Hydrogen generation from catalytic hydrolysis of alkaline sodium borohydride solution using Pt/C catalyst

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Abstract

Hydrogen generation from catalytic hydrolysis of aqueous NaOH-stabilized sodium borohydride solutions was investigated using platinum catalysts dispersed on active carbon, carbon black, and alumina supports. The Pt/C catalyst shows high catalytic activity due to the large BET surface area of active carbon support. The investigations on the effects of Pt loading and calcination temperature on the performance of Pt/C catalyst were also performed. After filtration from the reaction medium and rinsing with water, the used catalyst was re-evaluated and almost the same catalytic activities as fresh catalyst were obtained during several cycles.

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1. Introduction

Proton exchange membrane (PEM) fuel cells are attractive power sources for providing clean energy for transportation and stationary applications. However, their commercialization is still obstructed particularly by their high cost and a lack of hydrogen infrastructure. Recently, there is a growing demand for power systems for portable electronic equipments both in the consumer market and the military fields [1,2]. In that case, the storage and supply of fuel is an issue at least as big as the fuel cell performance. Hydrogen can be stored in tanks as compressed or liquefied H₂ or in hydrogen storage alloys. However, their volumetric and gravimetric efficiency are still too low to meet the requirements. The reforming of hydrocarbons is being considered as a viable method for “on-board” hydrogen production. But the difficulty in operating the high-temperature reforming process as well as the present of CO in the hydrogen stream which is a major poison to the anode electrocatalysts largely restricts its application in PEM fuel cells.

Recently, considerable efforts have been focused on the hydrogen generation from the hydrolysis of alkaline or alkaline earth metal hydrides (CaH₂, LiH, NaBH₄, MgH₂, LiAlH₄, etc.) [3]. Among these chemical hydrides, sodium borohydride (NaBH₄) offers the most promise for meeting the technical target of 6 wt% hydrogen capacity set by US Department of Energy (DOE) [4]. In addition, NaBH₄ is the least expensive metal hydride commercially available, and is easy to handle and store. The hydrolysis reaction can be initiated at ambient temperature and proceeds in an auto-thermal manner, indicating that no energy input is needed to sustain the reaction. By using catalysts, rapid hydrogen generation in response to demand can be achieved and its rate could also be easily controlled. The by-product of the hydrolysis reaction of sodium borohydride, NaBO₂, is environmentally benign and can be recycled as the raw material for regeneration to NaBH₄ [5]. These distinct advantages of hydrogen generation from NaBH₄ hydrolysis reaction make it an attractive and promising on-board hydrogen generation method for portable PEM fuel cells. Thus, extensive research has been...
performed on the hydrogen generation from hydrolysis of NaBH₄ solution [6–10].

To realize fast and controllable hydrogen generation and easy catalyst separation from reaction medium, heterogeneous catalysts with superior activity and durability should be developed. Up to now, the most studies on catalysts are mainly focused on the bulk metal [11], metal boronides [9,12], noble metal supported on anionic exchange resins [13] or TiO₂ [14], which are known as typical supports with low surface areas. The limited surface area of the heterogeneous catalyst restricts the catalyst performance as the catalyst activity is directly related to its surface area. In this study, the supported platinum catalysts were prepared using different supports with high surface areas and their performances for hydrolysis of base-stabilized NaBH₄ solution were investigated.

2. Experimental

2.1. Catalyst preparation

Active carbon was selected as the support due to its high surface area and high stability in a strongly alkaline medium. Pt/C catalyst was prepared by impregnation of the active carbon (BET surface area 1055 m²/g) with an aqueous solution of hexachloroplatinate hexahydrate. After drying at 80 °C in a vacuum oven for 8 h, the catalysts were calcined in 5% H₂–N₂ at 300 °C for 2 h. As prepared, Pt dispersed catalysts with metal contents of 2, 4, and 6 wt% were obtained, which are denoted as Pt/C-1, Pt/C-2, and Pt/C-3, respectively. To investigate the effect of calcination temperature on catalyst performance, a series of catalyst samples with the same metal content of 2 wt% but calcined at different temperatures were also prepared. The as-received catalysts calcined at 200 °C and 400 °C were denoted as Pt/C-4 and Pt/C-5, respectively. 2 wt% Pt/Al₂O₃ catalyst was prepared following the above procedure using γ-Al₂O₃ (BET surface area 248 m²/g) as the support. For comparison, 20 wt% Pt/C black (Carbot Vulcan XC-72) catalyst was also used as a catalyst. The catalyst was prepared by heating of ethylene glycol (EG) solutions of Pt salt. The procedure was as follows: 200 mg of Vulcan XC-72 was mixed with 50 ml ethylene glycol under ultrasonic treatment for 30 min. H₂PtCl₆/EG (6.5 ml; 48.6 mg, Pt) was slowly dropped into carbon containing beaker under ultrasonic treatment. The further treatment was performed by slow addition of 2 M NaOH/EG solution until the pH value was adjusted to above 12 and ultrasonated for 30 min. Then, the solution was heated in an oil bath at 130 °C for 3 h. The resulting suspension was filtered, and the residue was washed with deionized water and dried at 373 K over night in a vacuum oven.

2.2. Catalyst characterization

Nitrogen adsorption of the samples was measured at −196 °C with a Micromeritics ASAP 2010 surface area analyzer. The specific surfaces of the samples were determined from the N₂ adsorption–desorption isotherms by the BET method.

The Pt dispersion was determined from the H₂ chemisorption isotherm. This measurement was performed in a Micromeritics ASAP 2010 automated system. Prior to H₂ chemisorption, the sample was heated up to 300 °C under helium atmosphere and evacuated for 30 min. Then, the sample was flushed with H₂ at the same temperature for 30 min to ensure the overall reduction. After reduction, the sample was evacuated at 300 °C for 30 min to desorb any hydrogen and cooled down under vacuum to the adsorption temperature (30 °C) and evacuated for another 30 min. The concentration of exposed metal atoms on the surface was calculated by extrapolating the total and reversible adsorption isotherms to zero pressure, determining the amount of irreversible hydrogen chemisorbed from the difference, and assuming coverage of one H atom (irreversibly adsorbed) per reduced Pt atom exposed on the surface.

2.3. Catalyst testing

It is well-known that NaBH₄ undergoes self-hydrolysis at ambient temperature when stored in an aqueous solution. This hydrolysis can be greatly inhibited by the addition of base. In this work the generation of hydrogen was conducted using NaOH-stabilized NaBH₄ solutions. Fig. 1 shows a schematic diagram of the experimental setup. For simplification in catalyst screening, the hydrolysis reaction was carried out in batch operation and a 50 ml three-necked round-bottom flask was used as the reactor. The left-neck port was equipped with a thermometer inserted into the solution to monitor the temperature. In a typical H₂ generation experiment, 10 ml 5 wt% NaBH₄–5 wt% NaOH was initially put into the flask. The hydrolysis reaction was initiated by dropping the catalyst into the flask quickly through the right-neck port of the flask. The flask was immersed in a water bath to maintain the temperature within the range of 30 ± 0.2 °C. During the reaction, a wet gas meter was adopted to measure the cumulative volume of the generated hydrogen over time.
3. Results and discussion

It is known that the spontaneous hydrolysis of NaBH₄ can be greatly inhibited by addition of NaOH to the aqueous solution. Without using catalyst, the rate of hydrogen generation under the selected experimental conditions in this paper is negligible. However, the hydrolysis rate of NaBH₄ was accelerated dramatically in the presence of catalysts. The rate of hydrogen generation for various catalysts with 5 wt% NaBH₄–5 wt% NaOH solutions is shown in Fig. 2. To investigate the catalysts performance based on the same metal amounts, 0.025 g of Pt/Vulcan XC-72 catalyst and 0.25 g of Pt/C and Pt/Al₂O₃ catalysts were adopted because the platinum content of Pt/Vulcan XC-72 is 10 times that of the other two catalysts. The efficiency of catalysts is evaluated by the volume of hydrogen generated in a given time by the equivalent quantities of the active catalyst metals. As shown in Fig. 2, the reaction rate significantly depends on the catalysts employed. The hydrogen generation rate on active carbon supported catalyst is much higher than that on Al₂O₃ and Vulcan XC-72 supported catalysts. It must be noted that the active carbon and Al₂O₃ supports are crushed and sieved from the commercial supports and the Pt/C and Pt/Al₂O₃ catalysts are in the form of small particles of 20–40 mesh. In contrast to it, the Pt/Vulcan XC-72 catalyst is in the form of fine powders. It is suggested that finely divided powders are easily suspend in a liquid reaction medium, giving rise to a high external surface, low diffusion distances in the porous structure of each individual particle and consequently low mass transfer limitations [15]. However, the Pt/Vulcan XC-72 catalyst did not exhibit higher performance than other catalysts as expected, indicating the mass transfer play minor role under the employed reaction conditions. It is well documented that filling the support pores of carbons with the solution during the impregnation is accompanied by an intensive adsorption of H₂PtCl₆, the capacity of which increases linearly with an increase in their specific surface area [16]. Therefore, the good performance of Pt/C catalyst might be due to that the active carbon possesses very large BET surface area compared with the other two supports (Table 1). The cumulative volume of hydrogen generated with time for various catalysts is given in Fig. 3. It is shown that almost all the NaBH₄ hydrolyzed within 45 min on active carbon supported catalyst. However, only about 81% and 64% of hydrogen yields for the Al₂O₃ and Vulcan XC-72 supported catalysts, respectively, were obtained within the same time. According to these results, the characteristics of Pt/C catalyst were investigated in detail. The metal dispersions and the corresponding average particle sizes for different Pt/C catalysts are shown in Table 2.

Fig. 4 shows a plot of H₂ volumes generated as a function of time from a NaBH₄ solution catalyzed by Pt/C catalysts calcined in a reductive atmosphere at 200, 300, and 400 °C, respectively. As shown in Fig. 4, the hydrogen

![Fig. 2. Hydrogen generation rate with different catalysts in 10 ml 5 wt%NaBH₄–5 wt%NaOH solution.](image)

![Fig. 3. Cumulative hydrogen generation rate with different catalysts in 10 ml 5 wt%NaBH₄–5 wt%NaOH solution.](image)

![Fig. 4. H₂ volumes generated as a function of time from a NaBH₄ solution catalyzed by Pt/C catalysts calcined in a reductive atmosphere at 200, 300, and 400 °C, respectively.](image)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pt loading (%</th>
<th>Calcination temperature (°C)</th>
<th>Pt dispersion (%)</th>
<th>Mean Pt particle size (nm)</th>
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<tr>
<td>Pt/C-1</td>
<td>2.0</td>
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<td>35.6</td>
<td>2.7</td>
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<tr>
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<tr>
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<td>300</td>
<td>32.6</td>
<td>2.9</td>
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<tr>
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<td>32.1</td>
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<tr>
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<td>400</td>
<td>23.4</td>
<td>4.1</td>
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</table>

Table 1: BET surface area and porosity data

<table>
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<tr>
<th>Support</th>
<th>Surface area (m²/g)</th>
<th>Average pore diameter (nm)</th>
<th>Pore volume (cm³/g)</th>
</tr>
</thead>
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<tr>
<td>γ-Al₂O₃</td>
<td>0.45</td>
<td>7.2</td>
<td>248</td>
</tr>
<tr>
<td>Active carbon</td>
<td>0.61</td>
<td>3.2</td>
<td>1055</td>
</tr>
<tr>
<td>Vulcan XC-72</td>
<td>0.43</td>
<td>7.5</td>
<td>250</td>
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Table 2: Pt dispersions and crystallite sizes of the catalysts
evolution starts immediately without any induction period. The Pt/C-1 catalyst calcined at 300 °C exhibited better activity than Pt/C-4 and Pt/C-5 catalysts. It was reported by Kojima et al. [8] that the hydrogen generation rate increases as the Pt crystallite size decreases at the range of 2–50 nm and the maximum value was found for the catalyst with Pt particle size below 2 nm. Compared with Pt/C-4 and Pt/C-5 catalysts, the Pt/C-1 catalyst possesses high metal dispersion and small Pt crystallite size (Table 2), leading to its high performance. This indicated that appropriate calcination temperature plays an important role in preparing carbon supported platinum catalyst with optimum metal dispersions.

Fig. 5 shows the effect of Pt loading on the catalyst performance. Significant differences in hydrogen generation activities were observed for those Pt/C catalysts having different Pt loadings but almost similar Pt dispersions. As expected, the high Pt loading can produce more catalytic sites which are active for the hydrolysis of NaBH₄. It is apparent that the substrate surface is not completely occupied by platinum in these Pt/C catalysts. Therefore, increased Pt loadings are needed to optimize the reaction rate.

Catalyst durability is crucial for sodium borohydride based hydrogen application. Fig. 6 shows the cycle behavior on H₂ generation activity for 6 wt% Pt/C catalyst. After each experiment, the used catalyst was separated, washed with deionized water, and dried again. It is evident that the catalyst displayed very similar activity for hydrolysis of NaBH₄ during the six-cycle operations. It has been suggested that the precipitation of NaBO₂, a by-product of the hydrolysis reaction, would block the catalyst sites, thereby deteriorate the hydrolysis of NaBH₄ [7]. In this study, the concentration of NaBH₄ (5 wt%) is much lower than its saturated solubility (approximately 35 wt% at 23 °C), and the product of NaBO₂ may not exceed its solubility limit, thus no precipitation of NaBO₂ was observed. In addition, the rinsing of the used catalyst with water can help removing the NaBO₂ possibly remained on the pores of the used catalyst. In practice, another experiment results on successive hydrogen generation conducted in our lab have shown that the temperature of reaction medium can exceed 80 °C due to the exothermic reaction characteristics of the NaBH₄ hydrolysis reaction. It is suggested that the hot caustic reaction media coupled with possibilities of formation of large bulky sodium metaborate by-product constitutes significant challenges for chemical and mechanical stability of the catalyst [17]. Thus, the stability of Pt/C catalyst during long operating period for successive hydrogen generation, particularly in an auto-thermal reaction condition, needs to be studied in detail. Searching for new metal catalysts and optimizing their catalytic performance for successive hydrogen generation are in progress.

4. Conclusion

Hydrogen generation by hydrolysis of aqueous NaOH-stabilized sodium borohydride solutions has been studied using Pt catalysts supported on active carbon, alumina
and Vulcan XC-72. Active carbon supported catalyst exhibits the highest catalytic activity and the maximum hydrogen generation rate of 8.5 l/min · g Pt was achieved. The performances of Pt/C catalysts increase with Pt loading in the investigated range. The calcination temperature exhibits evident influence on the catalyst performance.

Acknowledgement

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References