

KINETIC STUDIES OF HYDROLYSIS REACTION OF NaBH_4 WITH $\gamma\text{-Al}_2\text{O}_3$ NANOPARTICLES AS CATALYST PROMOTER AND CoCl_2 AS CATALYST

Arshdeep Kaur^{1*}, Dasaroju Gangacharyulu¹ and Pramod K. Bajpai¹

¹ Thapar University, Department of Chemical Engineering, Patiala, India. E-mail: er.arsh87@gmail.com - ORCID: 0000-0002-1057-891X; ORCID: 0000-0003-0452-0225; ORCID: 0000-0002-8371-5022

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Abstract - Solid-state hydrogen storage is of considerable concern as a potential hydrogen source for portable fuel cell applications. This study mainly focuses on kinetics of $\text{NaBH}_4/\text{Al}_2\text{O}_3$ nanoparticles (20 nm)/ H_2O system with CoCl_2 as catalyst and the factors that affect the hydrogen generation rate (HGR). It is observed that the reaction rate increases considerably with increase in NaBH_4 , Al_2O_3 nanoparticle (20 nm), CoCl_2 and NaOH concentrations and the respective reaction orders are calculated. Hydrogen generation rate is also investigated at different temperatures (303, 313, 323 and 333 K) for constant NaBH_4 (1.25 moles/L), NaOH (1.4 moles/L), CoCl_2 (0.02 moles/L) and Al_2O_3 (0.09 moles/L) concentrations. Kinetics of the NaBH_4 hydrolysis reaction increases with $\gamma\text{-Al}_2\text{O}_3$ nanoparticles and the calculated activation energy is 29 kJ/moles. This study also reports that a combined dual-solid-fuel system is highly efficient in terms of hydrogen storage capacities compared with a single hydride based system. Maximum hydrogen generation efficiency, observed at a mass ratio of 0.09: 0.7 ($\text{Al}_2\text{O}_3/\text{NaBH}_4$), is 99.34%.

Keywords: Hydrogen; Energy; Nanoparticles; Sodium borohydride; Cobalt chloride; Alumina.

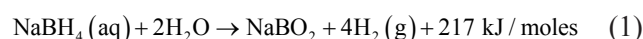
INTRODUCTION

Application of hydrogen as a fuel is considered to be a preeminent alternative to meet present energy demands. The primary technological barrier in the advancement towards implementation of a successful hydrogen economy is efficient hydrogen storage. Various hydrogen storage technologies are available like pressurized hydrogen storage and solid state hydrogen storage (Retnamma et al., 2011). Pressurized tank and cryogenic liquid hydrogen are energy intensive as well as are not preferred due to various safety concerns. In solid state hydrogen storage, H_2 is bonded with various chemicals and has a plethora of merits like high hydrogen storage densities and safe handling and storage (Demirci et al., 2010).

Detailed literature studies revealed that borohydrides are accepted as high potential storage materials with 4(B-H) bonds and hydrogen in the form of hydrides $\text{H}^{\delta-}$ that incorporate high hydrogen

densities (Moussa et al., 2013; Akdim et al., 2011). Therefore, it provides a key prospect to deal with pure hydrogen gas as fuel in the recharge aspects (Dai et al. 2011). Chemical release of hydrogen in hydrides is through thermolysis as well as the hydrolysis pathway. Table 1 represents some prominent hydrides releasing hydrogen by hydrolysis (releasing hydrogen from hydrides upon reaction with water).

Among all hydrides, sodium borohydride is a representative chemical hydride for hydrogen storage with distinct advantages as it is stable and safe to use and store. Furthermore, the NaBH_4 hydrolysis reaction initiates at room temperature and pressure in the presence of catalyst, as given in Equation 1. Moreover, the hydrogen released is a high purity gas (Amendola et al., 2000).



Considering the cost, byproduct recyclability and the “no-go” decision of the US Department of Energy

* Corresponding author: Arshdeep Kaur - E-mail: er.arsh87@gmail.com

Table 1. Chemical hydrogen storage in hydrides by hydrolysis.

S. No.	Hydrogen storage materials	H ₂ content (wt%)	Temperature (°C)	Limitations	Advantages	Reference
1.	LiH	25	Room temperature	Formation of LiH lowers HGR	High hydrogen density	Pitcher and Kavarnos (1997)
2.	LiBH ₄	18	Same	Unstable hydride	Same	Kojima et al. (2007)
3.	LiAlH ₄		Same	Unstable hydride	Same	Jang et al. (2006)
4.	Al and Al alloys (Powder)	3.7	Room temperature	Highly exothermic reaction, presence of coherent layer.	Can reduce production cost due to easy availability. Fast kinetics and reaction initiates at room temperature.	Hou (2006)
5.	NaBH ₄	10	Room temperature	Expensive		Dai et al. (2011)

for NaBH₄ for on-board vehicular hydrogen storage, studies are in progress to redefine NaBH₄ based hydrogen generation systems that can handle the technological barriers and improve hydrogen storage densities. To deal with the disadvantages of NaBH₄ as a prime hydrogen storage material, several coupling materials are studied as per the literature review given in Table 2.

Sodium borohydride is coupled with other probable materials as given in Table 2. As a result, fast kinetics and high efficiency are achieved. Specifically, alumina is added as a composite with sodium borohydride that increases the hydrogen generation rate and hydrogen yield.

It is further depicted that NaBH₄ has good affinity towards metal chlorides like iron(II) chloride, nickel(II) chloride, manganese(II) chloride, copper(II) chloride and cobalt(II) chloride that could act as an efficient catalyst for the NaBH₄ hydrolysis reaction (Schlesinger et al., 1953; Levy et al., 1960; Komova et al., 2008). Among cobalt-based salts like (CH₃COO)₂Co, CoSO₄, CoF₂, CoCl₂ and Co(NO₃)₂, for catalyzing the NaBH₄ hydrolysis reaction, CoCl₂ shows the highest hydrogen generation rate (HGR) (Akdin et al., 2011). Strong cationic charge and electrophilic nature of Co²⁺ and higher solubility of Cl⁻ in aqueous solution than other salts make it highly reactive.

Catalysts are also synthesized before use to obtain high hydrogen generation rates like a palladium complex catalyst (Sahin et al., 2016), Co(II)-Cu(II) complex catalyst (Kilinc et al., 2012) and salicyladimine-Ni complex catalyst (Kilinc et al.,

2017). Therefore, in this study a chemical hydride-based hydrogen storage system composed of NaBH₄/γ-Al₂O₃ nanoparticles (20nm)/H₂O with CoCl₂ as catalyst is reported. Here, γ-Al₂O₃ nanoparticles are used as catalyst promoter in the solution to achieve maximum hydrogen efficiencies. Previous studies also suggest that cobalt chloride is a promising catalyst that accelerates NaBH₄ hydrolysis and γ-Al₂O₃ nanoparticles form an activated complex with CoCl₂ that increases its catalytic activity (Kaur et al., 2017).

The present paper also demonstrates extended studies after selecting cobalt chloride as a promising catalyst and γ-Al₂O₃ nanoparticles as an appropriate catalyst promoter published in a previous work (Kaur et al., 2017). Extensive kinetic studies on the combination of alumina nanoparticles with NaBH₄ could further result in optimising operating conditions for high hydrogen generation rate and could facilitate cost reduction for a NaBH₄-based hydrogen storage system. Also, all the factors that influence the kinetics of this system are observed through a power law kinetic model that provides a detailed description of each kinetic parameter and adds novelty to the research work.

EXPERIMENTAL

Materials and methods

Materials used in the study were sodium borohydride (NaBH₄) (97% purity) and cobalt chloride hexahydrate (CoCl₂·6H₂O) (98% purity) procured from M/s Loba Chemie Ltd., sodium hydroxide pellets (NaOH) (97%

Table 2. Coupling materials with NaBH₄.

S. No.	Coupling materials	Observations	References
1.	(NaBH ₄ /Al) with CoCl ₂	90% fuel conversion	Dai et al. (2011)
2.	Composition of Al(10μm)/NaBH ₄ mixture activated by La and CoCl ₂	100% efficiency within 60min at 60°C	Jianbo et al. (2012)
3.	Al (10μm) Li/NaBH ₄ mixture activated by Ni powder	96% efficiency at 60°C	Shu et al. (2012)
4.	Composite of Al (10μm), Li, Co and NaBH ₄	100% hydrogen yield	Wang et al. (2013)

purity) and γ -alumina (Al₂O₃) (20nm, 99% purity) obtained from Merck Ltd.

Experiments were carried out in a 250 mL three-neck round bottom reaction flask under isothermal conditions. The reactor is cleaned and dried before starting the experiment. Predetermined amounts of reactants are added to the reactor that is attached to a pressure equalizing funnel from the middle port.

An aqueous solution of NaOH of amount 10 mL is added dropwise to the reactor via a pressure equalizing funnel. Hydrogen gas is evolved as soon as the aqueous solution of NaOH comes in contact with the reactants. Hydrogen generation is measured by displaced water volumes in a graduated cylinder as a function of time and corrected to the values at 298 K and 1 atm. The hydrogen measuring cylinder is attached to a water replacement system and homogeneous dispersion of catalyst is achieved in a short period of time due to the stirring action caused by evolved hydrogen gas bubbles. Evolved hydrogen gas was collected in an inverted graduated cylinder by downward displacement of water. Temperature in each experiment was maintained constant with the variation of $\pm 0.2^\circ\text{C}$.

Considering the constraints in the experimental facility and practical operating conditions, experiments were performed at specific concentrations of NaBH₄, CoCl₂, Al₂O₃ and NaOH. Four concentrations of NaBH₄ were taken for kinetic data: 1.00, 1.25, 1.30, 1.75 moles/L, for CoCl₂; 0.020, 0.024, 0.028, 0.032 moles/L; for Al₂O₃ 0.06, 0.07, 0.08, 0.09 moles/L; and for NaOH 1.16, 1.6, 2.06, 2.6 moles/L.

RESULTS AND DISCUSSION

Preliminary studies were carried out without addition of catalyst promoter in NaBH₄/H₂O system with CoCl₂ as catalyst varying the initial concentration of NaBH₄ and keeping the NaOH (1.4 moles/L) and CoCl₂ (0.02 moles/L) constant.

As shown in Figure 1, the hydrogen generation rate (HGR) increases with increase in NaBH₄ concentration at constant NaOH and CoCl₂ concentrations up to 1.7 moles/L. But at higher concentrations of NaBH₄ (2.00 and 2.25 moles/L) the hydrogen generation rate decreases. Maximum hydrogen generation is 13.5 moles/L. sec at 1.7 moles/L.

The hydrolysis kinetics are observed with addition of γ -Al₂O₃ nanoparticles. The kinetics are affected by multiple factors like concentration of stabilizer (NaOH), promoter (γ -Al₂O₃ nanoparticles), NaBH₄ and catalyst (CoCl₂.6H₂O). All these factors are observed by varying their concentrations and observing the change in HGR and keeping the concentration of other components constant. The change in concentration of each component will cause changes in viscosity and

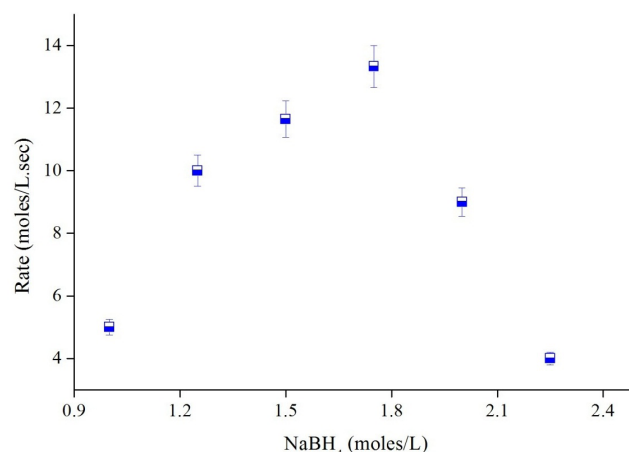


Figure 1. Variation of HGR with NaBH₄ with CoCl₂ as catalyst and without addition of (γ -Al₂O₃ nanoparticles).

density in the solution that will affect the HGR of the system as discussed below.

Effect of NaOH on hydrogen generation rate (HGR)

Sodium borohydride undergoes self-hydrolysis. Therefore, NaOH is used as stabilizer in the solution because NaOH considerably hinders spontaneous hydrolysis of NaBH₄. Additionally, the kinetics are dependent on solution pH and the solution pH is controlled by NaOH concentration, which affects the kinetics of the whole system. Therefore, the role of the stabilizer (NaOH) on the hydrolysis reaction of NaBH₄ is determined first and its effect on hydrogen generation is observed in the presence of CoCl₂ catalyst and γ -Al₂O₃ nanoparticles as promoter.

The effect of NaOH on the hydrogen generation rate was evaluated by performing a number of experimental runs at different NaOH concentrations as shown in Figure 2. In these experiments, the concentrations of NaBH₄, Al₂O₃ and CoCl₂ were kept constant at 1.25 moles/L, 0.09 moles/L and 0.02 moles/L, respectively.

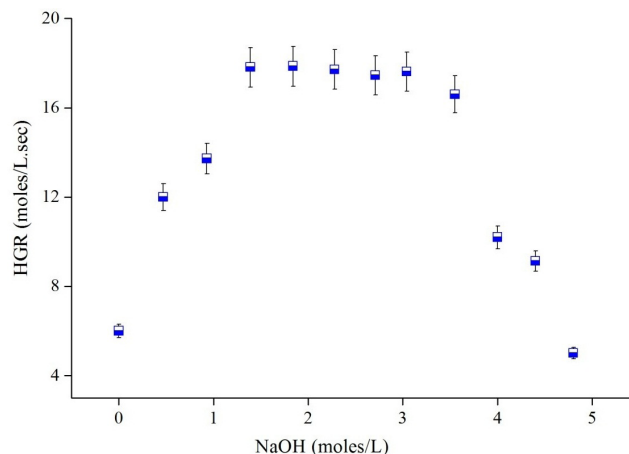


Figure 2. Variation of the HGR with NaOH concentration.

It is observed from the Figure 2 that, after 1.4 moles/L NaOH, the HGR is almost constant until 3.5 moles/L NaOH. As the concentration of NaOH exceeds 3.5 moles/L, the HGR decreases due to the high level of alkalinity in the solution that suppresses hydrogen release. Increasing the alkali concentration in the solution results in an increase in HG kinetics until the solution becomes highly viscous. Therefore, 1.4 moles/L of NaOH is selected to carry further kinetic studies.

Addition of NaOH increases the alkalinity of the solution, which results in formation of sodium aluminates in the solution and increases Al hydrolysis. This could be explained because the top oxide layer of the Al_2O_3 surface forms hydroxide after chemisorption of H_2O molecules in the solution (Deng et al., 2007). The surface hydroxyl groups show either acidic or basic behaviour depending on the pH of the solution. The pH of the present system is greater than 9. This could cause the adsorption of metal ions on the alumina surface and cationic adsorption of Co^{+2} or Na^+ could occur on the hydroxide layer of alumina, resulting in formations of sodium and cobalt based aluminates.

The presence of sodium aluminates in the solution prevents the formation of a passive layer on the aluminium surface (Gai et al., 2014; Gai et al., 2015). Therefore, sodium aluminate acts as a barrier to the formation of a hydroxide layer and speeds up the interaction of Co ions with alumina (Kaur et al., 2018; Kanturk et al., 2008; Li et al., 2005; Buchner et al., 1999). Thus, the concentration of NaOH is an important parameter for improving the hydrolysis of NaBH_4 and Al.

Effect of NaBH_4 on HGR

NaBH_4 is a prime component in the present hydrogen generation system. The effect of concentration of NaBH_4 on the hydrogen generation rate (HGR) was observed by conducting experiments at four different Al_2O_3 concentrations (0.06, 0.07, 0.08, 0.09 moles/L), 0.02 moles/L CoCl_2 and 1.40 moles/L NaOH and varying the NaBH_4 concentration. After 1.75 moles/L, the HGR decreases due to an increase in the viscosity of the solution. The reason behind this is that, initially, at lower concentrations of NaBH_4 , the contact time between BH_4^- ions and catalyst is higher. As the concentration of NaBH_4 increases, the formation of sodium metaborate by-product is high and it probably blocks the reactive sites of catalyst, thus increasing the viscosity of the solution and lowering the hydrogen generation rate (Saka et al., 2015).

The change in the HGR with increasing NaBH_4 concentration is demonstrated in Figure 3. Higher concentration of NaBH_4 in the system indicates high availability of a hydrogen source in the solution or higher concentration of sodium and borohydride

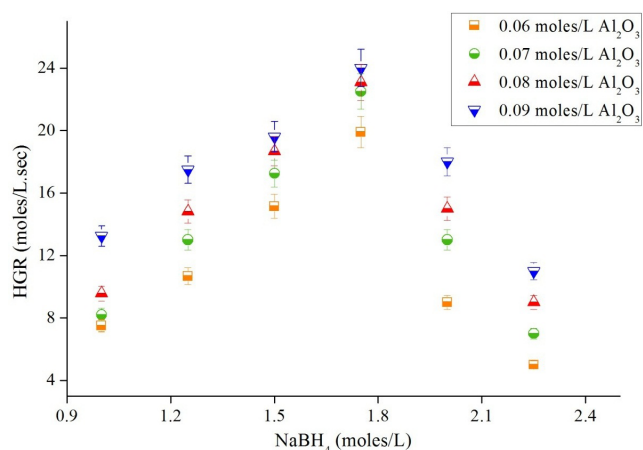


Figure 3. Effect of NaBH_4 concentration on HGR.

ions in the solution. The reaction rate with respect to NaBH_4 is dependent on the reactivity between borohydride ions and the catalyst surface (Holbrook and Twist 1971; Zhuang et al., 2013). Highly active CoCl_2 catalyst and Al_2O_3 nanoparticles efficiently help in the release of protons from borohydride ions in the solution.

The activated complex formed between Co/Al presents optimal electron density to weaken borohydride ions and help release hydrogen at a faster rate. Additionally, Na^+ ions form aluminates in the solution that promote Al hydrolysis (Kaur et al., 2017). Therefore, it can be concluded that an increase in NaBH_4 concentration increases the HGR of the system until the solution become highly viscous and results in a decrease of the HGR (after 1.75 moles/L of NaBH_4).

Effect of $\gamma\text{-Al}_2\text{O}_3$ nanoparticles on the HGR

To observe the role of Al_2O_3 nanoparticles on the HGR, the system was monitored at increasing Al_2O_3 concentration and keeping the other components constant as shown in Figure 4. Experiments were performed at four concentrations of NaBH_4 (1.00, 1.25, 1.50, 1.75 moles/L) with 0.02 moles/L CoCl_2 and 1.40 moles/L NaOH. As depicted in Figure 4, the HGR

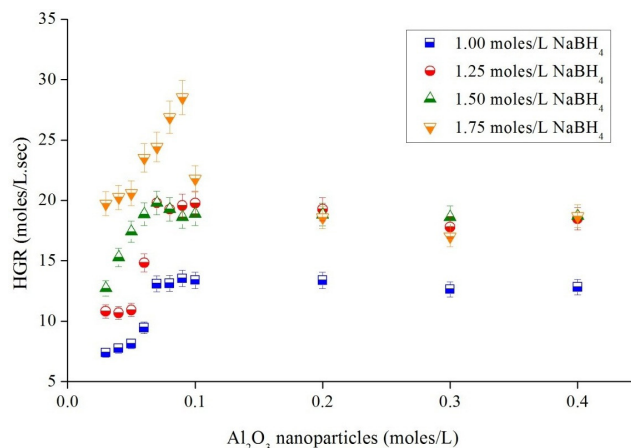


Figure 4. Effect of Al_2O_3 concentration on HGR.

increases with an increase in Al₂O₃ nanoparticles up to 0.09 moles/L. After 0.09 moles/L, the HGR is either constant (1.00 moles/L NaBH₄) or decreases (1.75 moles/L NaBH₄). Thus, on this basis, 0.09 moles/L Al₂O₃ is the selected concentration for further studies kinetic studies. The reason behind the phenomenon is consumption of reactants at a faster rate, that tends to increase the viscosity of the solution. Therefore, it could be concluded that the HGR increases with an increase in concentration of Al₂O₃ nanoparticles until the solution becomes highly viscous and all the reactants are consumed. Moreover, the amount of alumina as a promoter is higher in the solution than the amount of catalyst. Similar work is reported by Fan et al. (2012 a) and Fan et al. (2012 b) where the amount of promoter was more than the amount of catalyst, causing an increase in the HGR of the system.

Alumina concentration in the solution is an important factor that increases hydrogen generation and promotes the rate of the NaBH₄ hydrolysis reaction. Characteristics of alumina nanoparticles like particle size, hydrophilic, amphoteric nature and pH of the solution are also responsible for an increase in its solubility in the solution.

Furthermore, the interaction of the active complex (Co/Al) with Co_xB species promotes the activity of the catalyst (Fan et al., 2013). Thus, in the present system there exists a synergistic catalytic effect between Co_xB and hydroxylates of alumina that intensifies NaBH₄ hydrolysis. Hence, this is how γ -Al₂O₃ nanoparticles promote and affect overall HGR of the system.

Effect of CoCl₂ as catalyst on the HGR

Experiments were carried out at different concentrations of CoCl₂ (0.02, 0.024, 0.028, 0.032 moles/L) keeping other chemical components constant, i.e., 0.09 moles/L Al₂O₃, 1.25 moles/L NaBH₄ and 1.0 moles/L NaOH. It is observed that the kinetics of NaBH₄/H₂O is highly affected by CoCl₂. The effect of CoCl₂ on the HGR is presented in Figure 5, which shows that the HGR shoots to twice of its original value at 0.028 moles/L of CoCl₂. This means that the reaction time decreases to half of its original time as the CoCl₂ concentration increases in the solution.

Hydrogen generation is also observed at higher concentrations (0.036 and 0.046 moles/L) of CoCl₂ and the hydrogen generation rate increases with an increase in catalyst concentration. Although catalysts are not consumed by the reaction itself, they may change their form in further chemical reactions. Catalysts affect the reaction environment by binding to the reagents or by forming some specific intermediates (Masel, 2001). The increase in the concentration of CoCl₂ in solution results in the reduction of BH₄⁻ ions at a faster rate due to the formation of Co_xB active species in the solution due to the electrophilic nature of Co²⁺ that leads to

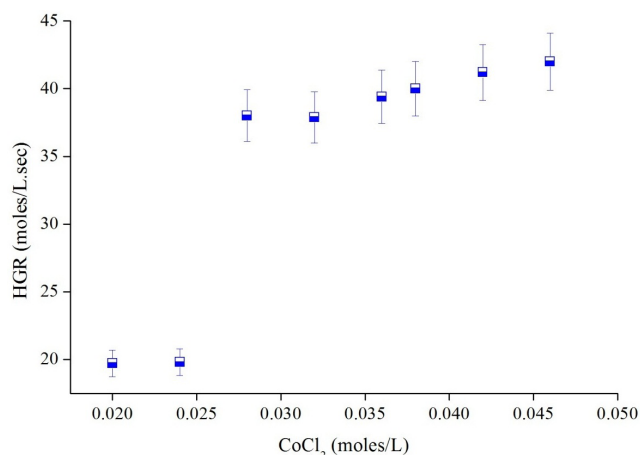


Figure 5. Effect of CoCl₂ concentration on HGR.

high reactivity towards BH₄⁻ ions. This affects the kinetics of the NaBH₄ hydrolysis reaction and results in an increase in the HGR (Akdım et al., 2009).

In the presence of γ -Al₂O₃ nanoparticles in the solution, cobalt forms active species with alumina (cobalt aluminate). An increase in CoCl₂ concentration increases the formation of the Co/Al activated complex and appreciably increases the HGR. Therefore, alumina promotes the catalytic activity of Co_xB active species in the solution. Moreover, Cl⁻ as an anion has maximum solubility in the solution based on the coefficient of diffusivity, that is higher for Cl⁻ ions when compared with anions of other salts like CoCl₂·6H₂O, CoSO₄·7H₂O, (CH₃COO)₂Co·4H₂O, Co(NO₃)₂·H₂O, CdSO₄, or CuSO₄·5H₂O (Kaur et al., 2018). This improves the kinetics of the system by significantly affecting the hydrolysis of NaBH₄. The reaction is highly vigorous and fast at higher concentrations of CoCl₂ (0.028 and 0.032 moles/L) and to obtain considerable kinetic data and, to observe the variation of the HGR with NaBH₄ and alumina, further kinetic studies were carried out at 0.02 moles/L of CoCl₂.

KINETIC STUDIES

The rate is related to temperature and concentrations of NaBH₄, Al₂O₃, catalyst and NaOH according to the following expression:

$$-4 \frac{d[\text{NaBH}_4]}{dt} = d \frac{[\text{H}_2]}{dt} = k_{\text{overall}} [\text{NaBH}_4]^a [\text{Al}_2\text{O}_3]^b [\text{CoCl}_2]^c [\text{NaOH}]^d \quad (2)$$

The overall hydrogen generation rate can be expressed as,

$$r_{\text{H}_2} \propto [\text{NaBH}_4]^a [\text{Al}_2\text{O}_3]^b [\text{CoCl}_2]^c [\text{NaOH}]^d \quad (3)$$

where, r_{H_2} is the hydrogen generation rate in moles L⁻¹ sec⁻¹, [NaBH₄] is the concentration of NaBH₄,

$[Al_2O_3]$ is the concentration of alumina, $[CoCl_2]$ is the concentration of cobalt chloride, $[NaOH]$ is the concentration of NaOH in moles L^{-1} and a, b, c, d are the apparent orders with respect to $NaBH_4$, Al_2O_3 , $CoCl_2$, NaOH concentrations, respectively. On the basis of kinetic studies, the overall order of reaction and activation energy was calculated.

Kinetics with respect to NaOH

To observe kinetic parameters with respect to NaOH, hydrogen generation (HG) versus time for different NaOH concentrations is shown in Figure 6 and the rate of reaction is represented by equation 4,

$$r_{H_2[NaOH]} = k_4[NaOH]^d \quad (4)$$

where $r_{H_2[NaOH]}$ is rate of hydrogen generation and k_4 is the rate constant with respect to NaOH concentration. HG is dependent on NaOH concentration and increases with time.

Plotting the HGR versus NaOH concentration on a logarithmic scale as shown in Figure 7 gives the slope as 0.15. Thus, the order of reaction with respect to NaOH is 0.15 with rate constant $16.44 \text{ (sec)}^{-1} \text{ (moles/L)}^{0.85}$. As observed, the order with respect to NaOH reduces to a very low value of 0.15. The explanation for this is that, with the increase in NaOH in solution, the pH of the solution increases to a value greater than 12. Accordingly, the hydrogen generation rate becomes less dependent on hydronium ion, resulting in a decrease in the value of the order to 0.15 (Davis and Swain, 1960; Davis et al. 1960; and Davis et al. 1962).

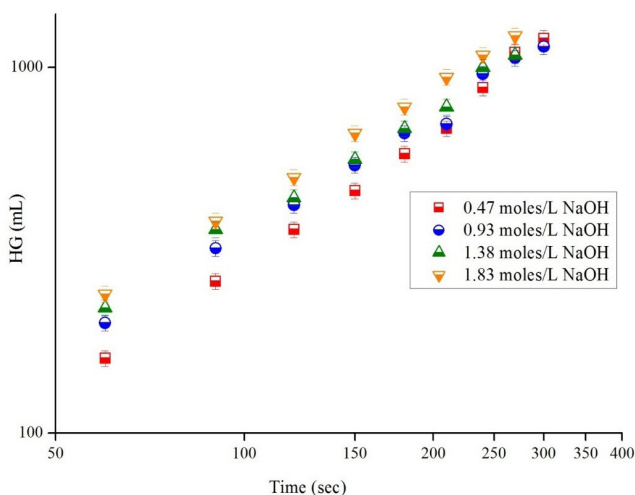


Figure 6. HG with time at different NaOH concentrations.

Kinetics with respect to $NaBH_4$

Hydrogen generated as a function of time for different $NaBH_4$ quantities is plotted in Figure 8. The rate of reaction with respect to $NaBH_4$ is given by Equation 5:

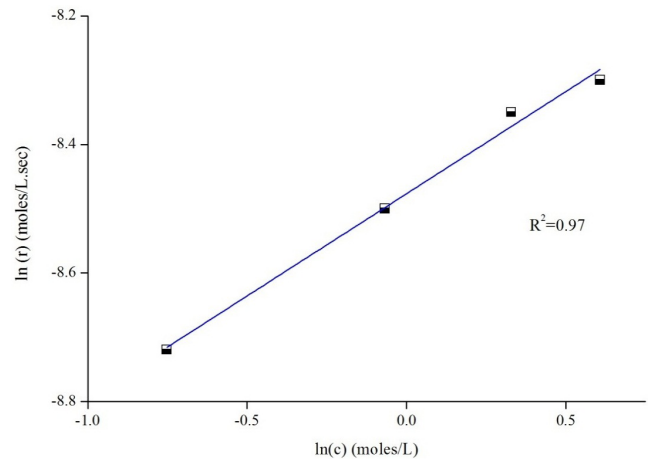


Figure 7. Hydrogen generation rate as a function of NaOH concentration.

$$r_{H_2[NaBH_4]} = k_1[NaBH_4]^a \quad (5)$$

Experiments were performed at $NaBH_4$ (1.00, 1.25, 1.50 and 1.75 moles L^{-1}), at constant $CoCl_2$ (0.02 moles L^{-1}), NaOH (1.4 moles L^{-1}) and Al_2O_3 (0.09 moles L^{-1}) concentrations.

The variation on a logarithmic scale of the HGR versus $NaBH_4$ concentration, Figure 9, gives the order of reaction of $0.9 \sim 1$, with $k_1 = 14.58 \text{ (sec)}^{-1}$. Various results are compared with the present result with an order equal to or less than 1 (Levy et al., 1960; Demirci and Garin 2008; Patel et al. 2009). These results indicate dependency of the rate on $NaBH_4$.

Rate kinetics with respect to Al_2O_3 nanoparticles

The hydrogen generation rate with respect to alumina varies according to the rate Equation (6):

$$r_{H_2[Al_2O_3]} = k_2[Al_2O_3]^b \quad (6)$$

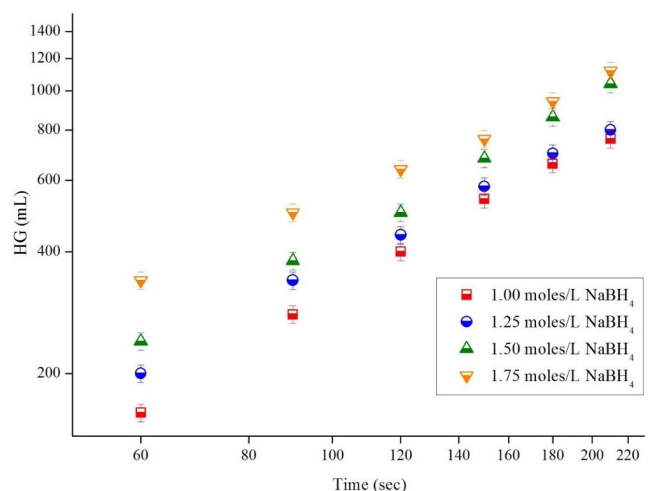


Figure 8. Hydrogen generation as a function of time at different $NaBH_4$ concentrations.

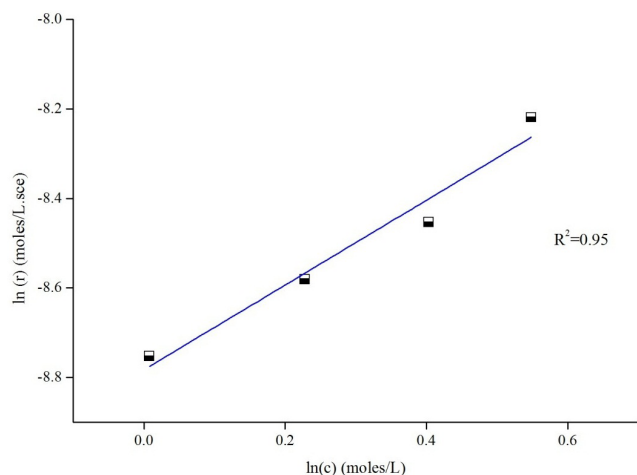


Figure 9. Hydrogen generation rate as a function of NaBH₄ concentration.

where $r_{H_2[Al_2O_3]}$ is the rate of hydrogen generation and k_2 is the rate constant with respect to alumina. The hydrogen generation versus time plot for different Al₂O₃ concentrations at constant NaBH₄ (1.25 moles L⁻¹), NaOH (1.4 moles L⁻¹) and CoCl₂ (0.02 moles L⁻¹) concentrations is shown in Figure 10. As the concentration of Al₂O₃ increases, HG increases with time.

Plotting the HGR versus alumina concentration on a logarithmic scale gives a slope of 0.45 ~ 0.5. Thus, the order of reaction with respect to alumina nanoparticles is 0.5 with rate constant k_2 of 69.43 (sec)⁻¹ (moles L⁻¹)^{0.5}, as shown in Figure 11. The result confirms that the HGR is dependent on Al₂O₃ concentration.

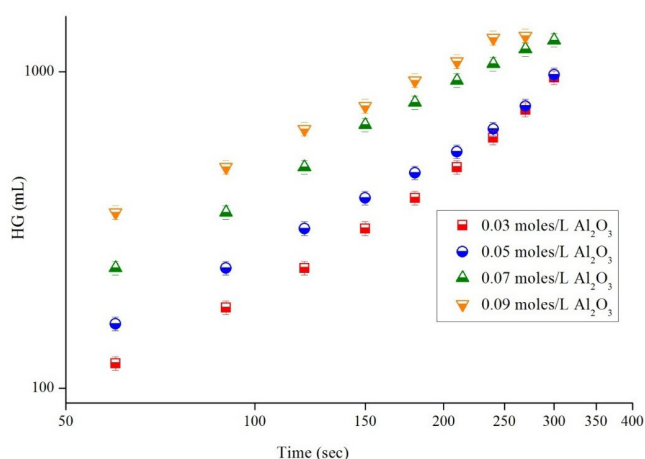


Figure 10. HG as a function of time at different alumina concentrations.

Effect of CoCl₂ concentration on HGR

According to the rate Equation 7, the hydrogen generation rate is related to catalyst, via:

$$r_{H_2[CoCl_2]} = k_3[CoCl_2]^c \quad (7)$$

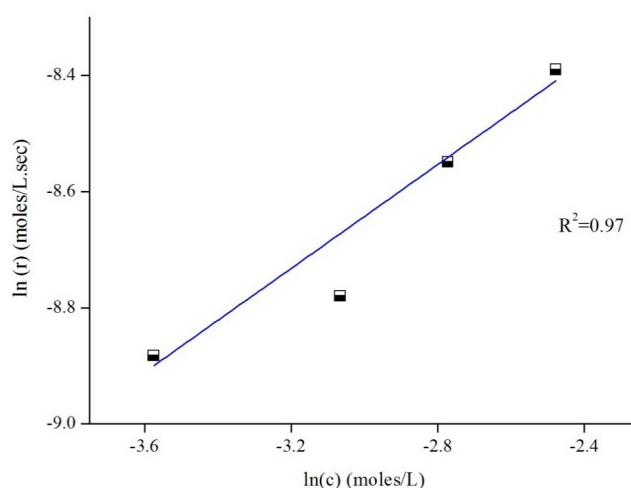


Figure 11. HGR as a function of alumina concentration.

where $r_{H_2[CoCl_2]}$ is the rate of hydrogen generation and k_3 is rate constant with respect to CoCl₂ concentration. The hydrogen generation versus time plot is presented in Figure 12. Accelerated hydrogen generation is observed with time, with the increase in catalyst concentration. The slope calculated by plotting the HGR versus CoCl₂ on a logarithmic scale, Figure 13,

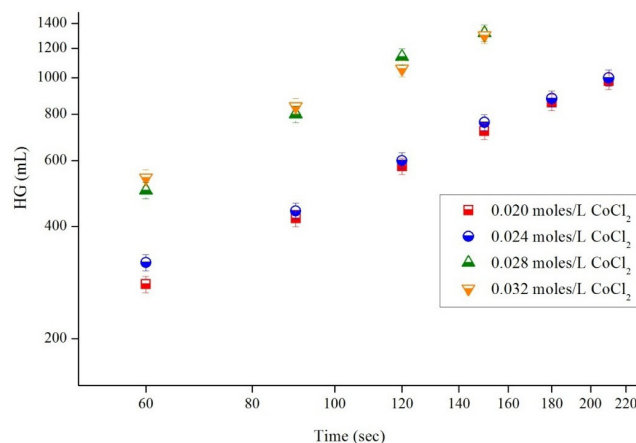


Figure 12. Hydrogen generation with time at different CoCl₂ concentrations.

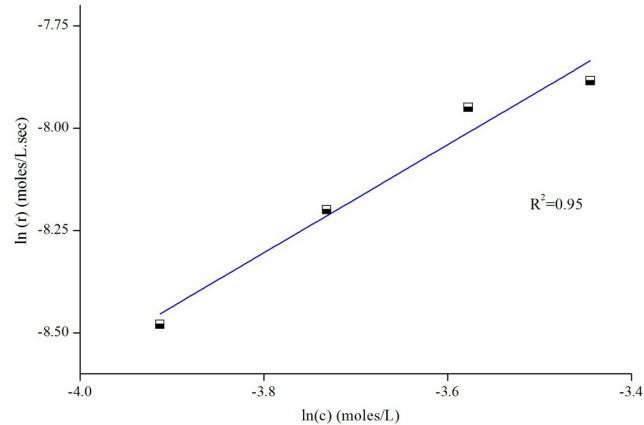


Figure 13. HGR as a function of CoCl₂ concentration.

is 1.5 with a rate constant of 12.088×10^3 (sec)⁻¹ (L/moles)^{0.5}.

In addition, the nature of the catalyst defines the variation in the order of the hydrolysis reaction. Demirci and Garin (2008), Patel et al. (2009) and Fernandes et al. (2009) reported orders of 1.27 for a Ru-promoted sulphated zirconia catalyst, 1.07 for a Co-P-B catalyst, and 1.05 for a (Co-P-B)-based catalyst, respectively, that show the compatibility of the present results with literature.

The rate equation with respect to the order of the individual factors affecting the overall order is presented as Equation 8.

$$r_{H_2} = k_{\text{overall}} [\text{NaBH}_4]^1 [\text{Al}_2\text{O}_3]^{0.5} [\text{CoCl}_2]^{1.5} [\text{NaOH}]^{0.15} \quad (8)$$

EFFECT OF TEMPERATURE ON THE HYDROGEN GENERATION RATE

Temperature is a substantial parameter that influences the kinetics of the system drastically. Thus, to observe change in the kinetics of the present system with the change in temperature, the HGR was investigated at different temperatures and at constant NaBH₄ (1.25 moles L⁻¹), NaOH (1.4 moles L⁻¹), CoCl₂ (0.02 moles L⁻¹) and Al₂O₃ (0.09 moles L⁻¹) concentrations. The slope of the HG versus time graph gives the rate at each temperature (303, 313, 323 and 333 K). Hence, k_{overall} is analysed at different temperatures. The activation energy is computed according to Equation 9 (Fogler, 2000):

$$\ln(k_{\text{overall}}) = \ln(A) - \frac{E}{RT} \quad (9)$$

where T is the absolute temperature (in Kelvin) and k_{overall} is overall rate constant at each temperature with units (sec)⁻¹(L/moles)^{2.15}. Different k values against temperature are shown in Table 3. Thus, $\ln(k_{\text{overall}})$ versus (1/T) is plotted as shown in Figure 14, to determine the activation energy for the present system. The activation energy evaluated is 29 kJ moles⁻¹ and A is 18.62×10^8 (sec)⁻¹(L/moles)^{2.15}. The activation energy of the NaBH₄/H₂O system without addition of alumina nanoparticles is calculated as 38 kJ/moles (Kaur et al., 2015).

The activation energy varies with the type of catalyst used in the system, catalyst promoter, reaction experimental conditions and the chemical and physical

Table 3. Values of k_{overall} at different temperatures.

S.No.	T (K)	k_{overall}	(1/T)	$\ln(k_{\text{overall}})$
1.	293	16.310×10^3	0.0034	9.70
2.	303	23.523×10^3	0.0033	10.06
3.	313	35.340×10^3	0.0032	10.47
4.	323	47.120×10^3	0.0031	10.70

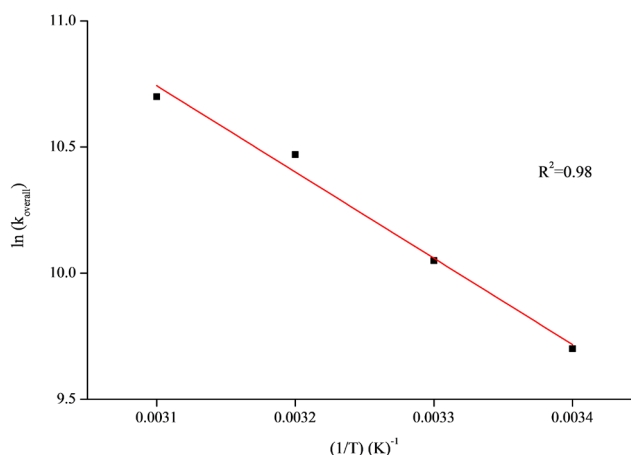


Figure 14. Arrhenius plot of $\ln(k_{\text{overall}})$ versus (1/T).

properties of the components incorporated in the reaction. Factors that help in lowering the activation energy are highly active γ -Al₂O₃ nanoparticles used as a promoter with CoCl₂ for the hydrolysis of NaBH₄.

THEORETICAL AND EXPERIMENTAL HYDROGEN CAPACITIES

For optimizing this HG system, maximum HG efficiencies are calculated at different mass ratios of Al₂O₃/NaBH₄. Hydrogen generation is dependent on the composition of various components of the system and, to optimize the composition, mass ratios of Al₂O₃/NaBH₄ are examined and the efficiency of NaBH₄/Al₂O₃/H₂O with CoCl₂ is calculated using equation 1.

The calculations are performed at constant CoCl₂ and NaOH concentrations. Theoretical and experimental hydrogen densities and efficiencies at different mass ratios of Al₂O₃/NaBH₄ are given in Table 4. Variation in the component ratio varies the efficiency for maximum hydrogen yield. Here the concentration of Al₂O₃ nanoparticles is kept constant and NaBH₄ is varied. It is envisaged that the efficiency increases with the increase in NaBH₄ and incredibly high efficiency of 99.34% is achieved at a mass ratio of 0.09:0.7 for Al₂O₃/NaBH₄. These results depict the maximum conversion of reactants to release hydrogen. In contrast, this efficiency is compared with the efficiency of the NaBH₄/H₂O system without addition of Al₂O₃ nanoparticles and there is a massive difference in the overall efficiencies of both the systems.

As reported in the literature, 90% efficiency is achieved with a 2:1 mass ratio of NaBH₄/Al using

Table 4. Theoretical and experimental H₂ densities.

S. No.	Al ₂ O ₃ :NaBH ₄ (g/g)	H ₂ Density (wt %)		Efficiency (%)
		Theoretical	Experimental	
1.	0.09 : 0.4	10.76	10.48	97.3
2.	0.09 : 0.5	10.76	10.56	98.14
3.	0.09 : 0.6	10.76	10.62	98.69
4.	0.09 : 0.7	10.76	10.69	99.34

CoCl₂ as catalyst (Dai et.al, 2011). It is envisaged that a composite of Al/La/CoCl₂:NaBH₄ gives 100% efficiency with mass ratio of 1:1 at 333K (Jinabo et al., 2012). Also, an efficiency of 96 % is achieved by a mixture of Al/Li/Ni:NaBH₄ with a mass ratio of 3:1 at 333K (Shu et. al, 2012). Hydrogen generation from Al/Li/Co:NaBH₄ powder and water results in 100% efficiency at 323K (Wang et al., 2013).

Maximum efficiency of 73% was obtained at 0.7 g NaBH₄ as shown in Table 5. Also, the variation in theoretical and experimental values of hydrogen density represents the need to add a promoter to the system that could efficiently release hydrogen from sodium borohydride. Hence, this work shows that Al₂O₃ nanoparticles added in the system increase the efficiency and describes the effectiveness of a system to be used in practical applications for hydrogen generation and storage.

Table 5. Theoretical and experimental H₂ capacities.

S. No.	NaBH ₄ (g)	H ₂ Density (wt %)		Efficiency (%)
		Theoretical	Experimental	
1.	0.4	10.76	6.6	61
2.	0.5	10.76	7.3	67
3.	0.6	10.76	7.5	69
4.	0.7	10.76	7.9	73

CONCLUSIONS

This work is an extensive study of the NaBH₄/ γ -Al₂O₃ nanoparticles/H₂O system with CoCl₂ as catalyst and the involvement of each component in solution that promotes the release of hydrogen, contributing towards increased system efficiency.

- The reaction rate of NaBH₄ hydrolysis increases with an increase in reactant (NaBH₄), catalyst promoter (γ -Al₂O₃ nanoparticles), stabilizer (NaOH) and catalyst (CoCl₂.6H₂O) concentrations.

- The kinetics of the system are analyzed using a power-law kinetic model. This model describes the change in rate of reaction with concentration so that the variation in the HGR could be predicted.

- The activation energy calculated for this system is 29 kJ/moles, which is lower than without addition of γ -Al₂O₃ nanoparticles (38 kJ/moles). Thus, addition of γ -Al₂O₃ nanoparticles accelerates the kinetics of this HG system.

- Incredibly high efficiency of 99.34% is achieved at a mass ratio of 0.09 : 0.7 for Al₂O₃ : NaBH₄ with a theoretical hydrogen density of 10.76 wt% and experimental hydrogen density of 10.69 wt%. This value is high enough to state that there is overall conversion of NaBH₄ in terms of hydrogen release in the system.

- In comparison with conventional NaBH₄/H₂O based hydrogen storage systems, in terms of HGR, activation energy and efficiency; the NaBH₄/ γ -Al₂O₃

nanoparticles/H₂O based HG system with CoCl₂ as catalyst is more effective and, therefore, it can be considered to be an efficient system to be used in fuel cell technologies for hydrogen generation and storage.

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