NaBH₄ 수용액 분해 수소 발생용 최적 촉매 개발

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Development of an Catalyst for Hydrolysis of Aqueous Sodium Borohydride Solution

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Abstract : Hydrogen generation by the hydrolysis of aqueous sodium borohydride (NaBH₄) solutions was studied using IRA-400 anion resin dispersed Pt, Ru catalysts and Lithium Cobalt oxide (LiCoO₂) supported Pt, Ru and PtRu catalysts. The performance of the LiCoO₂ supported catalysts is better than the ion exchange resin dispersed catalysts. There is a marked concentration dependence on the performance of the LiCoO₂ supported catalysts and the hydrogen generation rate goes down if the borohydride concentration is increased beyond 10%. The efficiency of PtRu- LiCoO₂ is almost double that of either Ru-LiCoO₂ or Pt-LiCoO₂ for NaBH₄ concentrations up to 10%.

1. Introduction

Proton exchange membrane fuel cells (PEMFC) are on the verge of commercialization and expected to replace the internal combustion engine in transportation as well as residential power production. However, efficient operation of the PEMFC needs hydrogenin pure form. Though hydrogen is mainly produced from the reformation of hydrocarbon feed stocks, the efficiency of the fuel cell is affected due to the presence of carbon monoxide which poisons the fuel cell catalyst. Moreover, low cost, safe hydrogen storage technologies are yet to be developed.

In view of the above, on site hydrogen production from the chemical hydrides is attractive, since the hydrogen will be purer without any fuel cell poisons [1,2]. Among the hydrides, sodium borohydride, NaBH4 is desirable due to its high hydrogen storage efficiency of 10.80% and the excellent stability of its alkaline solutions [3]. Schlesinger et al. [4] have reported that the alkaline borohydride solutions undergo hydrolysis in presence of various transition-metal catalysts to produce hydrogen. Based on this, various catalysts of Pt, Ru, Ni, Co etc., have been developed for hydrogen production from borohydride solutions and reported in recent years [5-7].

However, the application of Pt-alloy catalysts for the hydrolysis of NaBH4 is not reported in the literature.

The adsorption characteristics and the resulting catalytic activity of Pt-alloy catalysts may be better than the source metals. This prompted us to study PtRu as the hydrolysis catalyst for hydrogen generation from aqueous NaBH4 solutions as well as to investigate the influence of the support materials on catalysis. The IRA-400 anion exchange resin dispersed Pt, Ru catalysts as well as the Lithium Cobalt (II) oxide, LiCoO2 supported Pt, Ru and PtRu catalysts were prepared and tested for the borohydride hydrolysis. The preliminary results are discussed in this communication.

2. Results and Discussion

The rate of hydrogen generation for various catalysts

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with 5%NaBH4 (5%NaOH) solution is given in Fig.1. The hydrogen generation rate on LiCoO2 supported catalysts is higher than that of the ion exchange resin dispersed catalysts. The higher efficiency of LiCoO2 supported catalysts is reported to be due to the adsorption of water on the surface of the oxide support. Since, the H- from BH4- discharges electron through the catalyst which reduces H+ from water to generate hydrogen [7]. Hence, availability of water in the proximity of catalyst sites will facilitate the hydrolysis. The hydrogen generation rate with PtRu-LiCoO2 is almost double of that obtained with Pt-LiCoO2 and Ru-LiCoO2 catalysts. The superior performance of PtRu-LiCoO2 catalyst may be due to the favorable adsorption characteristics of the alloy catalyst coupled with the synergic effect of the oxide support.

The specific gravity of the 5%NaBH4 (5%NaOH) solution was determined to be 1.039g/ml. Considering the 10.80% hydrogen storage efficiency of NaBH4, 25ml of the above solution will contain 3.333 litters of hydrogen. The cumulative volume of hydrogen generated with time for various catalysts is given in Fig.2. With PtRu-LiCoO2 as the hydrolysis catalyst, almost all the NaBH4 got hydrolyzed within 15 min. Where as, it took around 30 and 45min. with Ru-LiCoO2 and Pt-LiCoO2 respectively. The cumulative hydrogen production rate of Pt-IRA-400 catalyst is slightly lesser than that obtained with Pt-LiCoO2 and Ru-LiCoO2 catalysts. In the case of Ru-IRA- 400 resin supported catalyst, only about 50% of the NaBH4 got hydrolyzed in 45min.

If the above performances could be sustained in concentrated NaBH4 solutions, the LiCoO2 supported catalysts especially the PtRu-LiCoO2 will be an excellent candidate to generate large quantity of hydrogen at the maximum rate from very small volume of concentrated NaBH4 solutions. In order to ascertain this, hydrogen generation experiments were carried out with various concentrations of NaBH4 solutions. The results will be discussed in the following sections.
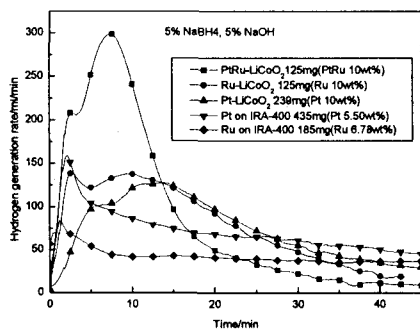

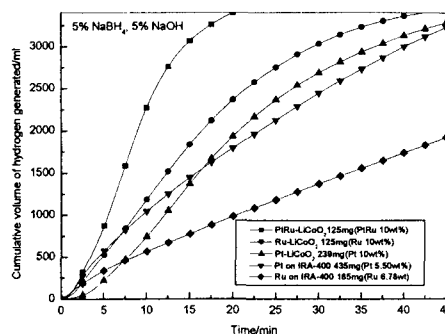Fig. 1 Hydrogen generation with different catalysts in 5%NaBH4 (5%NaOH) solution

Fig.2 The cumulative hydrogen generation rate with different catalysts in 5%NaBH4, 5%NaOH solution

The cumulative volume of hydrogen generated for Pt-IRA- 400 and Ru-IRA- 400 resin catalysts with various NaBH4 concentrations are plotted in Fig. 3. It can be seen that the hydrogen generation profile is more or less same on both the catalysts. The hydrogen generation rate with Pt-IRA- 400 is higher than that of Ru-IRA- 400 even though the catalyst metal equivalents are same. The hydrogen generation rate increased when the borohydride concentration was increased from 5 to 10%. The slower rate of hydrogen generation with 5% NaBH4 solution might be due to mass transport limitations inside the resin beads. The hydrogen generation rate was slightly reduced when the NaBH4 concentration was increased above 10%. This may be due to the increase in pH of the concentrated solutions with the resulting increase in their stability. However, the above catalysts can be used to produce hydrogen at a steady rate from 10-20% NaBH4 solutions.
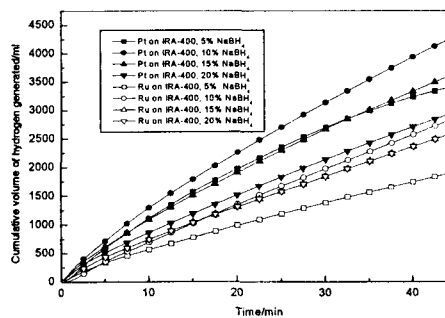

Fig.3 The effect of borohydride concentration on cumulative volume of hydrogen generated with Pt-IRA-400 and Ru-IRA-400 resin catalysts, Pt-IRA-400: 435mg (Pt 5.5 wt%) ; Ru-IRA-400: 185mg (Ru 6.78 wt %)

The effect of NaBH4 concentration on the cumulative hydrogen volumes with Ru-LiCoO2 and Pt-LiCoO2 catalysts are plotted in Fig.4. As noted earlier, for the same molar quantity of the active catalysts, hydrogen generation rate with the LiCoO2 supported catalysts is

higher than that of the IRA- 400 anion resin dispersed catalysts. Moreover, hydrogen generation rate with Ru-LiCoO2 is higher than that of Pt-LiCoO2 which is opposite to that observed with the IRA-400 resin dispersed catalysts. The above results show that the influence of LiCoO2 support material on the catalytic enhancement is more pronounced on Ru than Pt. Both Ru-LiCoO2, Pt-LiCoO2 show a marked concentration dependence which is also quite different from that observed on the ion exchange resin dispersed catalysts.
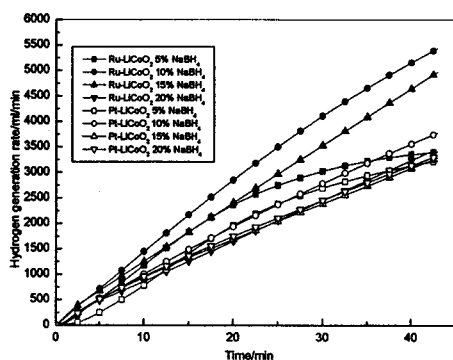

Fig.4 The effect of borohydride concentration on the cumulative volume of hydrogen generated with Ru-LiCoO2 and Pt-LiCoO2 catalysts, Ru-LiCoO2 : 125mg (Ru 10 wt%) ; Pt-LiCoO2 : 239mg (Pt 10.0 wt %

The hydrogen generation profile was similar on both the catalysts for the 5% NaBH4 solution. Even though, the temperature was maintained at a constant value, the rate of hydrogen generation was continuously increasing with time. Similar observation has been reported by the earlier workers on the oxide supported catalysts [7]. The exact cause for the above phenomenon is not clear at the moment. This may be due to the generation of additional catalyst sites by the reduction of surface oxides or the effect of changing solution composition on the rate of hydrolysis.

With 10% NaBH4 solution, the hydrogen generation profile was different on both the catalysts. In the case of Ru-LiCoO2 catalyst, the hydrogen generation rate increased when compared with that of 5% NaBH4 solution. But the maximum rate of hydrogen production could not be sustained for longer time and the rate gradually decreased with time, may be due to the decrease in concentration of NaBH4 solution. But with Pt-LiCoO2 catalyst, the hydrogen generation rate was reduced when compared with that of the 5% NaBH4 solution. When the NaBH4 concentration was increased beyond 10%, the hydrogen generation rate was decreased on both the catalysts, but the effect was more pronounced on Ru-LiCoO2. The effect of NaBH4 concentration on the rate of hydrogen production was less dramatic with Pt-LiCoO2 at higher concentrations. The hydrogen generation rate was more or less same for both 15% and 20% NaBH4 solutions. . However, it can be noted that

Ru-LiCoO2 will be an efficient catalyst up to borohydride concentration of 15%.

3. Conclusions

The performance of LiCoO2 supported catalysts is better than the ion exchange resin dispersed catalysts. There is a marked NaBH4 concentration dependence on the performance of LiCoO2 supported catalysts. The performance of PtRu-LiCoO2 is double than that of Ru-LiCoO2. The superior performance of the PtRu-LiCoO2 catalyst may be due to the favorable adsorption characteristics of the alloy coupled with the catalytic enhancement due to the LiCoO2 support. The LiCoO2 supported catalysts especially the PtRu-LiCoO2 will be an excellent candidate for the development of commercial catalysts for hydrogen generation from NaBH4 solutions of up to 15% concentration. It will be an ideal catalyst in stationary applications where handling of large volume of NaBH4 solutions may not be a constraint.

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