

XAFS study of Rh cocatalyst loaded on gallium oxide

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Introduction

Hydrogen attracts much attention as the energy of the next generation. Photocatalytic steam reforming of methane (PSRM; $\text{CH}_4 + 2\text{H}_2\text{O} \rightarrow 4\text{H}_2 + \text{CO}_2$) is one of the ideal hydrogen production methods since it has a potential to produce hydrogen from renewable resources and solar energy. We reported that Pt-loaded semiconductors showed the activity for the PSRM at room temperature and their activities increased with increasing the reaction temperature until ca. 343 K [1, 2]. In the present study, we examined the influence of thermal energy on the PSRM over the Rh/ $\beta\text{-Ga}_2\text{O}_3$. Especially, we discussed how the local structure of Rh cocatalyst would influence the thermal activation energy of the Rh/ $\beta\text{-Ga}_2\text{O}_3$ samples.

Experimental

Rh cocatalyst was loaded on $\beta\text{-Ga}_2\text{O}_3$ (Kojundo, 99.99%) by an impregnation method, followed by heating in a flow of hydrogen at various temperatures (373–673 K) for 0.5 h. Photocatalytic reaction was carried out with a fixed-bed flow-type reactor as the similar way to the previous studies [1, 2].

Rh K-edge XAFS spectra were recorded at the NW-10A station at KEK-PF in a transmission mode for Rh foil and Rh(1 wt%)/ $\beta\text{-Ga}_2\text{O}_3$ samples. The spectra were analyzed with REX 2000 software (Rigaku). The theoretical parameters were used for curve fitting analysis.

Result and Discussion

Fig. 1 shows Arrhenius plot for the hydrogen production rate over the Rh(0.05 wt%)/ $\beta\text{-Ga}_2\text{O}_3$ reduced at 473 K. As the reaction temperature increased, hydrogen production rate increased until 332 K and then became constant at higher temperatures. In the low temperature range, Arrhenius plot showed a straight line and the thermal activation energy (E_a) was 10.5 kJ mol⁻¹. This value was much smaller than that of the thermal steam reforming of methane. It was suggested that thermal energy would influence the mild activation steps such as the promotion of the migration of photoexcited carriers.

Hydrogen production rate and thermal activation energy of Rh(0.05 wt%)/ Ga_2O_3 samples treated at various temperatures were compared with non-treated one. Hydrogen production rate first increased with increasing the reduction temperature until 573 K but decreased at 673 K. On the other hand, thermal activation energy monotonically increased from 6.0 to 16.1 kJ mol⁻¹ with an increase of the reaction temperature.

Local structure of Rh cocatalyst was examined with XAFS. Rh K-edge XANES spectra of Rh(1 wt%)/ Ga_2O_3

samples reduced at various temperatures were very similar with that of Rh foil. No clear differences were observed among these samples. However, clear difference was observed from EXAFS as shown in Fig. 2. Fitting analysis showed that Rh cocatalyst existed as metal in the sample reduced at 573 K and lower temperatures but became alloy with Ga in the sample reduced at 673 K. This suggests that the surface of $\beta\text{-Ga}_2\text{O}_3$ should be reduced. Therefore, the formation of Rh-Ga alloy and the reduction of the $\beta\text{-Ga}_2\text{O}_3$ surface would be the reasons for the decrease of the production rate and the increase of the thermal activation energy in the sample reduced at 673 K.

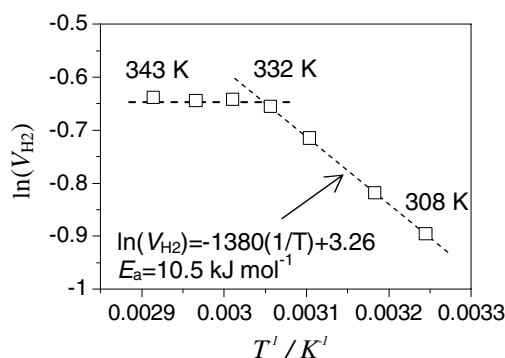


Fig. 1 Arrhenius plot for the hydrogen production rate (V_{H_2}) in the PSRM over the Rh(0.05 wt%)/ $\beta\text{-Ga}_2\text{O}_3$ reduced at 473 K.

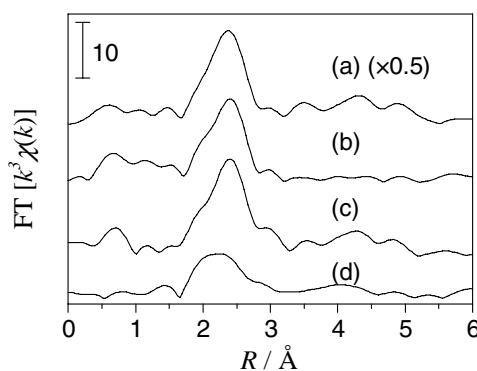


Fig. 2 Fourier transform of Rh K-edge EXAFS spectra of (a) Rh foil and (b)–(d) Rh(1 wt%)/ $\beta\text{-Ga}_2\text{O}_3$ samples reduced at various temperatures. Reduction temperature was (b) 373, (c) 573 and (d) 673 K.

References

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- [2] K. Shimura, et al., *J. Phys. Chem. C*, **114** 3493 (2010).

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