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Charge Separation and/or Hot Spots: Monitoring of Au Site Temperature of Au–ZrO_2 Photocatalysts for CO_2 Photoreduction in H_2O

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1 Introduction

In principle, photocatalysis proceeds owing to separated charges in molecule and/or solid to induce reduction (by electron) and oxidation (by hole) reactions. In contrast, 'hot spot' effects by irradiated light have been enigmatically suggested. If we assume 10 mg of Au nanoparticles dispersed in the area of 1 cm^2 are irradiated under the light of intensity 150 mW cm^{-2}, the temperature should increase at the maximum rate of 1.9 K s^{-1} based on the heat capacity $C_p^{\ominus}$ = 0.129 J K^{-1} g^{-1} [1].

To clarify these contrasting two effects, we reported temperature monitoring of Ni, Ru, and Zr sites of Ni–Ru–ZrO_2 photocatalysts under CO_2 and H_2 irradiated by UV–visible light. The reactor was immersed in ethylene glycol bath to suppress the heating of reactor by the light irradiation [1]. This study monitored Au site of Au–ZrO_2 photocatalyst in liquid H_2O saturated with CO_2. H_2O is the reactant, and also suppress the heating of photocatalyst.

2 Experimental Section

Au (5.0 wt %)–ZrO_2 photocatalyst was prepared via liquid phase reduction starting from $HAuCl_4 \cdot 4H_2O$ and ZrO_2 (JRC-ZRO-07, Catalysis Society of Japan) using $NaBH_4$.

Au L_3-edge XAFS spectra were measured at the Photon Factory, on the 9C beamline equipped with a Si (1 1 1) monochromator, a Rh-coated cylindrical mirror, and a piezo transducer. 40 mg of Au–ZrO_2 photocatalyst disk (φ = 10 mm) was set in Pyrex glass cell equipped with PET films on both sides. The cell was filled with H_2O (1.5 mL), CO_2 (2.3 kPa), and He (95 kPa), and the disk was irradiated by Xe arc lamp via quartz light guide. The light intensity was 1384 mW cm^{-2}. The distance between the light guide exit (φ = 5.0 mm) and the Au–ZrO_2 disk was kept at 10 cm.

3 Results and Discussion

Under the similar photocatalytic reaction conditions, steady formations of CO and CH_4 were confirmed as long as 48 h at the formation rates of 0.54 and 0.22 μmol h^{-1} g_{cat}^{-1}, respectively, at the irradiated light intensity of 673 mW cm^{-2}.

Before UV–visible light irradiation, the coordination number (N) of Au–Au interatomic pair was evaluated to 10.48 based on curve-fit analysis. We assumed that the N values did not change in the EXAFS monitoring under UV–visible light and the following light off.

The Au–Au interatomic peak intensity at 0.26 nm (phase shift uncorrected) in the Fourier transform quickly decreased when the UV–visible light irradiation started (Figure 1A). In contrast, as soon as the excitation light was turned off, the peak intensity partially recovered (Figure 1B).

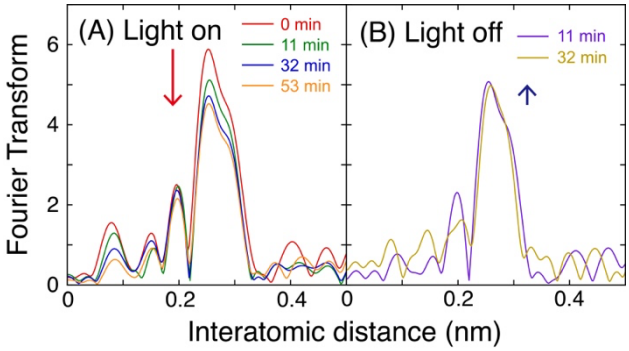

Figure 1. Time course changes of Fourier transform of Au L_3-edge EXAFS χ-function weighted by angular wave number k^3 using Au (5.0 wt %)–ZrO_2 photocatalyst under H_2O and CO_2. (A) Irradiated under UV–visible light for 66 min and (B) the light was turned off.

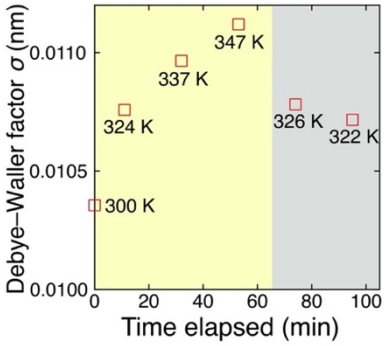

Figure 2. Time course changes of Au–Au Debye–Waller factor monitored based on Au L_3-edge EXAFS using Au (5.0 wt %)–ZrO_2 photocatalyst under H_2O and CO_2. Irradiated under UV–visible light (left) and the light was turned off (right).

The Au site temperature was evaluated based on correlated Debye model and translational movement model for metal nanoparticles [1–4]. The Au site temperature change is shown in Figure 2, in accord with the quick changes of Au–Au peak intensity upon light on and off in Figure 1.

The temperature of H_2O (liquid) seems to be well in thermal equilibrium with the temperature of Zr sites in Au–ZrO_2 disk because H_2O was in direct

contact with the disk throughout the monitoring. The Zr site temperature change was also evaluated: 314 K at the end of light irradiation and 303 K after the light was turned off for 44 min.

Based on these, Au was warmed by light energy as hot spots, and the Au–Au peak intensity partially recovered compared to initial intensity before light irradiation (Figure 1A and B) because of the warmed water by light energy. In view of photocatalysis, hot spot Au site can be promoted for hydrogenation toward CH_4, besides the charge separation effects induced by light.

References

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