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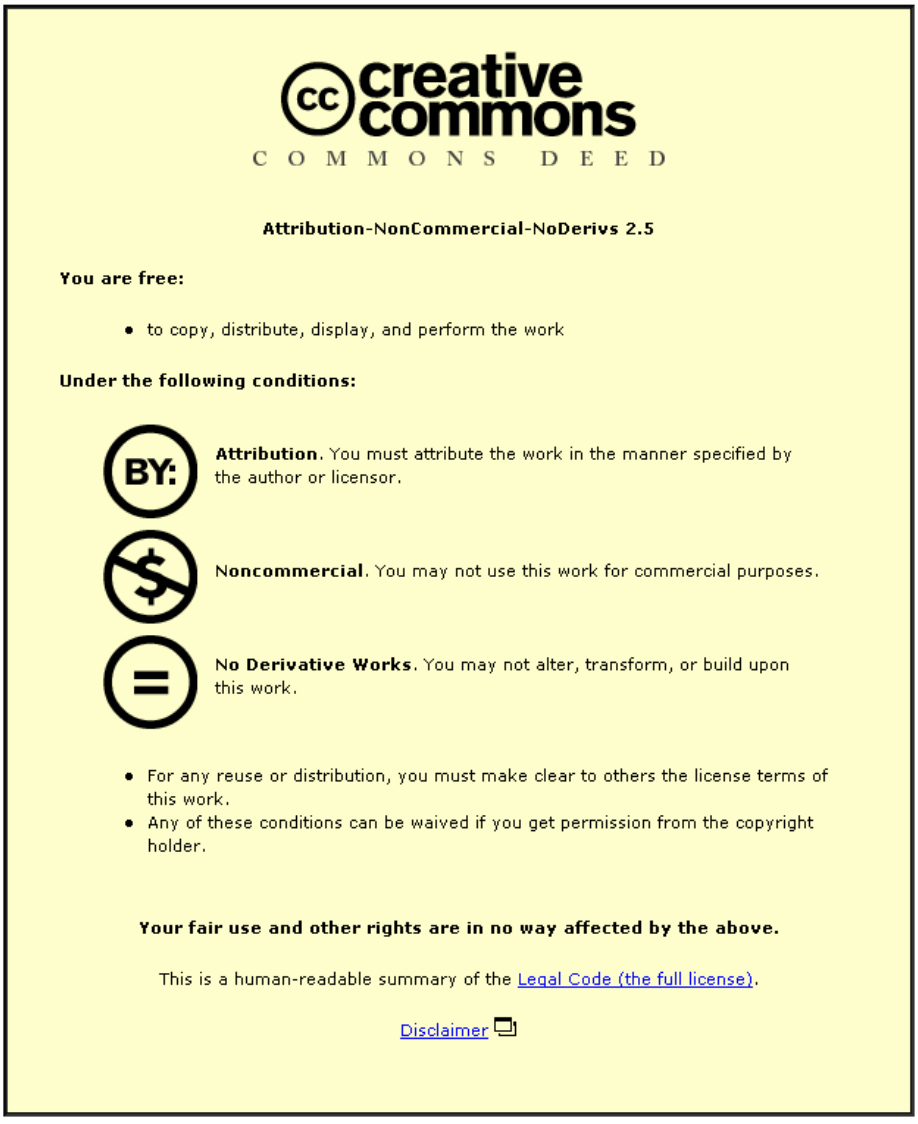

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Kinetic study of $NaBH_4$ hydrolysis over carbon supported ruthenium

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Abstract

The effects of temperature and the concentrations of $NaBH_4$, $NaBO_2$ and NaOH on the rate of $NaBH_4$ hydrolysis over carbon supported ruthenium catalyst were investigated using isothermal rate data extracted from non-isothermal reactions. It was shown that the hydrolysis was a zero-order reaction with respect to the concentration of $NaBH_4$ and the reaction rate decreased with the increase of OH^- concentration. A rate expression was then derived to correlate the hydrolysis rate with the temperature and NaOH concentration.

Key Words

Sodium borohydride, kinetics, hydrolysis, ruthenium

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1. Introduction

Extensive research has been performed for on-board hydrogen generation, such as pyrolysis of metal hydrides (e.g. LiH, MgH_2) [1], hydrogen storages in adsorption materials (e.g. carbon nanotubes and graphites) [2], compressed hydrogen tanks [3], and the hydrolysis of chemical hydrides [4]. Among these methods, the hydrolysis of $NaBH_4$ (Scheme 1) has attracted great attention due to the high stability of its alkaline solution and the relatively high energy density, which can reach 6% by weight [5]. The importance of $NaBH_4$ as an hydrogen carrier has been demonstrated in a promising bench scale hydrogen generator designed by Pozio et al [6] in Erredue srl (Italy). Earlier than Pozio's prototype generator, Amendola et al [7] and Zhang et al [8] in Millennium Cell (USA) designed several hydrogen generators up to 1 kWe using $NaBH_4$ aqueous solution.

$NaBH_4 + 2H_2O = NaBO_2 + 4H_2 + 285$ kJ

Scheme 1. The hydrolysis of sodium borohydride.

A suitable catalyst must be used for an efficient hydrolysis of $NaBH_4$ in alkaline conditions. The catalysts include BrØnsted acids, metal halides such as $NiCl_2$, $CoCl_2$, and transition metal catalysts [9]. Transition metals (usually supported on some carriers for practical applications) are regarded as the most efficient catalysts [9, 10], which is promising for on-board application. Recently, many new forms of transition metal catalysts have been developed, such as nickel based powder [11], metal alloy catalysts [12], Pd supported on carbon [13], nickel borides [14], filamentary nickel mixed Co catalyst [15] and Ru supported on a resin [7].

An accurate kinetic expression is essential to the rational design and analysis of a reactor on board. Although the kinetics of BrØnsted acid catalyzed $NaBH_4$ hydrolysis was extensively studied in the 1960s and 1970s [16-18], very few investigations have so far been contributed to the kinetics of the metal catalysis. Due to the lack of accurate kinetics, empirical methods were resorted to for predicting hydrogen generation rate from the hydrolysis of $NaBH_4$ [7, 19, 20]. Until very recently, some reports have appeared on the kinetics of metal catalysis [21-23]. However, the kinetics obtained was not consistent. Zhang et al [21] reported that the hydrolysis was zero-order at low temperatures and first order at high temperatures with respect to $NaBH_4$

when Ru catalyst was used, while Guella et al [22] reported that the hydrolysis was first order with respect to $NaBH_4$ when Pd catalyst was used.

There are two difficulties in investigating transition metal catalyzed $NaBH_4$ hydrolysis. First, the hydrolysis of $NaBH_4$ over transition metal catalyst is a strong exothermal heterogeneous reaction. In order to obtain rate data for a fixed temperature, an efficient temperature control method has to be designed to remove the heat generated. In investigating the kinetics of heterogeneous catalysis, efficient heat removal is usually implemented by minimizing the contact time between reaction mixture and the catalyst in one cycle by the use of the well-known Carberry reactor or reducing reactant concentration [24, 25]. Both Zhang et al [21] and Guella et al [22] used dilute solutions and small amount of catalyst to keep temperature constant. For investigating the hydrolysis of $NaBH_4$, minimizing the contact time for reaction mixture and catalyst will not work well especially for higher reaction temperatures since $NaBH_4$ has a significant hydrolysis rate at higher temperatures even in the absence of a catalyst, which would introduce a significant error for following the reaction. On the other hand, the kinetics obtained from low concentrations may not be the same as at higher concentrations due to the effect of high ionic strength. The investigation of the kinetics at high concentrations of $NaBH_4$ is therefore desirable. Another difficulty for investigating the kinetics of $NaBH_4$ hydrolysis is the control of pH value during reaction. The by-product $NaBO_2$ is a strong base. As soon as it is produced, the solution becomes basic as show in Scheme 2.

$B(OH)_4^- = H_3BO_3 + OH^-$

Scheme 2. Ionic equilibrium of $NaBO_2$ in aqueous solution. BO_2^- in aqueous solution exists in the form of $B(OH)_4^-$ [26].

In our work, instead of making an effort to control reaction temperature and pH value during following the hydrolysis, a data analysis method has been designed, which can be used to obtain rate data for a fixed reaction temperature and pH value from a set of hydrolysis experiments that temperature and pH value are not closely controlled. This paper reports the application of the data analysis method to study the kinetics of $NaBH_4$ hydrolysis. The effects of $NaBH_4$, $NaBO_2$ and NaOH concentrations and reaction temperature on $NaBH_4$ hydrolysis were investigated.

2. Experimental

2.1 Materials

$NaBH_4$ and NaOH (analytical grade) were purchased from Sigma-Aldrich. They were used as received. The catalyst was purchased from Johnson Matthey, with 3% (wt) Ru supported on carbon. The cylindrical catalyst particles had a diameter of 2 mm and a length of 3 mm with a specific area of around 1000 m^2g^{-1}.

2.2 Catalyst Grinding

The catalyst particle was ground using a pestle and mortar and then sieved using a set of sieves with different mesh apertures. Eight different sieves (Fisher Scientific) were stacked on top of each other, and the average diameters of the catalyst particles trapped in each sieve were assumed to match the average aperture sizes of the two adjacent sieves. The sieve set and the catalyst sizes are listed in Table 1.

2.3 Experimental procedure

The experimental rig consisted of two parts: a reaction system and a water replacement system to measure the volume of hydrogen generated. The reaction system consisted of a three-port reactor with a magnetic stirrer in it, a water bath that was used to adjust reaction temperature, and a feeding funnel. One side-port of the reactor was equipped with a thermocouple and another side-port was connected to the water replacement system. The middle port of the reactor was used to site the feeding funnel. The water replacement system consisted of a graduated cylinder full of water and a water reservoir that was used to immerse the cylinder.

A container was placed onto an electronic balance (A&D). Before starting the experiment, the water in the reservoir was filled to such a level that any extra water would overflow through a slope into the container on the balance. The electronic balance was connected to a computer using a standard RS232 connector. Software provided by the balance manufacturer was used to record the time and the weight of the water displaced from the cylinder. The time interval for recording the weight was one second.

The reactor was placed into the water bath with a fixed amount of catalyst inside (the amount of catalyst that was used was based on the convenience of reaction control

and the rate data was based on unit mass of catalyst). A pre-determined amount of $NaBH_4$ powder was then added into the reactor. After all these were ready, the cork of the feeding funnel was opened to add water or NaOH solution into the reactor to start the hydrolysis. The weight of the water that was displaced by the hydrogen produced and the reaction temperature were both recorded by using a computer.

2.4 Data analysis method

The relationship between reaction rate and temperature for any chemical reactions can be expressed using equation (1).

$$r = Ae^{-E/RT} f \tag{1}$$

where r is the reaction rate (cm^3 H_2 s^{-1} $gcat^{-1}$), A is the pre-exponential factor, E is the activation energy (J mol^{-1}), R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T is the temperature (K), and f is the kinetic function of the reaction, which may be a function of the concentrations of reactants and/or products (mol kg^{-1}). Taking the logarithms of both sides, yields

$$\ln r = \ln A + \ln f - \frac{E}{RT} \tag{2}$$

Since A and the expression of f is unique for a specific reaction at the same extent of reaction, ln$r$ against 1/T should have a linear relationship. The method to obtain rate data for a fixed temperature and pH value of the reaction medium from hydrolysis experiments without close temperature control is based on equation (2).

As an example for the data analysis method, the experimental program is given in Table 2 for obtaining the rate data for a constant temperature and pH value of reaction solution when varying $NaBH_4$ concentration. There are six sets of experiments A to F, each set having a different amount of $NaBH_4$ while other conditions are the same. In each set, there are five runs 1-5, each of which has a different starting temperature. The experimental data (v_{H2} ~ time and T ~ time) for E1 to E5 (1.2 g $NaBH_4$ in 10 ml water) are shown in Figure 1. The curves were then converted to r_{H2} ~ m_{NaBO2} (Figure 2a) and T ~ m_{NaBO2} (Figure 2b) respectively, where $NaBO_2$ concentration, m_{NaBO2}, was

calculated from the volume of hydrogen produced, v_{H2}. $\ln r_{H2}$ against $1/T$ were then plotted in Figure 3 (m_{NaBO2} = 0.2, 0.5, 0.7 and 1.0 mol kg^{-1} are shown). The slope of the line corresponds to $-E/R$, and the intercept on the vertical axis corresponds to $\ln A + \ln f$. Due to the good linearity for a fixed $NaBO_2$ concentration, the reaction rate at any temperature can then be reliably intrapolated at this concentration of $NaBO_2$.

Similarly, the reaction rate for a fixed temperature and $NaBO_2$ concentration was calculated for the other sets of experiments (A, B, C, D and F). It should be noted that $NaBH_4$ concentrations in each set of experiment are different at the same $NaBO_2$ concentration due to different initial $NaBH_4$ concentrations. Therefore, the rate data at various $NaBH_4$ concentrations was obtained for the same $NaBO_2$ concentration and temperature. In the same way, the rate data for various $NaBO_2$ concentrations can be obtained for the same $NaBH_4$ concentration and temperature. The effect of NaOH can be studied by altering the weight of NaOH in Table 2.

3. Results and Discussion

3.1 Removal of diffusion limitation

Heat and mass transfer effects frequently impact upon the overall performance of a heterogeneous catalytic reaction. Accurate kinetic rate equations can seldom be extracted from data obtained under the influence of significant heat and/or mass transport limitations. Thus it is important that the rate data be acquired in the regime of kinetic control. Since the hydrolysis of $NaBH_4$ is in a liquid system, heat transfer limitations can be ignored [27]. Two aspects of mass transfer should be considered: external mass transfer (from bulk liquid to catalyst surface) and internal mass transfer (from catalyst surface to the inside of the pores). The former can be eliminated by increasing stirring rate and the latter can be eliminated by decreasing catalyst particle size.

To find a stirring rate at which external mass transfer limitation can be removed, it is necessary to compare rate data at various stirring rates for a fixed temperature and initial $NaBH_4$ concentration. To this end, three groups of experiments were performed, each having a different stirring rate (0 rpm, 390 rpm, and 650 rpm). Each group consisted of five runs with the same initial $NaBH_4$ weight, catalyst and water but different starting temperatures. Isothermal reaction rate (cm^3 H_2 s^{-1} $gcat^{-1}$) versus

$NaBO_2$ concentration (i.e. extent of reaction) was obtained using the data analysis method introduced in section 2.4 and shown in Figure 4 for three temperatures (20°C, 30°C, and 40°C).

At each temperature, hydrogen generation rate decreased rapidly with the proceeding of the hydrolysis. This was due to the increase of the basicity of the reaction medium with the production of $NaBO_2$ as discussed in the next section. At any reaction temperatures, stirring rate showed little effect on reaction rate when the concentration of $NaBO_2$ was higher than 0.2 mol/kg (more than 10% of $NaBH_4$ was hydrolyzed). This was most likely due to the agitation of hydrogen gas, which made the effect of stirring rate not significant. Stirring rate did show some effect at early stages of higher reaction temperatures. The higher the stirring rate, the higher was the reaction rate, since the agitation of hydrogen did not contribute much to the mass transfer at earlier stages. It should be noted that the difference between reaction rate at 390 rpm and 650 rpm was very small, less than 10%, even at early stages. It can thus be concluded that 650 rpm was high enough for the removal of external diffusion limitation. The stirring rate was kept at 650 rpm in the following investigations.

By designing experiments similar to investigating the effect of stirring rate, the isothermal reaction rate was obtained for different particle sizes, as shown in Figure 5. At both temperatures (20°C and 40°C), the reaction rate increased significantly with the decrease of catalyst particle size until particle size reached 0.049 mm. With a further decrease in particle size, the reaction rate did not increase significantly. This indicates that the limiting effects of internal diffusion can be removed by using a catalyst particle size of less than 0.049 mm. The particle size was kept at 0.049 mm in the following investigations.

3.2 Effect of $NaBH_4$ and $NaBO_2$ concentrations

After obtaining the conditions at which the reaction is in the regime of kinetic control, the effects of $NaBH_4$, $NaBO_2$ and NaOH concentrations on the hydrolysis of $NaBH_4$ were investigated. Six groups of hydrolysis experiments were conducted, each group having a different initial $NaBH_4$ concentration. In each group, there were 5 runs, each having a different initial reaction temperature. The initial concentrations of the six groups were 1.32, 1.59, 2.11, 2.64, 3.17 and 3.97 kg mol^{-1} respectively. Isothermal

reaction rate versus $NaBH_4$ concentration were obtained for a fixed $NaBO_2$ concentration (pH value) using the data analysis method as illustrated in section 2.4.

Figure 6 shows the dependence of hydrogen generation rate on $NaBH_4$ concentration for three different temperatures and $NaBO_2$ concentrations. At a fixed temperature and $NaBO_2$ concentration, the rate of hydrogen generation did not vary significantly with the change of $NaBH_4$ concentration. Hence, this reaction is a zero-order with regard to $NaBH_4$ concentration.

Since the reaction rate did not depend on the concentration of $NaBH_4$, an average of the six rate data for a fixed $NaBO_2$ concentration in Figure 6 was taken to represent the reaction rate at that $NaBO_2$ concentration. The averaged rate data were then plotted against $NaBO_2$ concentration, as shown in Figure 7. With the increase of $NaBO_2$ concentration, the reaction rate decreased rapidly at first and then leveled off at later stages.

3.3 Effect of NaOH concentration

For investigating the effect of NaOH concentration, five groups of hydrolysis experiments were conducted, each group having a different NaOH concentration. In each group, there were five runs, each run having a different starting temperature. From the five runs in one group (one NaOH concentration), isothermal reaction rate versus $NaBO_2$ concentration were obtained using the data analysis method introduced in section 2.4. Figure 8 shows the dependence of reaction rate on NaOH concentrations and the temperature. It should be noted that $NaBH_4$ concentration decreased steadily with the increase of $NaBO_2$ concentration in Figure 8.

The reaction rate increased rapidly with the increase of temperature at a fixed NaOH concentration. At a fixed temperature, reaction rate decreased rapidly with the increase of NaOH concentration. When both the temperature and NaOH concentration were fixed, the reaction rate changed within a very small range. In the absence of NaOH, the basicity of the $NaBO_2$ solution undergoes a large change with the progress of the reaction, moving from neutral (pH = 7) to strongly basic (pH = 12.5 according to the equilibrium $B(OH)_4^- = H_3BO_3 + OH^-$, $K = 1.73 \times 10^{-5}$). However, the basicity of the solution does not change significantly in the presence of high concentration of

NaOH. The results in Figure 8 shows clearly that the reaction rate was constant when the temperature and the basicity of the solution were kept constant, which further confirms that the reaction is zero-order with respect to $NaBH_4$ concentration.

There are three main steps in the hydrolysis of $NaBH_4$ on the catalyst surface: adsorption of $NaBH_4$, hydrolysis reaction of $NaBH_4$ and desorption of H_2 from the catalyst surface. Zhang et al [21] showed that the adsorption of BH_4^- on catalyst surface was the rate-determining step. The decrease of the reaction rate with the increase of NaOH concentration implies that OH^- may adsorb competitively on the surface of the catalyst surface, resulting in the decrease of the reaction rate.

3.4 Rate expression

As discussed above, the reaction is zero-order with respect to the concentration of $NaBH_4$, and the reaction rate decreases with the increase of NaOH concentration due to the competitive adsorption of NaOH on the catalyst surface. The concentration of NaOH, [NaOH], would then appear in the denominator of the rate expression [28]. Hence, the hydrogen generation rate may be expressed using equation (3).

$$r_{H_2} = \frac{Ae^{-E/RT}}{1 + k[\mathrm{NaOH}]^{\beta}} \tag{3}$$

where r_{H_2} is the hydrogen generation rate ($cm^3\ s^{-1}\ gcat^{-1}$), k is the coefficient for the effect of NaOH concentration (mol kg^{-1}), and β is the power of NaOH concentration. In order to obtain the value of the parameters, equation (3) is rearranged, yielding

$$\frac{1}{r_{H_2}} = \frac{1}{Ae^{-E/RT}} + \frac{k}{Ae^{-E/RT}}[\mathrm{OH}^-]^{\beta} \tag{4}$$

Using the rate data in Figure 8, $1/r_{H_2}$ against $[\mathrm{NaOH}]^{\beta}$ was plotted to determine the values of the parameters in equation (4). A good linear relationship between r_{H_2} and $[\mathrm{NaOH}]^{\beta}$ was obtained when β was 0.3 as shown in Figure 9. The slope of the line is

$\frac{k}{Ae^{-E/RT}}$, and the intercept on vertical axis is $\frac{1}{Ae^{-E/RT}}$. The value of k for various temperatures was then determined by the ratio of the slope to the intercept, which was 1.31 ± 0.037. The values of E and A were obtained by plotting $\ln\left(Ae^{-E/RT}\right)$ against $1/T$, which were 64485 J mol^{-1} and 2.03 x 10^{12} cm^3 s^{-1} $gcat^{-1}$ respectively. The rate expression yields after substituting the values of A, E, β and k into equation (3).

$$r_{H_2} = \frac{2.03\times10^{12} e^{-7756.3/T}}{1+1.31[OH^-]^{0.3}} \qquad (5)$$

Equation (5) shows the dependence of hydrogen generation rate r_{H_2} (cm^3 H_2 s^{-1} gcat) on reaction temperature (K) and NaOH concentration (mol kg^{-1}) in the solution. Zhang et al [21] investigated the kinetics of $NaBH_4$ in the presence of the same type of catalyst. The activation value obtained in this research (64.5 kJ mol^{-1}) is similar to the value (66.9 kJ mol^{-1}) obtained by Zhang et al. However, their pre-exponential factor has a large difference from this research. This is because the effect of NaOH was not included in their rate expression.

4. Conclusions

The kinetics for the hydrolysis of $NaBH_4$ over ruthenium on carbon catalyst was investigated in this paper by using an alternative method to derive rate data for a fixed temperature and pH value from hydrolysis reactions, in which the temperature and pH value were not closely controlled. It has been shown that the hydrolysis of $NaBH_4$ over ruthenium catalyst is zero-order to $NaBH_4$ concentration when water is sufficient. The reaction rate depends strongly on alkaline concentration and reaction temperature as in equation (5).

References

1. Grochala W, Edwards PP. Thermal decomposition of the non-interstitial hydrides for the storage and production of hydrogen. Chem Rev 2004; 104: 1283-1315.
2. Bououdina M, Grant D, Walker GS. Review on hydrogen absorbing materials - structure, microstructure, and the thermodynamic properties. Int J Hydrogen Energy 2006; 31: 177-182.

3. Irani RS. Hydrogen storage: High-pressure gas containment. MRS Bull 2002; 27: 680-682.
4. Wu C, Zhang H, Yi B. Hydrogen generation from catalytic hydrolysis of sodium borohydride for proton exchange membrane fuel cells. Catal Today 2004; 93-95: 477-483.
5. Shang Y, Chen R. Hydrogen storage via the hydrolysis of $NaBH_4$ basic solution: Optimization of $NaBH_4$ concentration. Energy Fuels 2006; 20: 2142-2148.
6. Pozio A, De Francesco M, Montelecone G, Oronzio R, Galli S, Angelo CD, Marrucci M. Apparatus for the production of hydrogen from sodium borohydride in alkaline solution. Int J Hydrogen Energy 2008; 33: 51-56.
7. Amendola SC, Sharp-Goldman SL, Janjua MS, Spencer NC, Kelly MT, Petillo PJ, Binder M. A safe, portable, hydrogen gas generator using aqueous borohydride solution and Ru catalyst. Int J Hydrogen Energy 2000; 25: 969-975.
8. Zhang J, Zheng Y, Gore JP, Fisher TS. 1 kWe sodium borohydride hydrogen generation system. Part I: Experimental study J Power Sources 2007; 165: 844-853.
9. Kaufman CM. Catalytic generation of hydrogen from the hydrolysis of sodium borohydride: application in a hydrogen/oxygen fuel cell. Lousiana State University, USA. 1981.
10. Ye W, Zhang H, Xu D, Ma L, Yi B. Hydrogen generation utilizing alkaline sodium borohydride solution and supported cobalt catalyst. J Power Sources 2007; 164: 544-548.
11. Pinto AMFR, Falcao DS, Silva RA, Rangel CM. Hydrogen generation and storage from hydrolysis of sodium borohydride in batch reactors. Int J Hydrogen Energy 2006; 31: 1341-1347.
12. Park JH, Shakkthivel P, Kim HJ, Han MK, Jang JH, Kim YR, Kim HS, Shul YG. Investigation of metal alloy catalyst for hydrogen release from sodium borohydride for polymer electrolyte membrane fuel cell application. Int J Hydrogen Energy 2008; in press.
13. Patel N, Patton B, Zanchetta C, Fernandes R, Guella G, Kale A, Miotello A. Pd-C powder and thin film catalysts for hydrogen production by hydrolysis of sodium borohydride. Int J Hydrogen Energy 2008; 33: 287-292.

14. Hua D, Hanxi Y, Xinping A, Chuansin C. Hydrogen production from catalytic hydrolysis of sodium borohydride solution using nickel boride catalyst. Int J Hydrogen Energy 2003; 28: 1095-1100.
15. Kim J-H, Lee H, Han S-C, Lee J-Y. Production of hydrogen from sodium borohydride in alkaline solution: development of catalyst with high performance. Int J Hydrogen Energy 2004; 29: 263-267.
16. Kreevoy MM, Hutchins JEC. H_2BH_3 as an intermediate in tetrahydroborate hydrolysis. J Am chem Soc 1972; 94: 6371 - 6376.
17. Kreevoy MM, Jacobson RW. The rate of decomposition of $NaBH_4$ in basic aqueous solutions. Ventron Alembic 1979; 15: 2-3.
18. Kreevoy MM, Oh S-W. Relation between rate and equilibrium constants for proton-transfer reactions. J Am Chem Soc 1973; 95: 4805 - 4810.
19. Shang Y, Chen R. Semiempirical hydrogen generation model using concentrated sodium borohydride solution. Energy Fuels 2006; 20: 2149-2154.
20. Kim SJ, Lee J, Kong KY, Jung CR, Min I, Lee S, Kim H, Nam SW, Lim T. Hydrogen generation system using sodium borohydride for operation of a 400 W-scale polymer electrolyte fuel cell stack. J Power Sources 2007; 170: 412-418.
21. Zhang J, Delgass WN, Fisher TS, Gore JP. Kinetics of Ru-catalysed sodium borohydride hydrolysis. J Power Sources 2007; 164: 772-781.
22. Guella G, Zanchetta C, Patton B, Miotello A. New insights on the mechanism of palladium-catalyzed hydrolysis of sodium borohydride from ^{11}B NMR measurements. J Phys Chem B 2006; 110: 17024-17033.
23. Zhang Q, Wu Y, Sun X, Ortega J. Kinetics of catalytic hydrolysis of stabilized sodium borohydride solutions. Ind Eng Chem Res 2007; 46: 1120-1124.
24. Weekman VW. Laboratory reactors and their limitations. AIChE J 1974; 20: 833-840.
25. Vannice MA. Kinetics of Catalytic Reactions. New York: Springer Science + Business Media. 2005. p161.
26. Zachariasen WH. The crystal structure of postassium metaborate. J Chem Phys 1937; 5: 919-922.
27. Levenspiel O. Chemical Reaction Engineering. New York: John Wiley & Sons. 1999. p378.
28. Fogler HS. Elements of Chemical Reaction Engineering. 5th ed. Upper Saddle River, NJ, USA: Pearson Education International. 2006. p645-694.

Table captions

Table 1. Sieve set and catalyst size.

Table 2. Experimental program for deriving rate data for a fixed temperature and pH value.

Figure captions

Fig. 1. The v_{H2} ~ time (a) and temperature ~ time (b) for the hydrolysis of $NaBH_4$ at various starting temperatures ((1): 20°C; (2): 23°C; (3): 26°C; (4): 29°C; (5): 32°C). The hydrolysis was conducted using 1.2 g $NaBH_4$ in 10 cm^3 of 0% NaOH solution (water) with 0.3 g of catalyst of an average particle size of 0.049 mm.

Fig.2. The relationships between rate of hydrogen generation (r_{H2}) and $NaBO_2$ concentration (a) and reaction temperature and $NaBO_2$ concentration (b). They were transformed from Figure 2a and b respectively.

Fig. 3. $\ln r_{H2}$ versus 1/T at different $NaBO_2$ concentrations derived from Figure 3.

Fig. 4. Comparison of the effect of stirring rate on reaction rate. The catalyst particles used had an average size of 0.049 mm. The reaction was conducted using 0.5g $NaBH_4$ in 10 ml of water. The catalyst used was 0.3 g.

Fig. 5. Comparison of the reaction rate at various temperatures for different catalyst particle sizes. The reaction was performed using 0.5 g $NaBH_4$ in 10 ml of water. The catalyst used was 0.3 g.

Fig. 6. Hydrogen generation rate versus the molality of $NaBH_4$. The data was obtained by data analysis method introduced in section 2.4 after conducting the experimental programme in Table 2. The catalyst used was 0.3 g with an average particle size of 0.049 mm.

Fig. 7. The relationship between r_{H2} and the molality of $NaBO_2$. The data was obtained by taking the average of the six points as in Figure 6 at each temperature and $NaBO_2$ concentration.

Fig. 8. The effect of NaOH on the hydrolysis of $NaBH_4$ at various temperatures. The rate data was obtained by using the data analysis method introduced in section 2.4 after conducting the experimental programme in Table 2 by changing NaOH concentration from 0.23 to 9.2% (wt) and keeping the weight of $NaBH_4$ at 0.5g in each group. The catalyst was 0.3 g with an average particle size of 0.049 mm.

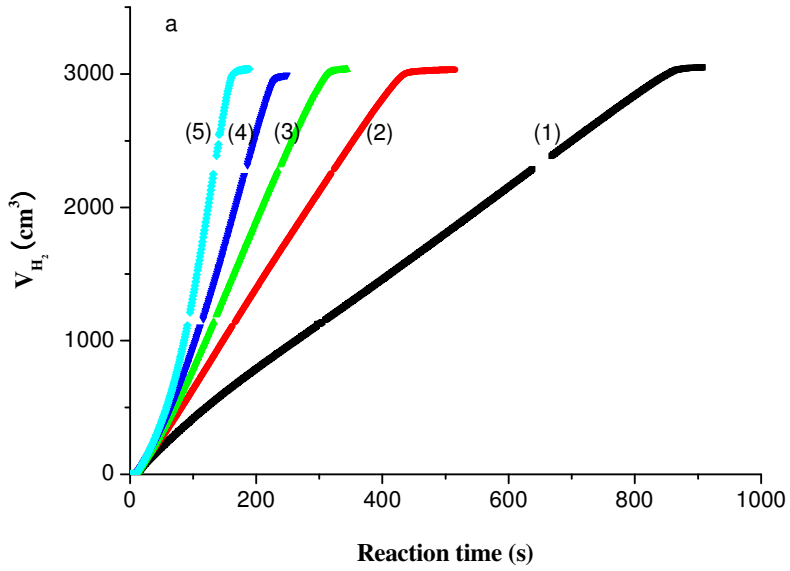
Fig.9. $1/r_{H2}$ versus $[OH^-]$ and their linear regressions at various temperatures.

Table 1. Sieve set and catalyst size.

Sieve aperture (μm)	Average catalyst size (μm)
600	-
500	550.
106	-
90	98
53	-
45	49
32	-
25	29

Table 2. Experimental program for deriving rate data for a fixed temperature and pH value.

Run#	Reaction conditions			
	$NaBH_4$ (g)	Catalyst (g)	NaOH solution (g)	Initial temperature (^oC)
A1	0.5	0.3	10	20
A2	0.5	0.3	10	23
A3	0.5	0.3	10	26
A4	0.5	0.3	10	29
A5	0.5	0.3	10	32
…	…	…	…	…
E1	1.2	0.3	10	20
E2	1.2	0.3	10	23
E3	1.2	0.3	10	26
E4	1.2	0.3	10	29
E5	1.2	0.3	10	32
F1	1.5	0.3	10	20
F2	1.5	0.3	10	23
F3	1.5	0.3	10	26
F4	1.5	0.3	10	29
F5	1.5	0.3	10	32



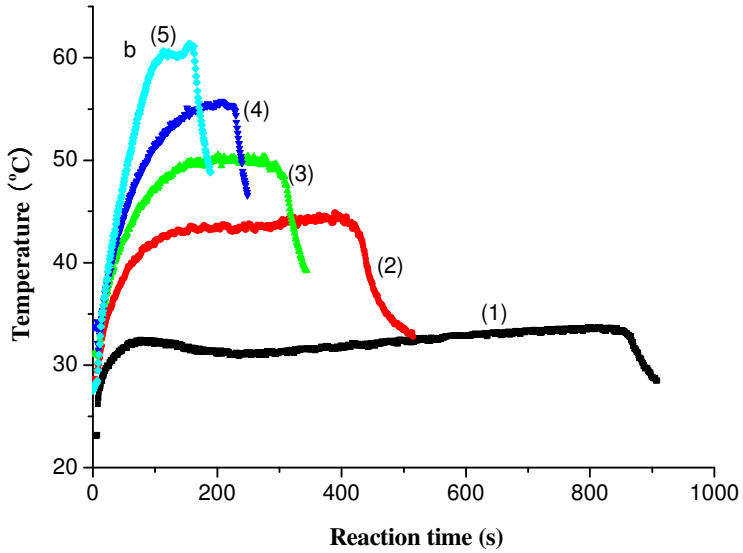


Fig. 1. The v_{H2} ~ time (a) and temperature ~ time (b) for the hydrolysis of $NaBH_4$ at various starting temperatures ((1): 20°C; (2): 23°C; (3): 26°C; (4): 29°C; (5): 32°C). The hydrolysis was conducted using 1.2 g $NaBH_4$ in 10 cm^3 of 0% NaOH solution (water) with 0.3 g of catalyst of an average particle size of 0.049 mm.

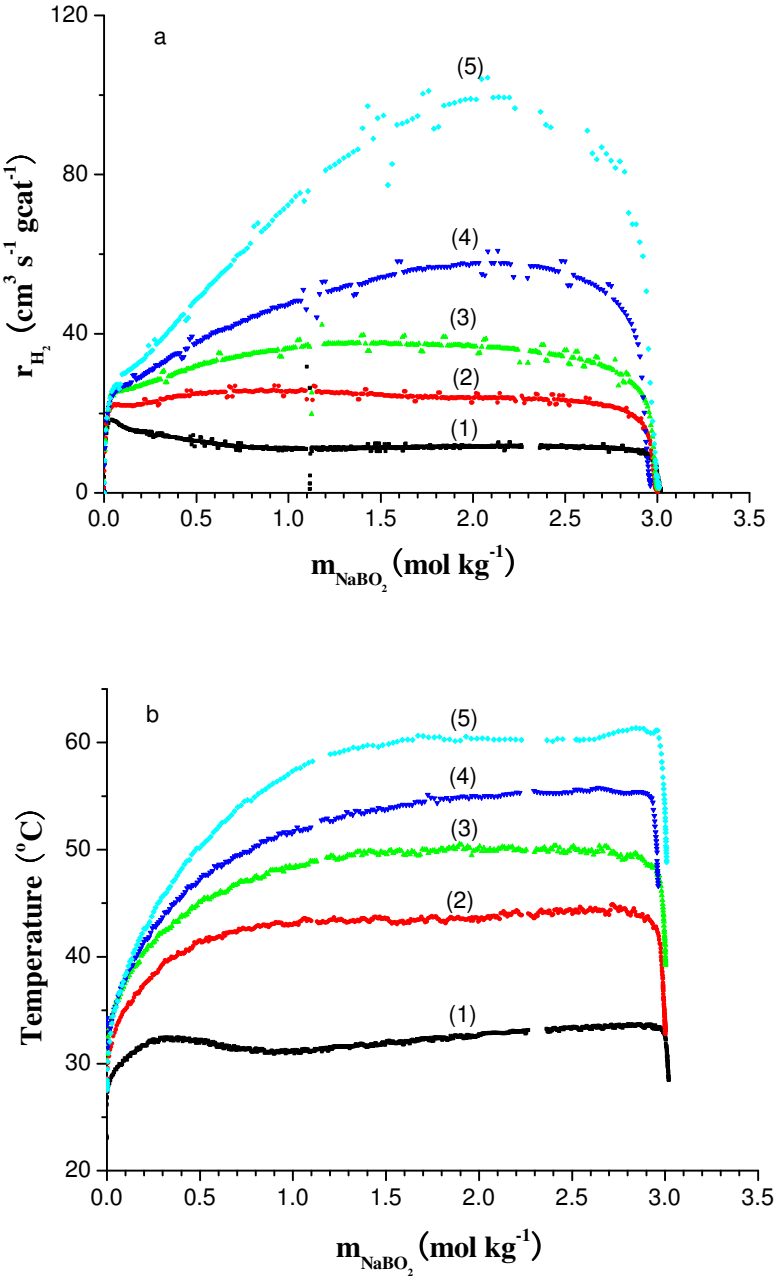


Fig.2. The relationships between the rate of hydrogen generation (r_{H2}) and $NaBO_2$ concentration (a) and reaction temperature and $NaBO_2$ concentration (b). They were transformed from Figure 1a and b respectively.

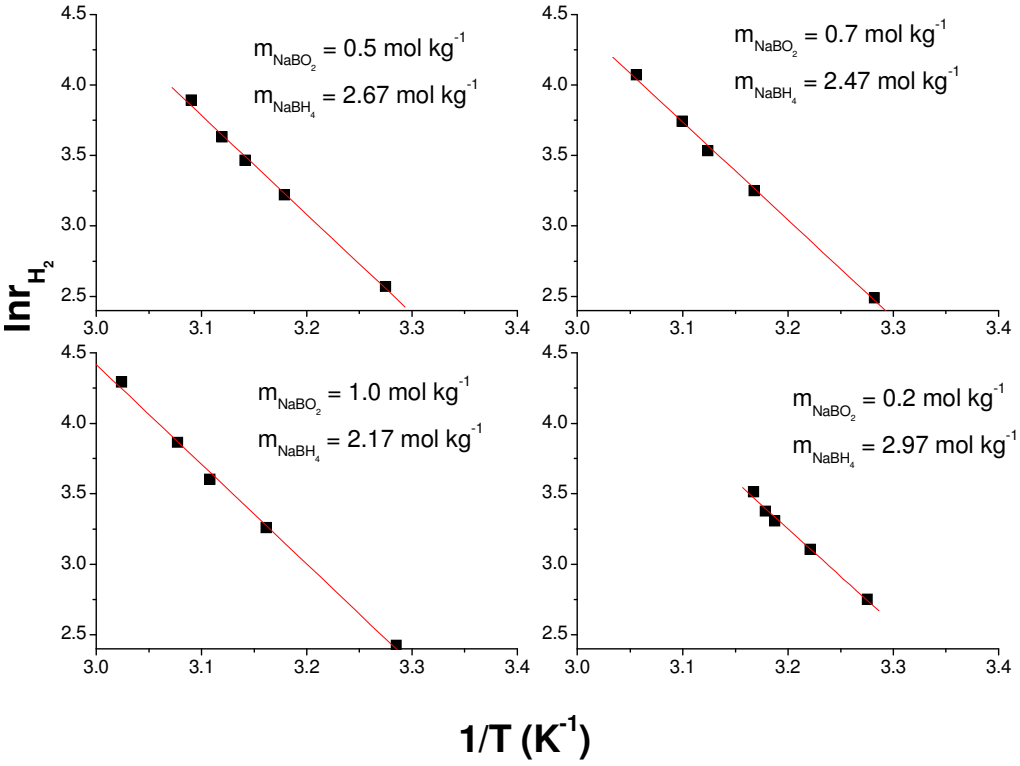


Fig. 3. lnr_{H2} versus 1/T at different $NaBO_2$ concentrations derived from Figure 3.

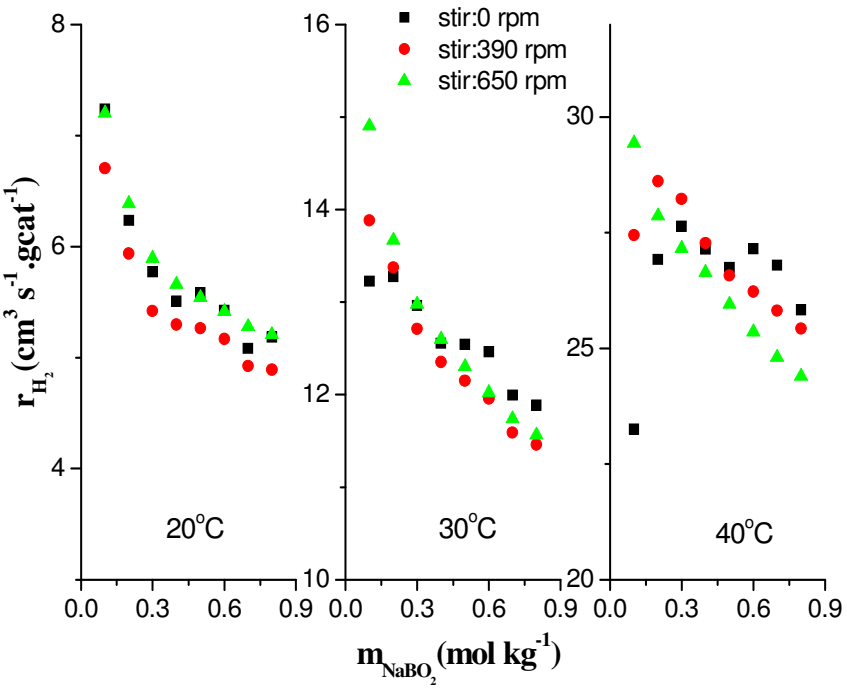


Fig. 4. Comparison of the effect of stirring rate on reaction rate. The catalyst particles used had an average size of 0.049 mm. The reaction was conducted using 0.5g $NaBH_4$ in 10 ml of water. The catalyst used was 0.3 g.

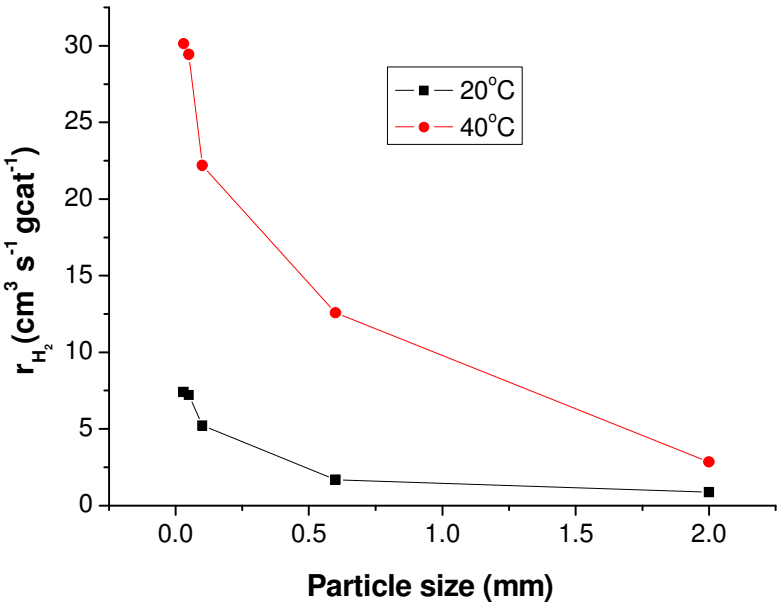


Fig. 5. Comparison of the reaction rate at various temperatures for different catalyst particle sizes. The reaction was performed using 0.5 g $NaBH_4$ in 10 ml of water. The catalyst used was 0.3 g.

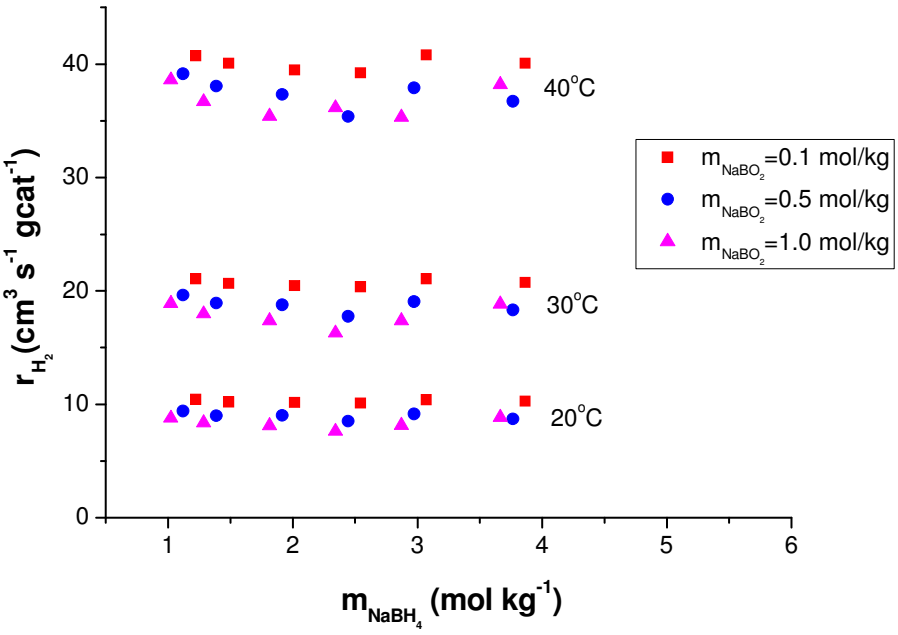


Fig. 6. Hydrogen generation rate versus the molality of $NaBH_4$. The data was obtained by data analysis method introduced in section 2.4 after conducting the experimental programme in Table 2. The catalyst was 0.3 g with an average particle size of 0.049 mm.

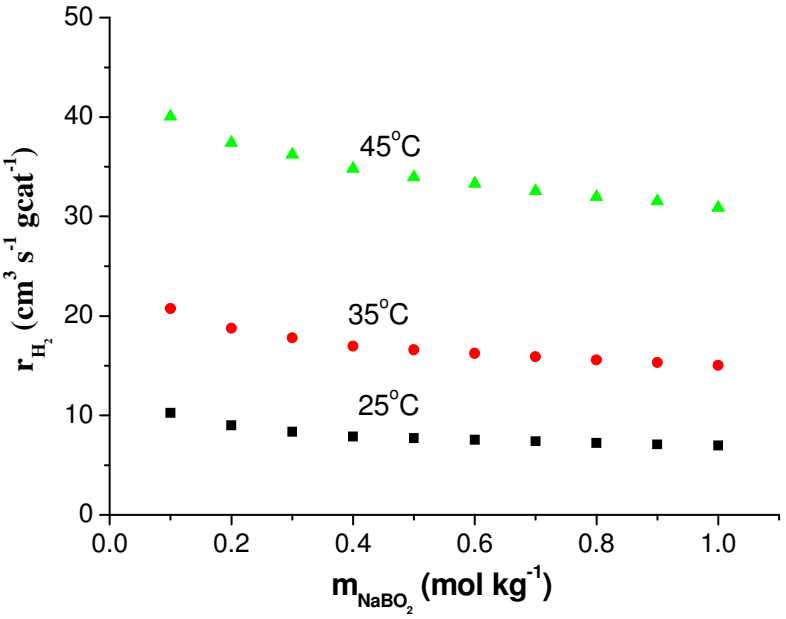


Fig. 7. The relationship between r_{H2} and the molality of $NaBO_2$. The data was obtained by taking the average of the six points as in Figure 6 at each temperature and $NaBO_2$ concentration.

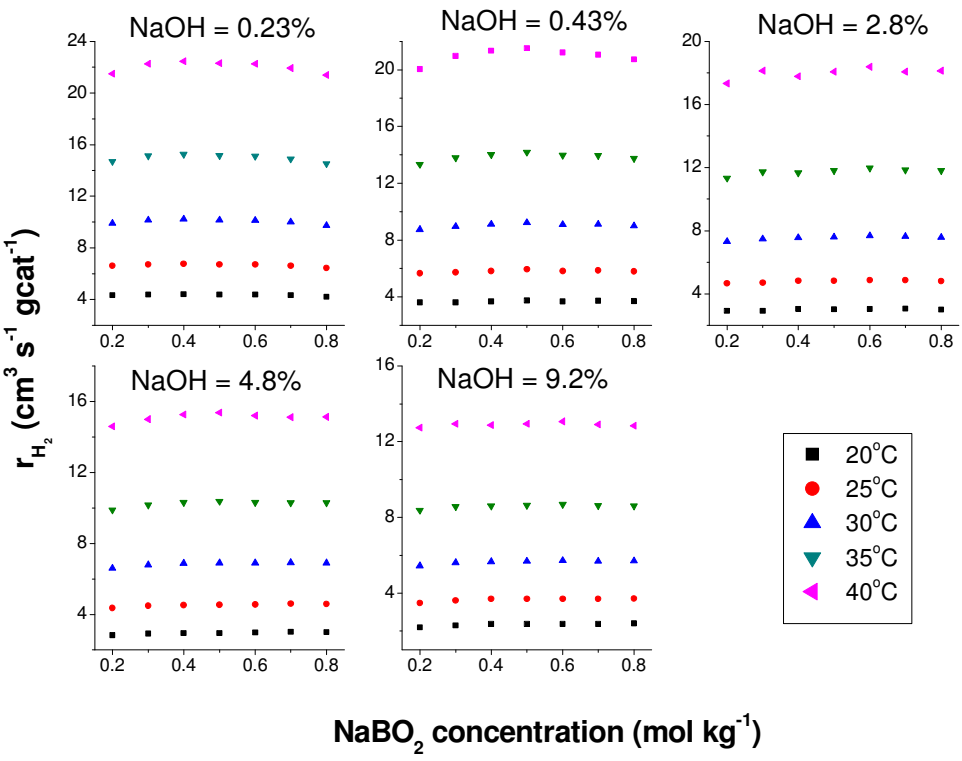


Fig. 8. The effect of NaOH on the hydrolysis of $NaBH_4$ at various temperatures. The rate data was obtained by using the data analysis method introduced in section 2.4 after conducting the experimental programme in Table 2 by changing NaOH concentration from 0.23 to 9.2% (wt) and keeping the weight of $NaBH_4$ at 0.5g in each group. The catalyst was 0.3 g with an average particle size of 0.049 mm.

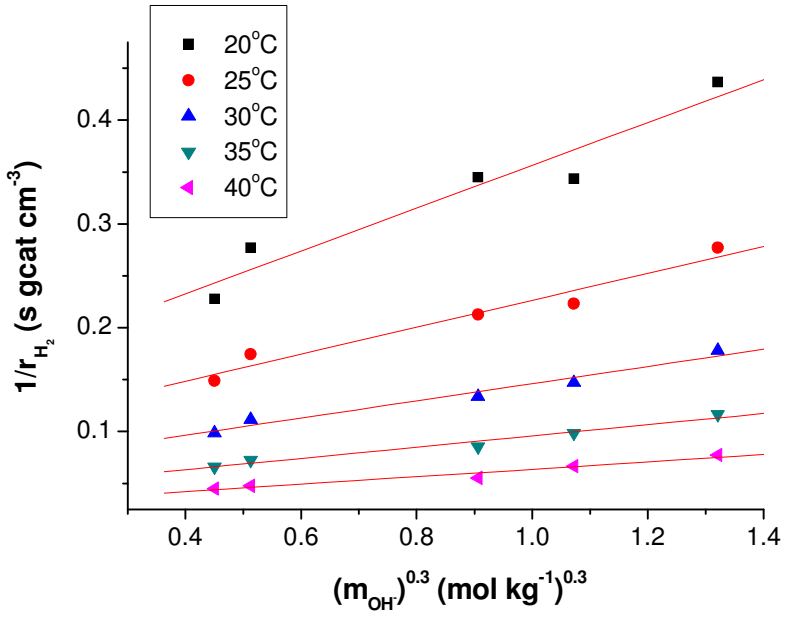


Fig. 9. $1/r_{H2}$ versus [OH^-] and their linear regressions at various temperatures.