

Study of nanosized Rh/Cr₂O₃ core/shell cocatalyst for over all water splitting using XAFS

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Introduction

Photocatalytic water splitting has attracted increasing attention as a means of energy conservation through the efficient use of solar energy. It is necessary to modify a photocatalyst with a H₂ evolution cocatalyst such as Rh/Cr₂O₃ core/shell composites[1, 2] to split water into H₂ and O₂ with reasonable efficiency. Recently, we found that nanosized Rh/Cr₂O₃ prepared via adsorption of nanoparticulate Rh clusters improved the photocatalytic activity of (Ga_{1-x}Zn_x)(N_{1-x}O_x) more than twice compared with Rh/Cr₂O₃ prepared by conventional photodeposition method. This improvement would result from differences in physicochemical properties such as valence and coordination states of the constituents of the composites. XAFS analysis is a suitable method to study relationship between structure and activity of nanoparticulate cocatalysts[2]. The purpose of this study is to clarify the detailed structure of the nanosized Rh/Cr₂O₃ using XAFS.

Experiments

(Ga_{1-x}Zn_x)(N_{1-x}O_x) and an aqueous solution of Rh nanocluster protected by polyvinylpyrrolidone were prepared based on the previously reported methods[1–3]. The (Ga_{1-x}Zn_x)(N_{1-x}O_x) powder was added to the Rh cluster solution (2.5 wt% of Rh to the (Ga_{1-x}Zn_x)(N_{1-x}O_x)). The suspension was stirred overnight and dried in vacuum. The dried powder was calcined in vacuum at 673 K to remove the protective group and then reduced in H₂ atmosphere at 573 K. Cr₂O₃ shell was formed over the Rh nanoparticles by the photodeposition method[1, 2], yielding the nanosized Rh/Cr₂O₃ core/shell supported on the (Ga_{1-x}Zn_x)(N_{1-x}O_x). The final amount of Rh loaded was confirmed to be 0.4 wt% by ICP-AES.

XAFS of the Rh-K edge was measured at the NW10A beamline. Appropriate amounts of the samples were packed in polyethylene packs. Using the packs, XAFS was recorded in fluorescent mode at ring energy of 2.5 GeV and stored current 60–36 mA.

Results and Discussion

Figure 1 shows Rh-K edge XANES spectra of the composite cocatalyst at each preparation stage. The spectrum of Rh species after calcination in vacuum was similar to that of Rh₂O₃. The edge position of the sample shifted to the same energy with Rh-foil after the H₂ reduction, indicating that the Rh^{III} species was reduced to metallic Rh. The spectral shape in the XANES region was not identical to that of Rh-foil due to the small particle

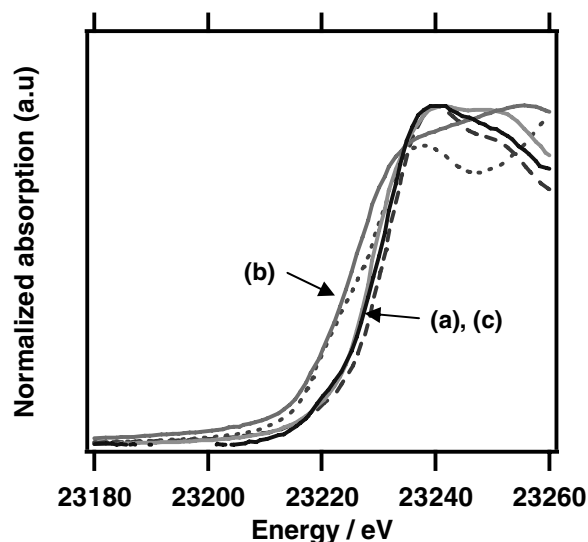


Figure 1. Rh-K edge XANES spectra of the R composite cocatalyst. (a) after calcination in vacuum, (b) (a) after the H₂ reduction, (c) (b) after the Cr₂O₃ shell formation. Spectra of Rh-foil and Rh₂O₃ are shown for reference by dot-line and dashed line, respectively.

size of the loaded Rh species (ca. 2 nm from TEM observations). The metallic Rh core was oxidized to trivalent Rh species during the photodeposition of Cr₂O₃ shell, which was different from the case of the Rh core prepared by the photodeposition method[2]. The Cr₂O₃ shell was formed as the result of photoreduction of Cr^{VI} species to Cr^{III} on Rh nanoparticles, or reduction reactions took place on the Rh core. Therefore, the formation of the nanosized Rh/Cr₂O₃ shell seems to involve some unconsidered processes causing oxidation of the Rh core. Our preliminary experiments revealed that metallic Rh worked better than trivalent Rh oxide as a core of the composite cocatalyst. Thus, higher activity could be attained by preventing the oxidation of Rh core. In-situ XAFS study will be useful to control valence of the Rh species.

References

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