XAS STUDY OF $LiCoO_2$ AND Pt-SUPPORTED ON $LiCoO_2$ CATALYSTS FOR HYDROGEN GENERATION FROM SODIUM BOROHYDRIDE SOLUTION

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Introduction

The fuel cells are promising technology for electrochemical power generation because they have efficiency much higher than that of other power generators.

Sodium borohydride can be used as hydrogen storage tank in both hydrogen and direct borohydride fuel cells [1-6]. Aqueous alkaline $NaBH_4$ solutions are non-toxic, non-flammable, stable and high volumetric and gravimetric energy-dense. The spontaneous reaction of sodium borohydride with water can be represented by equation:

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2 \qquad (1)$$

Sodium metaboride $NaBO_2$, which is produced during $NaBH_4$ hydrolysis, raises the pH of the solution and suppresses the reaction rate. Reaction products are environmentally safe and can be regenerated. The reaction rate can be easily controlled. Metal-metal oxide catalysts such as $Pt/LiCoO_2$ were found to be very effective for releasing hydrogen by hydrolysis of $NaBH_4$ solution at high pH [1-3].

In this paper, we report the results of our study on the catalyzed hydrolysis of $NaBH_4$ by $LiCoO_2$ and Pt-supported on $LiCoO_2$ using synchrotron radiation.

Results and discussion

Pt-supported on $LiCoO_2$ catalysts were prepared using a conventional impregnation method [1]. X-ray diffraction (XRD) and X-ray absorption near-edge structure (XANES) measurements were carried out using synchrotron radiation source of 01C2 beam line at National Synchrotron Radiation Research Center (NSRRC) in Taiwan.

Typical curves of hydrogen generation reaction rates of different catalysts are shown in Fig.1. The order of hydrogen generation reaction rates are shown as Pt-supported $LiCoO_2$ > Pt > $LiCoO_2$. This behaviour is similar to that of other catalysts, e.g. Pt-supported on carbon [6]. Therefore, the results obtained indicate that $LiCoO_2$ plays essential role similar to that of C in $NaBH_4$ hydrolysis.

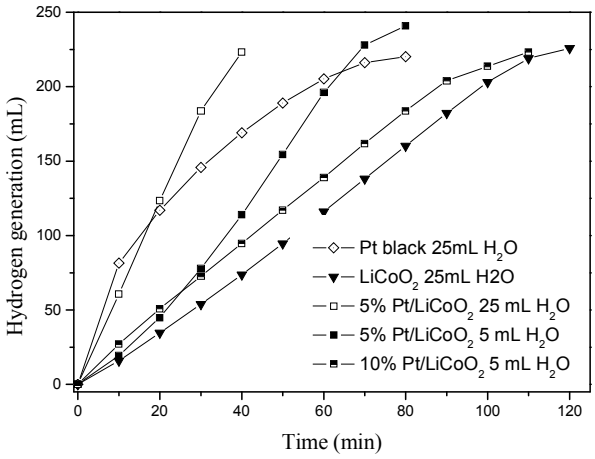

Fig.1. Hydrogen generation reaction rate from $NaBH_4$ (0.1 g) solution in H_2O for $LiCoO_2$, Pt and Pt-supported on $LiCoO_2$ catalysts (6.6 mg) at 22°C.

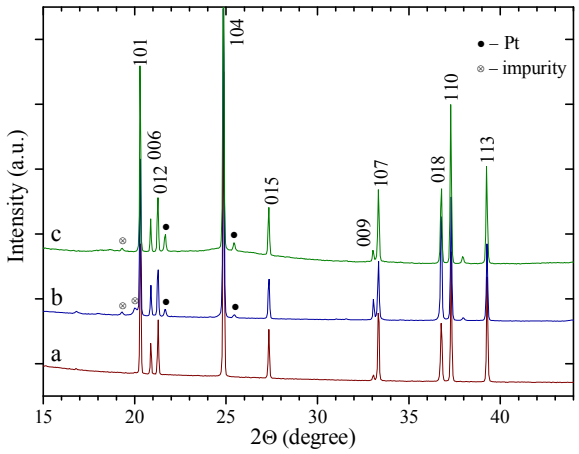

Fig.2. Powder XRD patterns of pure $LiCoO_2$ (a), Pt-supported on $LiCoO_2$ (5 wt.%) before (b) and after (c) reaction measured with monochromatic synchrotron radiation (λ = 0.8491Å) at 300K. Miller indexes for $LiCoO_2$ phase are shown.

The hydrogen generation rate decreases with increasing Pt loading, which can be caused by decreasing of the number of cobalt active sites on the surface of the catalyst. On the other hand, reaction accelerates with decresing the concentration of sodium borihydride. Therefore, the hydrolysis is supposed to be stepwise and different mechanisms could take place at different borohydride anion concentrations in the solution and Pt loading.

Crystal structure of $LiCoO_2$ is retained after the reaction for both types of catalysts used as shown in Fig.2. Moreover, the XRD peaks belonging to Pt (as indicated by "•" in Fig.2) appeared in the Pt-supported on $LiCoO_2$ samples before and after reaction.

Normalized XANES of cobalt K-edge spectra of $LiCoO_2$ and Pt-supported on $LiCoO_2$ catalysts before and after use in reaction (1) are shown in Fig.3.

For $LiCoO_2$ and Pt-supported on $LiCoO_2$ catalysts before reaction three peaks are plainly distinguishable (see, e.g. [7]). The first one, weak peak A represents 1s → 3d dipole-forbidden transition of a d-metal in slightly distorted octahedral coordination. Peak B is assign to 1s → 4p transition with simultaneous ligand-to-metal charge transfer. Finally, the strongest C peak is 1s → 4p transition. Considerable changes in XANES spectra of the cycled catalysts, especially Pt-supported on $LiCoO_2$, were detected indicating about changes of cobalt oxidation state and coordination geometry.

The position and the shape of XANES curves of cycled catalysts resemble that of Co metal. The changes in their structure are visualized by the inset to Fig. 3 where 1st derivative of the absorption spectra are shown.

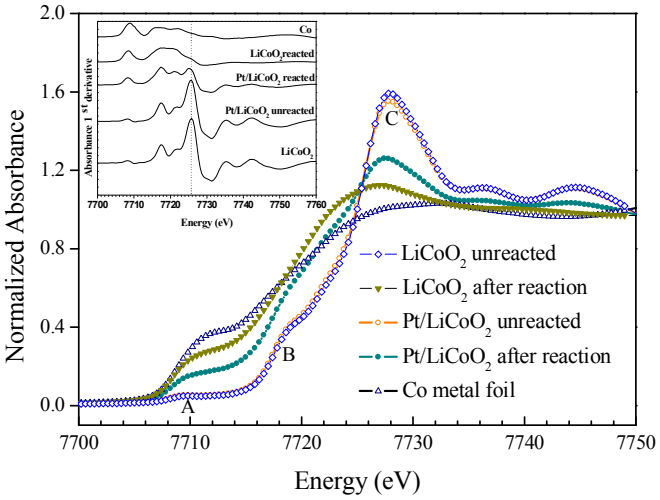

Fig.3. Normalized Co K-edge XANES spectra of $LiCoO_2$ and Pt-supported on $LiCoO_2$ (5 wt. %) catalysts before and after use in the reaction.

Conclusions

The catalytic reaction of sodium borohydride hydrolysis was studied using synchrotron XRD and XANES techniques. The results obtained suggest that the reduction of Co^{+3} in $LiCoO_2$ to lower oxidation states happens. Some more studies are now in progress to elucidate the mechanism of $LiCoO_2$ and Pt-supported on $LiCoO_2$ catalysts in the reaction of $NaBH_4$ hydrolysis.

Financial support from the Chung-Shan Institute of Science and Technology under the contract number of 94-S-C02 is fully acknowledged.

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