Kinetics of sodium borohydride hydrolysis reaction for hydrogen generation

Ai-Jen Hunga, Shing-Fen Tsai, Ya-Yi Hsub, Jie-Ren Kube, Yih-Hang Chen, Cheng-Ching Yua,*

aDepartment of Chemical Engineering, National Taiwan University, Taipei 106-17, Taiwan
bEnergy and Environment Research Laboratories (EEL), Industrial Technology Research Institute (ITRI), Hsinchu 310, Taiwan
cDepartment of Process Engineering, CTCI Corporation, Taipei 106, Taiwan

ARTICLE INFO
Article history:
Received 13 March 2008
Received in revised form 29 July 2008
Accepted 29 July 2008
Available online 11 September 2008

Keywords:
Kinetics
Sodium borohydride
Hydrolysis reaction
Hydrogen generation

ABSTRACT
In this work, a ruthenium catalyst was prepared for hydrogen generation from the hydrolysis reaction of an alkaline sodium borohydride solution. The reactions were carried out in a batch reactor at temperatures of 10, 30, 40 and 60°C for at least 70% conversion or 500 min, whichever came first. The experimental data was fitted to the following three kinetic models: zero-order, first-order, and Langmuir–Hinshelwood. The results indicate that the Langmuir–Hinshelwood model gives a reasonable description of the hydrogen generation rate over the entire temperature range studied as well as the time spans of the experiments. The zero-order model gives good behavior description only at relatively low temperature, i.e. 10°C. The first-order model works fairly well for a temperature range up to 30°C.

© 2008 International Association for Hydrogen Energy. Published by Elsevier Ltd. All rights reserved.

1. Introduction

Hydrogen has become one of the most promising future energy resources due to concerns about global warming and the depletion of fossil fuels. Hydrogen generation from the hydrolysis reaction of an alkaline sodium borohydride solution (NaBH₄) has drawn much attention due to its theoretically high hydrogen storage capacity (10.8 wt%). In addition, it is favored as the hydrogen supplier for proton exchange membrane (PEM) fuel cells due to the high purity of the hydrogen.

A hydrolysis reaction takes place only when an alkaline NaBH₄ solution is in contact with certain catalysts. Different catalysts such as ruthenium (Ru) [1–7], platinum (Pt) [8,9], palladium (Pd) [10], nickel (Ni) [11,12], cobalt (Co) [11,13,14], Co–B [15,16], Ni–B [17], Ni–Co–B [18], carbon nanotubes (CNT) [19] have been extensively studied.

For the design of reactors, it is essential to determine a reliable kinetic model for the hydrogen generation. Hydrogen generation from an alkaline NaBH₄ solution has been extensively investigated and three kinetic models have been proposed [1–7,10–13,15–19]. They are zero-order, first-order and Langmuir–Hinshelwood.

Several authors have used a zero-order model. Amendola et al. [1] used Ru on IRA-400 as the catalyst to study the effect of different temperatures on the kinetics of the hydrolysis reaction. Factors including the concentration of NaBH₄, the concentration of sodium hydroxide (NaOH) and the reaction temperature (which could affect the hydrogen generation rates) were investigated using the catalyst Ru on different supports in [2,3]. The catalysts Co [11,13], Ni [11], Co–B [15,16], Ni–B [17] and Ni–Co–B [18] were implemented for the hydrolysis reaction.

* Corresponding author. Fax: +886 2 2362 3040.
E-mail address: ccyu@ntu.edu.tw (C.-C. Yu).
0360-3199/$ – see front matter © 2008 International Association for Hydrogen Energy. Published by Elsevier Ltd. All rights reserved.
Nomenclature

- \( C \): concentration, mol L\(^{-1} \)
- \( C_{\text{NaBH}_4} \): initial concentration of NaBH\(_4\) based on maximum hydrogen generation rate, mol L\(^{-1} \)
- \( F_{\text{H}_2} \): filtered data for hydrogen generation rate, ml min\(^{-1} \)
- \( F_{\text{H}_2,\text{raw}} \): raw data for hydrogen generation rate, ml min\(^{-1} \)
- \( K_a \): adsorption constant, L mol\(^{-1} \)
- \( k \): reaction rate constant based on the solution volume for zero-order, mol L\(^{-1} \) min\(^{-1} \); for first-order, L g cat\(^{-1} \) min\(^{-1} \); for Langmuir–Hinshelwood, mol L\(^{-1} \) min\(^{-1} \)
- \( k' \): reaction rate constant based on the catalyst weight for zero-order, mol g cat\(^{-1} \) min\(^{-1} \); for first-order, L g cat\(^{-1} \) min\(^{-1} \); for Langmuir–Hinshelwood, mol cat\(^{-1} \) min\(^{-1} \)
- \( M_{\text{NaBH}_4} \): molecular weight of NaBH\(_4\), 37.8 g mol\(^{-1} \)
- \( M_{\text{H}_2O} \): molecular weight of H\(_2\)\(_O\), 18 g mol\(^{-1} \)
- \( M_{\text{NaBO}_2} \): molecular weight of NaBO\(_2\), 65.8 g mol\(^{-1} \)
- \( M_{\text{H}_2} \): molecular weight of H\(_2\), 2 g mol\(^{-1} \)
- \( N \): number of moles, mol
- \( r \): rate of reaction, mol L\(^{-1} \) min\(^{-1} \)
- \( R \): gas constant, 8.314 \times 10^{-3} \) kJ mol\(^{-1} \) K\(^{-1} \)
- \( R^2 \): correlation coefficient
- \( T \): reaction temperature, K
- \( t \): time, min
- \( V \): solution volume, L
- \( \omega_{\text{cat}} \): catalyst weight, g
- \( z \): discrete variable

Other authors have used a first-order model. Ozkar and Zahmakiran [4,5] used a water-dispersible Ru(0) nanocluster catalyst to increase activity. Shang and Chen [6] explored the effect of a concentrated NaBH\(_4\) solution on hydrogen generation rate. The synthesis and characterization of carbon nanotubes (CNT) as the catalyst for the hydrolysis reaction were investigated in Ref. [19]. The synthesis and characterization of a water-dispersible Ni(0) nanocluster catalyst was explored in Ref. [12] and the activity of Pd on the hydrolysis reaction was investigated in Ref. [10].

Finally, at least one author has used a Langmuir–Hinshelwood model. Zhang et al. [7] used the commercial catalyst Ru to analyze the effects of different substrates, the catalyst sizes, the stirring speed and the reaction temperature on the hydrogen generation rate. Table 1 summarizes published investigations of the kinetics of the

### Table 1 – Kinetic models for different catalysts, initial concentration of NaBH\(_4\)(aq) , temperature ranges, activation energy and time spans

<table>
<thead>
<tr>
<th>Catalyst/support</th>
<th>Initial concentration of NaBH(_4)(aq)</th>
<th>Kinetic model</th>
<th>Temp. range (°C)</th>
<th>Activation energy (kJ/mol)</th>
<th>Time span (min)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(5 wt%)/IRA-400</td>
<td>20 wt% NaBH(_4) + 10 wt% NaOH</td>
<td>Zero-order</td>
<td>25–55</td>
<td>47.0</td>
<td>27</td>
<td>Amendola et al. [1]</td>
</tr>
<tr>
<td>Ru(5 wt%)/IRA-400</td>
<td>7.5 wt% NaBH(_4) + 4 wt% NaOH</td>
<td>Zero-order</td>
<td>0–40</td>
<td>56.0</td>
<td>42</td>
<td>Amendola et al. [2]</td>
</tr>
<tr>
<td>Ru(1 wt%)/IR-120</td>
<td>5 wt% NaBH(_4) + 1 wt% NaOH</td>
<td>Zero-order</td>
<td>5–55</td>
<td>49.7</td>
<td>60</td>
<td>Hsueh et al. [3]</td>
</tr>
<tr>
<td>Ni</td>
<td>0.9 wt% NaBH(_4) + 10 wt% NaOH</td>
<td>Zero-order</td>
<td>10–50</td>
<td>62.7</td>
<td>150</td>
<td>Liu et al. [11]</td>
</tr>
<tr>
<td>Co</td>
<td>Zero-order</td>
<td>10–50</td>
<td>41.9</td>
<td>30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Raney Ni</td>
<td>Zero-order</td>
<td>10–30</td>
<td>50.7</td>
<td>50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Raney Co</td>
<td>Zero-order</td>
<td>10–30</td>
<td>53.7</td>
<td>50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Raney Ni(_{\text{CoS}_0})</td>
<td>Zero-order</td>
<td>10–30</td>
<td>52.5</td>
<td>30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co–B</td>
<td>20 wt% NaBH(_4) + 5 wt% NaOH</td>
<td>Zero-order</td>
<td>10–30</td>
<td>64.9</td>
<td>40</td>
<td>Jeong et al. [15]</td>
</tr>
<tr>
<td>Co–Al(_2O_3)</td>
<td>0.7 wt% NaBH(_4) + 4 wt% NaOH</td>
<td>Zero-order</td>
<td>25–40</td>
<td>57.8</td>
<td>14</td>
<td>Zhao et al. [16]</td>
</tr>
<tr>
<td>Ni–B</td>
<td>5 wt% NaBH(_4) + 5 wt% NaOH</td>
<td>Zero-order</td>
<td>30–50</td>
<td>32.6</td>
<td>80</td>
<td>Ye et al. [13]</td>
</tr>
<tr>
<td>Ni–Co–B</td>
<td>1.5 wt% NaBH(_4) + 10 wt% NaOH</td>
<td>Zero-order</td>
<td>20–60</td>
<td>56.0</td>
<td>35</td>
<td>Dong et al. [17]</td>
</tr>
<tr>
<td>Ru(0) nanoclusters</td>
<td>4.7 wt% NaBH(_4) + 15 wt% NaOH</td>
<td>Zero-order</td>
<td>8–27</td>
<td>62.0</td>
<td>50</td>
<td>Ingersoll et al. [18]</td>
</tr>
<tr>
<td>Ru(0) nanoclusters</td>
<td>0.5 wt% NaBH(_4)</td>
<td>First-order</td>
<td>30–45</td>
<td>28.5</td>
<td>5</td>
<td>Ozkar and Zahmakiran [4]</td>
</tr>
<tr>
<td>Ru(0) nanoclusters</td>
<td>0.5 wt% NaBH(_4) + 10 wt% NaOH</td>
<td>First-order</td>
<td>25–55</td>
<td>41.0</td>
<td>6</td>
<td>Shang and Chen [6]</td>
</tr>
<tr>
<td>Ru/C</td>
<td>5 wt% NaBH(_4) + 5 wt% NaOH</td>
<td>First-order</td>
<td>42–60</td>
<td>37.3</td>
<td>35</td>
<td>Pena-Alonso et al. [19]</td>
</tr>
<tr>
<td>Carbon nanotubes (CNT)</td>
<td>1 wt% NaBH(_4)</td>
<td>First-order</td>
<td>29–59</td>
<td>19.0</td>
<td>120</td>
<td>Metin and Ozkar [12]</td>
</tr>
<tr>
<td>Ni(C) nanoclusters</td>
<td>0.5 wt% NaBH(_4)</td>
<td>First-order</td>
<td>25–45</td>
<td>54.0</td>
<td>100</td>
<td>Patel et al. [10]</td>
</tr>
<tr>
<td>Pd/C</td>
<td>0.5 wt% NaBH(_4)</td>
<td>First-order</td>
<td>10–55</td>
<td>28.0</td>
<td>20</td>
<td>Zhang et al. [7]</td>
</tr>
<tr>
<td>Ru/Al(_2O_3)</td>
<td>0.8 wt% NaBH(_4) + 3 wt% NaOH</td>
<td>Langmuir–Hinshelwood</td>
<td>25–85</td>
<td>67.0</td>
<td>14</td>
<td>This work</td>
</tr>
<tr>
<td>Ru/t-Al(_2O_3)</td>
<td>12 wt% NaBH(_4) + 1 wt% NaOH</td>
<td>Zero-order</td>
<td>10–60</td>
<td>54.9</td>
<td>500</td>
<td>This work</td>
</tr>
<tr>
<td>Ru/Al(_2O_3)</td>
<td>12 wt% NaBH(_4) + 1 wt% NaOH</td>
<td>First-order</td>
<td>10–60</td>
<td>55.7</td>
<td>500</td>
<td>This work</td>
</tr>
</tbody>
</table>
hydrolysis of NaBH₄, including the kinetic models for different catalysts, initial concentration of the alkaline NaBH₄ solution, temperature ranges, activation energy and time spans. As shown in Table 1, the models are mostly zero-order or first-order with the exception of the work of Ref. [7]. Furthermore, the time spans of the experiments range from 5 to 150 min. Because we are interested in utilizing the kinetic model to design a hydrogen generation device, a model capable of describing the hydrogen generation rate over the entire batch reactor operation is preferred. The objective of this work is to determine an appropriate kinetic model of this hydrolysis reaction in a batch reactor based on experiments at four different temperatures.

Fig. 1 – Experimental setup for hydrogen generation from the hydrolysis reaction of an alkaline NaBH₄ solution.

![Experimental setup](image)

Fig. 2 – Hydrogen generation volume with respect to time at the concentration of NaBH₄ of 1, 12, 13 and 31 wt% at 30 °C with the concentration of NaOH at a constant 1 wt%.

![Graph](image)

Fig. 3 – Hydrogen generation volume with respect to time at the concentration of NaOH of 1, 5 and 10 wt% at 30 °C with the concentration of NaBH₄ at a constant 12 wt%.

![Graph](image)
2. Experimental

2.1. Hydrolysis reaction

A NaBH₄ solution with an alkaline stabilizer, NaOH, reacts with water to generate hydrogen and sodium metaborate (NaBO₂) in the presence of a catalyst. The catalytic hydrolysis reaction for hydrogen generation is irreversible, heterogeneous, and highly exothermic, with the heat of reaction of 210 kJ/mol [20]:

$$\text{NaBH}_4(\text{aq}) + 2\text{H}_2\text{O}(\text{ll}) \xrightarrow{\text{catalyst}} 4\text{H}_2(\text{g}) + \text{NaBO}_2(\text{aq}) \quad \Delta H_{\text{rxn}} = -210 \text{ kJ/mol}$$

(1)

This reaction system also has several advantages, including, hydrogen can be produced even when the temperature is 0°C, the hydrogen generation rate can be easily controlled, and an alkaline NaBH₄ solution is nonflammable and stable.

2.2. Preparation of Ru/γ-Al₂O₃ catalyst

The metal Ru was selected as a catalyst for hydrogen generation due to high hydrogen production [21,22] and gamma-alumina (γ-Al₂O₃) was used as the support. The catalyst Ru/γ-Al₂O₃ was prepared by the impregnation–reduction method. The synthesis procedure is summarized as follows:

1. Ten grams of γ-Al₂O₃ pellets (Alfa Aesar) were dehydrated at 600°C.
2. The γ-Al₂O₃ pellets were placed in 10 ml of 0.24 M RuCl₃·3H₂O (Sigma–Aldrich) for 24 h.
3. They were then dried for 2 h at 120°C in nitrogen and then calcined for 3 h at 550°C in nitrogen.
4. Finally, they were reduced for 6 h at 700°C in hydrogen, producing the catalyst Ru/γ-Al₂O₃.

2.3. Experimental setup

The experiments for the hydrolysis reaction were performed at the Industrial Technology Research Institute/Energy and Environment Research Laboratories (ITRI/EEL) facility in Hsinchu. Fig. 1 shows the experimental setup for hydrogen generation from the hydrolysis reaction of an alkaline NaBH₄ solution. The reaction took place in a round-bottomed glassware flask with three necks. A thermocouple in the first neck was used to monitor the solution temperature which was kept constant, via a thermostatic circulation water bath, to within ±0.1°C of the temperature set point. The second neck was connected to a funnel, which contained an alkaline NaBH₄ solution. The reaction was initiated when 30 ml of 12 wt% NaBH₄ solution, including 1 wt% NaOH solution as an alkaline stabilizer, was added to the flask to come into contact with 0.5 g of the catalyst Ru/γ-Al₂O₃. The catalyst was pre-soaked in 16 ml of de-ionized water. This level of solution concentration was used because it was found to produce the highest level of hydrogen generation, as shown in Figs. 2 and 3. As can be seen in Fig. 2, the hydrogen generation decreases with an increase in NaBH₄ concentration from 12 to 31 wt%. Similarly, as can be

Fig. 4 – Hydrogen generation volume with respect to time at temperatures of 10, 30, 40, and 60°C with the concentrations of NaBH₄ and NaOH at 12 and 1 wt%, respectively.

Fig. 5 – (A) Concentration of NaBH₄ with respect to time, (B) conversion of NaBH₄ with respect to time for four temperatures: 10°C, 30°C, 40°C, and 60°C.
seen in Fig. 3, the hydrogen generation decreases when the NaOH concentration is increased. The reagent solution was stirred by a magnet to maintain a uniform temperature. The hydrogen that was generated exited through the third neck into a coil condenser and then passed through a steam trap in order to remove the water vapor. During the experiments, the hydrogen generation rates were measured by a flow meter at the following temperatures: 10, 30, 40, and 60 °C. The sampling times for the temperature and flow measurements are 1.06 s.

3. Results and discussions

3.1. Kinetics

3.1.1. Data treatment

Because of the noise associated with measurements, it is desirable to use an exponential filter to smooth the raw data for hydrogen generation rates. Raw data was smoothed with a filter with a time constant of 0.42 min. The relatively small time constant will not alter the dynamic behavior of the reaction because the process time constant is much large, at least 40 min. The Appendix shows the hydrogen generation rate before and after the filtering at 30 and 60 °C. The cumulative volumetric hydrogen generation with respect to time is shown in Fig. 4 at temperatures of 10, 30, 40, and 60 °C.

For kinetic analysis, it is preferable to convert the hydrogen generation rate into the reactant (sodium borohydride) concentration – both as functions of time. From the reaction stoichiometry, the number of moles of NaBH₄ remaining in the batch reactor with respect to time can be expressed as:

\[
N_{\text{NaBH}_4}(z) = N_{\text{NaBH}_4}(0) - N_{\text{H}_2}(z)/4
\]

where \(N\) is the number of moles and \(z\) is the discrete variable.

The number of moles of H₂O remaining in the batch reactor with respect to time is:

\[
N_{\text{H}_2\text{O}}(z) = N_{\text{H}_2\text{O}}(0) - N_{\text{H}_2}(z)/2
\]

The number of moles of NaBO₂ remaining in the batch reactor with respect to time is:

\[
N_{\text{NaBO}_2}(z) = N_{\text{NaBO}_2}(0) + N_{\text{H}_2}(z)/4
\]

The solution volume with respect to time can then be evaluated as follows:

\[
V(z) = \frac{N_{\text{NaBH}_4}(z) \cdot M_{\text{NaBH}_4}}{\rho_{\text{NaBH}_4}} + \frac{N_{\text{H}_2\text{O}}(z) \cdot M_{\text{H}_2\text{O}}}{\rho_{\text{H}_2\text{O}}} + \frac{N_{\text{NaBO}_2}(z) \cdot M_{\text{NaBO}_2}}{\rho_{\text{NaBO}_2}}
\]

where \(V\) is the solution volume, \(\rho\) denotes the density, \(M\) stands for the molecular weight. Consequently, the concentration of NaBH₄ as a function of time can be obtained from \(C_{\text{NaBH}_4} = N_{\text{NaBH}_4}/V\) as shown in Fig. 5(A). The corresponding conversion of NaBH₄ can be calculated as shown in Fig. 5(B). In

Fig. 6 – Linear regression based on zero-order while the temperature is (A) 10 °C (B) 30 °C (C) 40 °C (D) 60 °C.
this work, the following three kinetic models were used to describe the behavior of the hydrolysis reaction for hydrogen generation using an integral method.

3.1.2. Zero-order
If the rate of consumption of NaBH₄ (C_{NaBH₄}) with respect to time is equal to a reaction rate constant, the reaction has zero-order kinetics (independent of any concentration).

\[
\frac{dC_{NaBH₄}}{dt} = -r_{NaBH₄} = -k(T)
\]  

(6)

where C is the concentration, r is the rate of reaction, k is the reaction rate constant based on the solution volume.

Integrating the differential Eq. (6) it then becomes:

\[
(C_{NaBH₄} - C_{NaBH₄}) = kt
\]  

(7)

A plot of \((C_{NaBH₄} - C_{NaBH₄})\) should be a linear function of time, where the slope is simply the reaction rate constant. Here, the maximum hydrogen generation rate was used as an initial condition. In theory, the maximum rate occurs while the concentration of the reactants is at its highest. Since the time delay to evolve the maximum amount of hydrogen caused by the pore diffusion resistance was only about 6 s, it is reasonable to assume that it can be applied as an initial condition. Fig. 6 shows plots of \((C_{NaBH₄} - C_{NaBH₄})\) versus time for four temperature settings. As can be seen in Fig. 6(A), data collected before the time of 50 min was excluded at the temperature of 10 °C for the linear regression due to the low reaction rate. The data at 10 °C could be linearly regressed in the range of 50–500 min with the correlation coefficient of 0.9991. The data at temperatures of 30, 40, and 60 °C could be linearly regressed only within the cut-off time, where the conversion of NaBH₄ is 50%, as shown in Fig. 6(B–D). As can be seen from Fig. 5(A), the concentration of NaBH₄ at 10 °C is always higher than 2.5 (mol/L) within the whole reaction time whereas the variations in the concentration of NaBH₄ at 30, 40, and 60 °C are greater. Therefore it is appropriate to apply the zero-order model while the concentration of NaBH₄ remains high. Table 2 summarizes the following

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Time span for regression (min)</th>
<th>k (mol/L/min)</th>
<th>Correlation coefficient ((R^2)) of regression</th>
<th>Correlation coefficient ((R^2)) for the entire range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zero-order</td>
<td>10</td>
<td>50-500</td>
<td>0.001455</td>
<td>0.9991</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0-265.86</td>
<td>0.006153</td>
<td>0.9947</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>0-107.50</td>
<td>0.01486</td>
<td>0.9987</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0-33.86</td>
<td>0.04628</td>
<td>0.9999</td>
</tr>
<tr>
<td>First-order</td>
<td>10</td>
<td>50-500</td>
<td>0.0004909</td>
<td>0.9999</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0-500</td>
<td>0.002356</td>
<td>0.9967</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>0-107.50</td>
<td>0.005347</td>
<td>0.9929</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0-33.86</td>
<td>0.01663</td>
<td>0.9859</td>
</tr>
<tr>
<td>Langmuir–Hinshelwood</td>
<td>10</td>
<td>50-500</td>
<td>0.001705</td>
<td>0.9993</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0-265.86</td>
<td>0.007287</td>
<td>0.9971</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>0-250</td>
<td>0.01729</td>
<td>0.9990</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0-100</td>
<td>0.05659</td>
<td>0.9997</td>
</tr>
</tbody>
</table>

\(a\) Full time span range: 0–500 min for 10 and 30 °C, 0–250 min for 40 °C, and 0–100 min for 60 °C.

Fig. 7 – Arrhenius plot for zero-order.

![Fig. 7 – Arrhenius plot for zero-order.](image)
3.1.3. First-order
Considering the case when the reaction rate is first-order in the concentration of NaBH₄, we have:

\[
\frac{dC_{NaBH_4}}{dt} = -r_{NaBH_4} = -kC_{NaBH_4}
\]  

(8)

Integrating the differential Eq. (8) it then becomes:

\[
\ln \left( \frac{C_{NaBH_4}}{C_{NaBH_4,0}} \right) = kt
\]  

(9)

A plot of ln(\(C_{NaBH_4}/C_{NaBH_4,0}\)) as a function of time should give a straight line, the slope of which is the reaction rate constant. Fig. 8(A) and (B) shows that plots of ln(\(C_{NaBH_4}/C_{NaBH_4,0}\)) versus time at temperatures of 10 and 30 °C produce good linear regression with correlation coefficients of 0.9999 and 0.9967. Nevertheless, the data at 40 and 60 °C could be regressed linearly only over the full cut-off time. The reason for this is that higher temperatures bring about higher reaction rates, thus this significantly increases the effect of the adsorption of NaBH₄ on the catalyst. Table 2 summarizes the following regression data for a first-order model: the reaction rate constant, the correlation coefficients from the linear regression; and the correlation coefficients for the full time span. According to the Arrhenius equation, the plot of ln(k) versus 1/T for four temperature settings as shown in Fig. 7 gave a good linear regression with the correlation coefficient of 0.9971. Therefore, the activation energy and the pre-exponential factor can both be determined, as shown in Table 3. Because of the gradual deterioration of the NaBH₄ concentration at higher temperatures toward the end of the time frame, e.g., 30, 40, and 60 °C, the first-order model is employed to compensate for this deterioration.

3.1.4. Langmuir–Hinshelwood
The Langmuir–Hinshelwood model [7,23] is commonly used to describe reaction kinetics for catalytic reactions. Consider the following rate expression:

\[
\frac{dC_{NaBH_4}}{dt} = -r_{NaBH_4} = -kC_{NaBH_4} \frac{K_a C_{NaBH_4}}{1 + K_a C_{NaBH_4}}
\]  

(10)

where \(K_a\) is the adsorption constant which is assumed to be a constant. Integrating Eq. (10), one obtains:

\[
\frac{1}{K_a} \ln \left( \frac{C_{NaBH_4,0}}{C_{NaBH_4}} \right) + \left( C_{NaBH_4} - C_{NaBH_4,0} \right) = kt
\]  

(11)
A plot of \( \frac{1}{K_a} \ln \left( \frac{C_{\text{NaBH}_4,0}}{C_{\text{NaBH}_4}} \right) \) as a function of time should give a straight line, the slope of which is the reaction rate constant. The objective function can be minimized by varying the adsorption constant using the data at 40 and 60°C. Therefore, it can be formulated as follows:

\[
\min_{K_a} f(K_a) = \left( 1 - R^2_{40°C} \right) + \left( 1 - R^2_{60°C} \right)
\]

where \( R^2 \) is the correlation coefficient. Fig. 10 shows that the optimal adsorption constant \( K_{a,\text{opt}} \) was obtained by minimizing Eq. (12) at temperatures of 40 and 60°C. In order to determine the reaction rate constant for Langmuir–Hinshelwood, the optimal adsorption constant was input into the data at temperatures of 10 and 30°C, as shown in Fig. 11(A) and (B). As can be seen in Fig. 11(C) and (D), the data at 40 and 60°C could be linearly regressed within the whole time span. Table 2 also shows the reaction rate constants, the correlation
coefficients of both regression and the entire range for Langmuir–Hinshelwood. Therefore from the Arrhenius plot of ln(\(k\)) versus 1/T as shown in Fig. 12, the activation energy and the pre-exponential factor could be determined to be 55.40 kJ/mol and 2.82 \(\times\) 10^7 mol/L/min. The reaction rate constants based on the solution volume and the catalyst weight for zero-order, first-order, and Langmuir–Hinshelwood are summarized in Table 3.

### 3.2. Batch reactor model

With the kinetic models available, a constant-pressure batch reactor model can be constructed. From the mole balance and

\[
\text{Fig. 13} - \text{Model predictions for zero-order, first-order, and Langmuir–Hinshelwood with the experimental data at 60 °C.}
\]
the stoichiometric relationship the variation of the number of moles of NaBH₄ with respect to time is the product of the rate of reaction and the solution volume, which can be expressed as follows:

\[
\frac{d(V_{\text{NaBH}_4})}{dt} = (-r_{\text{NaBH}_4}) \cdot V
\]  

(13)

The variation of the number of moles of H₂O with respect to time is:

\[
\frac{d(V_{\text{H}_2\text{O}})}{dt} = 2(-r_{\text{NaBH}_4}) \cdot V
\]  

(14)

The variation of the number of moles of NaBO₂ with respect to time is:

\[
\frac{d(V_{\text{NaBO}_2})}{dt} = r_{\text{NaBH}_4} \cdot V
\]  

(15)

The solution volume can be calculated in Eq. (5) and the concentration profiles of NaBH₄, H₂O, and NaBO₂ can then be obtained. The hydrogen generation rate can be computed as follows:

\[
F_{\text{H}_2} = 4(r_{\text{NaBH}_4} \cdot V \cdot \frac{M_{\text{H}_2}}{M_{\text{H}_2}})
\]  

(16)

where \( F_{\text{H}_2} \) is the hydrogen generation rate. Because of the constant reaction temperature, the energy balance equations are negligible in this system. Eqs. (13)–(15) can be solved by using the Euler method, the code is programmed in FORTRAN.

3.3. Validation of the kinetic model

The hydrogen generated from the hydrolysis reaction of an alkaline NaBH₄ solution can be used for PEM fuel cell applications due to its high purity. The operating fuel cell temperature is normally set at 60 °C for optimal performance. For this reason, the experimental data at 60 °C was used to validate the kinetic models, which are zero-order, first-order, and Langmuir–Hinshelwood. As can be seen in Fig. 13, the Langmuir–Hinshelwood model gave the best prediction among the three models.

4. Conclusions

In this study, the catalyst Ru/γ-Al₂O₃ was prepared by the impregnation–reduction method for the hydrogen generation from the hydrolysis reaction of an alkaline NaBH₄ solution. Next, the reaction was carried out in a batch reactor at 10, 30, 40 and 60 °C, respectively, until at least 70% conversion was achieved, except for the case of 10 °C when the reaction was terminated at 500 min. The results indicate that the zero-order model can only be applied for low conversion, e.g., \( x < 50\% \), and/or low temperature, e.g., 10 °C. The first-order model shows somewhat better applicability and gives a reasonably good concentration trajectory for temperatures up to 30 °C. The Langmuir–Hinshelwood model gives reasonable behavior description for the entire temperature range of interest, 10–60 °C. Therefore, the Langmuir–Hinshelwood model is recommended for the hydrogen generation device modeling and design.

Acknowledgement

This work is supported in part by the National Science Council of Taiwan.

Appendix

The raw data is filtered by an exponential filter with a time constant of 0.42 min, i.e., \( F_{\text{H}_2} = \frac{F_{\text{H}_2}}{0.42s + 1} \). Fig. A1 shows the hydrogen generation rate before (in blue) and after (in red) filtering at 30 °C (Fig. A1(A)) and 60 °C (Fig. A1(B)). (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

Fig. A1 – Raw data and filtered data at (A) 30 °C and (B) 60 °C.

References


