KINETIC STUDY OF SODIUM BOROHYDRIDE HYDROLYSIS USING LANGMUIR-HINSHELWOOD MODEL

Thesis

Submitted in the partial fulfilment for the award of degree

of

Masters of Science

In

Chemistry

Submitted by

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CERTIFICATE

This is to certify that the thesis entitled "**Kinetic Study of Sodium Borohydride Hydrolysis Using Langmuir-Hinshelwood Model"** being submitted by **Ms. Arushi Sudan** in the partial fulfilment for the requirement of degree of **Master of Science,** in **Chemistry,** in the Department of Chemical Engineering, Thapar University, Patiala is a record of candidate's own work carried out by her under our supervision and guidance. To the best of our knowledge, the content of this report does not form a basis for the award of any other degree.

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DECLARATION

I, **Arushi Sudan**, hereby declare that the work being presented in the thesis entitled "**Kinetic Study of Sodium Borohydride Hydrolysis Using Langmuir-Hinshelwood Model"** by me in the partial fulfillment of the requirement for the award of degree of Master of Science in Chemistry, from Department of Chemical Engineering, Thapar University, Patiala, is an authentic record of my own work carried under the supervision of **Dr. D. Gangacharyulu**, Professor and **Dr. R. K. Gupta,** Associate Professor and Head, Department of Chemical Engineering, Thapar University, Patiala, from January to July 2017.

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ABSTRACT

Hydrogen is an energy carrier that can be used in internal combustion engines or fuel cells and producing virtually no greenhouse gas when combusted with oxygen. The only significant emission is water vapour. The three main techniques for storing hydrogen are (a) as a compressed gas, (b) cryogenic liquid hydrogen and (c) solid-state hydrogen storage.

Compression of hydrogen at high pressure (150-200 bar) is the most common method of storing hydrogen. Liquid hydrogen is stored in cryogenic tanks at ambient pressure. Liquid hydrogen cannot be stored in open systems, due to low critical temperature of hydrogen. In solid state hydrogen storage method the hydrides have high hydrogen content and the stored hydrogen in them can be released by several pathways. $NaBH_4$ is considered best among all the chemical hydrides present for the generation of hydrogen.

In this work the rate and amount of hydrogen generation is studied at the different temperatures by taking four different concentrations of sodium borohydride. After the selection of all the chemicals, the kinetic parameters and affect on the hydrogen generation by changing concentration and temperature is determined. Increase in the hydrogen generation with temperature is observed.

Langmuir- Hinshelwood model is used for the estimation of kinetic parameters of sodium borohydride hydrolysis in the presence of cobalt chloride as a catalyst. This model is considered as a combination of zero and first order kinetic model, with adsorption coefficient K. Heat of adsorption ($\Delta H_{adsorption}$) was found to be -45 kJ/mol for the system. The Langmuir adsorption coefficients are calculated for four different temperatures.

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NOMENCLATURE

Symbol	Description	Dimensions
° C	Temperature	Degree Celsius
H_2	Hydrogen	
kg	Mass	Kilogram
G	Mass	Gram
L	Volume	Litre
T	Time	second

ABBREVATIONS

Abbreviation	Description
HGR	Hydrogen generation rate
CO	Carbon monoxide
Co	Cobalt
Cl^-	Chloride
H^-	Hydride
Aq	Aqueous

Chapter-1

Introduction

The increasing concern over the consequences of climate change is limiting the utilization of fossil fuels in the near future. Major economic crisis, environmental crisis or both could occur due to forced choice between energy and environment. Fossil fuels acts as one of the major source of world energy supply. Fossil fuel when combusted generates carbon dioxide, a green house gas which adversely affects the climate. Production of carbon dioxide in the atmosphere leads to climate change. Hence, the use of fossil fuels is in conflict with the global environmental concern [1].

According to the report submitted by International Panel on climate change, in which scientists came to a conclusion that global warming has already started and will increase in the coming years. This panel has alerted that by controlling the increase in amount of greenhouse gases like carbon dioxide, methane and CFC's, we can mitigate the global warming effect. The solar radiation entering the earth atmosphere gets adsorbed and warms the earth surface due to which a sharp increase in the temperature occurs as depicted in (Figure 1).

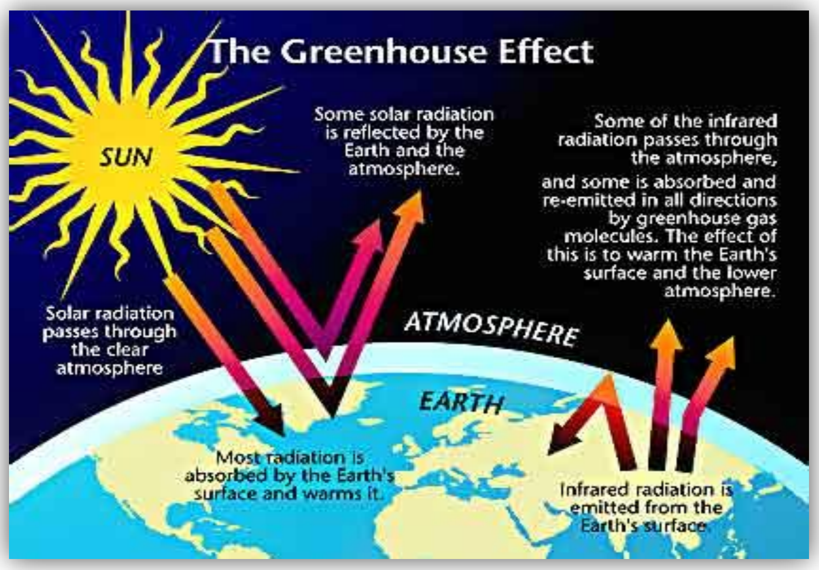


Figure 1: Greenhouse Effect [2].

To limit the carbon dioxide emission we can do the following :

1. Limit the population growth.
2. Improving the utilization of energy.

The hydrogen based economy reduces the dependence on fossil fuels, thus moving towards sustainable environment [3] which will replace the present energy dependency on fossil fuels.

1.1 Hydrogen energy

Hydrogen energy is considered as a substitute to replace fossil fuels which may reduce greenhouse gas emission and pollution although hydrogen is highly reactive in presence of sunlight [4]. Renewable energy sources like solar, wind and hydro are potential future energy sources. Producing hydrogen from renewable sources and utilizing hydrogen in engines may reduce greenhouse gas emission and pollution.

There are many benefits of replacing fossil fuels with hydrogen like the oil which is a fossil fuel used in heating and running our cars has a huge effect on our environment causing increase in particulate level which leads to global warming. The various reasons of replacing fossil fuels with hydrogen are as follows:

1. The by-product in case of Hydrogen powered cell is oxygen and water which will not cause any harm to human health or environment.
2. Hydrogen is non-polluting, non-toxic and renewable gas so it can easily replace fossil fuels.

Hydrogen is present in the form of chemical compounds such as water or hydrocarbons that need to be transformed so as to release hydrogen. The obstacles present while using hydrogen are as follows:

1. Apart from hydrogen production, the technologies which store hydrogen, carry and use it, should be developed so as to increase the hydrogen economy.
2. Hydrogen boils at -253° C and it is necessary to maintain this low temperature [5].

For hydrogen storage few criteria are to be considered like volumetric and gravimetric storage capacity, good mechanical, thermal stability and cost of operating system [6].

1.2 Hydrogen storage methods

The major challenge for efficient hydrogen economy is hydrogen storage and delivery. The three main techniques for storing hydrogen are in the form of (a) compressed gas, (b) cryogenic liquid hydrogen and (c) solid-state hydrogen storage. These techniques are described in the following paragraphs.

1.2.1 Hydrogen gas stored as a compressed gas and as a cryogenic liquid

Compressed gas and cryogenic liquid hydrogen storage involves various safety concerns and sophisticates technologies

High pressure hydrogen storage

Compression of hydrogen at high pressure (150-200 bar) is the most common method of storing hydrogen. In hydrogen vehicles compressed hydrogen gas is stored in tanks at 350 bar and 700 bar. The volumetric capacity of a gas tank increases as the temperature of the tank decreases at a fixed pressure and volume

The drawback of hydrogen storage under high pressure is that 20% of energy is lost during the storage process. Lightweight cylinders can help to cope up with the problem of loss of energy during hydrogen storage. The main problem in this method is embrittlement of cylinder material due to hydrogen gas filled in them and this process is called as Hydrogen embrittlement [7].

Liquefication

Energy density of hydrogen can be improved by storing the hydrogen in a liquid state. Liquid hydrogen can be combined with metal hydride, to minimize hydrogen loss. In this storage method, gas phase is condensed at high pressure than liquefied at cryogenic temperature in liquid hydrogen tank. The low temperature is maintained by using liquid helium cylinder. Liquefaction of hydrogen does not take place until -273^{0}C temperature is reached.

1.2.2 Solid state hydrogen storage

In this method molecules of hydrogen are stored in mesoporous materials by process of physical adsorption. The hydrogen capacity of a material is proportional to its specific surface area [8].

Hydrogen storage in metal hydrides

Some metals bond with hydrogen to form metal hydrides which leads to solid state storage of hydrogen under moderate temperature and pressure. It is a safe and volume-efficient storage method. Light metals like Li, Be, Na, Mg and Al form metal-hydrogen compounds out of all the chemical hydrides sodium borohydride is considered as the most attractive hydrogen storage material, it provides a safe and practical means of producing hydrogen and has high hydrogen content (10.7%).

Hydrolysis of sodium borohydride is a convenient method of hydrogen generation. The only by product, sodium metaborate is water soluble and environmentally benign. The reaction is fast in the presence of a catalyst, and external heat is not required for the reaction to take place.

Generation of hydrogen by hydrolysis of sodium borohydride is considered the best method due to high hydrogen capacity (10.8 wt percent), good storage capability of $NaBH_4$. Borax is the end product of $NaBH_4$ hydrolysis which does not cause any harm to the environment.

1.3 Catalyst for $NaBH_4$ hydrogen storage system

Experimental studies on $NaBH_4$ hydrolysis were conducted in the presence of catalysts such as cobalt chloride, nickel chloride, iron chloride and copper chloride, out of which Cobalt chloride is found to be the most active. Due to the high cost of noble metal catalysts like ruthenium and platinum, there use is limited [9].

For effective hydrogen generation system, extensive kinetics studies are required to be carried out using a chemical hydride material with high hydrogen storage capacity combined with a catalyst promoter that promotes hydrogen generation rate (HGR) of the system. Studying the effect of various parameters like temperature and concentrations of materials are important as these studies help in determining various factors that cause variation in rate of hydrogen generation.

Chapter-2
Literature review

Hydrogen energy is considered as a good alternative to fossil fuels as it has no negative impact on the environment. Hydride based hydrogen storage system is considered as potential hydrogen source for many applications. Technologies for hydrogen storage should be highly developed if a hydrogen based energy system is to be established particularly in transportation sector. Hydrogen has a low density, so storing hydrogen is a difficult task [10].

There are three techniques to store hydrogen (a) hydrogen stored as a compressed gas, (b) hydrogen as a cryogenic liquid, (c) hydrogen storage in solid form. In compressed and cryogenic techniques various safety measures are to be considered. In these techniques, energy is required to condense and change the hydrogen gas into liquid form. In solid state hydrogen storage the hydrogen is stored in metal hydrides and hydrogen is released through them by chemical pathways like hydrolysis and thermolysis [11].

In the past there were many hydrogen storage methods present like in solid state hydrogen storage method, hydrogen is stored in metal hydrides. Hydrides have a high percentage of hydrogen present in them which is released by chemical pathways [12].

$LiBH_4$, $NaBH_4$, $NaAlH_4$, and NH_3BH_3 have hydrogen storage densities of 18.5 wt%, 10.8%, 7.8% and 19.4%, respectively [13]. Single and multi-walled nanotubes also have hydrogen stored in them and are considered as hydrogen storage materials. Chemical hydrides are likely hydrogen storage materials. The bond formed between hydrogen and boron is responsible for high hydrogen density of metal hydrides [14].

2.1 Chemical hydrogen storage in hydrides

In chemical hydrogen storage system generation of hydrogen occurs through a chemical reaction. Hydrogen is released by thermolysis or hydrolysis.

2.1.1 Hydrolysis method for hydrogen generation

Release of hydrogen by reaction with water is called as hydrolysis. Non reversible hydrides undergo hydrolysis because they have high weight percent of hydrogen present in them. Sodium borohydride is proposed as an efficient hydrogen storage material due to the high weight percent of hydrogen present in it [15].

Hydrogen can be generated from the chemical hydrides by reacting them with water. The metal hydrides from which hydrogen can be released through hydrolysis are:

Lithium aluminium hydride

The reaction of $LiAlH_4$ with water is carried out in dry and inert environment as it reacts with water easily. It is highly unstable when compared with other hydrides [16].

Lithium hydride

Generation of hydrogen takes place when lithium hydride is reacted with water. Lithium hydroxide which is the by-product formed when the reaction occurs forms a thick layer on lithium hydride due to which its hydrogen generation rate decreases [17].

Ammonia borane (NH_3BH_3)

Ammonia borane as a hydrogen storage material is promising hydrogen storage hydride with gravimetric hydrogen storage capacity of 19.5 wt%. It is denoted as AB.

Sodium borohydride($NaBH_4$)

Sodium borohydride is also a promising material for hydrogen storage with gravimetric hydrogen storage capacity of 10.8 wt%. It is denoted as SB. Boron hydrides have high volumetric and gravimetric densities.

Out of all the chemical hydrides sodium borohydride is widely studied. In 1990’s sodium borohydride was widely studied because during that time hydrogen was considered as the only efficient renewable energy carrier. It is the best source of hydrogen. The hydrolysis of sodium borohydride is expressed in equation (1)

$$NaBH_4 + H_2O \rightarrow 4\ H_2 + NaBO_2\,(aq) + 217\ KJ \qquad (1)$$

In the above equation, ($NaBH_4 + H_2O$) is an energy dense water based fuel system. Catalyst induces rapid hydrogen generation and $NaBO_2$, borate formed can be recycled into sodium borohydride.

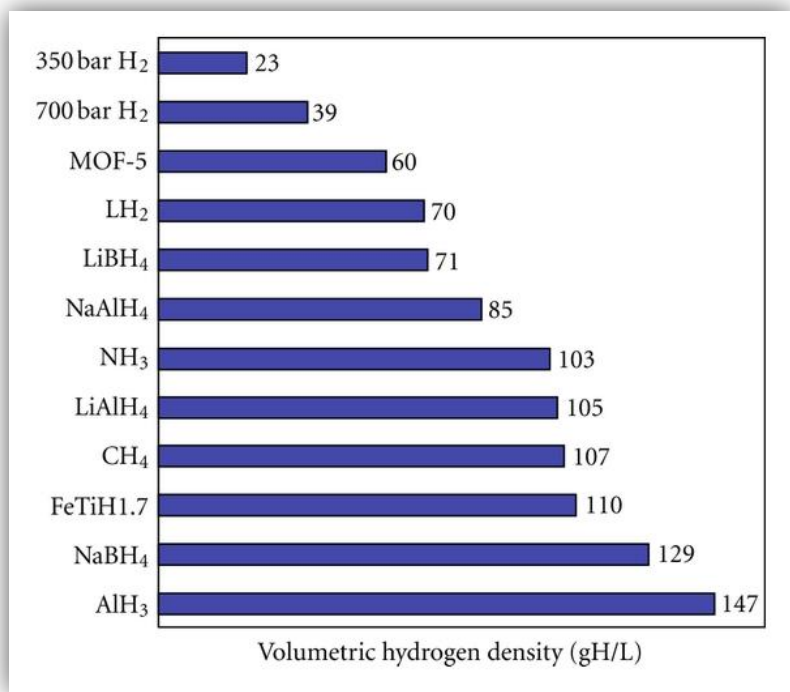


Figure 2: Volumetric hydrogen storage density of various hydrogen storage materials[18]

$NaBH_4$ is considered best among all the chemical hydrides present for the generation of hydrogen as depicted in (Figure 2). About 2.4 L of hydrogen is released by 1 g of sodium borohydride at normal temperature and pressure. Molecular formula of sodium borohydride is $NaBH_4$, it is a white in colour with molecular weight of 37.8 g/moles. It undergoes self hydrolysis and is moisture sensitive [19].

2.1.2 Hydrogen generation by thermolysis

Reaction which takes place in the presence of heat is called as thermolysis. It is a chemical pathway for the production of hydrogen from metal hydrides. The various hydrides in which production of hydrogen is reported are MgH_4 ,$LiBH_4$ etc. The reaction occurs at high temperature but slow and poor kinetics is a major disadvantage of this process.

Magnesium hydride contains around 14.9 wt% of hydrogen present in it and requires a temperature up to 270°C for thermolysis to occur. It shows slow and poor kinetics and reaction only takes place at higher temperature.

Production of hydrogen from metal hydrides by hydrolysis requires low temperature and the reaction kinetics is faster. So, it is concluded that chemical hydrogen by hydrolysis method is more effective than thermolysis method. Sodium borohydride contains 10 wt% hydrogen in it and hydrolysis occurs at room temperature.

2.1.3 Cryogenic hydrogen

Liquid hydrogen is stored in cryogenic tanks.Liquid hydrogen is present in rockets as rocket fuels. It is difficult to maintain a low temperature even when thermally insulated containers are present. Liquid hydrogen is highly flammable so, it should be kept away from flame.

Ritter and Ebner [20] reported a method in which hydrogen is pressurized upto 350-700 bar in specialized tanks. Density of cryogenic liquid hydrogen increases upto 70.8 kg/m^3, when hydrogen is condensed at 21.2 K. Liquefaction of hydrogen requires a large amount of energy.

2.1.4 Compressed hydrogen

At a high pressure of about 350 bar, hydrogen gas can be compressed easily and stored as compressed liquid hydrogen. For the storage of compressed liquid hydrogen special hydrogen cylinders are available to withstand high pressure. Hydrogen is stored in compressed form as it light in weight with low density of 0.084 kg/m^3.

Hydrogen storage tank is heavier than hydrocarbon storage tank as the energy content of hydrogen gas at ambient pressure and temperature is 10 MJ/m^3 because of which a larger hydrogen storage tank is required with larger volume. The embrittlement caused due to hydrogen diffusion requires a special attention for hydrogen storage. Due to the possibility of explosion of pressure vessels, compressed storage of hydrogen gas should be done with proper safety.

Compressed form of hydrogen is widely used in on-board mobile applications like in the vehicles for road transportation, at sites for stationary power generation etc. Hydrogen is stored in compressed form at 350 bar. Carbon composite cylinders store hydrogen at 700 bar, these cylinders are not manufactured in India. Total energy required to liquefy hydrogen is about 47 MJ/kg of hydrogen.

2.2 Catalyst used for hydrogen generation

Schlesinger et al. [21] were first to report increase in the hydrolysis of $NaBH_4$ reaction when metal chlorides are added to the reactant. Manganese, iron, cobalt and nickel react with sodium borohydride rapidly. It is seen out of all the metal chlorides, cobalt chloride is the most reactive one.

Formation of black precipitates after the reaction of cobalt chloride with sodium borohydride occurred. Gonzalez et al [22] reported that when cobalt chloride is present as a catalyst, decomposition of sodium borohydride occurs at a faster rate. The HGR of cobalt chloride was found to be more that other cobalt salts. It is a disagreement with the observation made by Kaufman and Sen [23] they stated that the catalytic activity of metal salts is not dependent on the anion present

Cobalt chloride dissociates into Co^{2+} and Cl^{-}. Chlorine is highly electronegative in nature and cobalt is more electrophillic when attached to cobalt chloride than another salt. In metal catalyst it is due to the presence of electrophillic character that strong positive charge attracts anions and strong polar molecules. Liu et al. [24] reported actual reaction mechanism which is different from that reported by Leavy et al. as the reactions taking place occur in parallel.

$$2\ Co^{2+} + 2\ BH_4^{-} + \rightarrow Co_2B + HBO_2 + 2\ H^{+} + \frac{9}{2}H_2 \qquad (2)$$

It is reported that hydrogen generation is increased as soon as cobalt chloride comes in contact with sodium borohydride, alumina and sodium hydroxide mixture.

One of the scientist suggested that sodium borohydride and cobalt chloride are mixed with each other in powdered form and water is added for the initiation of hydrolysis process.

2.3 Role of water

Hydrogen present in chemical hydrides is in reduced form or in electron rich state [25].Hydrides are of two types binary or complex hydrides. In simple hydrides (MH_n) the hydrogen contains negative charge and is bonded by covalent bond or ionic bond to metal.

$$MH_n + n\,H_2O \rightarrow M(OH)_n + nH_2 \quad (3)$$

Where, M is the metal present with valency 'n'.

The reaction product is hydroxide in chemical hydrides..

$$M(M^*H_4)n \;+\; (2n + X)H_2O \rightarrow M(M^*O_2)_n\;.xH_2o + 4nH_2 \quad (4)$$

Dissolution of sodium borohydride at 25°C requires extra water.

2.4 Effect of KOH on HGR

Sodium borohydride undergoes self hydrolysis so KOH is added to the reaction mixture in order to prevent hydrolysis of sodium borohydride.KOH is used as a stabilizer. With increase in the concentration of potassium hydroxide, hydrogen generation rate decreases as the alkaline nature of the solution is increasing.

2.5 Effect of Alumina (Al_2O_3) on HGR

HGR increases with increase in the concentration of alumina. γ-alumina nanoparticles promote and affect the HGR rate due to its size and hydrophilic nature of alumina particles [27].

2.6 Langmuir – Hinshelwood Model

Various models are studied to observe the hydrolysis of sodium borohydride system like zero order, first order, Langmuir-Hinshelwood model etc. The zero order model is based on linear behaviour of hydrogen generation. The graph obtained is a straight line [28]. According to Langmuir-Hinshelwood model the reaction consists of two steps: adsorption of adsorbent on the surface of catalyst and reaction of adsorbed species.

2. 7 Assumptions of Langmuir-Hinshelwood Model

Langmuir – Hinshelwood model deals with the adsorption of gases on the surface of a catalyst. The reaction occurs by following steps:

1. Reactants are diffused on the surface of the solid adsorbent.
2. Adsorption occurs on the surface of the solid.
3. Chemical reaction occurs at the surface followed by desorption of products.

This model is considered as a combination of zero and first order kinetic model, with adsorption coefficient K_{ads}[29].

2.8 Objectives

1. Determining amount of hydrogen generated at different sodium borohydride concentration.
2. Determining amount of hydrogen generated by changing the temperature of the system.
3. Determining of adsorption coefficient by applying Langmuir-Hinshelwood kinetic model.
4. Determination of heat of adsorption, during hydrolysis of sodium borohydride.

Chapter-3

Experimentation

Sodium borohydride undergoes hydrolysis to produce hydrogen and sodium borate as by-product. The by-product of the reaction is in aqueous form so it can be easily removed from the system. Self hydrolysis reaction of sodium borohydride occurs at low pH which makes is highly unstable, it can be made stable by reacting it with potassium hydroxide (KOH) as a solution stabilizer. A selected metal catalyst is required to speed up the reaction.

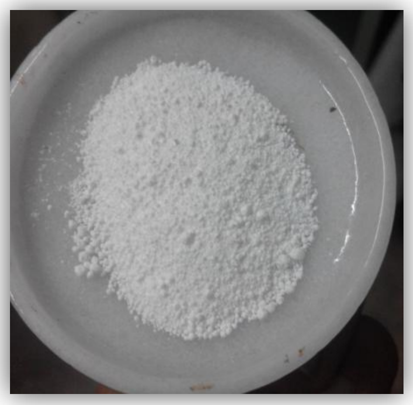
This chapter presents the experimental setup prepared to perform kinetic studies and calculate the heat of enthalpy by applying Langmuir Hinshelwood model.

3.1 Chemicals Required

Chemical required for the hydrolysis to take place are sodium borohydride 97% Purity, cobalt chloride hexahydrate 98% Purity from Lobachemical Ltd, Potassium hydroxide pellets (KOH) 97% Purity γ-alumina (Al_2O_3) (20nm, 99% purity).

Apparatus used for the study are Three-port reactor, heating mantle, pressure equalizing funnel, water container and measuring cylinder.

A) Cobalt chloride



B) Alumina powder

C) Sodium borohydride

D) Potassium hydroxide

Figure 3: Chemicals required for hydrogen generation

3.2 Experimental setup

A 250 mL three neck round bottom flask is used to carry the reaction. The left port of the flask has a thermometer attached to it so as to check the temperature of the system. Middle port is attached to pressure equalizing funnel and the right port with the help of a tube is connected to the water replacement system. Heating mantle used to control the reaction temperature. In the pressure equalizing funnel aq KOH is present which is used to prevent hydrolysis of sodium borohydride. A cylinder is present in a container with water in an inverted form. This cylinder measures the amount of hydrogen generated by the system.

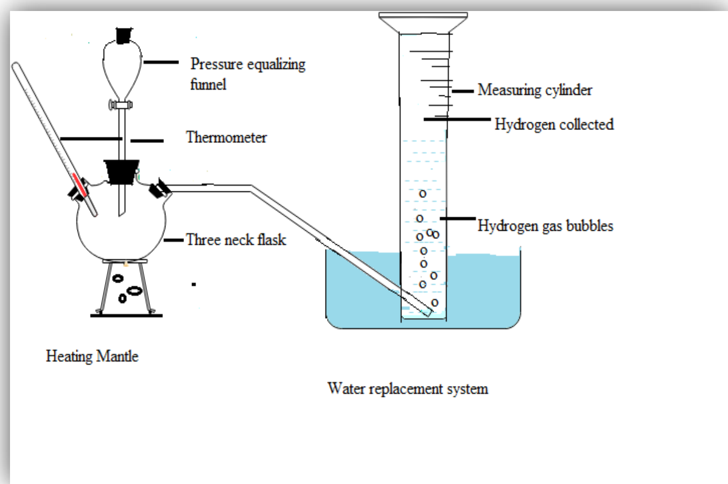


Figure 4: Diagrammatic representation of experimental setup for hydrogen generation

Figure 5: Three- neck flask with thermometer and pressure equalizing funnel

Figure 6: Experimental setup

3.3 Experimental procedure

In a 250 mL three neck round bottom flask sodium borohydride and alumina are added from the middle port. Cobalt chloride is added after this and then 10 mL of KOH solution is added drop wise to the mixture present in the flask with the help of pressure equalizing funnel. Generation of hydrogen gas bubbles occurs when KOH is added to the solution. Amount of hydrogen generated is measured by the amount of water displaced from the measuring cylinder.

Chapter-4

Hydrogen gas analysis

4.1 Properties of hydrogen gas

Hydrogen gas is a flammable gas and it can react with heat easily. Properties of hydrogen gas are as below [30].

1. Hydrogen is the smallest chemical element and consists of one proton only.
2. Hydrogen[H] atomic number is one.
3. Hydrogen has a melting point of -259.14°C.
4. Hydrogen density is 0.08988 g/L.
5. Hydrogen is less dense than air.

4.2 Qualitative analysis of hydrogen gas

Pop test is performed to perform the qualitative analysis of the hydrogen gas. It is a flame test. Hydrogen can be collected by heating water and placing a tube over the surface to collect hydrogen. Hydrogen is recognized by a pop sound when it burns.

Figure 7: Pop test [31]

Chapter- 5

Results and Discussion

For hydrogen generation, the main chemical used is $NaBH_4$ with hydrogen stored in it, cobalt chloride is used as catalyst, potassium hydroxide is used as stabilizer and alumina is used as catalyst promoter.

5.1 Effect of initial reactant concentration on hydrogen generation rate

Experiments were performed for analyzing the change in the amount of hydrogen generated at four concentrations of sodium borohydride (at reaction temperatures of 293 K, 303 K, 313K, and 323 K). The initial concentration of $NaBH_4$ was varied by increasing the amount of $NaBH_4$ in the reaction mixture.

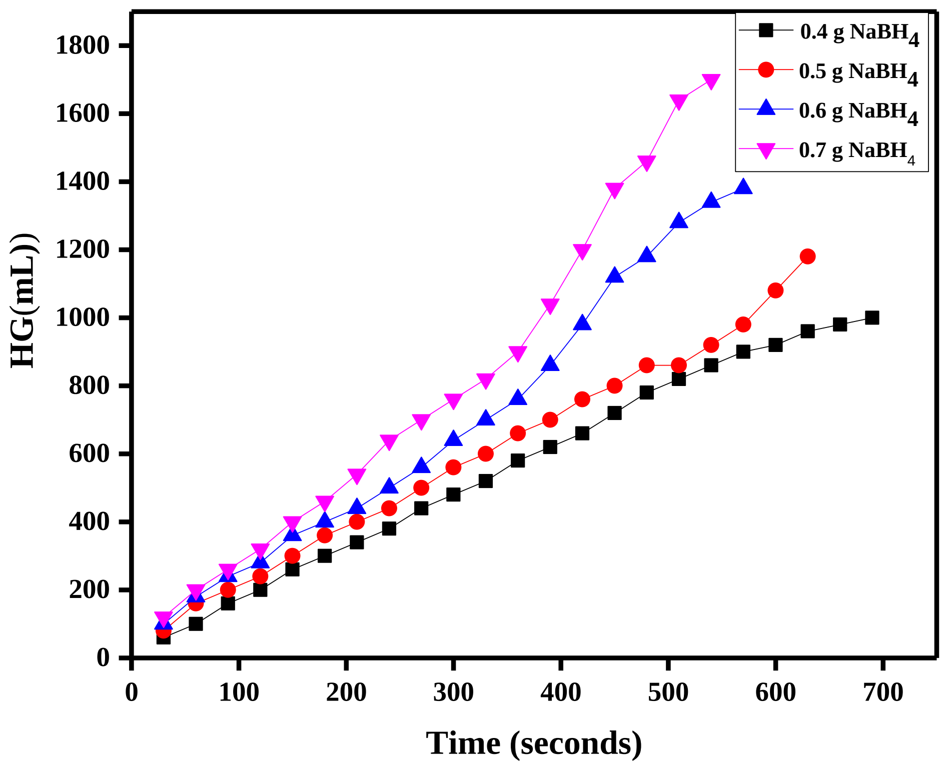


Figure 9: Hydrogen generation at 293 K with different $NaBH_4$ concentration

From Figure 9, it is observed that at a given reaction temperature, when the initial concentration of sodium borohydride was increased from 0.4 g to 0.7 g, the rate of hydrogen generation also increased.

At 293 K, 1000 mL of hydrogen was obtained from 0.4 g of $NaBH_4$, and 1700 mL hydrogen was obtained from 0.7 g $NaBH_4$ as shown in Table 1.

Table 1: HG at 293 K at different initial $NaBH_4$ concentrations

S. No	Time (seconds)	HG (0.4g $NaBH_4$)	HG (0.5g $NaBH_4$)	HG (0.6g $NaBH_4$)	HG (0.7g $NaBH_4$)
1.	30	60	80	100	120
2.	60	100	160	180	200
3.	90	160	200	240	260
4.	120	200	240	280	320
5.	150	260	300	360	400
6.	180	300	360	400	460
7.	210	340	400	440	540
8.	240	380	440	500	640
9.	270	440	500	560	700
10.	300	480	560	640	760
11.	330	520	600	700	820
12.	360	580	660	760	900
13.	390	620	700	860	1040
14.	420	660	760	980	1200
15.	450	720	800	1120	1380
16.	480	780	860	1180	1460
17.	510	820	860	1280	1640
18.	540	860	920	1340	1700
19.	570	900	980	1380	
20.	600	920	1080		
21.	630	960	1180		
22.	660	980			
23.	690	1000			

5.2 Effect of temperature on hydrogen generation rate

The temperature affects the kinetics of a system significantly. From the experiments conducted at four temperatures (293 K, 303 K, 313 K, and 323 K) it was observed that the amount of hydrogen generated increased with temperature (Tables 1-4).

Table 2: HG at 303 K at different $NaBH_4$ concentrations

S. No	Time (seconds)	HG(mL) ($NABH_4$0.4g)	HG(mL) ($NaBH_4$0.5g)	HG(mL) ($NaBH_4$0.6g)	HG(mL) ($NaBH_4$0.7g)
1.	30	100	140	180	240
2.	60	120	220	280	320
3.	90	180	320	380	380
4.	120	260	420	480	740
5.	150	300	660	580	940
6.	180	320	680	880	1120
7.	210	460	760	980	1420
8.	240	520	940	1080	1480
9.	270	580	980	1180	1560
10.	300	620	1070	1260	1680
11.	330	700	1110	1330	1740
12.	360	780	1170	1390	1740
13.	390	820	1200		
14.	420	840	1240		
15.	450	1040	1260		
16.	480	1040	1280		

Table 3: HG at 313 K at different $NaBH_4$ concentrations

S.No	Time (seconds)	HG(mL) ($NABH_4$0.4g)	HG(mL) ($NaBH_4$0.5g)	HG(mL) ($NaBH_4$0.6g)	HG(mL) ($NaBH_4$0.7g)
1	30	160	150	180	200
2	60	220	290	340	420
3	90	300	410	580	600
4	120	380	530	740	740
5	150	440	610	780	940
6	180	500	730	920	1120
7	210	580	770	980	1240
8	240	640	890	1040	1420
9	270	720	950	1140	1480
10	300	780	1070	1220	1580
11	330	840	1110	1400	1780
12	360	900	1170	1400	1780
13	390	960	1210		
14	420	1000	1290		
15	450	1080	1290		

Table 4: Hydrogen generation (HG) at 323 K at different $NaBH_4$ concentrations

S. No	Time (seconds)	HG(mL) ($NABH_4$0.4g)	HG(mL) ($NaBH_4$0.5g)	HG(mL) ($NaBH_4$0.6g)	HG(mL) ($NaBH_4$-0.7g)
1	30	200	220	280	320
2	60	240	260	340	420
3	90	280	300	440	520
4	120	340	400	580	620
5	150	360	420	600	800
6	180	420	500	680	1000
7	210	480	600	780	1060
8	240	500	640	880	1170
9	270	560	680	990	1380
10	300	600	790	1160	1560
11	330	680	890	1220	1820
12	360	780	990	1340	
13	390	880	1180		
14	420	990	1320		
15	450	1120			

From Tables 1-4 it is observed that the hydrogen generation per gram of $NaBH_4$ was maximum with 0.4 g initial concentration of $NaBH_4$. Figure 10 shows the increase in the hydrogen generation with temperature at 0.7 g $NaBH_4$ concentration at 293 K, 303 K, 313 K, and 323 K. This may be due to the reason that the solution becomes viscous towards the end of the reaction. At low temperature (293 K) the viscosity of this solution prevents effective contacting of the reactant with the catalyst as compared to the better contact at higher temperature (323K) and hence more hydrogen is generated at higher temperature.

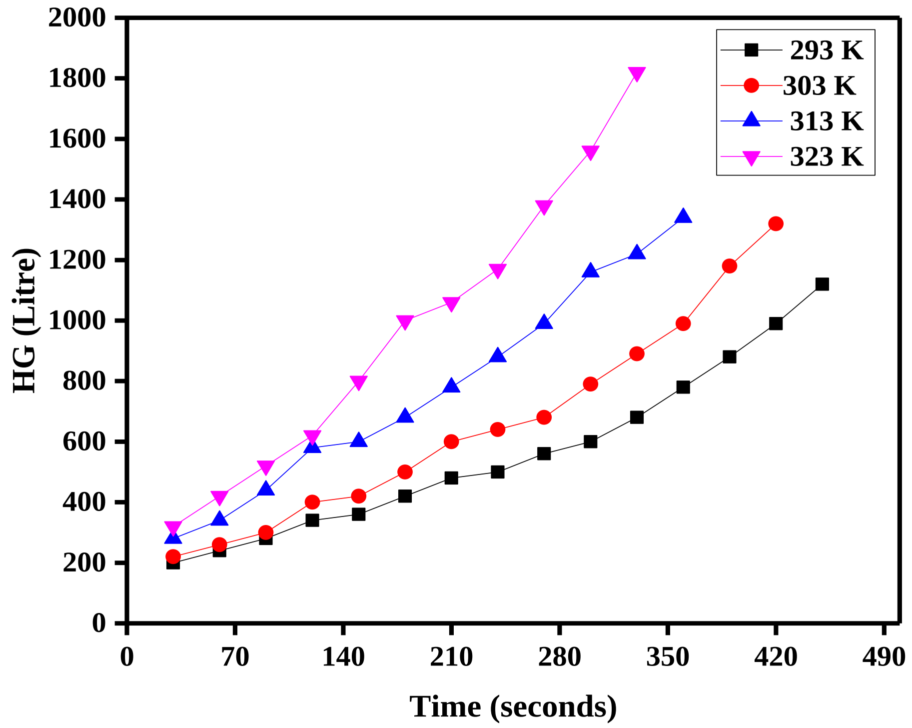


Figure 10: Hydrogen generation at different temperatures

5.3 Kinetics of metal catalyzed hydrolysis of $NaBH_4$

Experimental study of kinetics of sodium borohydride hydrolysis with $CoCl_2$ as a catalyst are studied and the reaction kinetics parameters are determined using Langmuir-Hinshelwood kinetic model.

5.3.1 Data analysis method

The change in concentration of sodium borohydride with time is:

$$C_A = C_{A0}\,(1 - \frac{V_{H2}}{V_{H2max}}) \qquad (5)$$

Where, C_{A0} is the initial concentration of $NaBH_4$ in mol/L. V_{H2} is the experimental value of hydrogen generated at each time point and V_{H2max} is the maximum amount of hydrogen that can be generated by the system in litres.

The maximum amount of hydrogen generated is calculated as follows,

$$V_{H2max} = \frac{amount\ of\ NaBH_4\ taken}{molecular\ weight\ of\ NaBH_4} \times 4 \times \frac{22.4}{273} \times T \qquad (6)$$

where T = Reaction Temperature in K, constant, 4, is the number of molecules of hydrogen generated when hydrolysis of sodium borohydride occurs given by equation(1)

$$NaBH_4 + 4\ H_2O \rightarrow NaBO_2 + 4\ H_2 + Heat$$

The initial value of C_A (C_{Ao}) at 293 K is 1.725 mol/L (for 0.7 g of sodium borohydride) and with time it decreased to 0.083 mol/L. This shows that more than 95% conversion took place.

5.3.2 Langmuir-Hinshelwood kinetics

Langmuir-Hinshelwood (L-H) model involves two steps. The first step involves adsorption of adsorbate species (BH^{4-}) on the catalyst surface [32].

$$BH_4^- + * \rightarrow BH_4^- \times * \qquad (7)$$

The fractional surface coverage by the adsorbate, $\theta_{NaBH4,}$ can be obtained by Langmuir adsorption isotherm,

$$\theta_{NaBH4} = \frac{K_{ads} C_A}{1 + K_{ads} C_A} \qquad (8)$$

Here, K_{ads} is the adsorption coefficient.

In second step surface reaction of the adsorbed species occurs to produce hydrogen:

$$BH_4^- \times * + 2\ H_2O \rightarrow BO_2^- \times * + 4\ H_2 \qquad (9)$$

The water is in excess, thus, change in water concentration may be assumed as insignificant, and the rate is proportional to the concentration of adsorbed species, θ_{NaBH4}. For reaction volume, V, and catalyst mass m_{cat}, the reaction rate may be written as,

$$-r_{NaBH4} = \frac{K_L \theta_{NaBH4} mcat}{V} \qquad (10)$$

Combining equations (8) and (10),

$$-r_{NaBH4} = \frac{dC_A}{dt} = \frac{m_{cat}}{V} K_L \frac{K_{ads} C_A}{1 + K_{ads} C_A} \qquad (11)$$

Equation (11) is a combination of Langmuir adsorption isotherm and first order reaction of the adsorbed species; this is Langmuir-Hinshelwood kinetic model.

On separating and integrating equation 11,

$$(C_{A0} - C_A) + \frac{1}{\mathrm{Kads}} \ln\left(\frac{C_{A0}}{CA}\right) = \frac{K_L mcat}{V}\ t \qquad (12)$$

Initial concentration of sodium borohydride is denoted by C_{A0}, C_A is the final concentration of $NaBH_4$, V is the volume of the reaction mixture and m_{cat} is the mass of the catalyst used. This model is considered as a combination of zero and first order kinetic model, with adsorption coefficient Kads.

In Equation (16), the term $(C_{A0} - C_A) + \frac{1}{K_{ads}} \ln\left(\frac{C_{A0}}{CA}\right)$ can be denoted by "Y". A graph between Y and T can be plotted to get a straight line for the evaluation of k_L. For plotting Y against T, K_{ads} should be known. The value of K_{ads} is assumed and plotted Y against T by changing the assumed value of K_{ads} till a straight line is obtained. From the slope obtained the value of K_L can be determined. The plots are shown in the Figures 11, 12 and 13.

$$K_{slope} = \frac{K_L m_{cat}}{V} \qquad (13)$$

At 293 K a plot (Figure 12) between $(C_{A0} - C_A) + \frac{1}{K_{ads}} \ln\left(\frac{C_{A0}}{C_A}\right)$ denoted as (Y) and time (T) at 0.4 g concentration of $NaBH_4$ gave a straight line for a value of $K_a = 46.8\ m^3 K mol^{-1}$

Table 5: Value of adsorption coefficient at different temperatures

S.No	K_{ads} (m^3 K mol^{-1})			
	293 K	303 K	313 K	323 K
1.	46.8	19.2	5.9	5.4
2.	33.4	13.9	9.7	4.2
3.	36.2	16.7	11.1	3.9
4.	42	18.1	12.5	2.8

Value of K_{ads} is decreasing with increase in temperature because the enthalpy of adsorption has negative value. Due to this at high temperatures, C_A is less than one and the reaction becomes first order.

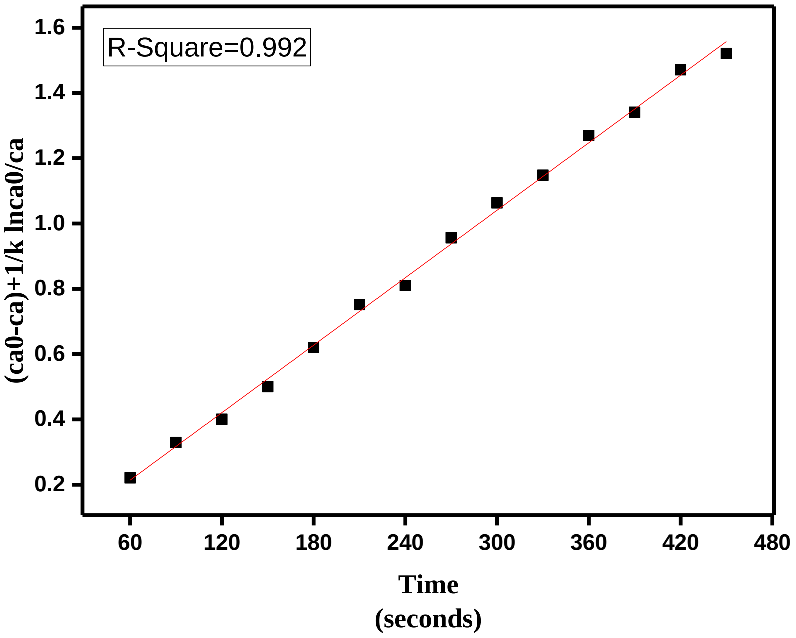


Figure 11: Graph between Y and Time at 293 K

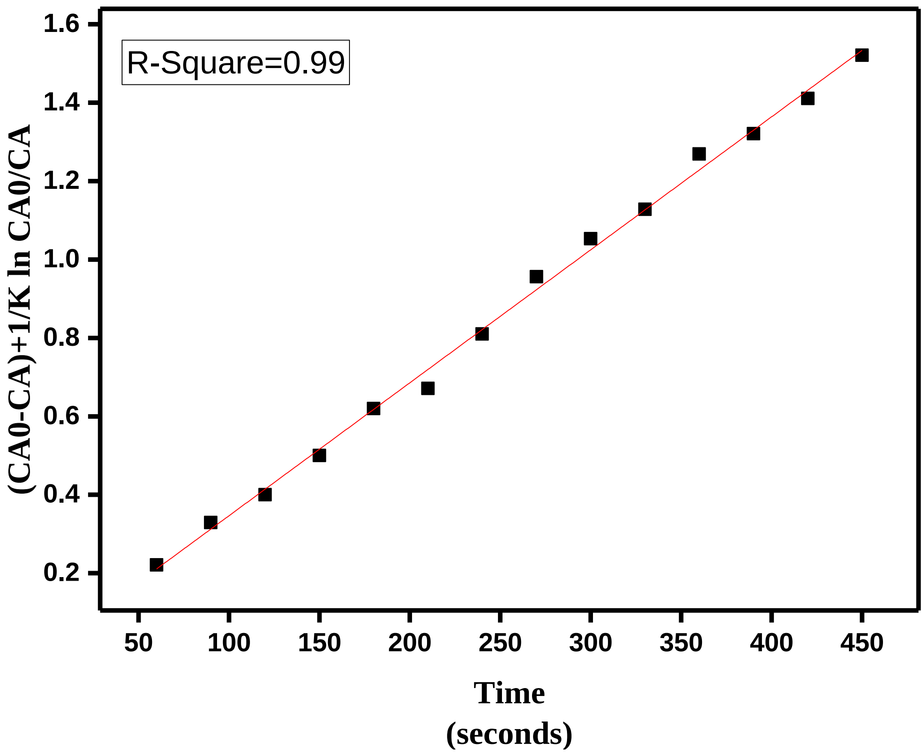


Figure 12: Graph between Y and Time at 303 K

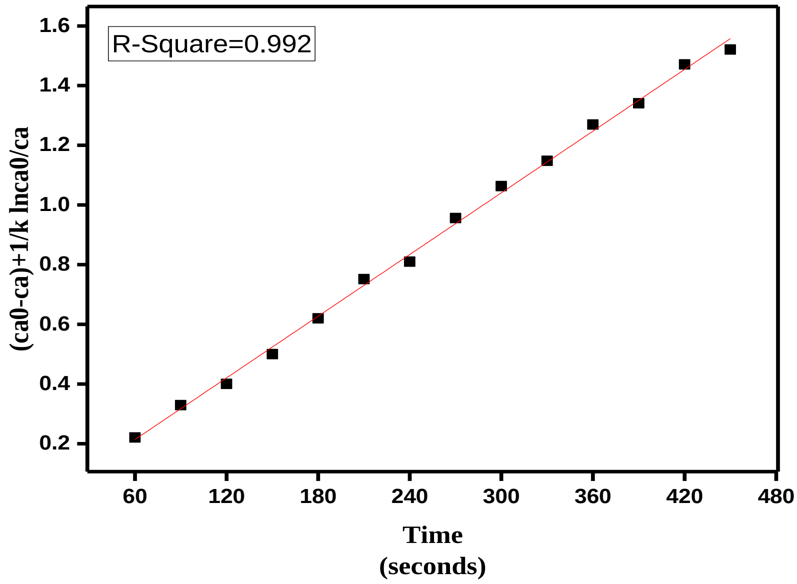


Figure 13: Graph between Y and Time at 313 K

Table 6: Vale of K_L at different temperature

S.No	Amount of $NaBH_4$ (g)	K_L (mol L^- sec^- g^-)			
		293 K	303 K	313 K	323 K
1.	0.4 g	0.0324	0.0432	0.0590	0.0600
2.	0.5 g	0.0426	0.0730	0.0660	0.079
3.	0.6 g	0.0524	0.0800	0.080	0.0812
4.	0.7 g	0.0660	0.0960	0.107	0.122

The value of K_L increases with increase in temperature as shown in Table 5. At 293 K for 0.4 g $NaBH_4$ concentration the value of K_L is 0.324 mol L^- sec^- g^- and it increases to 0.600 mol L^- sec^- g^- at 323 k.

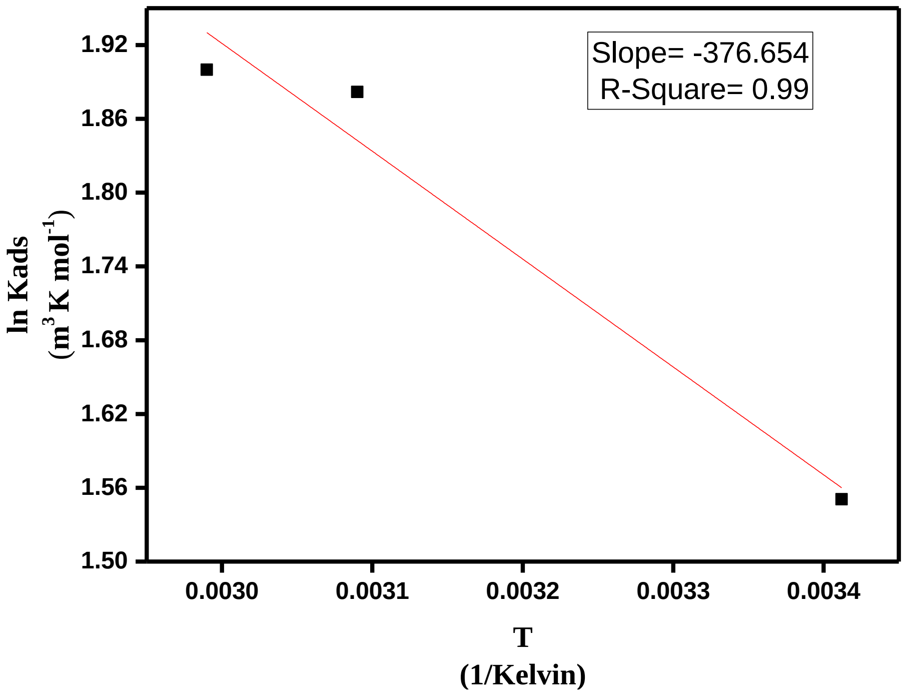


Figure 14: Plot between ln K_{ads} and $\frac{1}{T}$

Absorption coefficient K_{ads} varies with temperature according to equation (14):

$$K = A \exp\left(\Delta \frac{H_{ads}}{RT}\right) \qquad (14)$$

Where, A is the pre-exponential factor, ΔH_{ads} is the heat of adsorption, R is the gas constant and T is the temperature in Kelvin The value of heat of adsorption obtained from the graph is −45 kJ/mol which quite close to the value reported in the literature [33].

X-Ray Diffraction (XRD) of the residual material

For the determination of the composition of the sample, a finely ground homogenous sample is required.

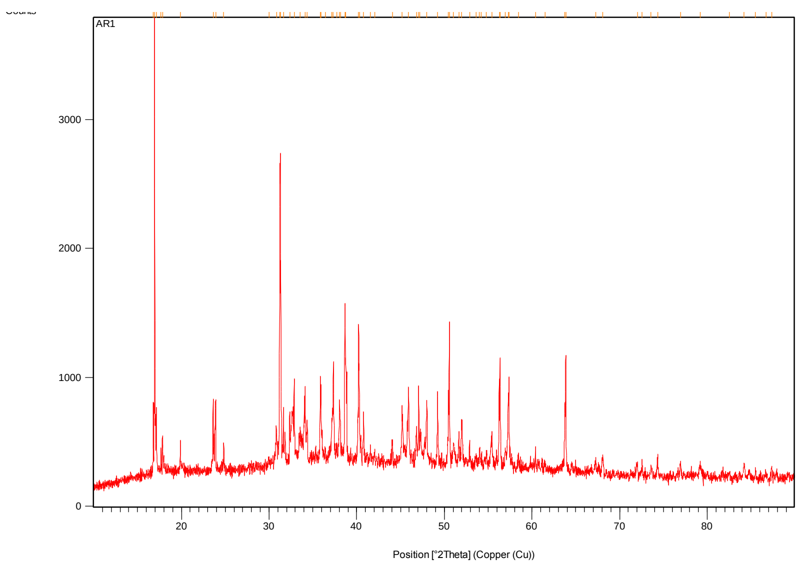


Figure 8: XRD of the residual material

From the XRD analysis it is observed that compounds containing boron are present in maximum amount in the residue. It has cobalt boride present in it and some other cobalt boride compounds with different oxidation state. The presence of cobalt boride confirms the presence of active catalytic site for hydrolysis to take place.

Chapter-6
Conclusion

1. Hydrolysis of sodium borohydride is increases with increase in the concentration of sodium borohydride.

2. The hydrogen generation rate increases with increase in temperature.

3. Langmuir -Hinshelwood model is used to obtain the adsorption coefficient K, which decreases with increase in temperature, due to which the concentration of sodium borohydride becomes less than one, hence the reaction is following first order.

4. From the Langmuir-Hinshelwood model, heat of adsorption is obtained.

5. It is concluded that adsorption is responsible for the variation of kinetic order from low to high temperatures.

Future scope of work

1. Study can be done on the methods to use the residue formed after sodium borohydride hydrolysis.
2. Study can be conducted for calculating the surface area covered by sodium borohydride by using Langmuir kinetic model.

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