Short communication

PtRu-LiCoO$_2$—an efficient catalyst for hydrogen generation from sodium borohydride solutions

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Abstract

Hydrogen generation by the hydrolysis of aqueous sodium borohydride (NaBH$_4$) solutions is studied using IRA-400 anion resin dispersed Pt, Ru catalysts and lithium cobalt oxide (LiCoO$_2$) supported Pt, Ru and PtRu catalysts. The performance of the LiCoO$_2$ supported catalysts is better than that of ion-exchange resin dispersed catalysts. There is a marked concentration dependence on the performance of the LiCoO$_2$ supported catalysts and the hydrogen generation rate decreases if the borohydride concentration is increased beyond 10 wt.%. The efficiency of PtRu-LiCoO$_2$ is almost double that of either Ru-LiCoO$_2$ or Pt-LiCoO$_2$ for NaBH$_4$ concentrations up to 10 wt.%.
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1. Introduction

Proton-exchange membrane fuel cells (PEMFCs) are on the verge of commercialization and are expected to replace the internal-combustion engine in transportation applications as in residential power production [1,2]. For efficient operation, however, the PEMFC requires hydrogen in a pure form. Though hydrogen is produced mainly from the reformation of hydrocarbon feedstocks, the efficiency of the fuel cell is affected due to the presence of carbon monoxide that poisons the fuel-cell catalyst. Moreover, low cost, safe hydrogen storage technologies have yet to be developed.

In view of the above, on-site hydrogen production from chemical hydrides is attractive, since the hydrogen will be pure and without any fuel-cell poisons [3–5]. Among the hydrides, sodium borohydride (NaBH$_4$) is desirable due to its high hydrogen content of 10.57 wt.% and the excellent stability of its alkaline solutions [6]. Schlesinger et al. [7] have reported that alkaline borohydride solutions undergo hydrolysis in the 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 [8–10].

The application of Pt-alloy catalysts for the hydrolysis of NaBH$_4$ has not been reported, despite the possibility that the adsorption characteristics and the resulting catalytic activity of such catalysts may be better than the source metals. This has prompted the study presented here of PtRu as a hydrolysis catalyst for hydrogen generation from aqueous NaBH$_4$ solutions, as well as the influence of the support materials on catalysis. IRA-400 anion-exchange resin dispersed Pt, Ru catalysts as well as lithium cobalt (II) oxide supported Pt, Ru and PtRu catalysts have been prepared and tested for borohydride hydrolysis.

2. Experimental

2.1. Catalyst preparation

2.1.1. Preparation of IRA-400 anion-exchange resin dispersed ruthenium and platinum catalysts

A ruthenium, catalyst dispersed on IRA-400 anion-exchange resin beads was prepared by ion exchange [8]. The

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Ru precursor, RuCl$_3$ (99.91 wt.%, Alfa-Aesar), was dissolved in deionized water and acidified with HCl. The acidified solution was added to a weighed amount of IRA-400 (Aldrich Chemicals) anionic resin beads. The resulting slurry was allowed to stand at ambient temperature for 24 h with occasional stirring. The impregnated resin was then reduced with 5 wt.% NaBH$_4$ solution. The slurry was filtered and the resin beads were then dried at 50 °C. The Ru content was calculated by elemental analysis (ICP) and found to be 6.78 wt.%. The platinum, dispersed catalyst was prepared by the same procedure using H$_2$PtCl$_6$ (99.90 wt.%, Alfa-Aesar) as the precursor. The Pt content was calculated by elemental analysis (ICP) and found to be 5.50 wt.%. The catalyst beads were then sieved using 50 μm sieve, packed in a 30 μm Titanium mesh container and used for the hydrogen-generation experiments.

2.1.2. *Preparation of lithium cobalt oxide (LiCoO$_2$) supported Pt, Ru and PtRu catalysts*

RuCl$_3$ and H$_2$PtCl$_6$ were used as precursors for catalyst preparation. The required amount of LiCoO$_2$ (Aldrich Chemicals) was suspended in deionized water and agitated with a magnetic stirrer. The precursors were dissolved in a sufficient quantity of deionized water and added to the LiCoO$_2$ suspension in a drop-wise manner. Then, the suspension was stirred for 30 min., heated to 80 °C and reduced with 5 wt.% NaBH$_4$ solution. The catalyst was filtered using a G4 sintered disc and dried at 80 °C under vacuum. The catalysts were prepared with 10 wt.% metal loading. The atomic percentages of Pt, Ru in the PtRu catalyst were calculated from ICP analysis and found to be 48.57 and 51.43 at.%, respectively.

For the hydrogen-generation experiments, a weighed amount of the catalyst (0.123 meq of active metal for Pt-LiCoO$_2$, Ru-LiCoO$_2$, and 0.084 meq for PtRu-LiCoO$_2$) was mixed with an equivalent quantity of deionized water. A 30 wt.% PTFE suspension was added to obtain a PTFE content equivalent to 20 wt.% of the catalyst. The contents were sonicated at room temperature for 30 min to achieve a homogeneous slurry. The slurry was then coated over a nickel mesh (4 cm × 2 cm) and dried at 105 °C to determine the catalyst loading. Then, it was heat treated at 320 °C for 30 min and used for the hydrogen generation-experiments.
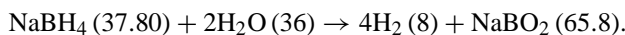
2.2. *Hydrogen generation*

In a typical hydrogen generation experiment, 25 cm^3 of the NaBH$_4$ solution was placed in a thermostatted tubular glass vessel. The catalyst template was tied to a stainless-steel rod and immersed into the solution through a rubber septum. A thermocouple was also inserted through the septum to measure the temperature. The hydrogen flow was measured using a mass flow meter. The output from the mass flow meter was connected to a Mobile recorder (MV100, Yokogawa Electric Corporation) for data storage. The temperature of the hydrolysis solution was maintained at 25 °C.

3. Results and discussion

The rate of hydrogen generation for various catalysts with 5 wt.% NaBH$_4$ (5 wt.% NaOH) solution is given in Fig. 1. The efficiency of catalysts is determined by the volume of hydrogen generated in a given time by the equivalent quantities of the active catalyst metals. The hydrogen-generation rate on LiCoO$_2$ supported catalysts is higher than that on ion-exchange resin dispersed catalysts. The higher efficiency of the LiCoO$_2$ supported catalysts is considered to be due to the adsorption of water on the surface of the oxide support. This is because the H$^-$ from BH$_4^-$ discharges electrons through the catalyst which reduces H$^+$ from water to generate hydrogen [10]. Hence, availability of water in the proximity of catalyst sites will facilitate the hydrolysis. The hydrogen-generation rate with PtRu-LiCoO$_2$ is almost double of that with Pt-LiCoO$_2$ and Ru-LiCoO$_2$ catalysts. The superior performance of the PtRu-LiCoO$_2$ catalyst may be due to the favourable adsorption characteristics of the alloy catalyst coupled with the synergic effect of the oxide support.

In the presence of catalysts, NaBH$_4$ will react with water to produce hydrogen according to the following reaction:

$$NaBH_4 \ (37.80) + 2H_2O \ (36) \rightarrow 4H_2 \ (8) + NaBO_2 \ (65.8).$$

The relative density of the 5 wt.% NaBH$_4$ (5 wt.% NaOH) solution was determined to be 1.039 g cm^{-3}. Twenty-five cubic centimetre of this solution will have 1.30 g NaBH$_4$ which can generate 0.27 g of hydrogen. When converted to volume, the generated hydrogen will be equivalent to 3.333 l at 25 °C. The cumulative volume of hydrogen generated with time for various catalysts is given in Fig. 2. With PtRu-LiCoO$_2$ as the hydrolysis catalyst, almost all the NaBH$_4$ becomes hydrolyzed within 15 min. Whereas, it takes around 30 and 45 min with Ru-LiCoO$_2$ and Pt-LiCoO$_2$, respectively. The cumulative hydrogen production rate of Pt-IRA-400 catalyst is slightly lesser than that obtained with Pt-LiCoO$_2$ and Ru-LiCoO$_2$ catalysts. For the Ru-IRA-400 resin supported

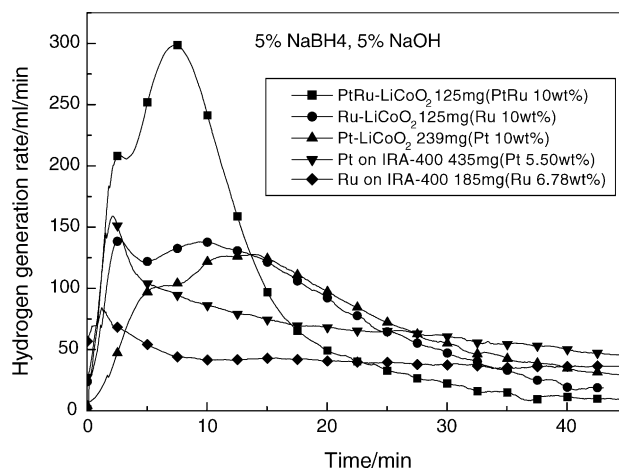Fig. 1. Hydrogen generation with different catalysts in 5 wt.% NaBH$_4$ (5 wt.% NaOH) solution.
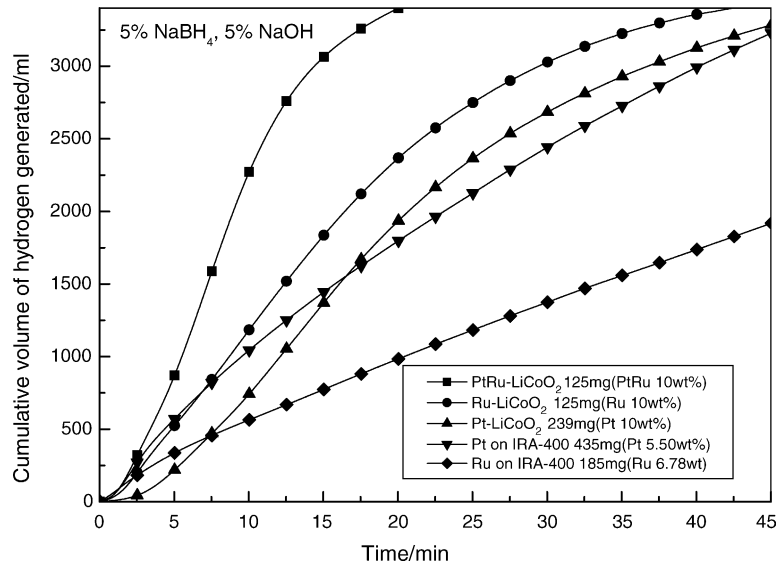
Fig. 2. Cumulative hydrogen generation rate with different catalysts in 5 wt.% NaBH$_4$, 5 wt.% NaOH solution.

catalyst, only about 50 wt.% of the NaBH$_4$ got hydrolyzed in 45 min.

If the above performances can be sustained in concentrated NaBH$_4$ solutions, the LiCoO$_2$ supported catalysts, especially PtRu-LiCoO$_2$, will be an excellent candidate to generate large quanties of hydrogen at the maximum rate from a very small volume of concentrated NaBH$_4$ solution. In order to ascertain this, hydrogen generation experiments were performed with various concentrations of NaBH$_4$ solutions. The results are discussed in the following sections.

The hydrogen generation rate for Pt-IRA-400 and Ru-IRA-400 resin catalysts with various NaBH$_4$ concentrations are plotted in Fig. 3. The respective figures of the cumulative volume of hydrogen generated are given in Fig. 4. 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 with Ru-IRA-400, even though the catalyst metal equivalents are same. The hydrogen generation rate increases when the borohydride concentration is raised from 5 to 10 wt.%. The slower rate of hydrogen generation with 5 wt.% NaBH$_4$ solution may be due to mass-transport limitations inside the resin beads. The hydrogen generation rate is slightly reduced when the NaBH$_4$ concentration is increased above 10 wt.%. This may be due to an increase in the pH of the concentrated solutions with a resulting increase in their stability. The above catalysts can, however, be used to produce hydrogen at a steady rate from 10 to 20 wt.% NaBH$_4$ solutions.
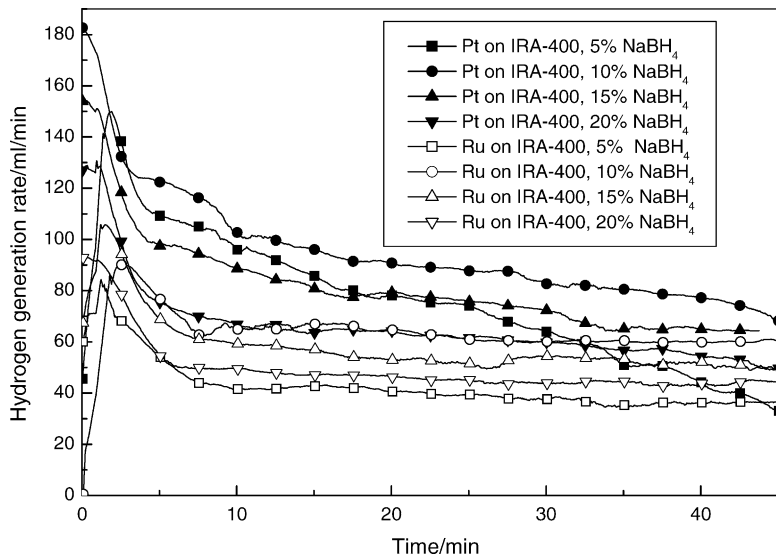

Fig. 3. Effect of borohydride concentration on hydrogen generation with Pt-IRA-400 and Ru-IRA-400 resin catalysts, Pt-IRA-400: 435 mg (Pt 5.5 wt.%); Ru-IRA-400: 185 mg (Ru 6.78 wt.%).
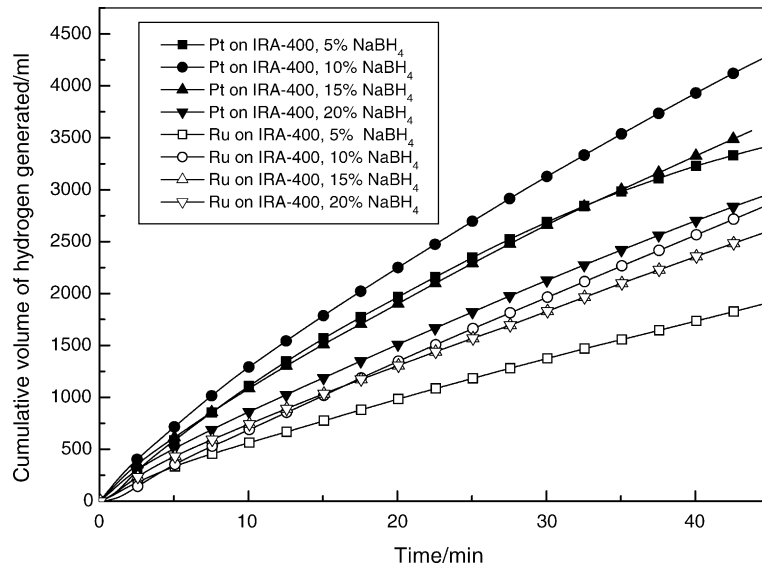
Fig. 4. Effect of borohydride concentration on cumulative volume of hydrogen generated with Pt-IRA-400 and Ru-IRA-400 resin catalysts, Pt-IRA-400: 435 mg (Pt 5.5 wt.%); Ru-IRA-400: 185 mg (Ru 6.78 wt.%).

The effect of $NaBH_4$ concentration on the hydrogen generation rate with Ru-LiCoO$_2$ and Pt-LiCoO$_2$ catalysts is presented in Fig. 5. The respective cumulative hydrogen volumes are given in Fig. 6. As noted earlier, for the same molar quantity of the active catalysts, the hydrogen generation rate with the LiCoO$_2$ supported catalysts is higher than that with the IRA-400 anion resin dispersed catalysts. Moreover, the hydrogen generation rate with Ru-LiCoO$_2$ is higher than that with Pt-LiCoO$_2$, which is opposite to that observed with the IRA-400 resin dispersed catalysts. These results show that the influence of LiCoO$_2$ support material on the catalytic enhancement is more pronounced on Ru than Pt. Both Ru-LiCoO$_2$, Pt-LiCoO$_2$ show a

marked concentration dependence that is also quite different from that observed on the ion-exchange resin dispersed catalysts.

The hydrogen generation profile is similar on both the catalysts for the 5 wt.% $NaBH_4$ solution. Even though the temperature is maintained at a constant value, the rate of hydrogen generation continuously increases with time. A similar observation has been made by other workers for oxide supported catalysts [10]. 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 to the effect of changing solution composition on the rate of hydrolysis.
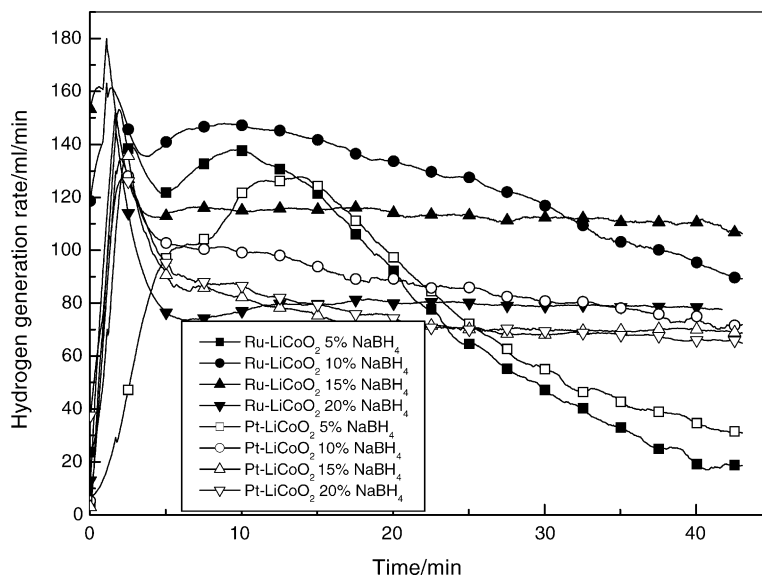

Fig. 5. Effect of borohydride concentration on hydrogen generation with Ru-LiCoO$_2$ and Pt-LiCoO$_2$ catalysts, Ru-LiCoO$_2$: 125 mg (Ru 10 wt.%); Pt-LiCoO$_2$: 239 mg (Pt 10.0 wt.%).
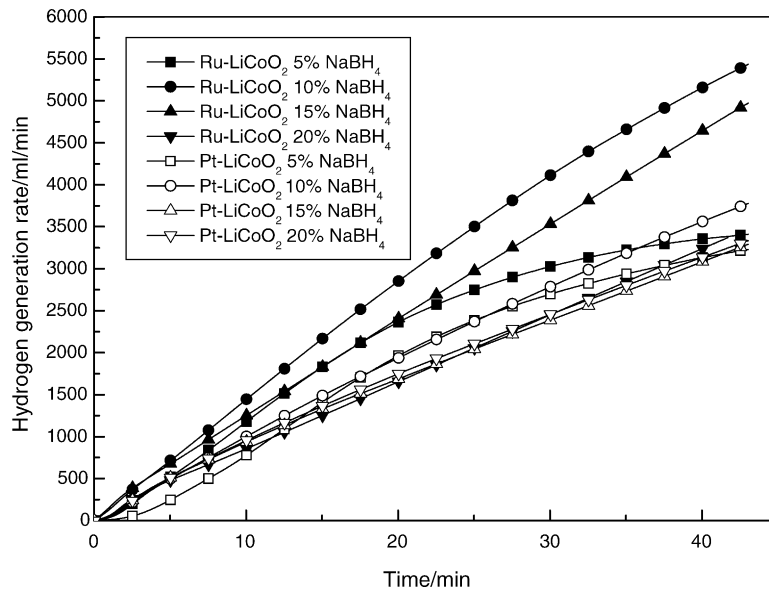
Fig. 6. Effect of borohydride concentration on the cumulative volume of hydrogen generated with Ru-LiCoO$_2$ and Pt-LiCoO$_2$ catalysts, Ru-LiCoO$_2$: 125 mg (Ru 10 wt.%); Pt-LiCoO$_2$: 239 mg (Pt 10.0 wt.%).

With 10 wt.% NaBH$_4$ solution, the hydrogen generation profile is different on both types of catalyst. For the Ru-LiCoO$_2$ catalyst, the hydrogen generation rate is greater than that with 5 wt.% NaBH$_4$ solution. The maximum rate of hydrogen production cannot, however, be sustained for a longer time and the rate gradually decreases with time. This may be due to the decrease in the concentration of the NaBH$_4$ solution. With Pt-LiCoO$_2$ catalyst, the hydrogen generation rate is lower than that for the 5 wt.% NaBH$_4$ solution. When the NaBH$_4$ concentration is increased beyond 10 wt.%, the hydrogen generation rate is decreased on both types of catalyst, but the effect is more pronounced on Ru-LiCoO$_2$. The effect of NaBH$_4$ concentration on the rate of hydrogen production

is less dramatic with Pt-LiCoO$_2$ at higher concentrations, i.e., it is more or less same for both 15 and 20 wt.% NaBH$_4$ solutions. It can be noted, however, that Ru-LiCoO$_2$ will be an efficient catalyst for borohydride concentrations up to 15 wt.%.

The hydrogen generation profile and the respective volume of cumulative hydrogen generated with the PtRu-LiCoO$_2$ catalyst is given in Figs. 7 and 8, respectively. The profile is the same as that obtained with either Ru-LiCoO$_2$ or Pt-LiCoO$_2$ catalysts. A remarkable observation is that the hydrogen generation rate with 5 and 10 wt.% NaBH$_4$ solutions is more than double that obtained with Ru-LiCoO$_2$. Nevertheless, the hydrogen generation rate is drastically reduced with increase
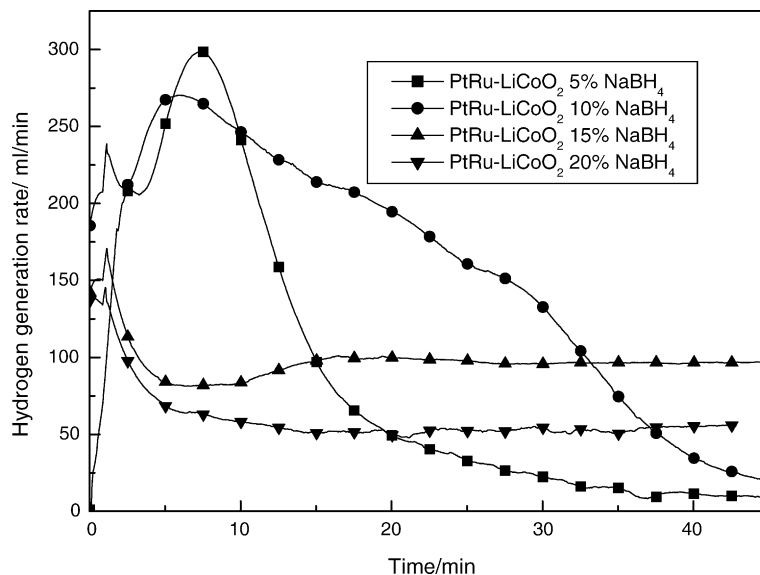

Fig. 7. Effect of borohydride concentration on hydrogen generation with 125 mg PtRu-LiCoO$_2$ catalyst (PtRu 10 wt.%).
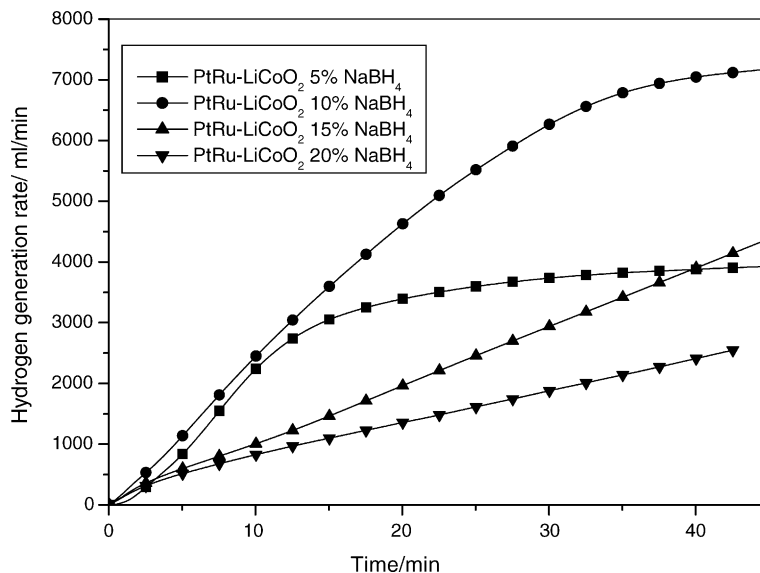
Fig. 8. Effect of borohydride concentration on cumulative volume of hydrogen generated with 125 mg PtRu-LiCoO$_2$ catalyst (PtRu 10 wt.%).

in NaBH$_4$ concentration and the rate with 20 wt.% NaBH$_4$ solution is less than that obtained with either Ru-LiCoO$_2$ or Pt-LiCoO$_2$ catalysts for the same NaBH$_4$ concentration. These results demonstrate that PtRu-LiCoO$_2$ is an excellent catalyst for hydrogen generation from dilute NaBH$_4$ solutions.

The above studies establish the marked influence of the LiCoO$_2$ support on the catalytic efficiency of Pt, Ru and PtRu catalysts. The LiCoO$_2$ support can enhance the performance of the catalysts by its own catalytic active sites, due to Brønsted acidic surface functional groups and metal–support interaction [11,12]. The number of Brønsted acidic surface functional groups will be reduced, however, at higher concentrations of NaBH$_4$ due to the increased alkalinity of the solution. If the catalytic enhancement by the LiCoO$_2$ support is mainly due to the surface acidic functional groups, the performance of the catalysts will decrease with increase in concentration of NaBH$_4$. The performance of the catalysts was indeed drastically reduced with increase in concentration of NaBH$_4$. Hence, the observations reveal that LiCoO$_2$ enhances the performance of the catalysts mainly by the Brønsted acidic surface functional groups. But the catalytic enhancement is not uniform for all the catalysts. In the case of PtRu-LiCoO$_2$, the alloying itself might also contribute in addition to the LiCoO$_2$ support, and hence gives rise to the superior performance of this catalyst.

4. Conclusions

Hydrogen generation by hydrolysis of NaBH$_4$ has been studied using IRA-400 anion resin dispersed Pt, Ru catalysts and LiCoO$_2$ supported Pt, Ru and PtRu catalysts. The performance of LiCoO$_2$ supported catalysts is better than that of the ion-exchange resin dispersed catalysts.

There is a marked NaBH$_4$ concentration dependence on the performance of LiCoO$_2$ supported catalysts. The performance of PtRu-LiCoO$_2$ is double that of Ru-LiCoO$_2$. The superior performance of this catalyst may be due to the favorable adsorption characteristics of the alloy coupled with catalytic enhancement due to the LiCoO$_2$ support.

LiCoO$_2$ supported catalysts, especially PtRu-LiCoO$_2$, are potentially be an excellent candidates for the development of commercial catalysts for hydrogen generation from NaBH$_4$ solutions of up to 15 wt.% concentration. In particular, it may prove to be an ideal catalyst for stationary applications where handling of a large volume of NaBH$_4$ solutions may not be a constraint.

Further studies of PtRu catalysts with various support materials are in progress to develop catalysts with superior performance.

Acknowledgement

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