

XAFS Study of Rhodium Cocatalyst Loaded on $K_2Ti_6O_{13}$ Photocatalyst

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1 Introduction

Some photocatalysts have been found to promote the photocatalytic steam reforming of methane (PSRM; $2 H_2O_{(g)} + CH_4 \rightarrow 4 H_2 + CO_2$) around room temperature [1-5]. The activity was much influenced by not only the properties of semiconductor but also the metal cocatalyst loaded on the surface. Although the platinum loaded $K_2Ti_6O_{13}$ photocatalyst show high activity, unfavorable formation of carbon monoxide and gradual deactivation were observed. On the other hand, a rhodium-loaded $K_2Ti_6O_{13}$ photocatalyst showed two times higher activity than the platinum-loaded one did, and promoted the PSRM selectively without deactivation for many hours [6]. Further, the activity strongly depended on the loading method for the cocatalyst. In this study, we investigated the local structure of rhodium cocatalysts on the $K_2Ti_6O_{13}$ photocatalyst by using XAFS spectroscopy.

2 Experiment

A $K_2Ti_6O_{13}$ photocatalyst was prepared by the solid-state reaction method. Four rhodium-loaded samples were prepared: three $Rh(0.03 \text{ wt\%})/K_2Ti_6O_{13}$ samples were prepared by impregnation and successive different thermal treatments, i.e., reduction at 473 K (*sample a*), calcination at 773 K before reduction at 473 K (*sample b*), and calcination at 773 K (*sample c*). The other sample was prepared by the photodeposition method in the presence of dissolved oxygen (*sample d*).

Rh K-edge XAFS spectra were recorded at the NW-10A station [7] of KEK-PF at room temperature with a Si(311) double crystal monochromator in a transmission mode and in a fluorescence mode by using the Lytle-detector (100 mm ion chamber filled with krypton) with a ruthenium filter ($\mu t=6$). The spectra were analyzed with a REX 2000 software (Rigaku).

3 Results and Discussion

Among these four samples, the catalyst prepared by the photodeposition method (*sample d*) showed the highest activity. The activity of the four samples was in the following order, *sample d* > *sample a* > *sample b* > *sample c*.

The Rh K-edge XANES spectra (Fig. 1A) revealed that the Rh cocatalyst would be almost metallic on both the *sample a* and the *sample b*. On the other hand, large edge shifts to higher energy suggested that the Rh cocatalyst would be almost oxidized on both the *sample c* and the *sample d*.

Fig. 1B shows the Rh K-edge EXAFS spectra of them. The curve-fitting analysis of EXAFS clarified that the peaks observed at 1.6 and 2.8 Å were assignable to the Rh–O and Rh–Rh shells in rhodium oxide, respectively.

The atomic distance of the Rh–O shell was 2.06 Å, which is close to the Rh–O distance in Rh_2O_3 (2.03–2.05 Å, ICSD #108941) but different from that in RhO_2 (1.93–2.02 Å, ICSD #28498). The curve-fitting analysis also provided that the peak observed at 2.4 Å was assignable to the Rh–Rh shell with atomic distance of 2.70 Å, which is consistent with the Rh–Rh distance in rhodium metal (2.69 Å, #650218). For the *sample a*, a very small peak and a large peak were observed at 1.6 and 2.4 Å, respectively, although the intensity of the latter peak (the Rh–Rh shell) was not so large as compared with that for the rhodium foil. These results indicate that the Rh species on the *sample a* would dominantly exist as relatively large metal nanoparticles. For the *sample b*, two peaks at 1.6 and 2.4 Å were observed, suggesting that both small metal and oxide moieties would coexist on it. For the *sample c*, a large peak at 1.6 Å and a small peak at 2.8 Å were observed, while the peak at 2.4 Å was hardly observed, showing that the Rh species would mainly exist as relatively large oxide particles. For the *sample d*, a clear peak at 1.6 Å, a relatively small peak at 2.4 Å and a shoulder at 2.8 Å were observed, showing that there were small metal and large oxide moieties.

From this result and other evidences, it is suggested that this coexistence of the rhodium metal and oxide particles as cocatalyst would enhance the photocatalytic activity.

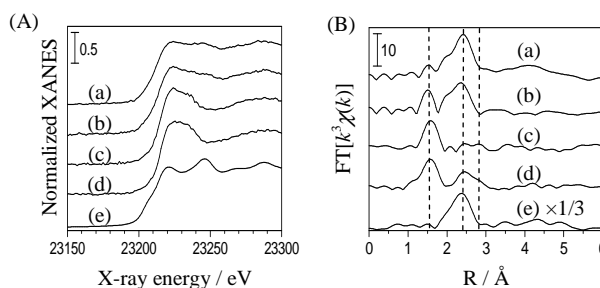


Fig. 1 (A) Rh K-edge XANES, and (B) Fourier transforms of Rh K-edge EXAFS spectra for the $Rh(0.1)/K_2Ti_6O_{13}$ photocatalysts, *samples a–d* in the text (a)–(d), and rhodium foil (e).

References

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