NW10A/2006G326

in situ XAFS analysis of Ru cocatalyst deposited on $SrTiO_3$:Rh photocatalyst

Hideki KATO[1], Yasuyoshi SASAKI[2], Wang-Jae Chun[3], Kiyotaka ASAKURA[4], Akihiko Kudo*[2]
[1]Tokyo Institute Tech., Midori-ku, Yokohama 226-8503, Japan
[2]Tokyo Univ. Science, Shinjuku-ku, Tokyo 162-8601, Japan
[3]International Christian Univ., Mitaka, Tokyo 181-8585, Japan
[4]Hokkaido Univ., Kita-ku, Sapporo 060-0811, Japan

Introduction

Overall water splitting under visible light irradiation has been achieved by Z-scheme type photocatalysis systems composed of two kinds of photocatalysts, Pt/$SrTiO_3$:Rh and $BiVO_4$, and an Fe^{3+}/Fe^{2+} electron mediator[1,2]. The authors have recently found that Ru is a better cocatalyst than Pt for use in the Z-scheme systems because Ru is inactive for reverse reactions between H_2 and O_2 or Fe^{3+} [3]. Characterization of the Ru cocatalyst is important to clear the mechanism.

In the present research, the authors carried out in situ XAFS analysis for Ru cocatalysts deposited on the $SrTiO_3$:Rh photocatalyst using suspension system with visible light irradiation.

Experiments

XAFS measurement at Ru K-edge was carried out for Ru/$SrTiO_3$:Rh and $RuCl_3$-$SrTiO_3$:Rh suspension systems containing methanol using a glass cell with and without visible light irradiation. Concentration of Ru in the suspension was 100 ppm. The suspended solution was continuously stirred by a magnetic stirrer during XAFS measurements. XAFS spectra were mainly collected in a fluorescence mode using a multi-channel solid state detector. The incident beam was monitored by an ionization chamber filled with N_2(50%)/Ar(50%).

Results

EXAFS measurements using dried disk samples have revealed that Ru cocatalysts were deposited as oxide clusters on $SrTiO_3$:Rh photocatalysts in the samples prepared by a photodeposition method. However, this result does not guarantee that the Ru oxide cluster is the active cocatalyst in photocatalytic reactions. There is a possibility that Ru oxide clusters can be reduced by photogenerated electrons under working condition because the Ru cocatalyst functions as reduction sites to produce hydrogen molecules. Therefore, the authors conducted in situ EXAFS measurements to clear active species of Ru cocatalyst in the Ru/$SrTiO_3$:Rh photocatalysts. The suspended solution containing methanol of an electron donor was irradiated with visible light to measure in situ EXAFS for H_2 production over the Ru/$SrTiO_3$:Rh photo-catalyst. No significant difference between disk and irradiated suspension samples was observed. It indicates that Ru oxide clusters on $SrTiO_3$:Rh are not reduced to metallic particles during photocatalytic H_2 production even in the presence of methanol. Thus, it has been revealed from in situ EXAFS that the Ru oxide cluster is an active cocatalyst for $SrTiO_3$:Rh.

Next, in situ EXAFS of irradiated $RuCl_3$-$SrTiO_3$:Rh suspension containing methanol was measured to clarify the change in the Ru state in the photodeposition process (Fig. 1). Contribution of Ru-Cl bonds was dominantly observed in an aqueous $RuCl_3$ solution. Ru-O bonds appeared when $SrTiO_3$:Rh powder was dispersed in the solution. But, the contribution of Ru-Cl bonds still remained. It indicates that hydrolysis takes place partly due to rising pH with elution of Sr ions. In the irradiated suspension, the contribution of Ru-Cl bonds disappeared and the EXAFS of the suspension became similar to that of Ru oxide cluster in the dried Ru/$SrTiO_3$:Rh sample. Thus, it has been found that Ru oxide cluster formed in the photodeposition process even in the presence of methanol.

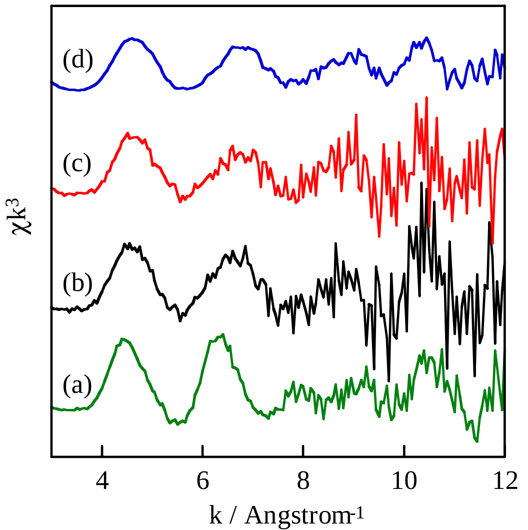

Fig. 1 EXAFS of (a) an aqueous $RuCl_3$ solution (100 ppm) containing 10 vol% of methanol, $RuCl_3$-$SrTiO_3$:Rh suspension; (b) in the dark, (c) under irradiation, and (d) a dried Ru/$SrTiO_3$:Rh disk.

References

[1] H. Kato et al., Chem. Lett. 33, 1348 (2004).
[2] H. Kato et al., Bull. Chem. Soc. Jpn. 80, 2457 (2007).
[3] Y. Sasaki et al., J. Catal., 259, 133 (2008).

*hkato@tagen.tohoku.ac.jp