

Valence and structural analysis of cobalt nanoparticles on ZrO₂ for CO₂ photoconversion using XAFS

Tarik Loumissi, Hongwei Zhang, 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 CO₂ into fuels is expected to be one of the key solutions to global warming and energy problem in a sustainable society. However, the catalytic activities for this reaction are still low, and the selectivity to preferable fuels, e.g., methane, is not high enough for practical use. Therefore, it is essential to clarify the reaction mechanism to solve these problems.

We tested Co₃O₄, CoO, and Co supported on ZrO₂. Among these catalysts, CoO–ZrO₂ exhibited the highest catalytic activity to form CH₄ from CO₂ at a rate of 140 μmol · h⁻¹ · g_{cat}⁻¹. This fact indicates that Co(II) is the major active site combined with ZrO₂. The Co site valence and structure were analyzed by Co K-edge X-ray absorption fine structure.

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-ray to two-thirds of the maximum intensity to suppress higher harmonics. The Co K-edge absorption energy was calibrated to 7709.5 eV using the spectrum of Co metal foil with 10 μm thickness. 150 mg of Co (5.0 wt %)–ZrO₂ photocatalyst was located in a reactor equipped with Kapton film windows. XAFS spectra were measured for samples under CO₂, H₂, and UV–visible light on the beamline. X-rays transmitted the disk perpendicularly while the incident angle of UV–visible light was 45°.

3 Results and Discussion

As shown in Figure 1, XANES data for Co nanoparticles on ZrO₂ before photoreduction test was fitted well with those of Co (75 mol%) and CoO (25 mol%) (Figure 1). The coordination number of Co–Co was 7.2 based on EXAFS analysis, suggesting the presence of mean 1.3 nm-size Co particles (dispersion 0.56) [1].

Then, the Co–ZrO₂ sample (150 mg) was exposed to CO₂ (2.3 kPa) and H₂ (21.7 kPa). XANES data for the Co nanoparticles were fitted well with those of Co (35 mol%) and CoO (65 mol%). The coordination number of Co–Co was 4.3 based on EXAFS analysis, suggesting that mean 0.74 nm of Co nanoparticles covered with CoO shell under CO₂ and H₂.

The change under CO₂ and H₂ can be quantitatively understood based on the reaction of surface Co sites with CO₂. Surface Co sites among 75 mol% Co before

photoreduction test are $75 \times 0.56 = 42$ mol%. Therefore, Co(II) sites became $42 + 25 = 67$ mol% by the reaction with CO₂. Remained Co⁰ sites was $75 \times 0.44 = 33$ mol%, in good agreement with 65 and 35 mol% based on Figure 1.

The mixed phase of metallic Co and CoO for the photoactivation of CO₂ and/or Co needs to be investigated further based on semiconducting nature of CoO (band gap 2.6 eV) and Co₃O₄ (1.57 eV) combined with H activation over metallic Co surface [2].

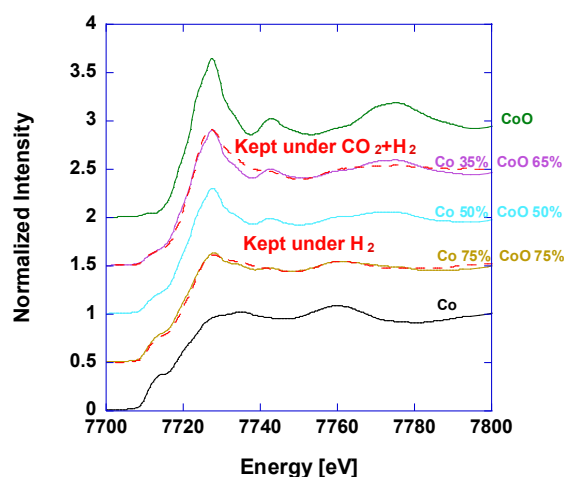


Figure 1. XANES spectra of Co K-edge for Co (5.0 wt %)–ZrO₂ under H₂ (21.7 kPa) and that under CO₂ (2.3 kPa) + H₂ (21.7 kPa).

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Reference

- [1] B. J. Kip, F. B. M. Duivenvoorden, D. C. Koningsberger, R. Prins, *J. Catal.*, **105**, 26–38 (1987).
- [2] H. Zhang, T. Itoi, T. Konishi, Y. Izumi, *Angew. Chem. Int. Ed.*, **60**, 9045–9054 (2021).

* yizumi@faculty.chiba-u.jp