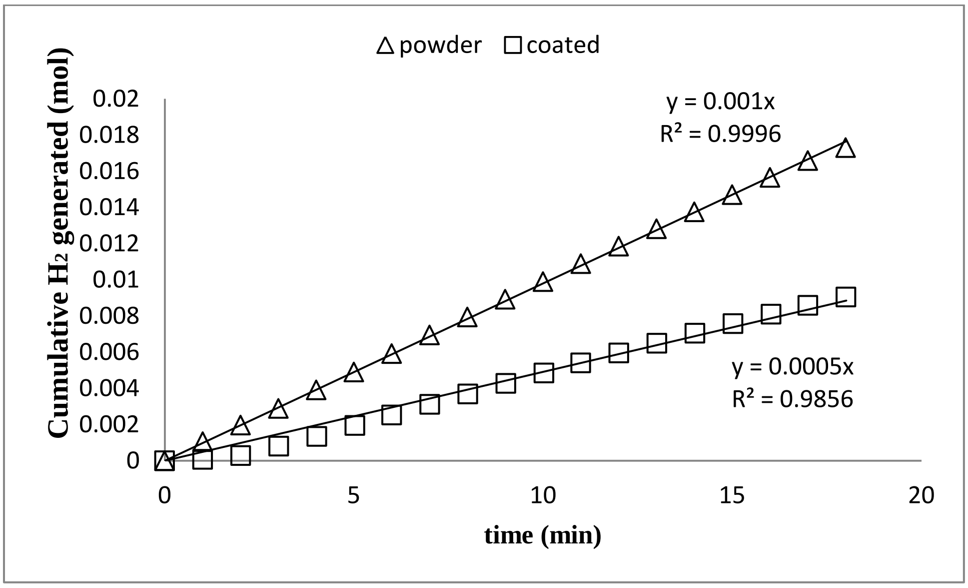


Figure 4-15 Effect of catalyst placement on H_2 generation for initial $NaBH_4$ concentration is 1wt%, NaOH concentration is 0.3wt% at feed rate of 1mL/min and 0.015g Pt/C catalyst (solid line represents best fitting line)

Hydrogen generation rate is estimated from the slope of the best fitting line to the cumulative H_2 generated mol versus time data by the following equation:

$$r'_{H_2,coated} = \frac{0.0005\left(\frac{mol}{\min}\right)\left(\frac{10^3 mmol}{mol}\right)}{0.015 gcat} = 33.3 \frac{mmol}{\min . g_{cat}} \tag{4.22}$$

$$r'_{H_2,powder} = \frac{0.001(\frac{mol}{\min})(\frac{10^3 mmol}{mol})}{0.015 gcat} = 66.7 \frac{mmol}{\min .g_{cat}} \tag{4.23}$$

H_2 generation rate is higher for powder catalyst than the H_2 generation rate of the coated catalyst. This result indicates the significance of the diffusional mass transfer limitations.

The effectiveness factor for this catalyst is estimated from the Equation 4.24:

$$\eta_{eff} = \frac{apperant\ H_2\ generation\ rate}{actual\ H_2\ generation\ rate} = \frac{r'_{H_2,coated}}{r'_{H_2,powder}} \tag{4.24}$$

as;

$$\eta_{eff} = \frac{33.3 mmol / \min g_{cat}}{66.6 mmol / \min g_{cat}} = 0.5 \tag{4.25}$$

Thus, for further experiments 0.015g powder form of Pt/C was selected to be used.

4.2.1.2 Effect of $NaBH_4$ concentration

The variation in hydrogen generation rate with the concentration of $NaBH_4$ is shown in Figure 4.16. The raw experimental data is given in Appendix B.

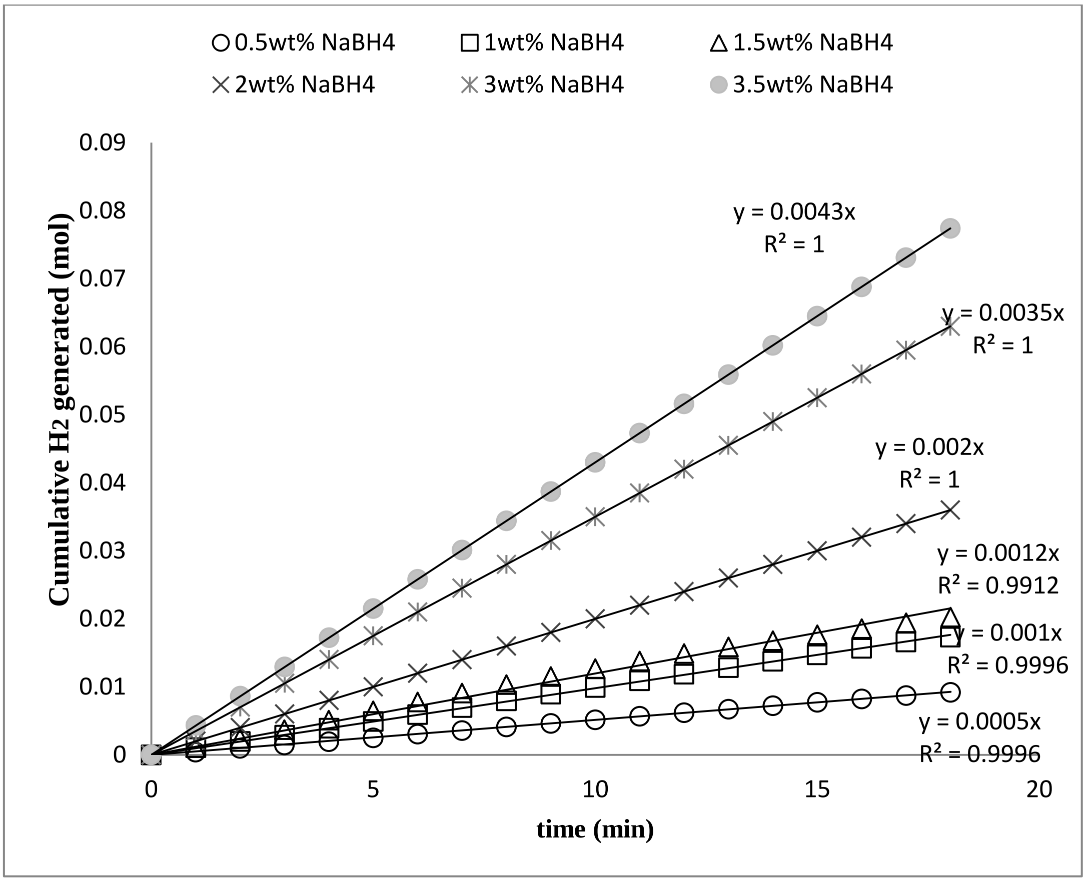


Figure 4-16 Linear fit of cumulative H_2 generation versus time

The amount of hydrogen generated in terms of moles is calculated based on Peng-Robinson Equation of State. The calculation procedure is discussed in Appendix A.1.

The hydrogen generation rates are estimated from the slope of the best lines fitted to the H_2 generated versus time data shown in Figure 4.16. The steady state hydrogen generation rates of 0.5, 1, 1.5, 2, 3 and 3.5 wt.% $NaBH_4$ solutions were 33.3, 66.7, 80,133.3, 233.3 and 286.7 mmol·min^{-1}·g$_{cat}^{-1}$, respectively. For these sets of experiments 0.015g of Pt/C is placed in the reactor in powder form. The reactor is operated for 20 minutes at continuous mode. It is observed that it reaches steady state after approximately 5 minutes.

The rate equation shows the effect of $NaBH_4$ concentration can be written as:

$$r'_{H_2} = k'[NaBH_4]^{\alpha} \tag{4.26}$$

Equation (4.26) is linearized by taking the natural logarithm of both sides.

$$\ln(r_{H_2}) = \alpha \ln([NaBH_4]) + \ln(k') \tag{4.27}$$

From the Figure 4.17, the linear fit gives the following equation:

$$\ln(r_{H_2}) = 1.1\ln([NaBH_4]) - 1.98 \tag{4.28}$$

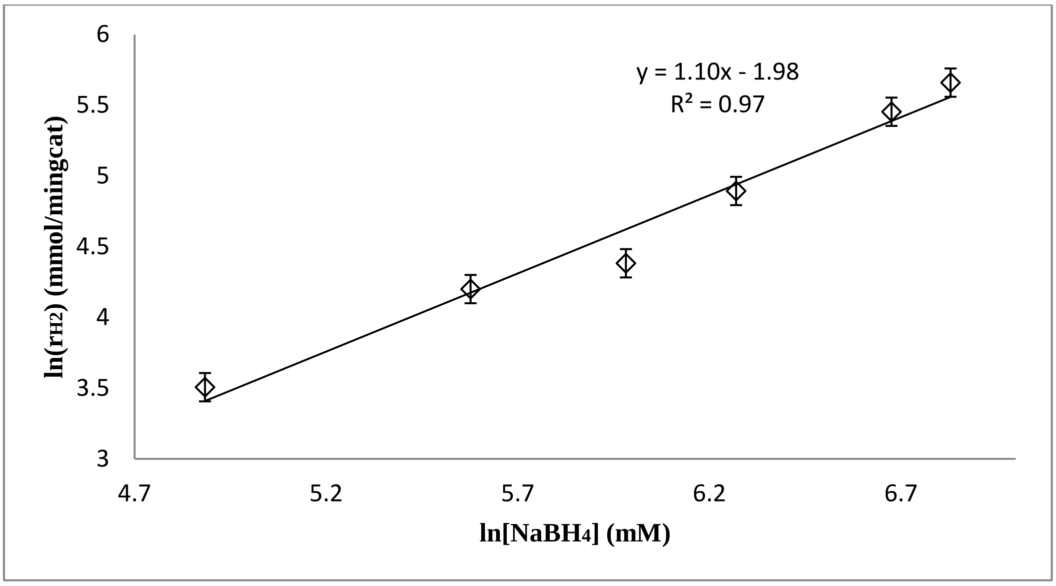


Figure 4-17 $\ln(r'_{H_2})$ versus $\ln[NaBH_4]$ graph for 0.015g Pt/C catalyst NaOH=0.3wt% and flow rate=1mL/min

Equation (4.28) shows the order of magnitude effect of the $NaBH_4$ concentration on the hydrogen generation rate.

When the concentration of $NaBH_4$ in the feed solution is increased, the hydrogen generation rate increases resulting that hydrolysis reaction rate strongly depends on the initial $NaBH_4$ concentration. The concentration range that is worked is appropriate for measurable quantities since the graduated cylinder limits the amount of H_2 generated. In order to achieve higher rates, solutions must be prepared as high $NaBH_4$ concentrations as possible. However, in the literature, Kojima et al. (2004) reported that when the concentration of $NaBH_4$ increases above 26 wt. %, the solubility of $NaBO_2$ decreases as it does not exist in a solution form. This is due to the increase in solution viscosity which causes a decrease in the hydrogen generation rate (Kim et al., 2007). Therefore, hydrogen generator should be designed according to the solubility limits of $NaBH_4$ and $NaBO_2$.

4.2.1.3 Effect of NaOH concentration

The hydrolysis reaction in a flow reactor without adding NaOH to the feed was tested. For this experiment, desired amount of catalyst and solid $NaBH_4$ is placed in the reactor in a powder form to eliminate the self-hydrolysis in the syringe pump. De-ionized water is fed to the reactor at a rate of 1mL/min for 20 minutes.

Figure 4.18 illustrates cumulative H_2 generation versus time data obtained without NaOH added to the feed solution.

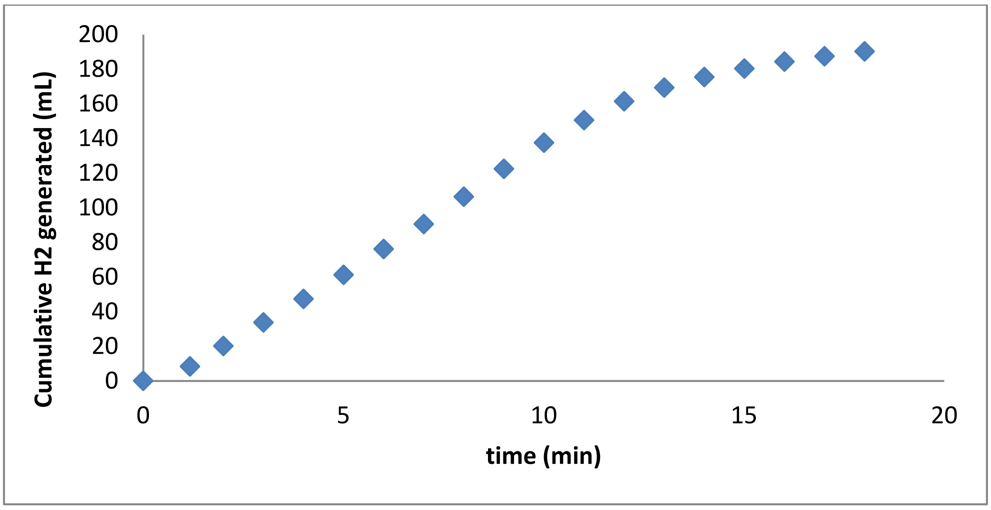


Figure 4-18 Cumulative H_2 generated versus time in a flow reactor for $NaBH_4$=1wt%, flow rate=1mL/min and without NaOH

The cumulative H_2 generated (mL) data are converted to the moles of H_2 generated by using Peng-Robinson Equation of state. Hydrogen generation rate changes with time. Figure 4.19 illustrates the best linear fit to the moles of hydrogen generated versus time.

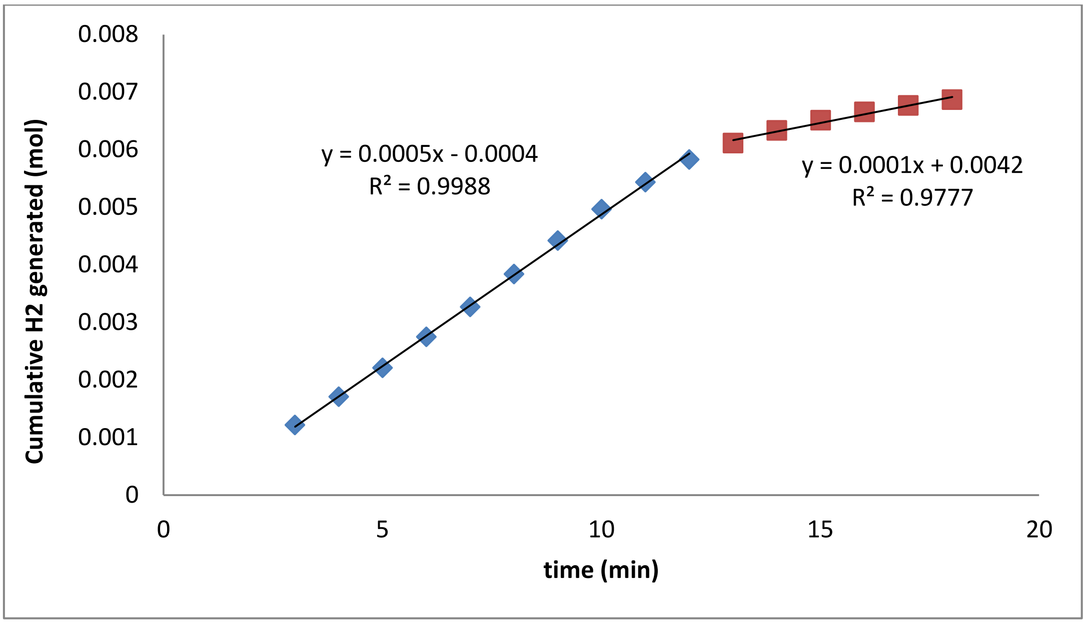


Figure 4-19 Linear fit of cumulative H_2 generation versus time

The H_2 generation rate is estimated from the slope of the best fitting line. The hydrogen production rate is 33.3 mmol/min.g_{cat} up to 10 minutes. Afterwards, the rate drops to 6.7 mmol/min.g_{cat}. A similar result is reported by Kim et al., 2007. They have explained the cause of this behavior as the “disturbance of flow by hydrogen bubbles and resulting irregular supply of water in case of no NaOH added to solution”.

However, the change of hydrogen generation rate with time may be result of the variation of the concentration of $NaBH_4$ in the flow reactor, which might be affected by the dissolution rate of $NaBH_4$.

It is interesting to note that steady state cannot be reached in a flow reactor if the feed does not contain NaOH. So, NaOH must be added to the feed solution. The self-hydrolysis of $NaBH_4$ has to be eliminated in the feed solution. In order to prevent hydrolysis reaction without catalyst, NaOH has to be added to the feed that contains $NaBH_4$ solution. Amendola et al. (2000) reported that the decrease in weight percent of NaOH makes the hydrogen generation rate faster by increasing solubility of $NaBO_2$.

The hydrogen generation rates are estimated from the slope of the best lines fitted to the H_2 generated versus time data shown in Figure 4.20.The steady state rates of 0.3, 0.5, 1 and 2 wt.% NaOH concentrations are 66.7, 60.0, 53.3 and 46.7 $mmol \cdot min^{-1} \cdot g_{cat}^{-1}$, respectively.

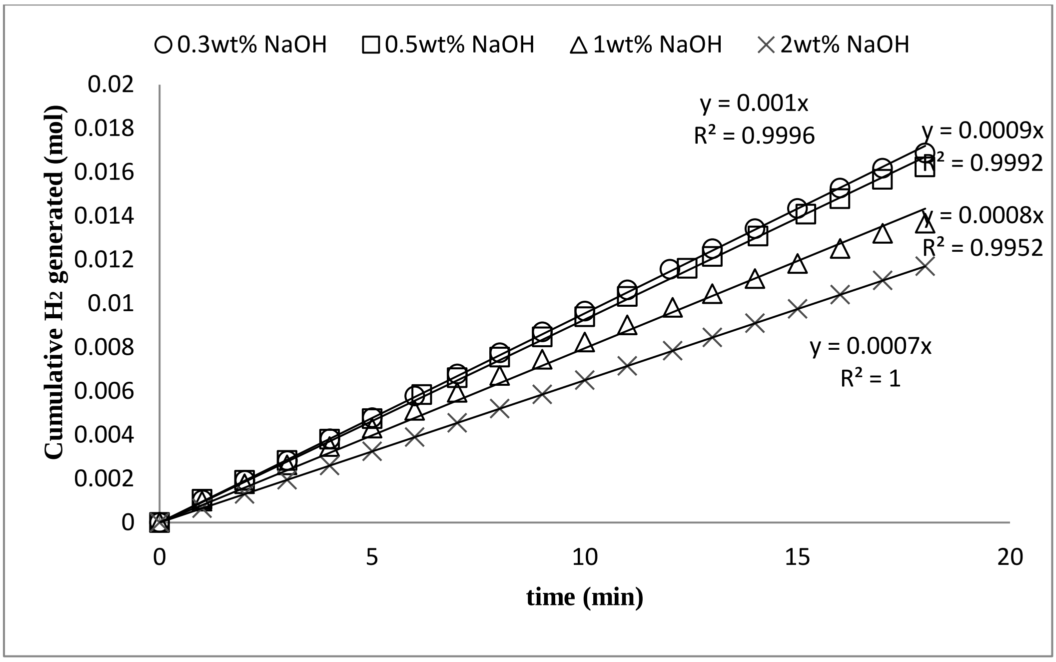


Figure 4-20 Effect of NaOH concentration on H_2 generation for $NaBH_4$=1.0 wt.%. Flow rate=1 $mL.min^{-1}$ and 0.015g Pt/C catalyst (solid line represents the best fitting line).

For the effect of NaOH concentration on the rate of hydrogen generation was expressed by the following equation:

$$r_{H_2} = k^{"}[NaOH]^{\beta} \tag{4.29}$$

Equation 4.29 is linearized by taking natural logarithm of taking both sides:

$$\ln(r_{H_2}) = \beta \ln([NaOH) + \ln(k^{"}) \tag{4.30}$$

Figure 4.21 shows the linear fit of the ln(r_{H2}) versus ln[NaOH] graph.

$$\ln(r_{H_2}) = -0.22 \ln([NaOH]) - 1.74 \tag{4.31}$$

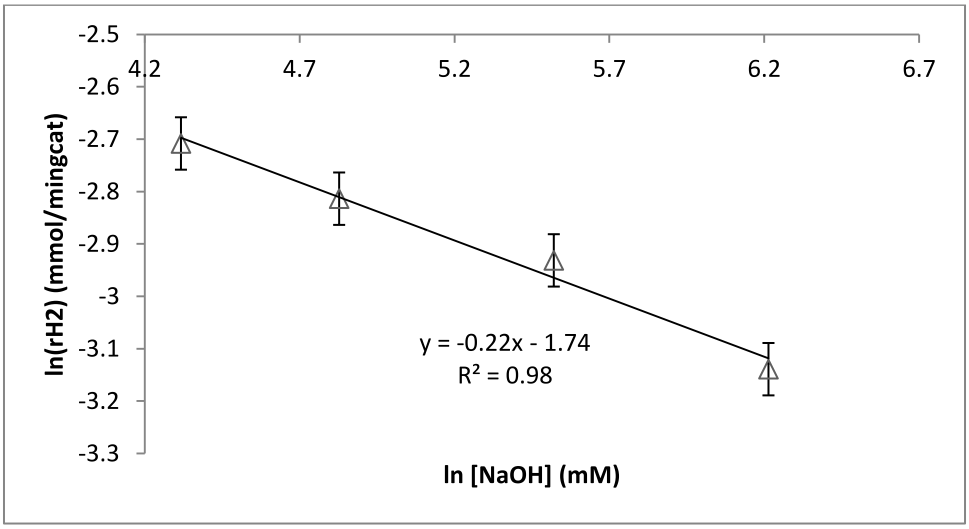


Figure 4-21 ln($r^{'}_{H_2}$) versus ln[NaOH] graph for 0.015g Pt/C catalyst $NaBH_4$=1wt% and flow rate=1mL/min

Equation 4.27 shows the order of magnitude effect of NaOH concentration on H_2 generation rate.

4.2.1.4 Effect of feed flow rate

Figure 4.22 shows the effect of feed flow rate of on the cumulative hydrogen generation for initial $NaBH_4$ concentration of 1wt%, NaOH concentration of 0.3wt% and temperature is 25°C.

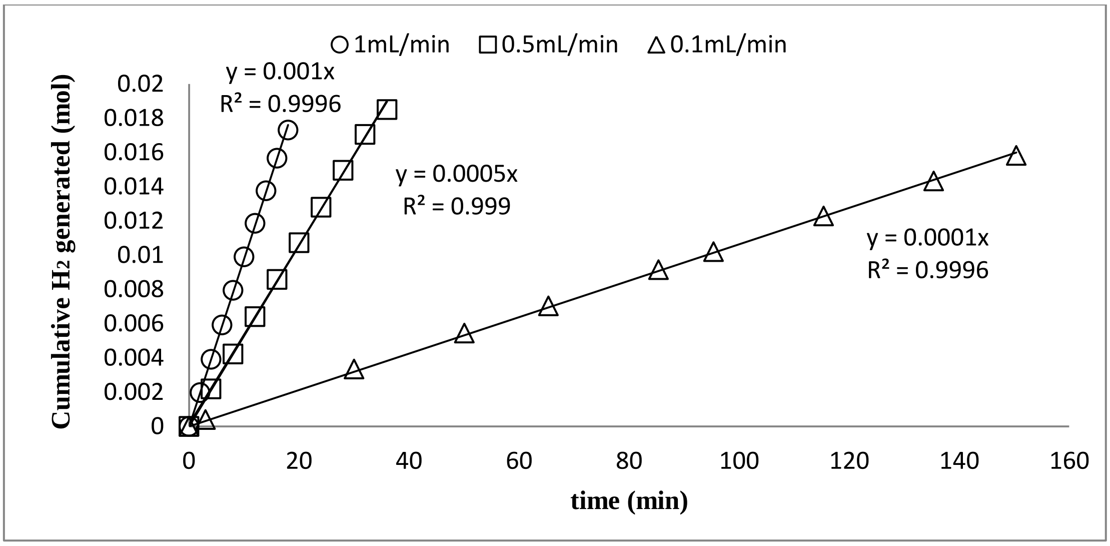


Figure 4-22 Linear fit to the cumulative H_2 generated versus time data

The increase in the feed flow rate enhances the hydrogen production rate. The hydrogen generation rates obtained for solution flow rates 0.1, 0.5 and 1 $mL\cdot min^{-1}$ are, 6.7, 33.3, 66.7 $mmol\cdot min^{-1}\cdot g_{cat}^{-1}$, respectively. This result may indicate the significance of external mass transfer on the hydrogen generation rate. Thus, the rate can be adjusted by changing the feed flow rate.

Table 4.2 summarizes the results obtained by using commercial 20% Pt/C Vulcan (ETEK®) catalyst in a flow reactor.

The hydrogen generation efficiencies were calculated based on the following equation:

$$\eta = \frac{\text{actual moles of } H_2 \; generated}{theoretical \text{ moles of } H_2 \; generated} = \frac{n_{H_2,actual}}{n_{H_2,theoretical}} \qquad (4.32)$$

A sample calculation for the H_2 generation efficiency is shown in Appendix B.3.

Table 4-2 Summary of the results obtained for 0.015g Pt/C catalyst in a flow reactor

$NaBH_4$ concentration (wt.%)	**NaOH concentration (wt.%)**	**Solution flow rate ($mLmin^{-1}$)**	**H_2 gen. rate ($mmolmin^{-1}g_{cat}^{-1}$)**	**H_2 generation efficiency, η**
0.5	0.3	1	33.3	0.94
1	0.3	1	66.6	0.95
1.5	0.3	1	80.0	0.76
2	0.3	1	133.3	0.95
3	0.3	1	233.3	0.98
3.5	0.3	1	286.7	1.0
1	0.5	1	60.0	0.85
1	1	1	53.3	0.76
1	2	1	46.7	0.66
1	0.3	0.5	33.3	0.47
1	0.3	0.1	6.7	0.095

From Table 4.2, it can be concluded that increasing the NaOH concentration decreases the H_2 generation efficiency. Also, when the flow rate decreases, the generation efficiency decreases accordingly. So, in prototype reactor low NaOH concentrations at high feed flow rates is recommended to be used.

4.2.1.5 Kinetic Model

The general mole balance equation for H_2 in a flow reactor can be written as:

$$F_{H_{2,0}} - F_{H_2} + \int r_{H_2} dW = \frac{d(N_{H_2})}{dt} \tag{4.33}$$

At steady state accumulation term will be zero. Also, the most critical assumption is that the hydrogen generation rate is same everywhere in the reactor since reactor has a very small volume (differential reactor). So, Equation (4.33) becomes:

$$-F_{H_2} + r_{H_2} W = 0 \tag{4.34}$$

By inserting definition of molar flow rate into Equation 4.34, Equation 4.35 is obtained.

$$F_{H_2} = \frac{n_{H_2}}{t} = r_{H_2} W \tag{4.35}$$

$$r_{H_2} = \frac{n_{H_2}}{t} \times \frac{1}{W} \tag{4.36}$$

Similarly, $NaBH_4$ mole balance can be written in a differential flow reactor.

$$F_{NaBH_{4,0}} - F_{NaBH_4} - r_{NaBH_4}.W = \frac{d(N_{NaBH_4})}{dt} \tag{4.37}$$

At steady state,

$$\Delta F_{NaBH_4} - r_{NaBH_4}.W = 0 \tag{4.38}$$

The stoichiometry between the rates given in Equation 4.3 is inserted into Equation 4.38 to get:

$$\Delta F_{NaBH_4} = \frac{r_{H_2}}{4}.W \tag{4.39}$$

So, according to the mentioned assumption above that concentration and rate does not change within the reactor, ΔF_{NaBH4} must be very small. To validate this assumption, the case discussed in section 4.2.1.1 using powder form catalyst of 0.015g is taken as a sample example. The H_2 generation rate for this sample case is 66.7 $mmol.min^{-1}.gcat^{-1}$. So, from Equation 4.39, Equation 4.40 can be obtained by inserting the definition of molar flow rate as:

$$\Delta F_{NaBH_4} = \frac{66.7 \times 10^{-3} mol / \min g_{cat}}{4} \times 0.015 g = \nu (C_{NaBH_{4,in}} - C_{NaBH_{4,out}}) \tag{4.40}$$

The υ denotes the feed rate of the solution (mL/min), which is 1mL/min for this specific case. Then,

$$(C_{NaBH_{4,in}} - C_{NaBH_{4,out}}) = \frac{0.00025}{1 mL / \min} = 0.00025 \tag{4.41}$$

The percent change in the concentration is calculated as:

$$\frac{(C_{NaBH_{4,in}} - C_{NaBH_{4,out}})}{C_{NaBH_{4,in}}} \times 100 = \frac{0.00025}{13.2} \times 100 = 0.002\% \tag{4.42}$$

Equation 4.42 validates the assumption.

The H_2 generation rate depends on feed flow rate, $NaBH_4$ and NaOH concentrations. At feed flow rate of 1 $mL \cdot min^{-1}$, rate is only proportional to the $NaBH_4$ and NaOH concentrations since temperature and catalyst amount is kept constant. So, rate equation can be expressed by using power law as follows:

$$r_{H_2}{}' = k C_{NaBH_4}^{\alpha} C_{NaOH}^{\beta} \qquad \text{for } \nu = 1 mL \min^{-1} \tag{4.43}$$

From the Figure 4.17, α is found to be 1.1 with a standard error of 0.97. Similarly, β is found as -0.22 from the graph of ln[NaOH] versus ln(rate) (Figure 4.21). Thus, rate equation can be expressed as follows:

$$r_{H_2}{}' = 0.163\frac{C_{NaBH_4}^{1.1}}{C_{NaOH}^{0.22}} \quad \frac{\text{mol}}{\text{min g}_{\text{cat}}} \quad \text{when } \nu\text{=1mL/min at } 25^0\text{C} \quad R^2 = 0.98 \qquad (4.44)$$

The unit of the concentrations of $NaBH_4$ and NaOH is mol/L in Equation 4.44. The effect of the catalyst amount and temperature is included in the rate constant.

4.2.2 Intrazeolite Co(0) nanocluster experiments

4.2.2.1 Comparison of Co(0) nanoclusters with Pt/C

Figure 4.23 shows the variation of hydrogen generation rate with type and amount of catalyst.

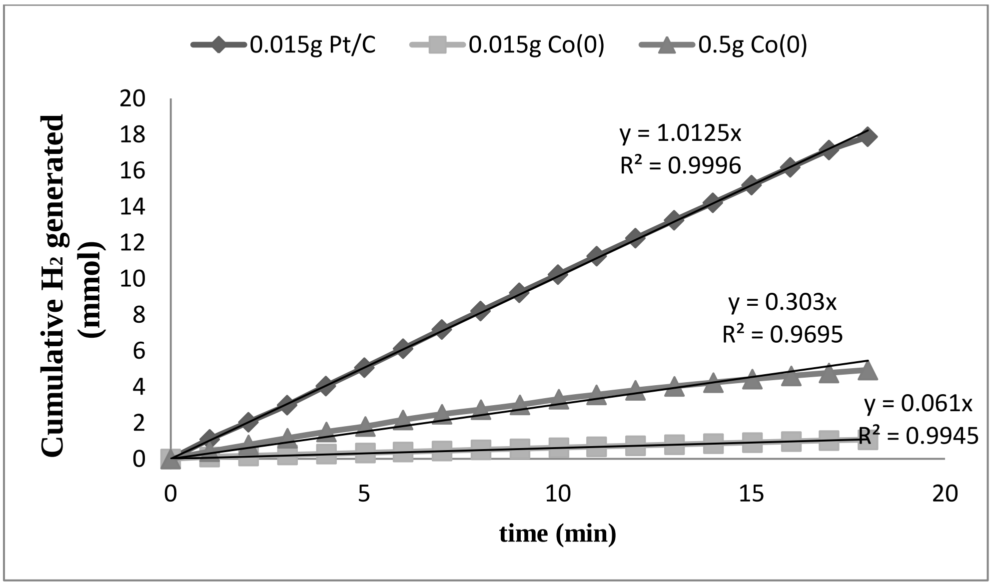


Figure 4-23 Comparison of H_2 generation rate of intrazeolite Co(0) nanoclusters with that of Pt/C catalyst, $NaBH_4$=1wt%, NaOH=0.3wt%, flow rate=1mL/min

The H_2 generation rate rate is calculated from the slope of the best fitted line to the cumulative H_2 generated versus time data shown in Figure 4.23. When 0.015g of Co(0) was placed in the reactor in powder form, the rate is found as 4.07 $mmol.min^{-1}g_{cat}^{-1}$. As the amount of Co(0) nanoclusters increased to 0.5 g, the rate becomes 0.61 $mmol.min^{-1}.g_{cat}^{-1}$. For the same reaction conditions, for Pt/C catalyst, the H_2 generation rate is calculated as 66.6 $mmol.min^{-1}.g_{cat}^{-1}$.

Although the activity of Co(0) catalysts is relatively slow with respect to Pt/C catalyst, it offers cheap and effective alternative to sodium borohydride system. Therefore, it meets the main requirement for portable applications.

4.2.2.2 Effect of $NaBH_4$ and NaOH concentration

The effect of $NaBH_4$ concentration is shown in Figure 4.24. The solution has initial NaOH concentration of 0.33wt% is fed at a flow rate of $1mL.min^{-1}$. 0.21g Co(0) is used and reaction is carried out at a room temperature of 25°C.

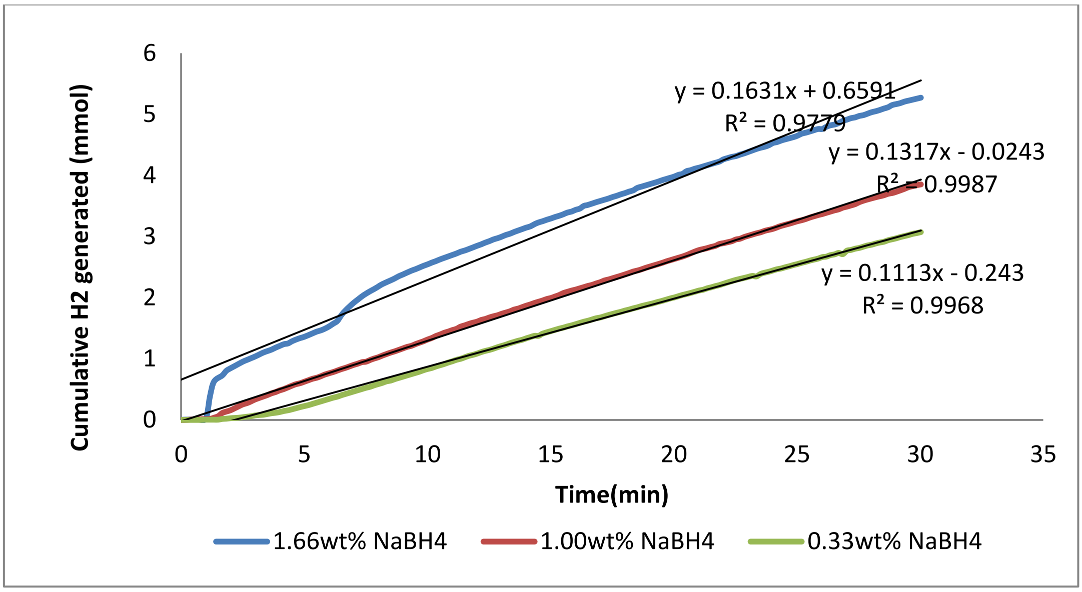


Figure 4-24 Best fitted line to the cumulative H_2 generated (mmol) versus time (min) data for different $NaBH_4$ concentrations

The H_2 generation rate is found from the slope of the best fitting line to the data. A sample calculation is shown in the Appendix B.2. For 1.66wt%, 1.0wt% and 0.33wt% $NaBH_4$ concentrations, the H_2 generation rates are calculated as 0.78, 0.63 and 0.53 $mmol.min^{-1}g_{cat}^{-1}$ respectively. As can be seen in Figure 4.24, for experiments conducted with intrazeolite Co(0) nanoclusters as catalyst, longer start-up period is observed when compared to the Pt/C experiments. This behavior may be result of very small Co(0) particles that creates pressure drop within the reactor. It takes approximately 5 minutes to reach steady state. Thus, the feed flow rate can be increased in order to overcome the pressure drop easily.

Figure 4.25 illustrates the best fitted line to the cumulative H_2 generated data for different NaOH concentrations. The initial $NaBH_4$ concentration is 1wt%, fed at a flow rate of 1mL/min using 0.21g Co(0) catalyst.

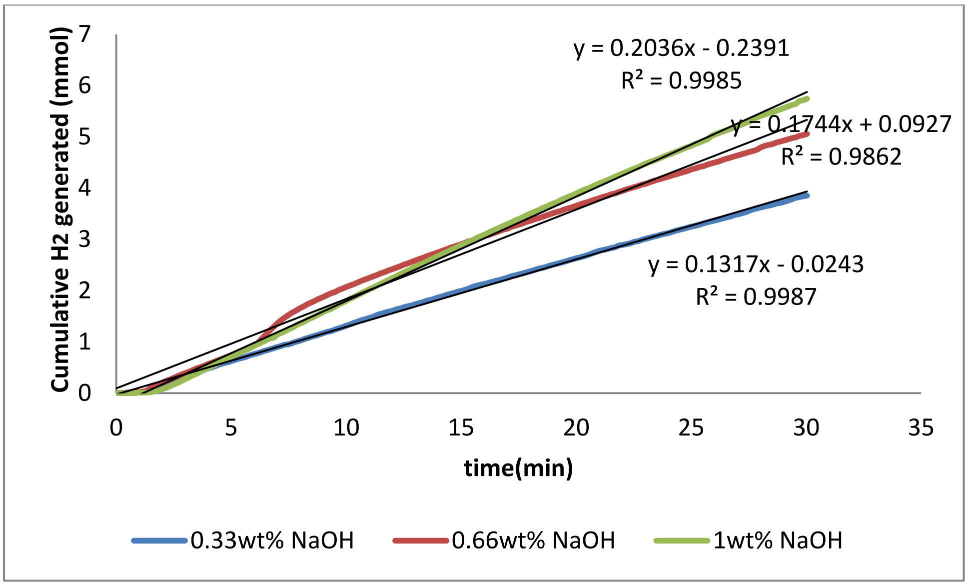


Figure 4-25 Effect of NaOH concentration on cumulative H_2 generated

The H_2 generation rate is calculated from the slope of the linear fit that is shown in Figure 4.25. The H_2 generation rate is found as 0.63, 0.83 and 0.97 $mmol.min^{-1}g_{cat}^{-1}$ for 0.33wt%, 0.66wt% and 1wt% NaOH concentrations respectively. It is observed that the increase in the NaOH concentration enhances the reaction rate.

4.2.2.3 Effect of flow rate

Figure 4.26 shows the influence of feed flow rate of liquid solution on the cumulative hydrogen generated. The initial concentration of the solution is 0.33wt% $NaBH_4$ and 0.33wt% NaOH. 0.21g Co(0) catalyst is used for all experiments at a reaction temperature of 25°C. The raw data of the cumulative H_2 generated (mL) versus time (min) is shown in Appendix B.2.

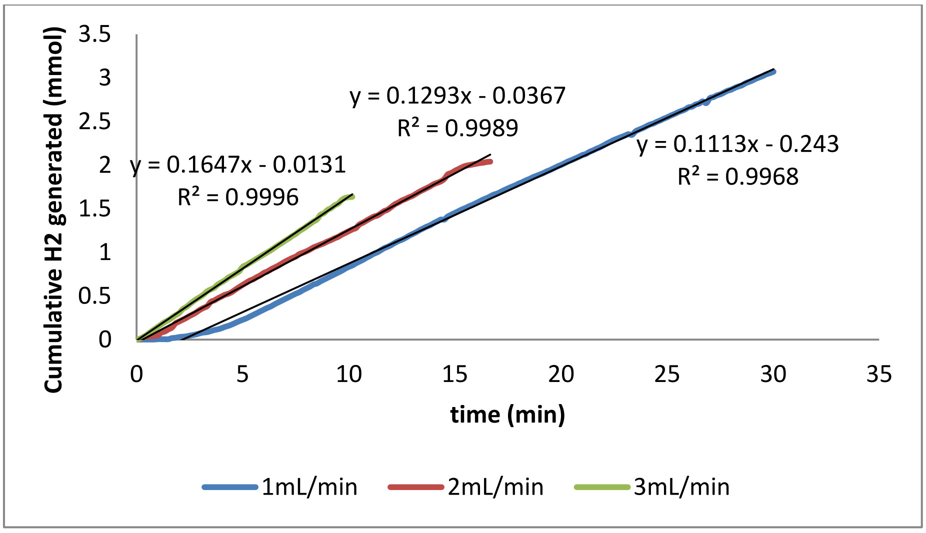


Figure 4-26 Linear fit to the cumulative H_2 generated versus time data

As flow rate increases, generation rate of hydrogen also increases, which provides an easy control of reaction and on demand production. The hydrogen generation rates obtained for solution flow rates 1, 2 and 3 $mLmin^{-1}$ were 0.53, 0.62, and 0.79 $mmol.min^{-1}g_{cat}^{-1}$ respectively.

Table 4.4 summarizes the results obtained with intrazeolite Co(0) nanoclusters in a flow reactor. The hydrogen generation efficiency is calculated from Equation 4.32 and a sample calculation shown in Appendix B.3.

Table 4-3 The results of experiments conducted with 0.21g Co(0) nanoclusters in a flow system

$NaBH_4$ concentration (wt.%)	NaOH concentration (wt.%)	Solution flow rate ($mLmin^{-1}$)	H_2 gen. rate ($mmolmin^{-1}g_{cat}^{-1}$)	H_2 generation efficiency, η
0.33	0.33	1	0.53	0.32
1.0	0.33	1	0.63	0.13
1.66	0.33	1	0.78	0.09
1.0	0.66	1	0.83	0.16
1.0	1.0	1	0.97	0.19
0.33	0.33	2	0.62	0.37
0.33	0.33	3	0.79	0.48

4.2.2.4 Kinetic model for intrazeolite cobalt nanocluster catalyst

The hydrogen generation rate is dependent on $NaBH_4$ and NaOH concentrations.

$$r_{H_2} = kC_{NaBH_4}^{\alpha} C_{NaOH}^{\beta} \tag{4.45}$$

Figure 4.21 shows ln[$NaBH_4$] versus ln(rate) graph.

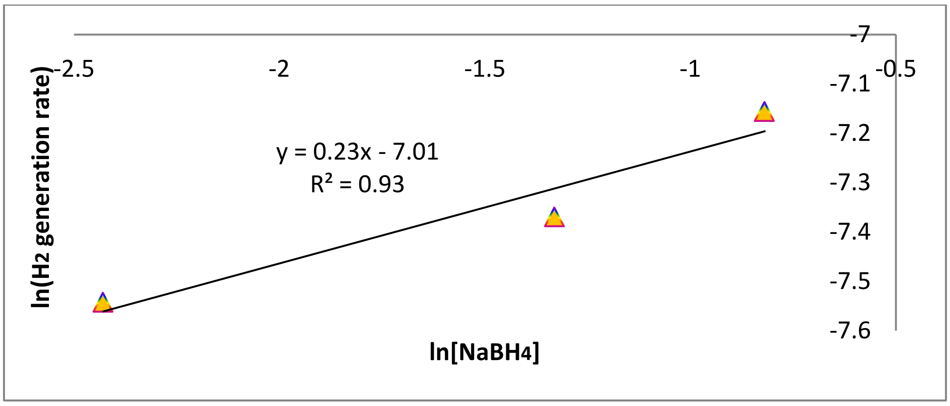


Figure 4-27 The ln[$NaBH_4$] versus ln(r_{H2}) graph for effect of $NaBH_4$ concentration

From Figure 4.27 α value, which shows the order of magnitude effect of $NaBH_4$ concentration, is found as 0.23. Similarly natural logarithm of NaOH concentration versus natural logarithm of H_2 generation rate is drawn and illustrated in Figure 4.28.

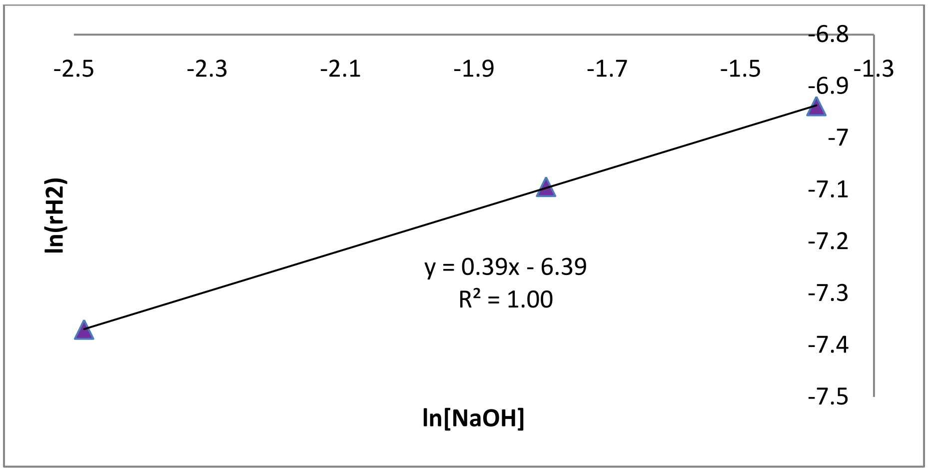


Figure 4-28 ln[NaOH] versus ln(r_{H2}) graph for effect of NaOH concentration

From Figure 4.28 the β is found as 0.39 and k is calculated as 2.38×10^{-3} $mol^{0.38}/L^{0.62}.ming_{cat}$.

So, Equation 4.42 expresses the kinetic model for intrazeolite Co(0) nanoclusters in a flow system for constant catalyst weight of 0.21g and flow rate of 1mL/min .

$$r_{H_2} = 2.4\times10^{-3}\times C_{NaBH_4}^{0.29} C_{NaOH}^{0.34} \frac{mol}{\min g_{cat}} \tag{4.46}$$

4.3 Mechanism of the hydrolysis reaction

For hydrolysis reaction may take place by the following mechanism purposed:

1. The external mass transfer associated with the diffusion of sodium borohydride to the catalyst surface.
2. Pore diffusion of $NaBH_4$ in order to reach active sides of the catalyst.
3. Surface reaction. The following surface reaction may take place on Pt catalyst:

   $$BH_4^- + Pt \rightarrow BH_4^-.Pt$$

   $$BH_4^-.Pt + 2H_2O \rightarrow BO_2^-.Pt + 4H_2$$

   $$BO_2^-.Pt \rightarrow BO_2^- + Pt$$

4. Back diffusion of H_2 from the pore to the external surface of the catalyst
5. External mass transfer of H_2 from catalyst surface
6. H_2 desorbs from the solution and bubble formation
7. Gas bubbles leave the reactor.
8. The rate of step 3 is considered as intrinsic kinetics.

4.4 Prototype Reactor Experiments

4.4.1 Run 1

Figure 4.29 shows the performance of prototype reactor with 1wt%$NaBH_4$, 0.5wt% NaOH and circulation flow rate is 3 mL/s.

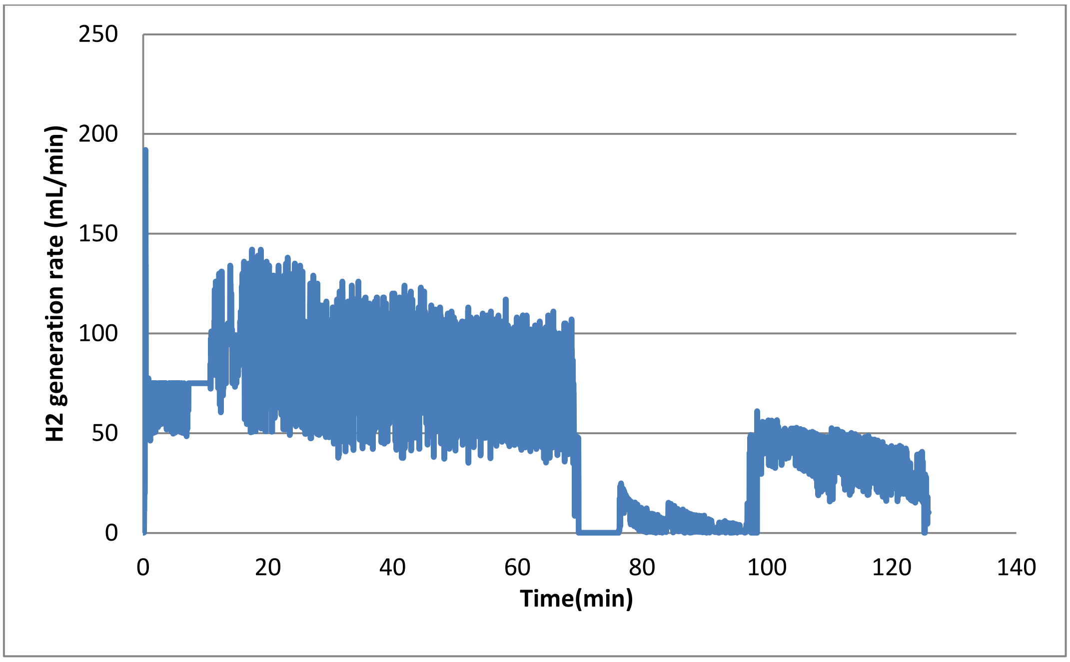


Figure 4-29 H_2 generation rate with respect to time for 1wt% initial NaBH4 concentration circulates at a rate of 3mL/s

As shown in Figure 4.29, the first 15 minutes belongs to the start-up of the reactor. Time between 15 and 75 minutes, the reactor begins to operate at 120mL/min as an average hydrogen generation rate. This rate decreases during the reaction to approximate 80mL/min till the time 75min. After 75 minutes, the pump is stopped and the reactor is allowed to produce its hydrogen in the remaining solution in the reactor. After 25 minutes, this remaining solution stops producing hydrogen. Then, the pump is started again, the reactor produces 50mL/min H_2 and again the rate is decreased till reaction terminates.

4.4.2 Run 2

In the Run 2 experiment, 710mL of 3 wt% $NaBH_4$ and 0.5wt% NaOH solution is circulated. The performance obtained from the reactor is shown in Figure 4.30.

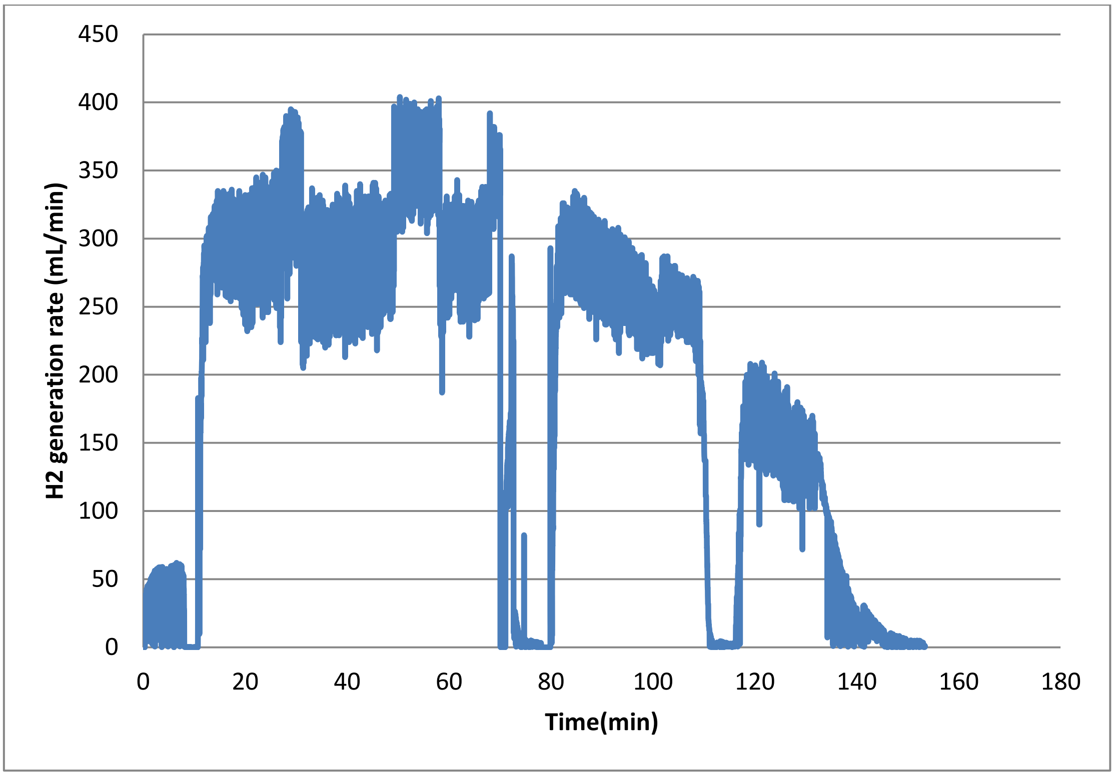


Figure 4-30 Change of H_2 generation rate with respect to time for 3wt% $NaBH_4$

As can be seen from Figure 4.30, the Run 2 composed of 3 operation steps. The first 10 minutes is start-up period. In the first step reactor is operated for 60 minutes. Then, the pump is stopped. The solution remaining in the reactor is sent back to the storage portion by the help of the pump. By this way, no H_2 is lost during the waiting period of the reactor. Then, as a second step pump is started again for 30 minutes. The solution remaining in the reactor again is fed to the storage portion. Finally, pump is started again and as a final step, reactor is operated for 30 minutes. It must be noted that between these steps, no refreshment of the solution is done.

In the first step, the average reaction rate is 350mL/ming$_{cat}$ and decreased to 300 mL/ming$_{cat}$ after 60 minutes of operation. In the second step, reaction starts with a rate of 300 mL/ming$_{cat}$ and decreased to 230 mL/ming$_{cat}$. Finally, in the third step average reaction rate of 175 mL/min is achieved before the termination. Figure 4.25 shows the temperature profile during the Run 2.

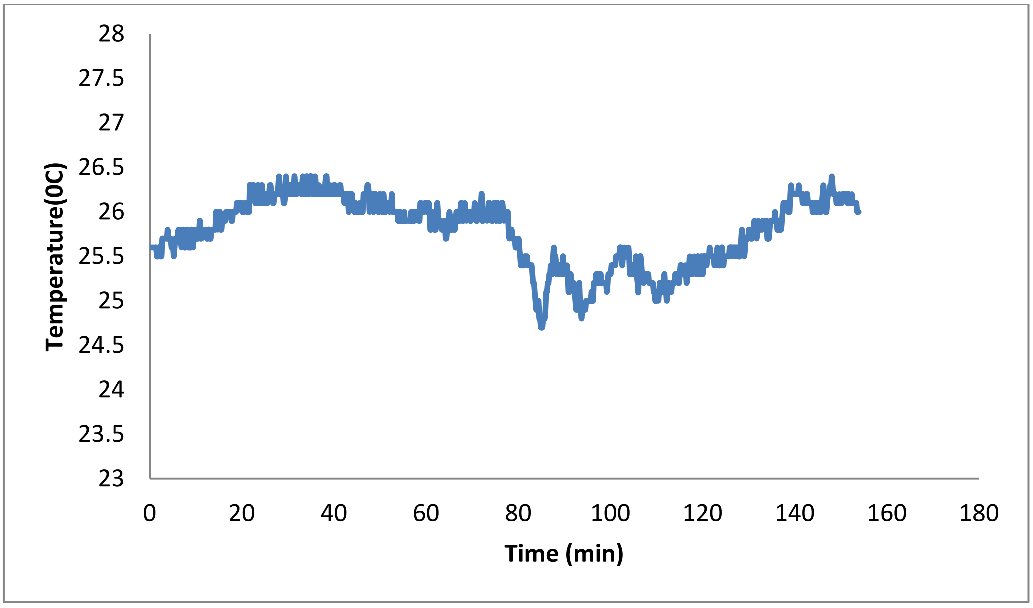


Figure 4-31 Temperature variation within the storage in the prototype system

4.4.3 Run 3

For the final run, 700mL of 5 wt% $NaBH_4$ solution circulated by using the same parameters in previous runs, but different strategy is followed. The reaction is started and waited until the hydrolysis reaction is completed. The hydrogen generation rate is obtained as an average of 950 mL/ming$_{cat}$. After 100 minutes the rate started to decrease and stopped after 4 hour and 10 minutes. The performance of the reactor in run 3 is shown in Figure 4.26.

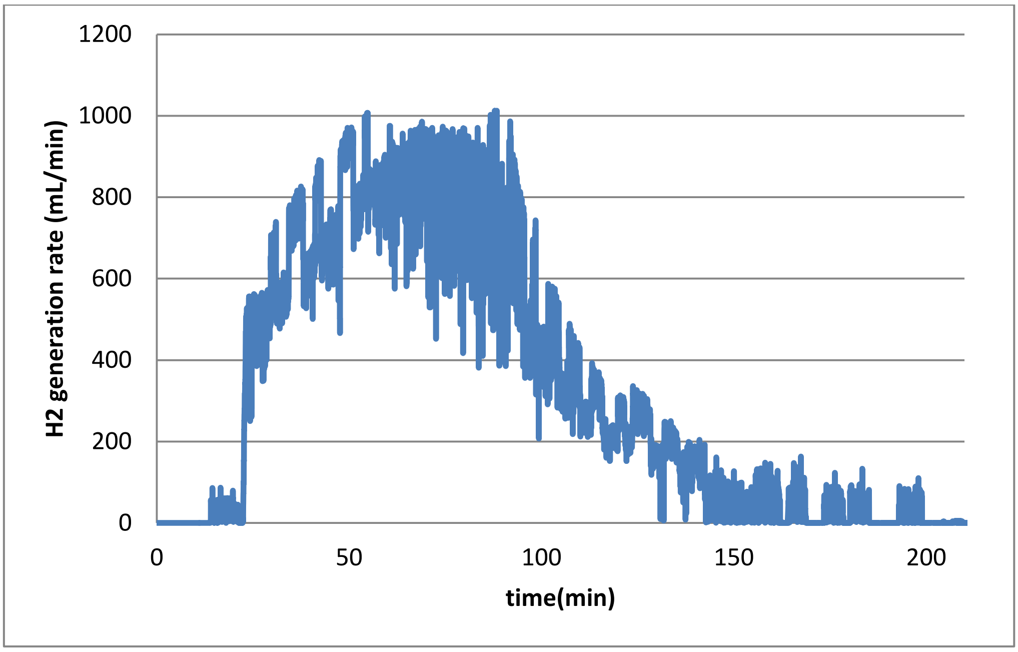


Figure 4-32 H_2 generation rate profile for solution initially contains 5 wt% $NaBH_4$

4.5 Comparison of results with literature

The activation energy for Pt/C catalyst (ETEK) was calculated as 48±1 kJ/mol. For comparison, activation energies reported by other authors for various catalysts are shown in Table 4.4.

Table 4-4 Comparison of experimentally determined activation energies of hydrolysis reaction

Catalyst	**E_a (kJ/mol)**	**Reference**
Pt/C (ETEK®)	46±1	Present Work
Co_3B	19	Walter, 2007
Pt/Pd-Si	19	Pena-Alonso et al., 2007
Ni_xB	38	Hua et al., 2003
Ru/C	66.9	Zhang et al., 2006
Ni–Ru/50WX8	52.7	Liu et. al, 2009

The activation energy calculated for Pt/C catalyst is higher than Co_3B and Pt/Pd-Si and Ni_xB catalysts. The measured value is lower than the values reported for commercially available Ru/C.

Table 4.5 shows the overall comparison of results with literature.

When the results were compared with other studies, lower hydrogen generation rates are obtained for kinetic experiments. However, in prototype reactor, the much better results are achieved. Also, in kinetic experiments, highest hydrogen generation rate was obtained in batch system. However, the prototype reactor was designed based on flow system parameters because in flow system we can control the reaction rate. In batch system, when hydrolysis reaction starts, it continues till the end with no control.

Table 4-5 Comparison with literature

Catalyst	**System**	**Flow rate (mL/min)**	**Temp (°C)**	**Solution composition**	**H_2 gen. rate (mmol/ming$_{cat}$)**	**Reference**
Pt/C (ETEK)	Batch	-	25	0.17M $NaBH_4$ 0.27M NaOH	5.16×10^{-3}	Present Work
Pt/C (ETEK)	Flow	1	25	0.17M $NaBH_4$ 0.27M NaOH	2.80×10^{-3}	Present Work
Intrazeolite Co(0) nanoclusters	Flow	1	25	0.17M $NaBH_4$ 0.27M NaOH	1.05×10^{-5}	Present Work
Pt/C (coated) (ETEK)	Recycle (prototype)	180	25	1.32M $NaBH_4$ 0.15M NaOH	35.70	Present Work
Intrazeolite Co(0) nanoclusters	Batch	-	25	1.2M $NaBH_4$ 2.5M NaOH	0.96	Rakap et. al, 2009
Co-B on Ni foam	Flow (Packed Bed)	17.5	25	5.2 M $NaBH_4$ 0.25M NaOH	119.2	Kim et al, 2007
Pt/C	Flow (Packed Bed)	10	25	2.64M $NaBH_4$ 1.25M NaOH	1321	Bai et al, 2006
Ni–Ru/50WX8	Batch	-	35	2.64M $NaBH_4$ 1.25M NaOH	17.85	Liu et al, 2009

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

The kinetics of catalytic hydrolysis of sodium borohydride was successfully analyzed in a batch and flow system.

For batch system, reactor with a volume of 30mL made up from glass was used to systematically investigate parameters such as $NaBH_4$ concentration, stabilizer (NaOH) concentration, solution temperature and catalyst amount. The increase in the $NaBH_4$ concentration increases the rate at an order of 0.26 while the increase in the NaOH concentration decreases the rate at an order of 0.31. The proposed kinetic model was:

$$r'_{H_2} = 13.4 \times 10^6 \times e^{-\frac{46.0}{RT}} \times \frac{C_{NaBH_4}^{0.26}}{C_{NaOH}^{0.31}} \qquad \frac{mol}{\min g_{cat}} \text{ with } R^2 = 0.986$$

It should be emphasized that the effect of catalyst amount is considered in the reaction rate constant. For further analysis, it is recommended that nonlinear square fit analysis may be done to the kinetic model with using the parameters that were found by using method of initial rates as initial estimates.

For a flow system, 5mL differential reactor made from glass was used. Flow system experiments were conducted at constant temperature and different from the batch system the effect of feed rate of the solution was investigated. In flow system, commercial Pt/C (ETEK®) and intrazeolite Co(0) nanoclusters synthesized by Prof. Dr. Saim Özkar’s research group were compared. The hydrogen generation rate obtained from the 0.015g Pt/C catalyst was 1mmol/min whereas 0.3mmol/min hydrogen generation rate was obtained from 0.5g intrazeolite Co(0) nanoclusters while all other parameters are kept constant. Although the activities of Co(0) catalysts are relatively slow with respect to Pt/C, it offers cheap and effective alternative to sodium borohydride system. Therefore, it meets the main requirement of being used in portable applications.

Moreover, for Pt/C catalyst, it was observed that placing catalyst as a powder form is favorable since the generation rate is affected by the diffusion limitations if catalyst is coated on a carbon cloth. The effectiveness factor was calculated as 0.5. In addition, the hydrolysis reaction shows approximately first order kinetics with respect to $NaBH_4$ concentration whereas it is inversely proportional to NaOH concentration to the power of 0.22. The rate model for Pt/C catalyst in a flow system was:

$$r_{H_2}{}' = 0.163 \frac{C_{NaBH_4}^{1.1}}{C_{NaOH}^{0.22}} \quad \frac{\text{mol}}{\text{min g}_{\text{cat}}} \quad \text{when } \nu\text{=1mL/min at } 25^0\text{C} \quad R^2 = 0.98$$

It should be emphasized that the hydrogen evolution rate is directly proportional to superficial solution velocity. This indicates that the rate is limited by external mass transfer that is most probably due to the desorption rate of hydrogen from the catalyst surface. It is concluded that for on demand production of hydrogen in such a flow reactor the H_2 generation rate can be controlled by the solution feed rate.

Also, for intrazeolite Co(0) nanoclusters, as a result of controlled experiments, the rate expression was found as:

$$r_{H_2}^{'} = 2.4\times10^{-3} \times C_{NaBH_4}^{0.29} C_{NaOH}^{0.34} \; \frac{mol}{\min g_{cat}}$$

Finally, recycle type prototype reactor with internal volume of $122cm^3$ and storage volume of 1336 cm^3 was designed, manufactured from Delrin® and operated successfully.

From prototype experiments, maximum 950mL/min hydrogen generation rate was obtained with 700mL 5 wt% NaBH4, 0.5wt% NaOH solution with circulation flow rate of 3mL/s. The H2 requirement for 100W PEM fuel cell is 1.5L/min. From these experiments, it may be concluded that with an increase in $NaBH_4$ concentration will give enough for 100W power fuel cell. The reason that we cannot increase the concentration was the limits of the flow meter. It is recommended to conduct experiments with a flow meter of high capacity.

In the operation of prototype reactor different strategies were followed. By successive operation of the same solution, it was observed that the reaction rate is decreased. This decrease is due to the fact that, after the operation is terminated that means pump is stopped, some of the solution remains in the reactor. So, in the waiting period, the remaining solution continues to produce its hydrogen. Therefore, it is more convenient that the remaining solution must be discharged back to the storage portion by the help of the pump during the waiting time. It is recommended that pump must be changed with two way pump in order to be able to do this discharging and to prevent hydrogen loss when it is not needed for operation of the reactor.

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APPENDIX A

BATCH REACTOR EXPERIMENTS

The raw data that was used in analysis of $NaBH_4$ effect on hydrogen generation rate is shown in Table A.1.

Table A.1 The raw data of experiments with constant 0.27M NaOH concentration and catalyst amount of 0.048g Pt/C at 20°C and 0.94atm

0.17M $NaBH_4$		0.23M $NaBH_4$		0.3M $NaBH_4$	
Time(s)	V_{H2}(mL)	Time(s)	V_{H2}(mL)	Time(s)	V_{H2}(mL)
0	0	0	0	0	0
20	38.9	20	41.2	20	46
40	73.3	40	78.3	40	84.9
60	103.6	60	111.5	60	120.3
80	133.3	80	143.2	80	156.7
100	158.9	100	175	100	189.9
120	183.1	120	204.6	120	223.5
140	204.1	140	232.1	140	255.6
160	220.5	160	256	160	284.4
180	233.8	180	278.8	180	312.9
200	241.9	200	297.4	200	338.2
220	246.2	220	313.8	220	362.4
240	247.6	240	325.7	240	383.1
260	247.9	260	334	260	402.1
280	-	280	337.6	280	417.3
300	-	300	338.7	300	429.2

Figure A.1 shows the raw data graph of effect of $NaBH_4$ concentration on H_2 generation rate.

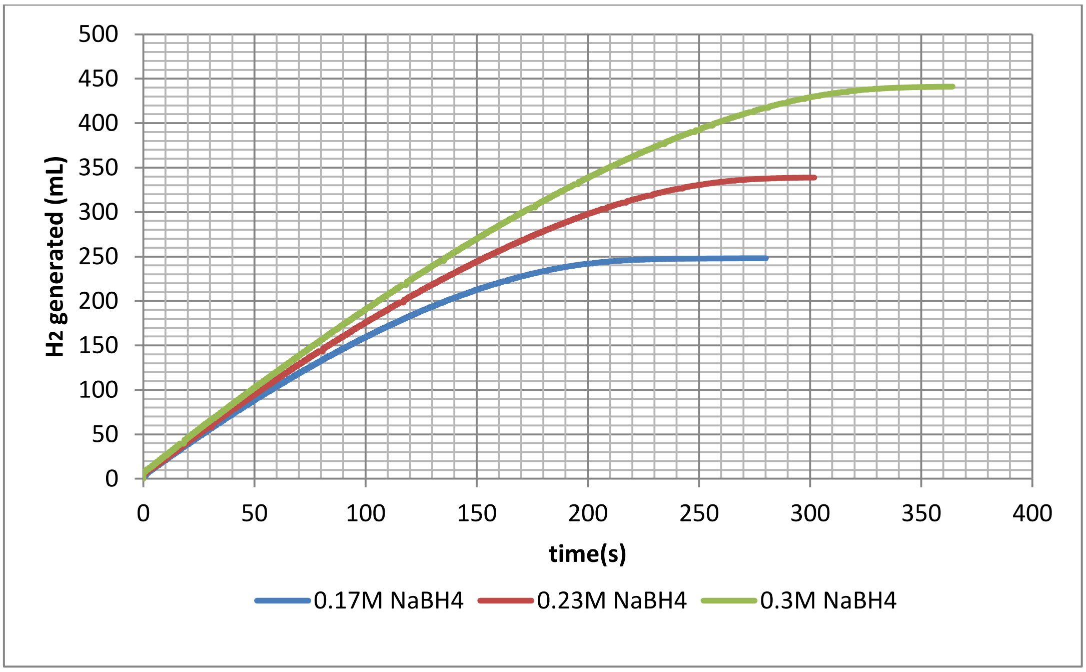

Figure A.1 The raw data for comparison of different $NaBH_4$ concentrations

A.1: ***Sample Calculation of moles of H_2 generated from the experiment data***

For 0.17M $NaBH_4$ solution with 0.27M NaOH the hydrogen generated was read from the table A.1 is 38.9 mL at 20s. The reaction temperature is 20°C and at a constant pressure of 0.94atm.

In order to calculate the moles of hydrogen produced, take ideal gas law as:

$$PV = nRT \tag{A.1}$$

$$(0.94atm) \times (38.9mL \frac{1L}{1000mL}) = n(0.082)(20 + 273.15) \tag{A.2}$$

$$n = 1.52 \times 10^{-3} mol\, \mathrm{H_2} \tag{A.3}$$

If we use Peng Robinson Equation of state in order to determine the moles of hydrogen produced:

$$P = \frac{RT}{V_m - b} - \frac{a\alpha}{V_m^2 + 2bV_m - b^2} \tag{A.4}$$

$$a = \frac{0.457235 R^2 T_c^2}{P_c} \tag{A.5}$$

$$b = \frac{0.077796 RT_c}{P} \tag{A.6}$$

$$\alpha = (1 + \kappa(1 - T_r^{0.5}))^2 \tag{A.7}$$

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 \tag{A.8}$$

$$T_r = \frac{T}{T_c} \tag{A.9}$$

Where ω is the accentric factor, V_m is the molar volume, T_r is the reduced temperature, T_c and P_c are the critical temperature and pressure respectively.

For 20°C and 0.94 atm pressure the molar volume of the hydrogen is calculated from the Peng Robinson equation of state as 0.0256 m^3/mol. So taking back the case of 38.9 mL of gas produced, the moles of H_2 was calculated as:

$$n_{H_2} = 38.9 mL \times \frac{1L}{1000mL} \times V_m = \frac{38.9mL}{10^6 \frac{mL}{m^3} \times 0.0256 \frac{m^3}{mol}} = 1.52 \times 10^{-3} mol \tag{A.10}$$

So, ideal gas assumption can be done. For the rest of the experiments all calculations were done with Peng-Robinson equation of state.

For rate calculation from the graph of cumulative hydrogen generated versus time, the slope of the linear portion is considered. This time we take the case of constant NaOH concentration.

To understand this, all these experiments were repeated and Figure A.2 shows the results of the repetition for the specific case of 0.17M $NaBH_4$ solution at 20°C.

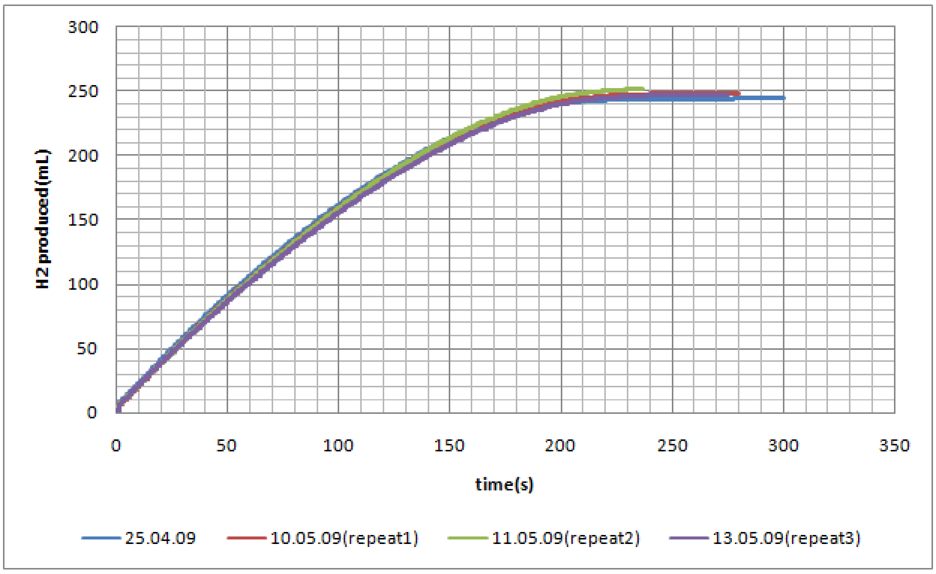

Figure A.2 Reproducibility of the experiments

For all cases near 100% reproducibility was obtained that proves our system was good working and appropriate for practical purposes.

A.2: *Sample calculation for the hydrogen generation rate*

Figure 4.2 shows the cumulative hydrogen generated versus time graph for initial concentration of NaOH is 0.27M, 0.048g Pt/C catalyst at 20°C.The slope of the curve gives the rate of hydrogen generation. For rate analysis the first 90 seconds are taken into account.

For 0.3M $NaBH_4$, the hydrogen production rate is calculated as:

$$r'_{H_2} = \frac{0.078(\frac{mmol}{s})(\frac{60s}{1\min})}{0.048gcat} = 97.50\frac{mmol}{\min .gcat} \tag{A.11}$$

Figure A.3 shows the raw data obtained for the comparison of different NaOH concentrations. During all the experiments, the initial $NaBH_4$ concentration is 0.17M, 0.048g Pt/C catalyst is used in a reactor at 20°C.

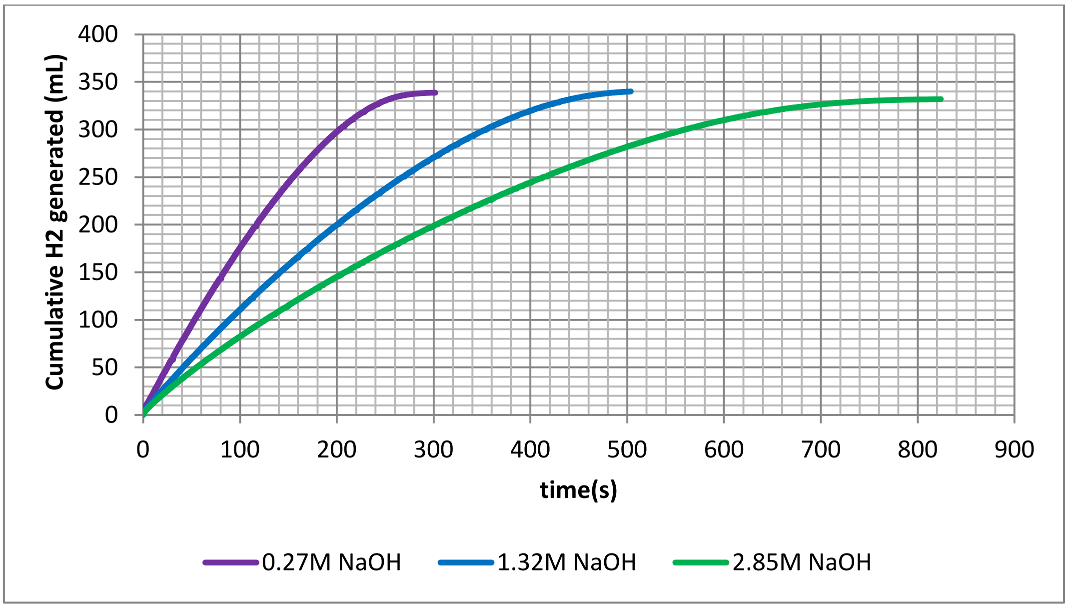

Figure A.3 The raw data for NaOH concentration effect

The best fitting line for the calculation of rate for the different NaOH concentrations is shown in Figure 4.5.

For 2.85M NaOH, the rate is calculated as:

$$r'_{H_2} = \frac{0.0345(\frac{mmol}{s})(\frac{60s}{1\min})}{0.048gcat} = 43.13\frac{mmol}{\min .gcat} \tag{A.12}$$

Figure A.4 shows the raw data for comparison of different catalyst amounts. During the experiments initial $NaBH_4$ and NaOH concentration are 0.17M and 0.27M respectively at 20°C.

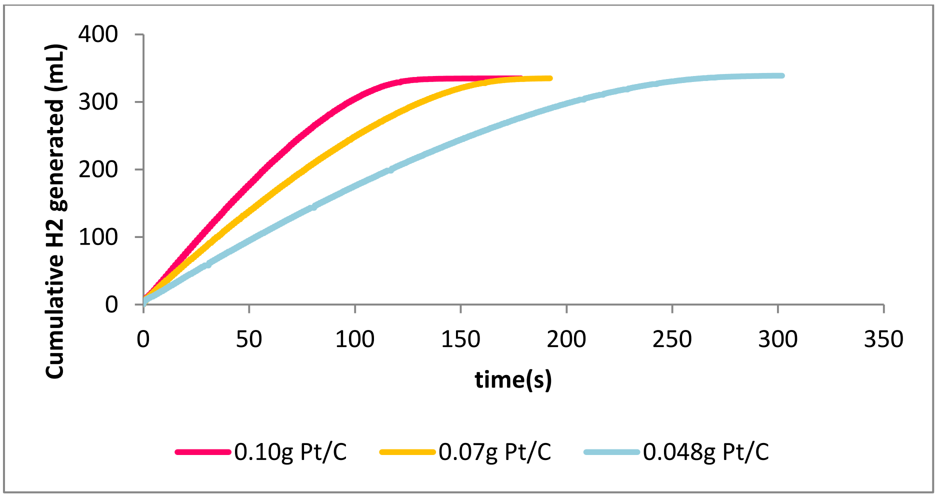

Figure A.4 Raw data for effect of catalyst amount

For 0.1g Pt/C catalyst, the hydrogen generation rate was calculated as:

$$r'_{H_2} = \frac{0.132(\frac{mmol}{s})(\frac{60s}{1\min})}{0.048gcat} = 165.00\frac{mmol}{\min.gcat} \tag{A.13}$$

Figure A.5 shows the raw data for the effect of temperature. During the experiments, 0.17M $NaBH_4$, 0.27M NaOH initially is used with 0.048g Pt/C.

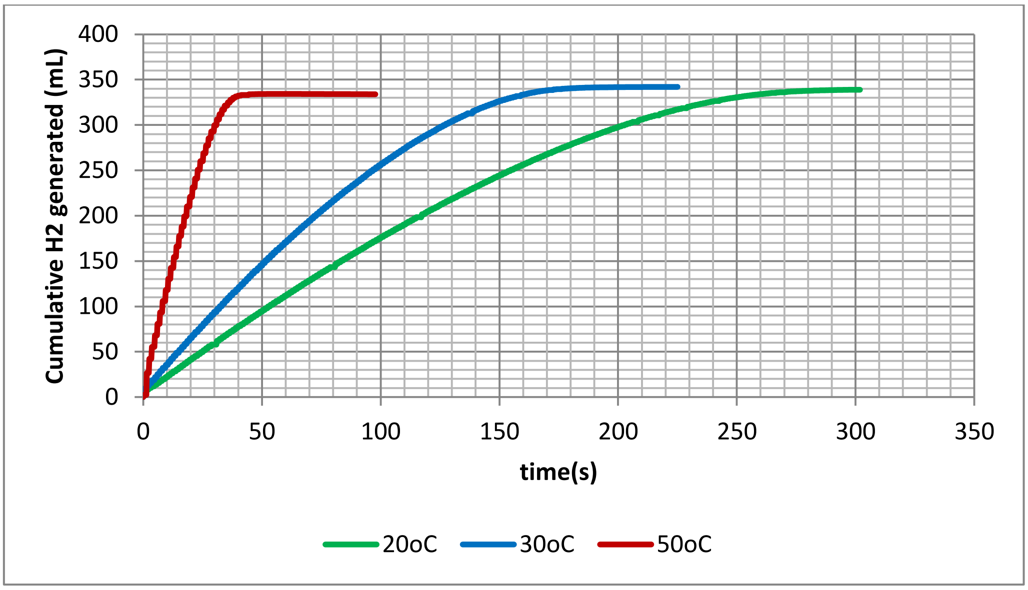

Figure A-5 Raw data for effect of temperature

The best fitting line to the cumulative H_2 generated versus time data is shown in Figure 4.10 after the raw data is converted into mmoles of hydrogen generated. From the slope of the Figure 4.10, for 50°C, the H_2 production rate is calculated as:

$$r_{H_2}^{'} = \frac{0.4045(\frac{mmol}{s})(\frac{60s}{1\min})}{0.048gcat} = 505.63\frac{mmol}{\min .gcat} \tag{A.14}$$

APPENDIX B

FLOW REACTOR EXPERIMENTS

B.1: *Experimental data for the experiments conducted with Pt/C catalyst*

Table B.1 and Table B.2 show the variation of cumulative H_2 generated (V_{H2},mL) versus time (min) at same initial NaOH concentration (0.3wt%), feed flow rate was1mL/min and catalyst amount was 0.015g Pt/C. The initial $NaBH_4$ concentration varied as 0.5, 1, 1.5, 2, 3 and 3.5wt% for each run.

Table B.1 Cumulative hydrogen generated versus time for 0.5, 1 and 1.5wt% $NaBH_4$

0.5wt% $NaBH_4$		1wt% $NaBH_4$		1.5wt% $NaBH_4$	
Time(min)	V_{H2}(mL)	Time(min)	V_{H2}(mL)	Time(min)	V_{H2}(mL)
0	0	0	0	0	0
2	1.7	2	1.9	2	1.5
4	25.8	4	52.9	4	65
6	52.2	6	105.2	6	137.8
8	82.3	8	160	8	210
10	110.9	10	214.6	10	279
12	139.2	12	267.4	12	342.6
14	167.3	14	320.3	14	402.3
16	195.1	16	371.6	16	453.3
18	222	18	423	18	501.1
20	248.1	20	467.4	20	546.7

Table B.2 Cumulative hydrogen generated versus time for 2, 3 and 3.5wt% $NaBH_4$

2wt% $NaBH_4$		3wt% $NaBH_4$		3.5wt% $NaBH_4$	
Time(min)	V_{H2}(mL)	Time(min)	V_{H2}(mL)	Time(min)	V_{H2}(mL)
0	0	0	0	0	0
2	108.4	2	189.8	2	233.2
4	216.3	4	378.8	4	465.4
6	324.2	6	567.3	6	697.0
8	432.0	8	756.3	8	929.2
10	540.2	10	945.3	10	1161.4
12	648.2	12	1134.4	12	1393.6
14	756.1	14	1323.4	14	1625.8
16	864.2	16	1512.3	16	1858.0
18	972.2	18	1701.4	18	2090.2

Figure B.1 shows the graph obtained from the raw data for the effect of $NaBH_4$ concentration.

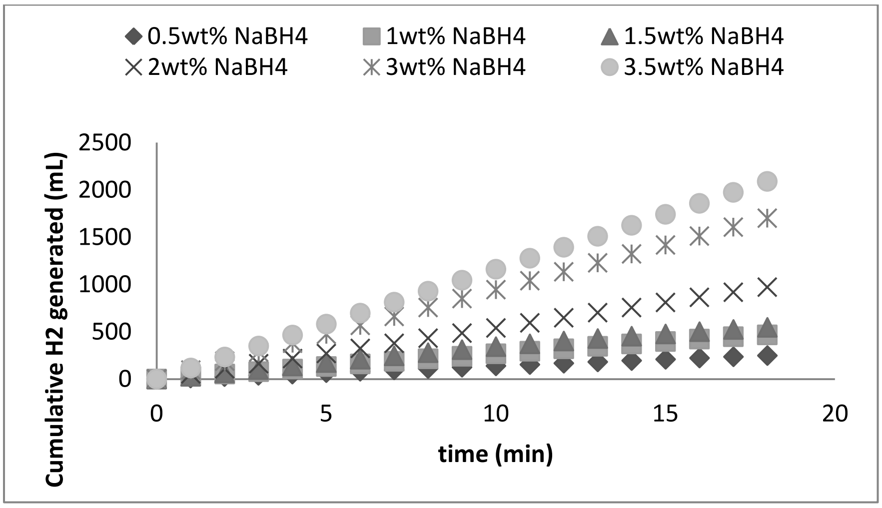

Figure B.1 Cumulative H_2 generation versus time for different concentrations of $NaBH_4$ in a flow reactor.

Sample Calculation: Hydrogen generation rate

Cumulative hydrogen generated is converted into moles of hydrogen generated by equation A.4. Cumulative H_2 generated (mol) versus time (min) data are fitted by using Microsoft Office EXCEL 2007. The rate of hydrogen production is estimated from the slope of the best fitting line.

Figure 4.16 illustrates the best fit equations and the data. The slope for 3 wt% $NaBH_4$ concentration is 0.0035. Hydrogen generation rate (mmol/min.g_{cat}) is calculated as:

$$r'_{H_2} = \frac{0.0035(\frac{mol}{\min})(\frac{10^3 mmol}{mol})}{0.015 gcat} = 233.3\frac{mmol}{\min .g_{cat}} \tag{B.1}$$

The experiments are repeated 3 times. The error bars shown in Figure 4.17 are estimated from the repeated runs. Figure B.2 shows the reproducibility of the experiment carried out with 1wt% $NaBH_4$, 0.3wt% NaOH concentration at 1mL/min feed rate using 0.015g Pt/C catalyst.

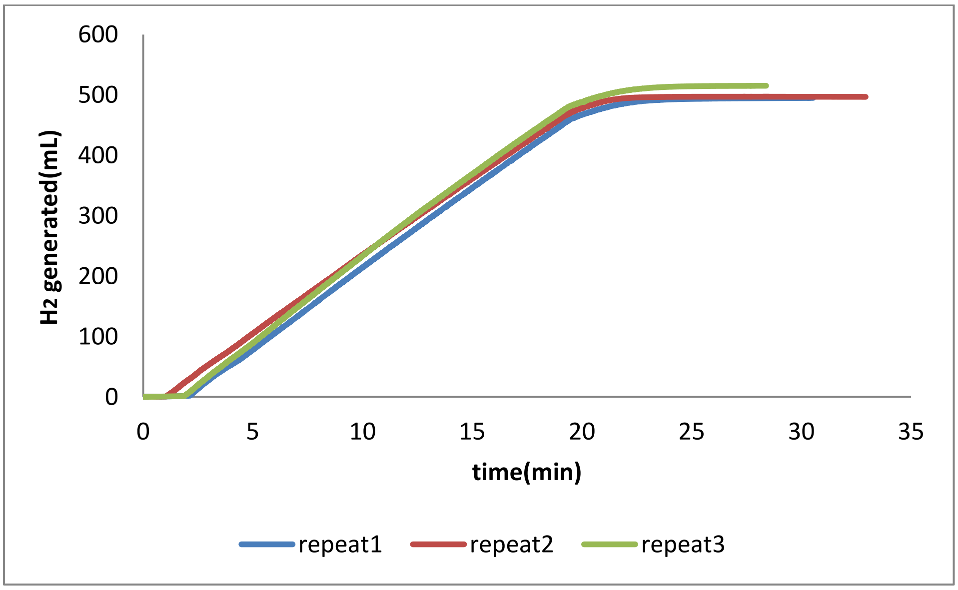

Figure B.2 Reproducibility of experiment

Figure B.3 shows the variation of generated hydrogen for the effect of NaOH concentration while keeping initial $NaBH_4$ concentration as 1wt%, flow rate is 1mL/min using 0.015gPt/C catalyst.

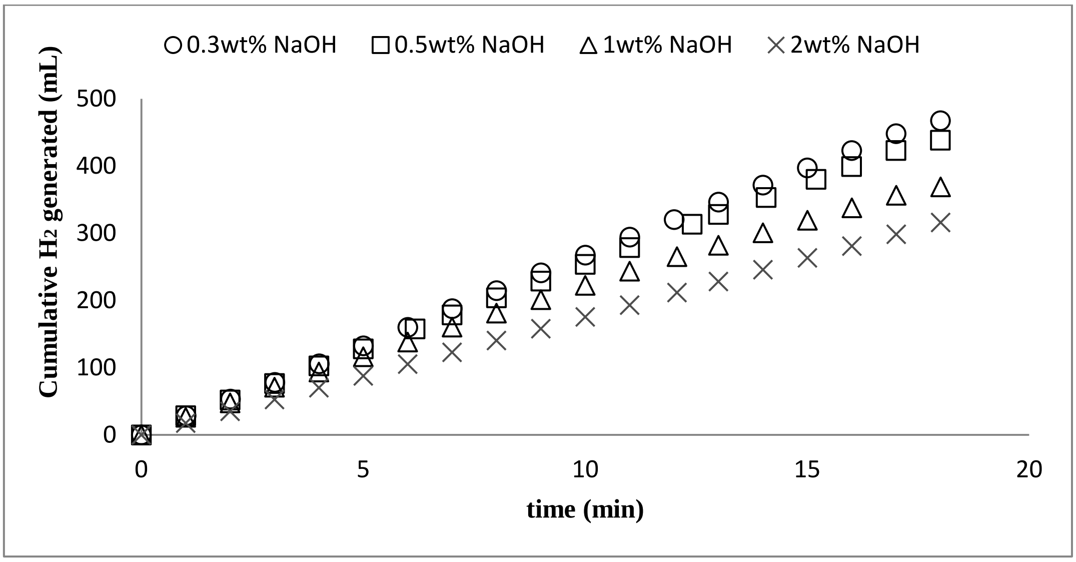

Figure B.3 Effect of NaOH concentration on cumulative H_2 generated versus time

Figure 4.20 shows the best fit equations and the data. The slope of best fit line for 1 wt% $NaBH_4$ concentration is 0.0008. Hydrogen generation rate ($mmol/min.g_{cat}$) is calculated as:

$$r'_{H_2} = \frac{0.0008(\frac{mol}{\min})(\frac{10^3 mmol}{mol})}{0.015 gcat} = 53.3 \frac{mmol}{\min . g_{cat}} \tag{B.2}$$

Figure B.4 shows the cumulative H_2 generated (mL) versus time data for different flow rates. The initial $NaBH_4$ and NaOH concentration is 1wt% and 0.3wt% respectively at a constant feed flow rate of 1mL/min. 0.015g Pt/C catalyst is used in these three experiments conducted at a constant temperature of 25°C.

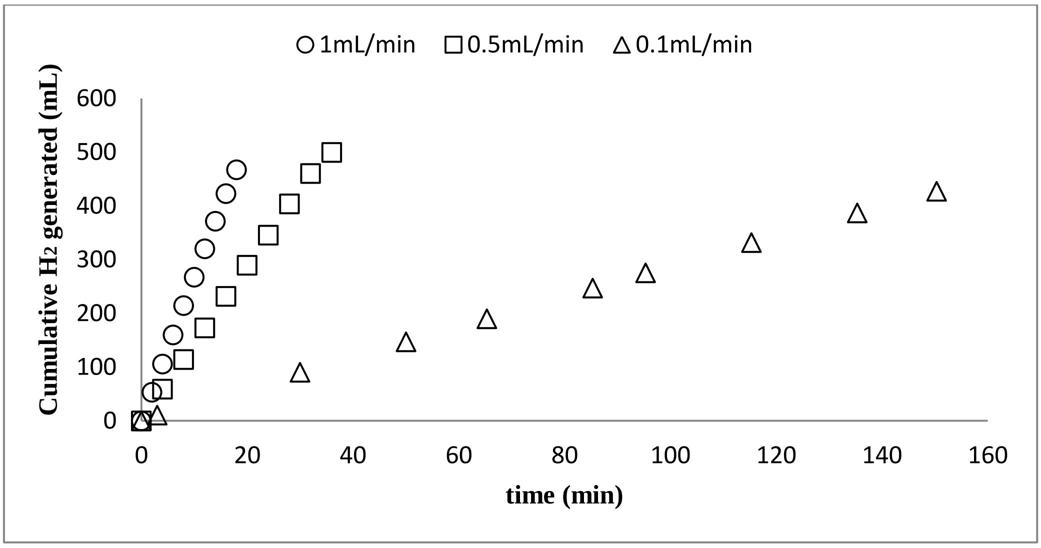

Figure B.4 The variation of cumulative H_2 production versus time for different flow rates

Figure 4.22 illustrates the best fitted line to the cumulative H_2 generation (mol) versus time (min) data. Hydrogen generation rate (mmol/min.g_{cat}) is calculated from the slope of the best fitting line. The slope of linear line is 0.0005 for the case, which solution initially contains 0.1wt% $NaBH_4$ and 0.3wt% NaOH is fed at a flow rate of 0.5mL/min. Thus, H_2 production rate is calculated as:

$$r'_{H_2} = \frac{0.0005\left(\frac{mol}{\min}\right)\left(\frac{10^3\,mmol}{mol}\right)}{0.015 g_{cat}} = 33.3 \frac{mmol}{\min . g_{cat}} \tag{B.3}$$

B.2: ***Experimental data for the experiments conducted with Intrazeolite Co(0) nanocluster catalyst***

Figure B.5 shows the cumulative H_2 generated (mL) versus time data for different $NaBH_4$ concentrations. The initial concentration of NaOH is 0.33wt% feed at a rate of 1mL/min using 0.21g Co(0) nanoclusters as catalyst.

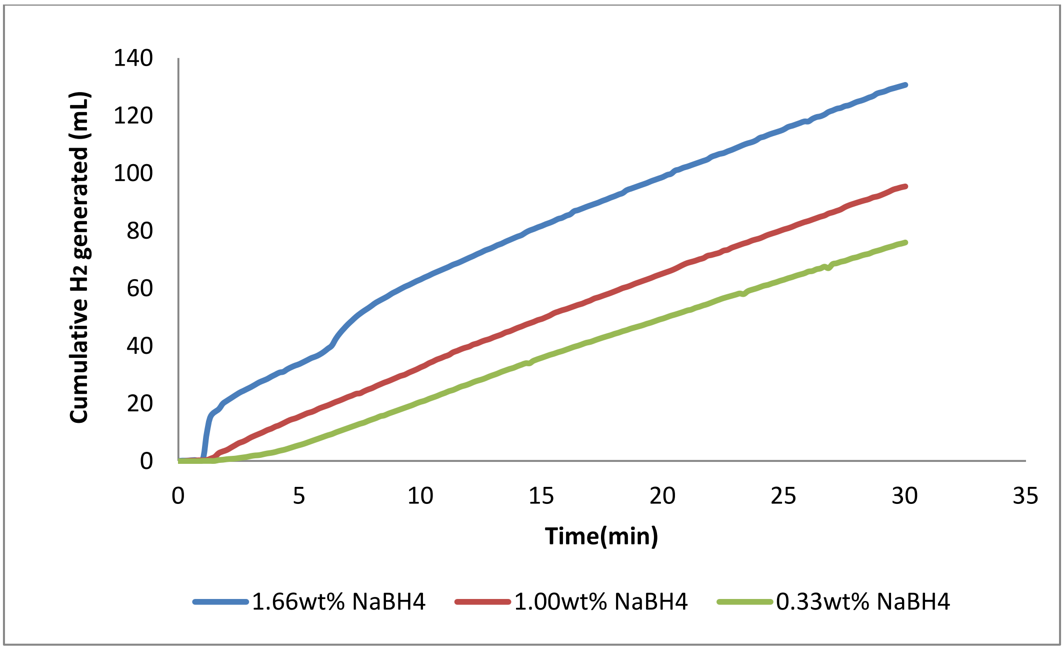

Figure B.5 Cumulative H_2 generated versus time for different $NaBH_4$ concentrations

H_2 generated (mL) data is converted into mmoles of H_2 by using Peng-Robinson equation of state. The procedure is explained in Appendix A.1. Figure 4.24 illustrates the best linear fit to the cumulative H_2 generated (mmol) data. Hydrogen generation rate (mmol/min.g_{cat}) is calculated from the slope of the best fitting line. The slope of linear line is 0.1317 for the solution initially contains 0.33wt% NaBH4 and 0.33wt% NaOH is fed at a 1mL/min. Thus, H_2 production rate is calculated as:

$$r'_{H_2} = \frac{0.1317(\frac{mmol}{\min})}{0.21gcat} = 0.63\frac{mmol}{\min .g_{cat}} \quad \text{(B.4)}$$

Figure B.6 illustrates the raw data obtained for different NaOH concentrations with initial $NaBH_4$ concentration of 1wt% feed at a flow rate of 1mL/min using 0.21g catalyst.

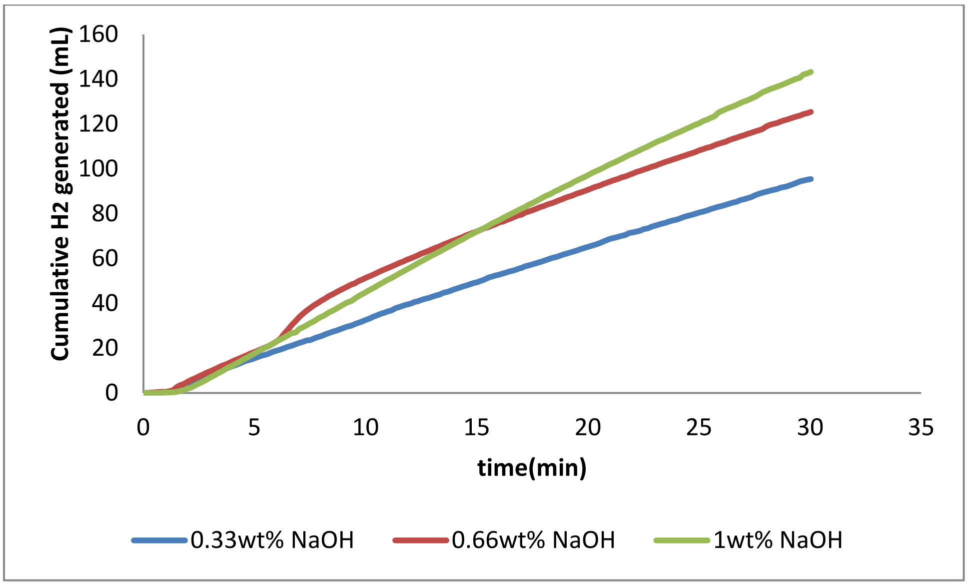

Figure B.6 Cumulative H_2 generated versus time graph for different NaOH concentrations

The H_2 generation rate is calculated from the slope of the best fitting line to the data shown in Figure 4.25. As a sample case, the slope of linear line is 0.2036 for the solution initially contains 1wt% $NaBH_4$ and 1wt% NaOH, fed at a flow rate of 1mL/min. So, H_2 production rate is calculated as:

$$r'_{H_2} = \frac{0.2036(\frac{mmol}{\min})}{0.21gcat} = 0.97\frac{mmol}{\min .g_{cat}} \quad \text{(B.5)}$$

Figure B.7 shows the raw data obtained for the effect of flow rate on H_2 generation rate. The solution initially contains 0.33wt% $NaBH_4$ and 0.33wt% NaOH. The reaction temperature is 25°C and 0.21g Co(0) is used during the experiments.

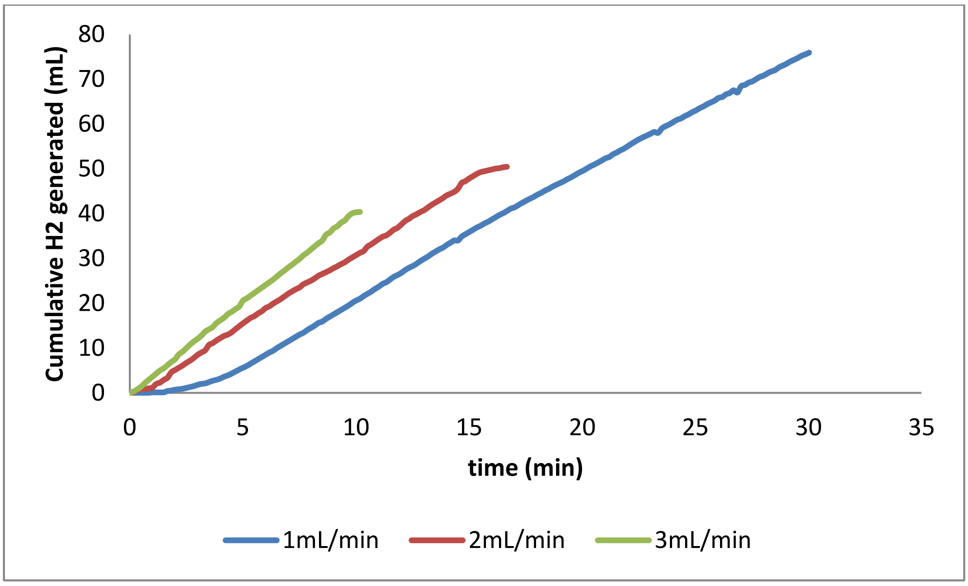

Figure B.7 Cumulative H_2 generated versus time graph for different flow rates

The H_2 generation rate is calculated from the slope of the best fitting line to the data shown in Figure 4.26. As a sample case, the slope of linear line is 0.1293 for the solution initially contains 0.33wt% $NaBH_4$ and 0.33wt% NaOH, fed at a flow rate of 2mL/min. So, H_2 production rate is calculated as:

$$r'_{H_2} = \frac{0.1293(\frac{mmol}{\min})}{0.21 gcat} = 0.62 \frac{mmol}{\min . g_{cat}} \qquad (B.6)$$

B.3: *Sample Calculation for the H_2 generation efficiency*

The H_2 generation efficiency is calculated from the Equation 4.22. The actual amount of H_2 generated is calculated as:

$$n_{H_2,actual} = r_{H_2}(mmol/\min g_{cat}) \times \{reaction\ time\}(\min) \times W(g) \tag{B.7}$$

The theoretical amount of H_2 generated is calculated from the reaction stoichiometry, knowing the initial $NaBH_4$ concentration.

$$n_{H_2,theoretical} = n_{NaBH_4} \times 4 \tag{B.8}$$

$$n_{NaBH_4} = V_{solution}(mL) \times \frac{w(wt\%)}{100} \times \frac{1mol}{37.83g} \tag{B.9}$$

For 20 mL solution that has 0.5wt% initial $NaBH_4$ concentration, 0.3wt% NaOH concentration using 0.015g Pt/C catalyst at a feed flow rate of 1mL/min, the hydrogen generation rate is estimated as 33.3 mmol/min.g_{cat}. So, efficiency is calculated as:

$$\eta = \frac{n_{H_2,actual}}{n_{H_2,theoretical}} \tag{B.10}$$

$$n_{H_2,actual} = r_{H_2} \times time \times W = 33.3 \times 10^{-3} \times 20 \times 0.015 = 9.99 \times 10^{-3} mol \tag{B.11}$$

$$n_{H_2,theoretical} = V_{solution} \times \frac{w}{100} \times \frac{1mol}{37.83g} \times 4 = 20 \times \frac{0.5}{100} \times \frac{1}{37.83} \times 4 = 0.0106 mol \tag{B.12}$$

$$\eta = \frac{n_{H_2,actual}}{n_{H_2,theoretical}} = \frac{9.99 \times 10^{-3}}{0.0106} = 0.94 \tag{B.13}$$