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Electron Injection to Ru and the Polarization toward Surface for Photocatalytic Ammonia Synthesis

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1 Introduction

Ammonia is a fundamental chemical for fertilizers and raw material to Nylon and acrylonitrile. Apart from such traditional uses, ammonia is expected as hydrogen carrier in sustainable society. To achieve the application, it is essential to synthesize ammonia based on only renewable energy, in contrast to Fe-based catalysts at the high temperature.

Based on the difference of catalytic performance, Ru performs as effective catalysts for ammonia synthesis at lower temperature, e.g. 588 K compared to Fe-based catalysts [1]. To explore the possibility of reviewable energy source for ammonia synthesis, this study investigated the origin of accelerating effects of UV–visible light irradiation for ammonia synthesis over Ru–CeO_2 photocatalyst.

2 Experimental Section

Ru–CeO_2 photocatalyst was prepared from Ru(III) nitrosyl nitrate and CeO_2 powder (Daiichi Kigenso Kagaku Kogyo, Type A) via impregnation. The dried sample was heated at 673 K under H_2 before photocatalytic ammonia synthesis tests.

Ru K-edge XAFS spectra were measured at the Photon Factory Advanced Ring, on the NW10A beamline equipped with a Si (3 1 1) monochromator, a Pt-coated cylindrical mirror, and a piezo transducer. The photocatalyst samples were set in quartz cell equipped with PET windows filled with N_2 and H_2, and irradiated by UV–visible light.

3 Results and Discussion

Fluorescence spectra were measured for Ru–CeO_2 photocatalysts excited by the UV light at wavelength λ = 200 nm. As the Ru content increased from 1.25 wt % to 10 wt %, the fluorescence peak intensity significantly decreased (not shown), suggesting increased charge separation if the band-gap excited electrons in CeO_2 (conduction band, CB) transfer to Ru nanoparticles. The size of Ru nanoparticles were analyzed to be sub-nm, presumably comprising a few Ru atoms based on EXAFS analysis [2].

The Ru K-edge was monitored using Ru (2.5 wt %)–CeO_2 photocatalyst under the irradiation of UV–visible light at the beamline (Figure 1A). The progressive shift of absorption edge to lower energy side was clearly observed during 0–116 min of light irradiation. This tread demonstrates that the injection of light-excited electrons from CB of CeO_2 to Ru sub-nanoparticles gradually occurred.

Then, the UV–visible light was turned off at beamline. The Ru K-edge position of Ru (2.5 wt %)–CeO_2 photocatalyst essentially remained constant (Figure 1B). This result indicated that the CeO_2 and Ru were effectively polarized in the direction of these connection toward surface even after the light was turned off. This polarization facilitated the electron injection from Ru atom to π^* orbital of adsorbed N_2 molecule for the dissociation [1].

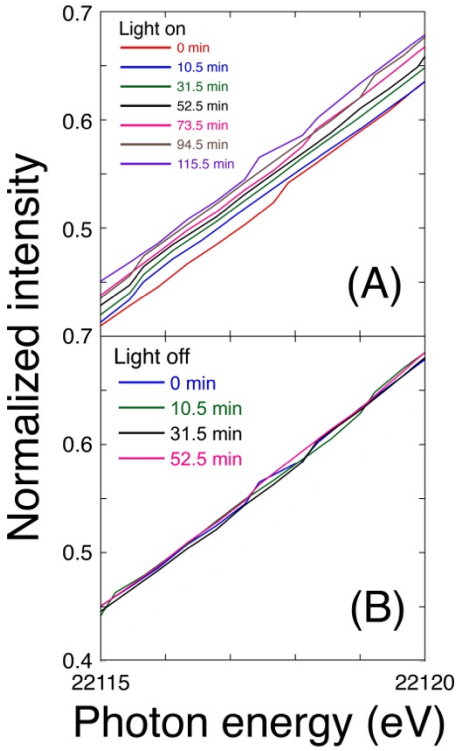

Figure 1. (A) Ru K-edge spectra measured for Ru (2.5 wt %)–CeO_2 photocatalyst heated at 673 K under H_2 irradiated by UV–visible light and (B) the light was turned off.

References

[1] Izumi, Y.; Iwata, Y.; Aika, K. Catalysis on Ruthenium Clusters Supported on CeO_2 or Ni-doped

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