

# Debye–Waller factor analysis of Co<sup>0</sup> site on ZrO<sub>2</sub> under CO<sub>2</sub>, H<sub>2</sub>O, H<sub>2</sub>, and UV–visible light irradiation

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## 1. Introduction

In contrast to the irreversible consumption of fossil fuel and raw materials, the conversion of CO<sub>2</sub> into fuels and/or valuable chemicals using a sustainable energy represents a pivotal step toward establishing a new carbon-neutral cycle. The economically viable photocatalytically formed C<sub>2</sub> and C<sub>3</sub> hydrocarbons derived from photocatalytic CO<sub>2</sub> reduction have emerged as key chemicals (0.9–8 \$ kg<sup>-1</sup>) compared to CO and CH<sub>4</sub> (0.06–0.18 \$ kg<sup>-1</sup>). We reported the EXAFS analysis for the switchover of photocatalytic pathways from CO<sub>2</sub> to C<sub>1-3</sub> paraffin versus from CO to selective C<sub>2</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>6</sub>, using a Co<sup>0</sup>–ZrO<sub>2</sub> catalyst [1,2]. In this report, the valence state, structure, and the temperature of the Co site was monitored under CO<sub>2</sub>, H<sub>2</sub>O, H<sub>2</sub>, and UV–visible light irradiation.

## 2. Experimental section

Cobalt K-edge XAFS spectra were measured in the transmission mode at the Photon Factory, High Energy Accelerator Research Organization (Tsukuba, Japan) on the 9C beamline using a Si(1 1 1) monochromator, a Pt-coated mirror, and a piezo transducer. The Co–ZrO<sub>2</sub> samples were treated in a quartz U-tube and transferred to a Pyrex cell filled with reaction gases, which was equipped with a polyethylene terephthalate film (Toyobo, Japan, G2, 50 μm thick) on both sides for both UV–visible light and X-ray transmission. A 500 W Xe arc lamp (Model SX-UID502XAM, Ushio) was used as the light source, with the distance between the fiber light exit of the Y-shaped quartz light guide and the photocatalyst set at 2 cm.

The obtained Co K-edge XAFS data were analyzed using the XDAP software package version 3.2.9 [3]. Multiple-shell curve-fit analyses were performed with the data obtained on the EXAFS using the empirical amplitude extracted from the EXAFS data for the Co metal foil (10 μm thick).

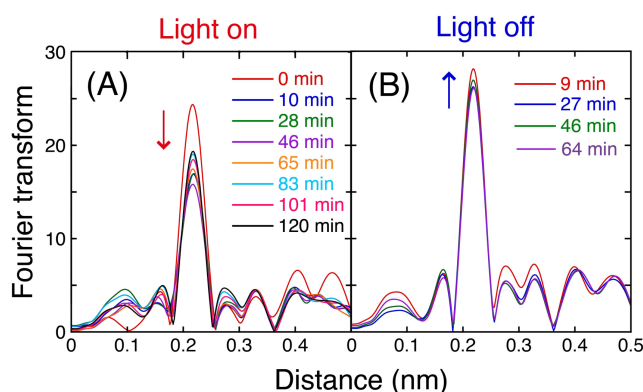
## 3. Results and Discussion

<sup>13</sup>CO<sub>2</sub> (2.3 kPa) photoreduction using D<sub>2</sub>O (2.2 kPa), H<sub>2</sub> (21.7 kPa), and Co–ZrO<sub>2</sub> photocatalyst reduced in H<sub>2</sub> at 823 K formed <sup>13</sup>C-methane with a D ratio of 9.2 mol%, which agrees with a D ratio in the reactants (9.1 mol%) [4]. This suggests that D<sub>2</sub>O and H<sub>2</sub> reached equilibrium more rapidly and were shuffled over Co<sup>0</sup> more efficiently than the progressive hydrogenation steps to C<sub>2,3</sub> paraffin common under either H<sub>2</sub> or H<sub>2</sub>O.

The methane formation rate was the 9.6% of that observed using H<sub>2</sub> owing to the competitive adsorption of OH on the Co<sup>0</sup> surface and/or H<sub>2</sub>O adsorption at the oxygen

vacancy site of ZrO<sub>2</sub> [4]. However, during photocatalytic CO<sub>2</sub> reduction tests under H<sub>2</sub>O (2.3 kPa) and H<sub>2</sub> (21.7 kPa; Figure 1) through Co K-edge EXAFS, the Co<sup>II</sup> species could not be detected. This demonstrates that the metallic Co surface effectively activates H<sub>2</sub>O for C<sub>2,3</sub> paraffin photosynthesis using either H<sub>2</sub> or H<sub>2</sub>O (g).

Furthermore, the quick temperature increase when the UV–visible light was turned on (Figure 1A) and quick temperature decrease when the light was turned off (Figure 1B) were also demonstrated based on the peak intensity change in the Fourier transform owing to the change of Debye–Waller factor for the Co–Co interatomic pair.



**Figure 1.** Time–course change of the Fourier transform of the angular wave number  $k^3$ -weighted EXAFS  $\chi$ -uncion for the Co (7.5 wt %)–ZrO<sub>2</sub> photocatalyst reduced in H<sub>2</sub> at 973 K under CO<sub>2</sub> (2.3 kPa), H<sub>2</sub>O (2.3 kPa), and H<sub>2</sub> (21.7 kPa) (A) during irradiation under UV–visible light and (B) under dark.

## References

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