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Development of an active platine-based catalyst for the reaction of H_2 production from $NaBH_4$

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Abstract

In this study, the effects of preparation parameters for $LiCoO_2$ support and reaction conditions on H_2 production from $NaBH_4$ over 1.5 wt% Pt/$LiCoO_2$ were studied to develop an effective Pt/$LiCoO_2$ catalyst. $LiCoO_2$ was prepared by solid-state reaction of lithium and cobalt precursors. Equal amount of heat generating material to the reactants was determined as optimum amount. Samples calcined between 500 and 700 °C almost gave approximate H_2 production rates, but samples calcined at higher temperatures showed less activity. Investigated hydrolysis reaction parameters were $NaBH_4$ and NaOH concentrations, reaction temperature and catalyst amount. Decreasing $NaBH_4$ and NaOH concentrations increased the production rate of H_2. Also the increase in reaction temperature and catalyst amount increased the production rate of H_2, as expected.

Keywords: $NaBH_4$; Hydrogen production; Pt/$LiCoO_2$; $LiCoO_2$ preparation; Solid-state reaction

1. Introduction

In the search for an efficient, clean and safe energy resource, hydrogen draws attention with its advantages such as high energy density (142 kJ/g) and high electronegative properties. The hydrogen production technologies have been developed parallel to the developments in fuel cell technologies. As a pollution-free and a high efficiency energy conversion device, fuel cells are considered to be one of the most attractive energy conversion technologies of the future. Especially, PEM fuel cells are attractive for producing clean energy by using hydrogen as fuel. Hydrogen needed for PEM fuel cell can be produced from a source on demand, since a low cost and safe hydrogen storage method has not been developed yet. Currently used hydrogen is mostly produced from natural gas via catalytic reforming, which produces a mixture of H_2, H_2O, N_2, CO_2, and CO [1,2]. PEM fuel cells are sensitive to the concentration of carbon monoxide in hydrogen. Even a few parts per million CO can cause the catalyst poisoning in PEM fuel cell [2]. At this point a chemical hydrate sodium borohydrate, which contains 10.8 wt% hydrogen, is seen as a safe and portable alternative route for H_2 storage because it is stable under ordinary conditions and liberates pure H_2 in specific conditions, which can be created in safe and controllable way. In the presence of a selected catalyst, hydrolysis reaction of $NaBH_4$ solution gives 4 mol of H_2 and the half of the produced hydrogen comes from water. The by-product $NaBO_2$ does no harm to the environment, and can be recycled as the raw material for producing $NaBH_4$ [2,3]. Thus, the hydrolysis reaction of $NaBH_4$ is an environmentally friendly and renewable process and without a catalyst the reaction is very slow (half-life is about 430 days in pH 14 and 25 °C) [4]. Therefore, development of an effective catalyst is the focal point of the researches in the literature.

Various type of catalysts are being used by different researchers such as metal halides ($NiCl_2$, $CoCl_2$), colloidal platinum, Co and Ni boride, active carbon, Raney nickel, Ru supported on ion exchange resin beads, and Mg-based material [3–8]. Pt–$LiCoO_2$ was found to work as an excellent catalyst for releasing hydrogen by hydrolysis of $NaBH_4$ solution [5,9,10]. In all these studies, Pt–$LiCoO_2$ catalysts were prepared by impregnation of Pt precursor on commercial $LiCoO_2$ support material.

In this study, the effects of preparation conditions for $LiCoO_2$ support were studied to develop an effective Pt/$LiCoO_2$ catalyst. $LiCoO_2$ was prepared by solid-state reaction of lithium and cobalt precursors, and the effects of preparation parameters such as the amount of reactants, the existence and the type of the heat generating material and calcination temperature on hydrogen production (i.e. hydrolysis reaction) rate were investigated. The effects of reaction conditions such as $NaBH_4$

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and NaOH concentrations, reaction temperature and catalyst amount were also investigated.

2. Experimental

2.1. Catalyst preparation

$LiCoO_2$ was prepared as support material by solid-state reaction of Li_2O and $Co(NO_3)_2{\cdot}6H_2O$. Commercial $LiCoO_2$ was also used for comparison. In solid-state reaction method, Li_2O, $Co(NO_3)_2{\cdot}6H_2O$ precursors and heat generating material were mixed in appropriate amounts and heated in a muffle furnace as described in the literature [8]. Amount of reactants, existence and type of the heat generating material and calcination temperature were chosen as preparation parameters. Ammonium nitrate and urea were used as HGM in this study. Calcination was performed for all $LiCoO_2$ materials prepared in two steps. In the first step all samples prepared by using equal amounts of ammonium nitrate and precursors were calcined at 300 °C for 3 h. Then in the second step $LiCoO_2$ supports were heated to 500, 600, 700, 800 and 900 °C and kept there for 5 h.

1.5 wt% $Pt/LiCoO_2$ catalysts were prepared by Pt impregnation on $LiCoO_2$ support by using incipient to wetness impregnation method. $Pt(NH_3)_4(NO_3)_2$ and $Pt(NH_3)_4(OH)_2{\cdot}xH_2O$ were chosen as Pt precursors. $LiCoO_2$ supports were crushed and sieved to 150–200 μm particle sizes before impregnation. After impregnation all catalysts were dried at 250 °C for 5 h and then calcined at 450 °C for 2 h. Also, commercial $LiCoO_2$ was also used for comparison.

In order to investigate the effect of Pt addition method, in addition to impregnation, the catalyst was also prepared by adding $Pt(NH_3)_4(NO_3)_2$ to initial mixtures of Li_2O, $Co(NO_3)_2{\cdot}6H_2O$ and HGM. The sample was calcinated first at 300 °C for 3 h and then 700 °C for 5 h.

2.2. Catalyst characterizations and activity measurement

XRD analysis was performed to determine $LiCoO_2$ structure in the prepared support materials by using a Rigaku D/MAX-Ultimat PC XRD equipment in Boğaziçi University Advanced Technologies R&D Center. The activities of catalysts in the hydrolysis of $NaBH_4$ were measured in a semi-batch jacketed reactor at atmospheric pressure and room temperature. Prepared catalysts were placed into the reactor and $NaBH_4$ solution was fed to the reactor by a peristaltic pump. Since reaction is highly exothermic, the reactor was cooled by using a cold water jacket in order to maintain isothermal reaction conditions. Reaction mixture was stirred 500 rpm by a magnetic stirrer. H_2 was collected in a volumetric flask and amount of H_2 versus time data were recorded.

3. Results and discussion

3.1. Effects of catalyst/support preparation parameters

1.5 wt% Pt was impregnated over $LiCoO_2$ support, which was prepared by solid-state reaction of lithium and cobalt precursors. The effects of $LiCoO_2$ preparation parameters such as the amount of reactants, the presence and the type of heat generating material (HGM), and calcination temperature on H_2 production were investigated.

HGM is an important parameter in the preparation of $LiCoO_2$, although it is not a precursor. It supplies heat by decomposing with an exothermic reaction during calcinations and it changes the structure of the support, which may come in two forms: a hexagonal structure and a cubic structure. The cubic form of $LiCoO_2$ was defined as low temperature (LT-$LiCoO_2$) and the hexagonal form $LiCoO_2$ was defined as high temperature (HT-$LiCoO_2$) in the literature [7]. The hexagonal and cubic structures are based on the same oxide sublattice, and are distinguished by the spatial arrangement of actions [11,12].

Ammonium nitrate and urea were used as HGM in this study. If the amount of HGM used was equal to the total amount of precursors, it was defined as 1×, while the HGM amount, which is twice higher than the amount of precursor, was defined as 2×. Some samples containing higher amounts of HGM were also prepared. However, these samples scattered to the furnace during calcination step due to higher heat generation rate.

Therefore, Fig. 1 illustrates XRD patterns of the samples prepared in the absence and in the presence of different amount and type of two HGMs. Crystal diameters (*L*) of all the samples were calculated by using XRD patterns shown in Fig. 1 together with Scherrer equation. Scherrer equation was adopted to evaluate

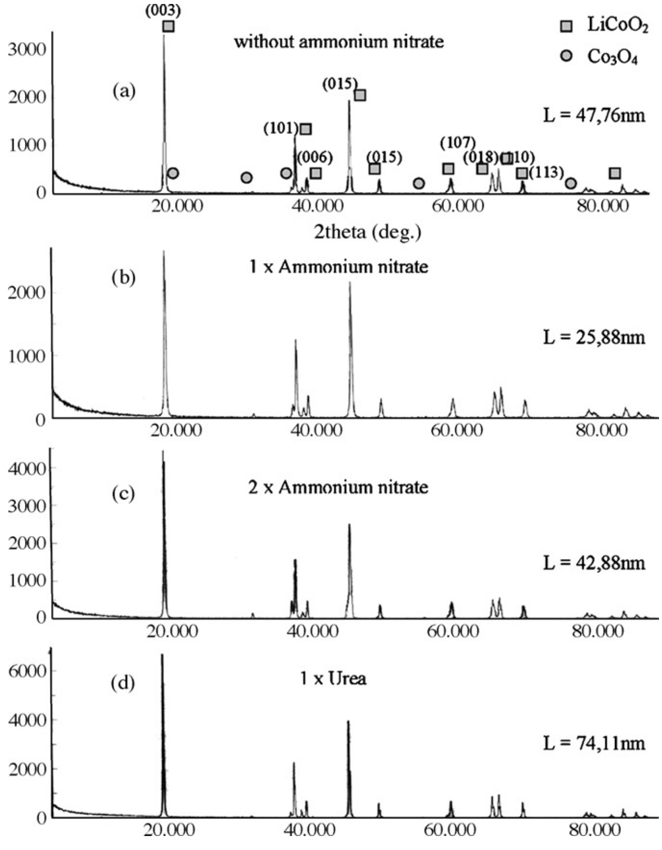

Fig. 1. XRD patterns of $LiCoO_2$ prepared by solid-state reaction method (calcinated at 3 h 300 °C then 5 h 700 °C): (a) without ammonium nitrate, (b) 1× ammonium nitrate, (c) 2× ammonium nitrate, and (d) 1× urea.

the average particle sizes of the catalysts, as described by Eq. (1):

$$L = \frac{0.9\lambda_{K\alpha_1}}{B_{2\theta}\cos\theta_{\max}} \qquad (1)$$

where $\lambda_{K\alpha_1}$ presents the wavelength of Cu $K\alpha_1$ radiation (1.54056 Å) and $B_{2\theta}$ is the half-width of the diffraction peak. Another parameter $\theta_{\max}$ is the 2θ degree of the diffraction peak. The value of the average particle size L can be calculated through Eq. (1). Since the $LiCoO_2(0\,0\,3)$ and $LiCoO_2(0\,1\,5)$ diffraction peaks might overlap with those peaks of the Co_3O_4, here we chose the parameters of $LiCoO_2(1\,0\,1)$ peak to carry on the evaluation.

As shown in Fig. 1, all samples have similar patterns indicating mostly HT-$LiCoO_2$ structure, since the miller index of HT-$LiCoO_2$ and LT-$LiCoO_2$ was given in the literature [7] as (0 0 3), (1 0 1), (0 0 6), (0 1 5), (1 0 7), (0 1 8), (1 1 0) and (1 1 1), (3 1 1), (2 2 2), (4 0 0), (3 3 1), (3 3 0), (4 4 0), respectively. Comparing XRD patterns in Fig. 1a and b, sample with HGM has showed smaller particle diameter. After Pt impregnation, both samples gave the similar hydrogen production profiles in the activity test performed at 20 °C, with 50 mg Pt/$LiCoO_2$ and 20 wt% $NaBH_4$ + 10 wt% NaOH solution, as seen in Fig. 2. Sample with a smaller particle diameter produces hydrogen in less time.

As seen in Fig. 1b and c, increasing the amount of ammonium nitrate increases the crystalline diameter of prepared $LiCoO_2$. An interesting situation was observed here, because use of ammonium nitrate decreased the particle diameter as shown in Fig. 1a and b. Reaction tests also showed that H_2 production rate was slightly lower for the samples prepared by using high ammonium nitrate, as shown in Fig. 2. Therefore, although existence of ammonium nitrate did not affect hydrogen production rates significantly, it was concluded that optimum value for amount of ammonium nitrate, within the experimental region studied, was equal mass with mass of precursors (Li_2O and $Co(NO_3)_2{\cdot}6H_2O$).

The effect of HGM type was also investigated. When urea was used instead of ammonium nitrate, $LiCoO_2$ particles with larger diameter were produced. XRD patterns in Fig. 1d show that urea-used sample gives a well-developed HT-$LiCoO_2$ structure. However, hydrogen production experiments could not be done with urea-used catalysts. Since during preparation of $LiCoO_2$ with urea, support samples could not obtained in proper amounts due to scattering of samples to furnace, as what happened in the case of the sample prepared with 3× ammonium nitrate, because of high heat of decomposition reaction of urea.

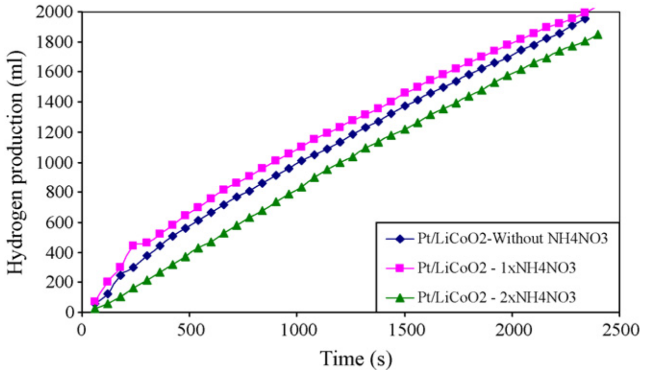

Fig. 2. Effects of heat generating material (20 wt% $NaBH_4$ + 10 wt% NaOH, solution at 50 mg Pt/$LiCoO_2$ catalyst, T = 20 °C).

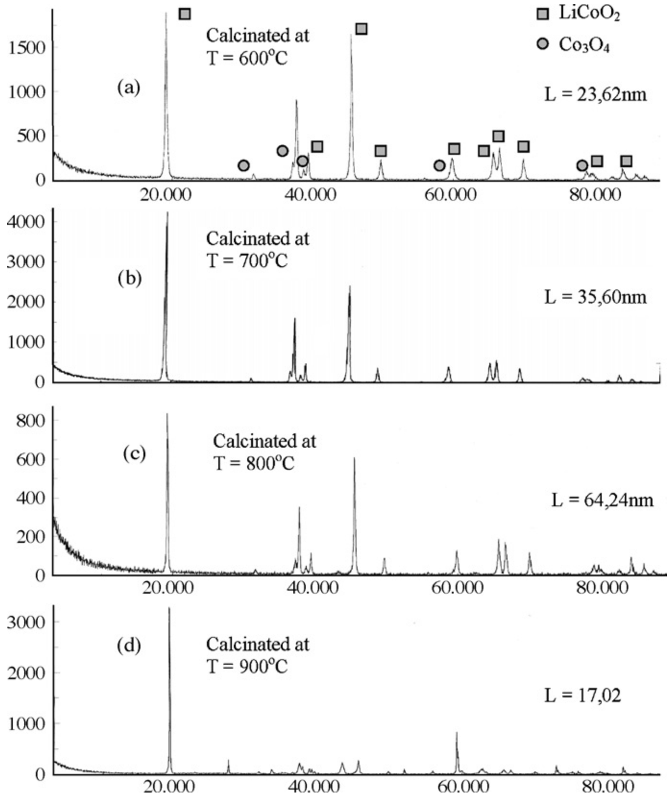

Fig. 3. XRD patterns of $LiCoO_2$ samples calcined at different temperatures (Li_2O, $Co(NO_3)_2{\cdot}6H_2O$ and 1× HGM): (a) 600 °C, (b) 700 °C, (c) 800 °C, and (d) 900 °C.

Calcination temperature was another preparation parameter investigated in this study. XRD patterns of $LiCoO_2$ supports calcined at different temperatures are seen in Fig. 3. Yoon and Kim reported that the structure of the $LiCoO_2$ materials varies from low temperature (LT) phase to high temperature (HT) phase as calcination temperature increases [12]. This argument was also validated by our results since increasing calcination temperature ensured a well-developed HT-$LiCoO_2$ phase. The sample calcined at the highest temperature also has small particle diameters due to sintering.

As shown in Fig. 4, it is clear that increasing calcination temperature decreases H_2 production rate. Samples calcined between 500 and 700 °C almost gave approximate H_2 production rates, (20.9 ml/(s g)) but samples calcined at 800 °C and 900 °C showed less production rates such as 14.51 ml/(s g) catalyst, and 9.07 ml/(s g), respectively. The reason for low production rate may be explained probably due to some structural changes and sintering of the sample calcined at 900 °C.

The effect of Pt salt type on catalyst activity was also investigated. $Pt(NH_3)_4(NO_3)_2$ and $Pt(NH_3)_4{\cdot}(OH)_2{\cdot}xH_2O$ were chosen as Pt precursors. Both samples gave almost same H_2 production profile shown in Fig. 5. Therefore, $Pt(NH_3)_4(NO_3)_2$

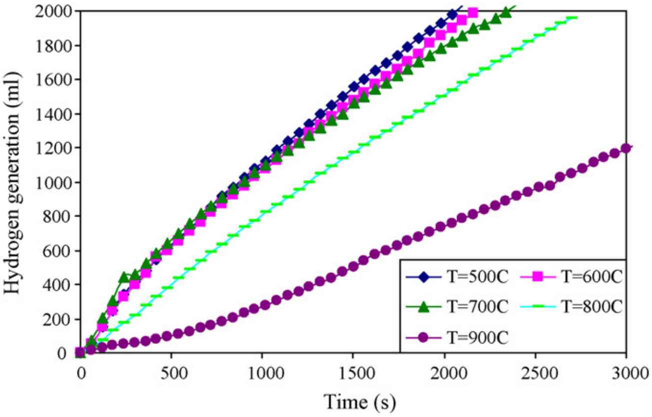

Fig. 4. Effect of calcination temperature on H_2 generation (20 wt% $NaBH_4$ + 10 wt% NaOH, solution at 50 mg Pt/$LiCoO_2$ catalyst, $T = 20\,^{\circ}C$).

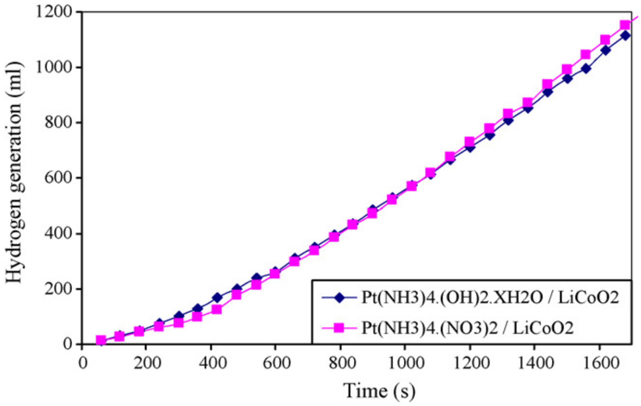

Fig. 5. Effect of Pt precursor on H_2 generation (20 wt% $NaBH_4$ + 10 wt% NaOH, solution at 50mg Pt/$LiCoO_2$ catalyst, $T = 20\,^{\circ}C$).

was preferred in the preparation of Pt/$LiCoO_2$ catalysts, due to its higher solubility in water.

The effect of Pt addition method to the prepared support was also studied. In addition to impregnation, the catalyst was also prepared adding Pt into the initial mixtures of solid-state reaction. In the comparison of H_2 production profiles of two catalysts, impregnated one has shown higher production rate (98.54 ml/(s g) compare to 66.55 ml/(s g)) (Fig. 6). This may be explained with very small diameters of Pt particles embedded in bulk phase of support $LiCoO_2$.

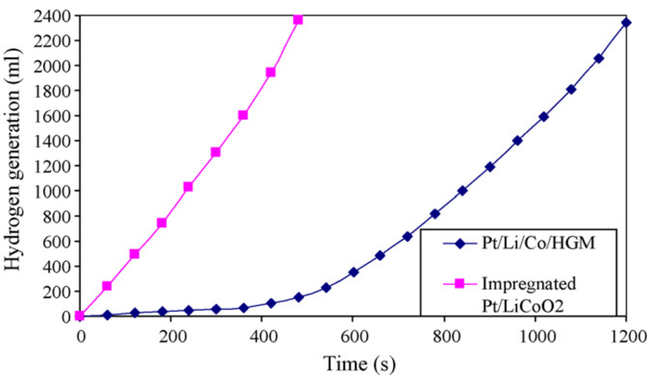

Fig. 6. Effect of Pt in $LiCoO_2$ structure on H_2 generation (20 wt% $NaBH_4$ + 10 wt% NaOH, solution at 50 mg Pt/$LiCoO_2$ catalyst, $T = 40\,^{\circ}C$).

3.2. *Effects of reaction conditions*

The effects of hydrolysis reaction parameters such as $NaBH_4$ and NaOH concentrations, reaction temperature and the amount of catalyst on hydrogen production rate were also investigated. The catalyst used in these experiments were prepared by Pt impregnation (using $Pt(NH_3)_4(NO_3)_2$ as precursor) on $LiCoO_2$ support, which is prepared by equal amounts of ammonium nitrate and precursors. $LiCoO_2$ support was calcined first at 300 °C for 3 h and then heated to 700 °C and kept there for 5 h before Pt impregnation.

3.2.1. *Effect of $NaBH_4$ solution concentration*

Concentration of $NaBH_4$ is one of the most important parameter of the process considering that it is one of the hydrogen source in addition to water. According to the results of the H_2 production tests performed with 5, 10, 15 and 20 wt% $NaBH_4$ solutions, decreasing amount of $NaBH_4$ in solution increases the H_2 production as illustrated in Fig. 7. The highest H_2 production rate (31.11 ml/(s g)) was obtained with 5% $NaBH_4$ solution at 20 °C and 10% NaOH concentration with 50 mg catalyst.

The results similar to ours were observed and reported by various investigators such as Jeong et al. [13], Amendola et al. [3,4] and Kim et al. [14]. It was explained that the decrease in the production rate caused by the increase in the viscosity of reaction medium [3,4]. At lower viscosity, the amount of $NaBH_4$ molecules contacted with catalyst particles was much more than the ones at higher viscosity. Therefore, higher reaction rate was observed.

3.2.2. *Effect of NaOH concentration*

Although NaOH is not a reactant of the process, it is important to increase the pH of reaction solution to prevent uncontrolled hydrolysis of $NaBH_4$. The effects of NaOH concentration on H_2 production rate were investigated by using reaction solutions which include 5, 10, 15 and 20 wt% NaOH and 20 wt% $NaBH_4$ at the reaction temperature of 20 °C using 50 mg 1.5%

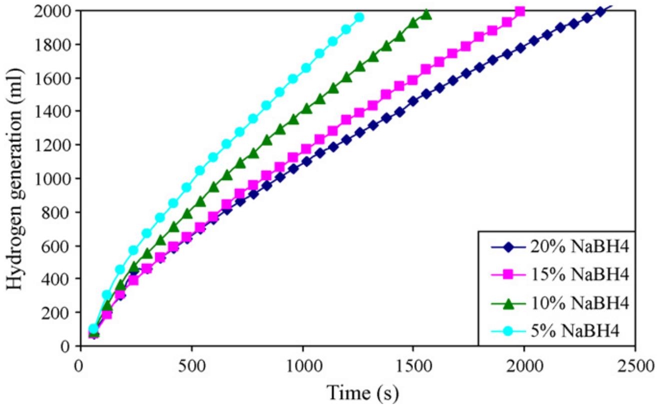

Fig. 7. Effects of $NaBH_4$ concentration on H_2 production rate (x wt% $NaBH_4$ + 10 wt% NaOH solution at 50 mg Pt/$LiCoO_2$ catalyst, $T = 20\,^{\circ}C$).

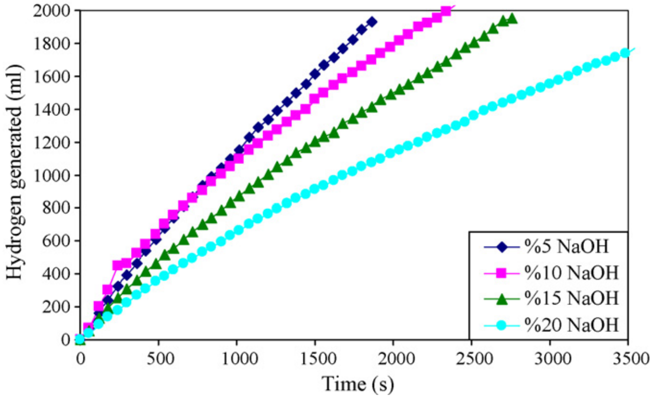

Fig. 8. Effects of NaOH concentration on H_2 production rate (x wt% NaOH + 20 wt% $NaBH_4$ solution at 50 mg $Pt/LiCoO_2$ catalyst, $T = 20\,°C$).

$Pt/LiCoO_2$ catalyst. As seen in Fig. 8, the increase of NaOH concentration decreases the reaction rate (20.8 ml/(s g) at 5% NaOH, 10.0 ml/(s g) at 20%) as also reported in the literature with different types of catalysts [3,15]. Higher concentrations of NaOH decrease the amount of free water required for the reaction, and therefore it decreases the production rate of H_2.

3.2.3. *Effect of reaction temperature*

In order to see the effect of temperature on H_2 production rate, hydrolysis of $NaBH_4$ was carried out at 20, 30 and 40 °C. Another experiment was made at non-isothermal conditions starting at room temperature in order to compare our results with the literature [5]. Since reaction rate increases with temperature (17.42, 39.46 and 98.55 ml/(s g), for 20, 30 and 40 °C, respectively) according to Arrhenius equation, our results showed Arrhenius behaviour as illustrated in Fig. 9. On the other hand, the result of non-isothermal experiment did not show linear profile since reaction was exothermic causing temperature rise and therefore rise in the reaction rate. Instead, it showed a parabolic profile similar to those in the literature [3,4,13,15].

3.2.4. *Effect of catalyst amount*

H_2 production by different amounts of catalyst was also investigated. Using more catalyst increases the H_2 production as expected and results are shown in Fig. 10.

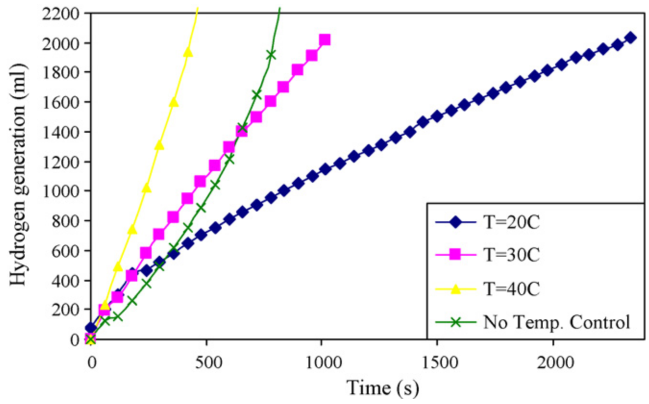

Fig. 9. Effects of temperature on H_2 production rate (10 wt% $NaBH_4$ + 10 wt% NaOH solution at 50 mg $Pt/LiCoO_2$ catalyst).

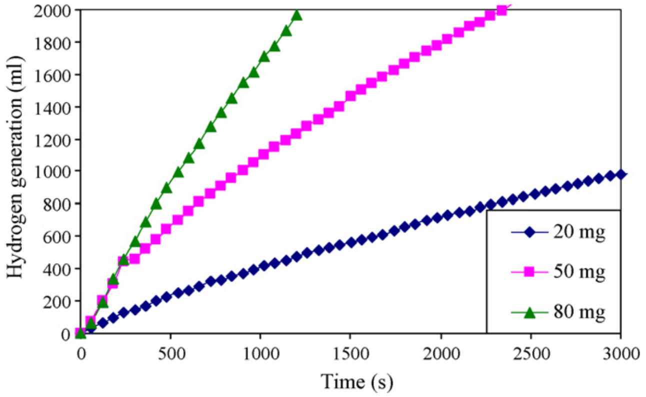

Fig. 10. Effects of temperature on H_2 production rate (20 wt% $NaBH_4$ + 10 wt% NaOH solution at 50 mg $Pt/LiCoO_2$ catalyst).

3.2.5. *Comparison of results with the literature*

The results of this study were compared with the literature studies and showed in Fig. 11. The result of the experiment performed with the catalyst prepared by Pt impregnation on commercial $LiCoO_2$ support is also shown in Fig. 11. Experimental conditions were almost similar with different studies in the literature. The highest H_2 production rate (20.9 ml/(s g) at 20 °C), as shown in Fig. 11, was obtained by using the catalyst prepared in this study. In the literature, Kojima et al. studied different types of metal supported catalysts and found that $Pt/LiCoO_2$ catalysts (50 mg) give higher H_2 production compared to others [5]. Catalysts used in the study of Kojima et al. had been prepared by impregnation of Pt on commercial $LiCoO_2$ and reaction tests were done in non-isothermal conditions showing a parabolic H_2 production rate profile. In the comparison of our results with the studies of Kojima et al. and other studies in the literature, preparation of $LiCoO_2$ by solid-state reaction improved the activity of $Pt/LiCoO_2$ catalysts for the hydrolysis reaction of the $NaBH_4$.

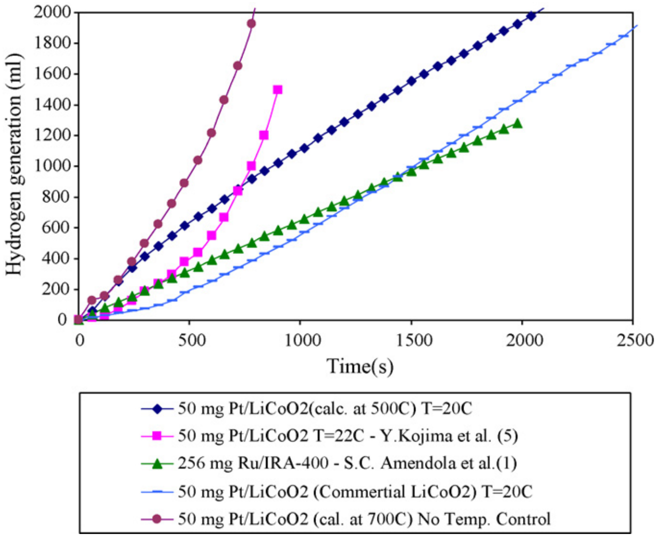

Fig. 11. Comparison of the H_2 production rates of different catalysts.

4. Conclusion

The effects of $LiCoO_2$ preparation parameters and reaction conditions on H_2 production from $NaBH_4$ over 1.5 wt% $Pt/LiCoO_2$ were studied and it was found that:

- In the preparation of support $LiCoO_2$, the catalysts prepared by using ammonium nitrate as HGM gave higher H_2 production rates and equal amount of HGM to the reactants was determined as optimum.
- Samples calcined between 500 and 700 °C gave approximately the same H_2 production rates, while the samples calcined at higher temperatures showed lower activity towards.
- Decreasing $NaBH_4$ and NaOH concentrations, increased H_2 production rate.. The H_2 production rate was also decreased by increasing reaction temperature and amount of catalysts expected.

Acknowledgements

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