

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

Tomoki Oyumi, 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

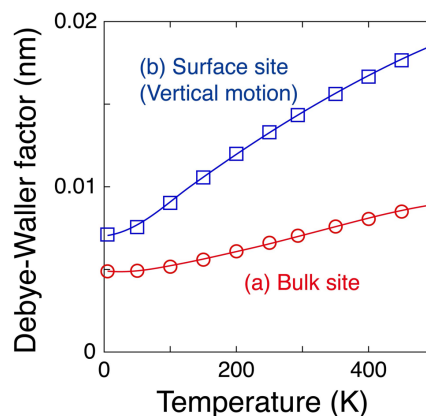
In contrast to irreversible fossil fuel consumption as fuels and resources, CO<sub>2</sub> reduction into fuels and/or valuable chemicals using a sustainable energy source completes a new carbon-neutral cycle [1,2]. Photocatalytic CO<sub>2</sub> reduction has the advantage of being direct and simple; however, the products have been limited to CO, CH<sub>4</sub>, and CH<sub>3</sub>OH, in contrast to the electrochemical production of formate, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, CH<sub>3</sub>CHO, C<sub>2</sub>H<sub>5</sub>OH, C<sub>3</sub>H<sub>8</sub>, C<sub>3</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>7</sub>OH, acetate, and oxalate from CO<sub>2</sub> and/or CO owing to the concentrated electrons supplied from electricity. The photocatalytically formed C<sub>2</sub> and C<sub>3</sub> hydrocarbons (HCs) from CO<sub>2</sub> have recently been economically viable 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>) [3]. This study reports the EXAFS analysis for the switchover of photocatalytic pathways from CO<sub>2</sub> to C<sub>1–3</sub> paraffins 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.

## 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) using a Si(1 1 1) monochromator, a Pt-coated mirror, and a piezo transducer [4,5]. The Co–ZrO<sub>2</sub> samples were treated in quartz *U*-tube and transferred to Pyrex cell filled with reaction gases, which was equipped with a Kapton film (Dupont, Wilmington, DE, USA; 50 μm thick) on one side for X-ray transmission and a polyethene terephthalate film (Toyobo, Japan, G2, 50 μm thick) on the other side for both UV–visible light and X-ray transmission. The distance between the fiber light exit of the Y-shaped quartz light guide and the photocatalyst was 20 mm.

The obtained Co K-edge XAFS data were analyzed using the XDAP software package [6]. The pre-edge background was approximated with a modified Victoreen function,  $C_2/E^2 + C_1/E + C_0$ , where  $E$  is the photon energy and  $C_0$ ,  $C_1$ , and  $C_2$  are constants. 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). The interatomic distance ( $R$ ) and coordination number ( $N$ ) values for the Co–Co and Co–O interatomic pairs were set to 0.2502 nm and 12 [7] and 0.2131 nm and 6 [8], respectively.

The temperature dependence of the Debye–Waller factor ( $\sigma$ ) was calculated for the bulk site and surface site of Co metal (Figure 1) using the correlated Debye model with the ab initio multiple-scattering calculation code, FEFF8 [9], and bulk and surface Debye temperatures.



**Figure 1.** Correlation between the Debye–Waller factor ( $\sigma$ ) and temperature for (a) bulk sites (circle, ○) and (b) surface sites (vertical motion; square, □) in/on the Co metal generated using the correlated Debye model with a FEFF8 code [9].

## 3. Results and Discussion

The  $\sigma$  value was calculated based on the correlated Debye model for bulk and surface Co sites (vertical motion versus surface) and the Debye temperature for bulk  $\theta_{D(\text{Bulk})}$  (445 K [10]) and surface  $\theta_{D(\text{Surface}, \perp)}$  for the vertical motion of freedom (211 K [11]). We approximated the mean Co nanoparticle temperature ( $T$ ) as the arithmetic mean value based on  $\theta_{D(\text{Surface}, \perp)}$  weighted using  $1/2 \cdot 1/3 D$  for vertical translational motion at a free hemisphere surface and  $\theta_{D(\text{Bulk})}$  weighted using  $(1-D) + (1/2)D + (1/2 \cdot 2/3)D$  for the bulk site, nonfree hemisphere in contact with ZrO<sub>2</sub>, and horizontal translational motion at a free hemisphere surface.

$$T_{\text{nanoparticle}} = T_{\text{Surface}, \perp} \times 1/6 D + T_{\text{Bulk}} \times (1 - 1/6 D) \quad (1)$$

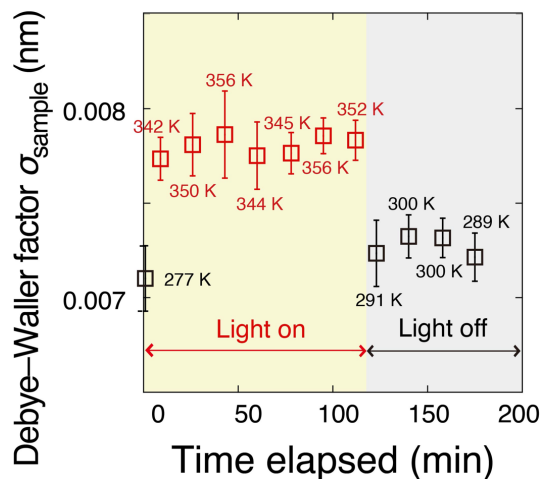
The  $\sigma$  value for samples ( $\sigma_{\text{sample}}$ ) was calculated using eq. 2, taking the contribution of structural disorder ( $\sigma_{\text{disorder}}$ ) and the difference of the  $\sigma_{\text{sample}}$  value from the Co metal foil ( $\sigma_{\text{XDAP}}$ ) into account.

$$\sigma_{\text{sample}}^2 = \sigma_{\text{Co metal, correlated Debye}}^2 + \Delta(\sigma_{\text{disorder}}^2) + \Delta(\sigma_{\text{XDAP}}^2)$$

At 296 K,  $\sigma_{\text{sample}}$  and  $\sigma_{\text{Co metal, correlated Debye}}$  values were 0.007 (28) and 0.007 (05) nm, respectively, for the nanoparticle model above based on the correlated Debye model (Figure 1) and eq. 1. The  $\sigma_{\text{XDAP}}$  value was given as 0.001 (00) nm. Thus,  $\sigma_{\text{disorder}}$  was evaluated as 0.001 (82) nm.

The time course of Fourier transform,  $\sigma$  value, and Co<sup>0</sup> site temperature under CO (2.3 kPa), H<sub>2</sub> (2.3 kPa), Co (7.5 wt %)–ZrO<sub>2</sub> reduced under H<sub>2</sub> at 973 K, and UV–

visible light (Figure 2) behaved very similarly to the report last year under CO<sub>2</sub> (2.3 kPa), H<sub>2</sub> (2.3 kPa), Co (7.5 wt %)-ZrO<sub>2</sub> reduced under H<sub>2</sub> at 973 K, and UV-visible light [12], irrelevant to reactants [3]. Thus, the temperature change was concluded mostly owing to light energy.



**Figure 2.** Time course of Debye–Waller factor based on the Co K-edge EXAFS analysis and the evaluated temperature of Co nanoparticles in Co (7.5 wt %)-ZrO<sub>2</sub> reduced under H<sub>2</sub> at 973 K using CO (2.3 kPa), H<sub>2</sub> (2.3 kPa), and UV-visible light irradiation based on correlated Debye model.

## References

- [1] Izumi, Y. Recent Advances in Photocatalytic Conversion of Carbon Dioxide into Fuels with Water and/or Hydrogen Using Solar Energy and Beyond. *Coord. Chem. Rev.* **2013**, 257, 171–186.
- [2] Izumi, Y. Recent Advances (2012–2015) in the Photocatalytic Conversion of Carbon Dioxide to Fuels Using Solar Energy: Feasibility for a New Energy, in ACS Books "Advances in CO<sub>2</sub> Capture, Sequestration, and Conversion", Volume 1194, F. Jin, L.-N. He, and Y. H. Hu, Eds., Chapter 1, pp 1–46.
- [3] Loumissi, T.; Ishii, R.; Hara, K.; Oyumi, T.; Zhang, H.; Hirayama, R.; Niki, K.; Itoi, T.; Izumi, Y., under review.
- [4] Zhang, H.; Itoi, T.; Konishi, T.; Izumi, Y. Efficient and Selective Interplay Revealed: CO<sub>2</sub> Reduction to CO over ZrO<sub>2</sub> by Light with Further Reduction to Methane over Ni<sup>0</sup> by Heat Converted from Light. *Angew. Chem. Int. Ed.* **2021**, 60, 9045–9054.
- [5] Zhang, H.; Itoi, T.; Konishi, T.; Izumi, Y. Dual Photocatalytic Roles of Light: Charge Separation at the Band Gap and Heat via Localized Surface Plasmon Resonance To Convert CO<sub>2</sub> into CO over Silver–Zirconium Oxide. *J. Am. Chem. Soc.* **2019**, 141, 6292–6301.
- [6] Vaarkamp, M.; Linders, H.; Koningsberger, D. XDAP Version 3.2.9.; XAFS Services International: Woudenberg, The Netherlands, 2022.
- [7] [https://www.webelements.com/cobalt/crystal\\_structure.html](https://www.webelements.com/cobalt/crystal_structure.html) (checked on June 25, 2023).
- [8] Jauch, W.; Reehuis, M.; Bleif, H. J.; Kubanek, F. Crystallographic Symmetry and Magnetic Structure of CoO. *Phys. Rev. B* **2001**, 64, 052102.
- [9] Ankudinov, L.; Ravel, B.; Rehr, J. J.; Conradson, S. D.; Real Space Multiple-Scattering Calculation and

Interpretation of X-Ray-Absorption Near-Edge Structure. *Phys. Rev. B Condens. Matter Mater. Phys.* **1998**, 58, 7565–7576.

- [10] American Institute of Physics Handbook, 3<sup>rd</sup> Ed; Gray, D. E., Billings, B. H., Frederikse, H. P. R., Bleil, D. F., Lindsay, R. B., Cook, R. K., Marion, J. B., Crosswhite, H. M., Zemansky, M. W., Eds.; McGraw-Hill: New York, 1972; p 4-115.
- [11] Hou, M.; El Azaoui, M.; Pattyn, H.; Verheyden, J.; Koops, G.; Zhang, G. Growth and Lattice Dynamics of Co Nanoparticles Embedded in Ag: A Combined Molecular-Dynamics Simulation and Mössbauer Study. *Phys. Rev. B* **2000**, 62(8), 5117–5128.
- [12] Loumissi, T.; Oyumi, T.; Yu, J.; Ishii, R.; Izumi, Y. *Photon Fac. Act. Rep.* 2021 **2022**, 39, 2019G141. [http://pfwww.kek.jp/acr/2021pdf/u\\_reports/pf21b0145.pdf](http://pfwww.kek.jp/acr/2021pdf/u_reports/pf21b0145.pdf)

\* yizumi@faculty.chiba-u.jp