

Monitoring of the Active Site of Photoreduction from CO to Ethene and Propene using Metallic Co–ZrO₂ Photocatalyst

To create a new C-neutral cycle, it is economically viable to convert CO₂ to C_{2,3} hydrocarbons utilizing renewable energy. Co⁰–ZrO₂ photocatalyst converted CO into C₂H₄ and C₃H₆ by the irradiation of UV–visible light, and the key reaction steps were followed by EXAFS. By reducing at 973 K, Co was metallic particles of mean 2.9 nm. At the Co K-edge, Debye–Waller factor increased quickly from 0.0071 to 0.0078 nm by the temperature increase to 350 ± 8 K by the irradiation of UV–visible light, elucidating reaction steps from CO to CH₂ species then to C₂H₄ and C₃H₆.

In contrast to the irreversible consumption of fossil fuels and raw materials, the conversion of CO₂ reduction into fuels and/or valuable chemicals using a sustainable energy represents a pivotal step toward establishing a new C-neutral cycle [1, 2]. The economically viable nature that formed C₂ and C₃ hydrocarbons derived from photocatalytic CO₂ reduction has emerged as key chemicals (0.9–8 \$ kg^{−1}) compared to CO and CH₄ (0.06–0.18 \$ kg^{−1}). A comprehensive understanding of the reaction pathways of the photocatalytic synthesis of C₂ and C₃ hydrocarbons from CO₂ remains elusive, hindering precise control of reaction. This study reports selective photocatalytic pathway from CO to C₂H₄ and C₃H₆ using a Co⁰–ZrO₂ catalyst.

The local electronic and geometric structures associated with the thermal behavior of active metallic Co sites essential for CO photoreduction were monitored via Co K-edge EXAFS. The analysis was conducted under UV–visible light irradiation using CO (2.3 kPa), H₂ (21.7 kPa), and Co (7.5 wt %)-ZrO₂ reduced at 973 K under H₂. In the Fourier transform of EXAFS before UV–visible light irradiation, the curve-fit analysis revealed an intense peak observed at 0.21 nm (Fig. 1(a), 0 min) owing to a Co–Co inter-

atomic distance of 0.249 nm with a surface dispersion was 0.43.

The Debye–Waller factor (σ) was calculated using the correlated Debye model for bulk and surface Co sites (vertical motion versus surface), considering the Debye temperature for bulk (445 K) and surface for the vertical motion of freedom (211 K). We approximated the mean temperature of Co nanoparticle as the arithmetic mean value, considering vertical translational motion at a free hemisphere surface, the bulk site, nonfree hemisphere in contact with ZrO₂ surface, and horizontal translational motion at a free hemisphere surface.

Then, the temperature of the Co site was inversely evaluated based on the monitored σ value (Fig. 1(c)). This specific approach directly monitored the local Co site temperature. The Co sites were initially at 277 K before exposure to UV–visible light. Upon irradiation, the temperature of the Co sites quickly increased to 350 ± 8 K, rapidly decreasing once the light was turned off after 117 min (Fig. 1(b)). The temperature elevation in Fig. 1(c) stemmed from the transformation of light energy into heat at the Co⁰ surface, quickly reaching the heat equilibrium and dissipating into ZrO₂ support/the reactor/EXAFS cell.

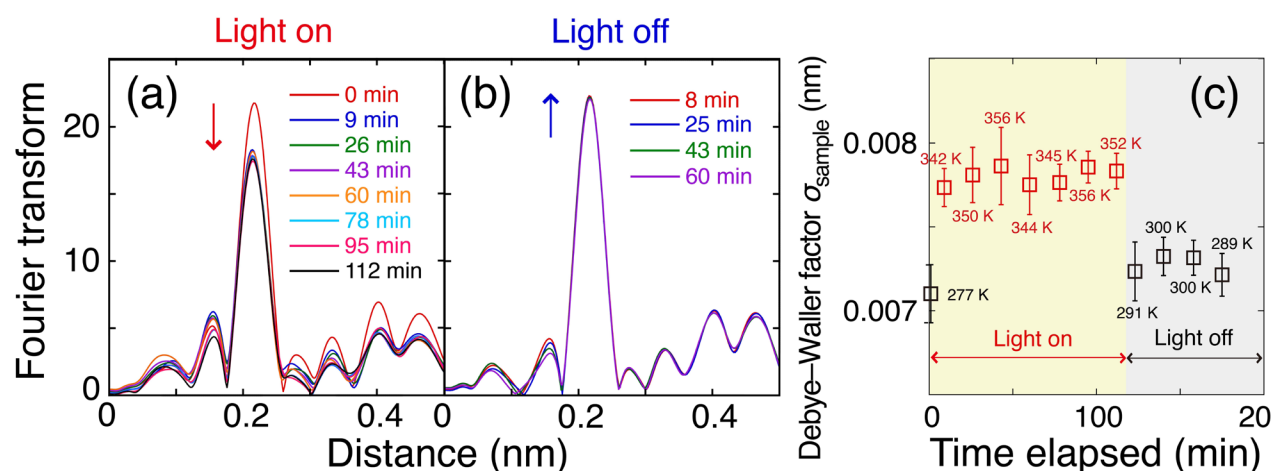
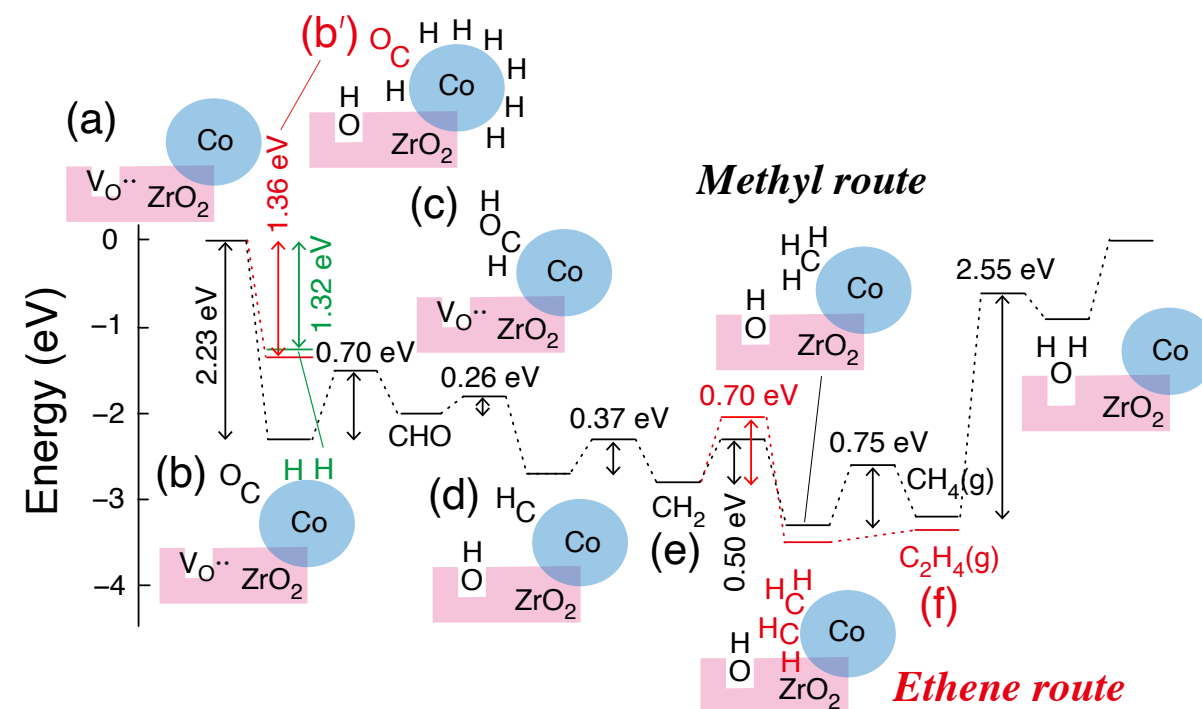


Figure 1: Time-course evolution of the Fourier transform of the angular wave number k^2 -weighted Co K-edge EXAFS X-function for the Co (7.5 wt %)-ZrO₂ photocatalyst under CO (2.3 kPa) and H₂ (2.3 kPa) (a) during UV–visible light irradiation (142 mW cm^{−2}) and (b) under dark and (c) Debye–Waller factor derived from the EXAFS analysis and the determined temperature of Co nanoparticles based on the correlated Debye model.



Scheme 1: Energy diagram over monoclinic ZrO₂ (1 1 1) surface combined with Co₁₉ cluster exposing hcp (0 1 0) surface calculated under CO and H₂. Ethene route was also drawn compared to methyl route^a.

The suggested reaction route of CO photoreduction to C₂H₄ was confirmed by DFT calculations. CO is adsorbed on the Co⁰ site (Scheme 1(b)), followed by the formation of CHO and HCOH species at the interface of the ZrO₂ surface and Co⁰ (Scheme 1(c)). It is energetically advantageous when the hydroxy group fills the neighboring surface O vacancy (V_O^{••}) site to form CH (Scheme 1(d)). In the following Methyl route, the barrier for CH₃ hydrogenation to form CH₄ is highest (0.75 eV). In comparison, the Ethene route via the coupling of CH₂ was more favorable (activation energy 0.70 eV, Scheme 1(e) and (f)), which aligns with the specific formation of ¹³C₂H₄ and ¹³C₃H₆ from ¹³CO [3]. The isotopic shuffling of ¹³C/¹²C was also plausible between CO adsorbed on the Co⁰ surface and ¹²CO₂ adsorbed at the V_O^{••} sites from the air (Scheme 1(a–c)).

The advantageous CO adsorption in the first stage transitions to competitive adsorption of CO (adsorption energy 1.36 eV; Scheme 1(b)) and H (1.32 eV; Scheme 1(b')) in the second step of consecutive photocatalysis. The increased population

of H on Co⁰ sites kinetically explains the transition to form C_{1–3} paraffin and C₃H₆ after 4 h of the photocatalytic reaction. Selective C_{2,3} olefin formation proceeded during initial 4 h of reaction while on later stage, CH₄ was a major product with minor C₂H₆, C₃H₆, and C₃H₈ [3].

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BEAMLINES

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