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Debye–Waller factor analysis of Co^0 site on ZrO_2 under UV–visible light irradiation for CO_2 photoconversion

Tarik Loumissi, Tomoki Oyumi, Jingwei Yu, Rento Ishii, and Yasuo Izumi*
Department of Chemistry, Graduate School of Science, Chiba University, Yayoi 1-33, Inage-ku
Chiba 263-8522, Japan

1 Introduction

Photocatalytic conversion of CO_2 into fuels is expected to be one of the key solutions to global warming and energy problem in a sustainable society. However, the catalytic activity for this reaction is still low, and the selectivity to preferable fuels, e.g., methane, is not high enough for its practical use. Therefore, it is essential to clarify the reaction mechanism to feedback and solve the problems.

We tested Co_3O_4, CoO, and Co supported on ZrO_2 as photocatalysts for CO_2 photoreduction. Among these, Co–ZrO_2 photocatalyst heated at 823 K under H_2 exhibited the highest CH_4 formation rate: 300 μmol h^{-1} g_{cat}^{-1}. However, Co^0 and Co^{II} sites coexisted in the photocatalyst as reported in our Activity Report 2020 [1]. In this report, Co–ZrO_2 photocatalyst was heated at 973 K under H_2, and the valence, local structure, and thermal behavior were analyzed by EXAFS.

2 Experimental section

Co K-edge XAFS spectra were measured at 290 K in transmission mode. A Piezo transducer was used to detune the X-rays to two-thirds of the maximum intensity. The Co K-edge absorption energy was calibrated to 7709.5 eV for Co metal foil. Co (7.5 wt %)–ZrO_2 photocatalyst powder heated at 973 K under H_2 was located in a Pyrex glass reactor equipped with Kapton film windows. XAFS spectra were measured for samples under CO_2, H_2, and UV–visible light on the beamline. X-rays transmitted the disk perpendicularly while the incident angle of UV–visible light was 45° using Y-shaped fiber light guide.

3 Results and Discussion

Co (7.5 wt %)–ZrO_2 photocatalyst powder heated at 973 K under H_2 effectively formed $^{13}CH_4$ at the rate 190 μmol h^{-1} g_{cat}^{-1} using $^{13}CO_2$, H_2, and UV–visible light that was comparable to the rate using Co (7.5 wt %)–ZrO_2 photocatalyst powder heated at 823 K under H_2.

The Co state was exclusively metallic, valence zero at the interatomic distance of 0.2502 nm based on the EXAFS curve fit analysis.

Furthermore, the time course of the Debye–Waller factor during CO_2 photoreduction for 138 min and the period later than the light off was monitored (Figure 1). Initial value 0.0071 nm corresponded to 296 K of Co site based on correlated Debye model taking both bulk and surface Debye temperature into account [2,3]. During UV–visible light irradiation, the value increased to 0.0076–0.0080 nm corresponding to 341–371 K of Co site.

After the UV–visible light was turned off, the data indicated gradual temperature decrease to room temperature (Figure 1, right). Such trend strongly suggested that the heated Co^0 surface site owing the light energy proceeded the hydrogenation reaction of CO to methane and the other hydrocarbons (ethene, ethane, propene, and propane). CO was formed on ZrO_2 suface under UV–visible light [2.3].

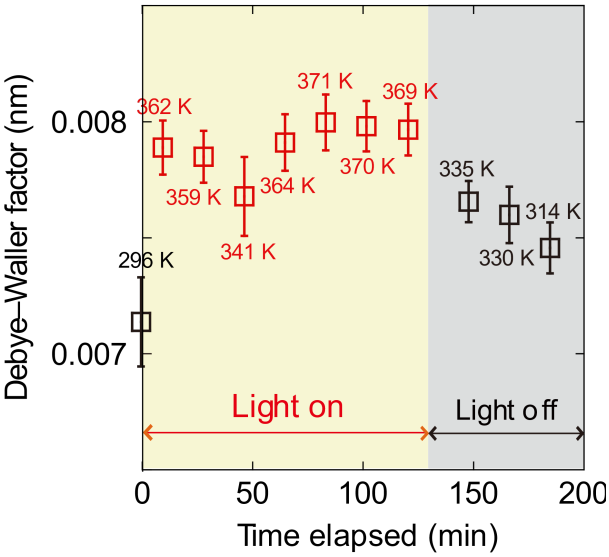

Figure 1. Time course of Debye–Waller factor for Co K-edge EXAFS measured for Co (7.5 wt %)–ZrO_2 heated at 973 K under H_2. The sample was under CO_2 (2.3 kPa) and H_2 (21.7 kPa) during the measurement.

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References

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* yizumi@faculty.chiba-u.jp