

Monitoring of Fe site on ZrO₂ to form C₁₋₃ hydrocarbons under CO₂, H₂, and UV–visible light irradiation

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1. Introduction

Photocatalytic CO₂ reduction establishes a novel C-neutral cycle and is considered a potential environmental solution for a sustainable society. However, its near-term implementation is hindered by economic challenges, primarily due to the costs of photocatalysts and reactor design. Among first-row transition metals, Fe is the most abundant and cost-effective. Consequently, Fe-based photocatalysts for CO₂ photoreduction have been widely studied. However, nearly all reported systems employ Fe in the form of metal ions within metal–organic frameworks, covalent organic frameworks, porphyrins, or as Fe₂O₃, functioning primarily as redox mediators. In this study, metallic Fe surface was monitored by EXAFS for CO₂ photoreduction catalyst forming C₁₋₃ hydrocarbons in combination with semiconductor ZrO₂ [1].

2. Experimental section

Fe K-edge X-ray absorption fine structure spectra were measured at beamline 9C. A Si (1 1 1) double-crystal monochromator was used to analyze X-rays emitted from the storage ring via a bending magnet. The monochromator was adjusted using a piezo transducer and focused using a bent cylindrical mirror coated with Rh. Photocatalyst samples were pretreated in a quartz U-tube and transferred to a Pyrex cell filled with reaction gas (CO₂ + H₂). The cell was equipped with polyethylene terephthalate film (Toyobo, Japan, Type G2, 50 μm thick) on both sides. A 300 W Xe arc lamp (Model MAX-350, Asahi spectra) served as the light source, with a fiber light exit positioned 2 cm from the photocatalyst.

The obtained Fe K-edge XAFS data were analyzed using the XDAP version 3.2.9 [2]. 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 Fe metal foil (4 μm thick).

3. Results and Discussion

¹³CO₂ (2.3 kPa) photoreduction using H₂ (21.7 kPa) by metallic Fe⁰–ZrO₂ photocatalyst reduced in H₂ at 973 K (Fe⁰–ZrO₂-973R) was carried out under UV–visible light irradiation at 110 mW cm⁻². Only the photoreduction of ¹³CO₂ to ¹³CO proceeded after 5 h of reaction. Increasing the UV–visible light intensity to 322 mW cm⁻² switched to the reduction of ¹³CO₂ to ¹³CH₄, and further increasing the UV–visible light intensity to 472 mW cm⁻² induced a selective photoreduction to ¹³C_{2,3} paraffins (15 mol%) after 20 h of reaction.

To identify the active sites responsible for these reaction steps, Fe K-edge EXAFS was measured for Fe⁰–ZrO₂-973R. Unexpectedly, ~20% of the Fe⁰ sites reduced at 973 K were oxidized upon reaction with ¹³CO₂ in the dark (Fig. 1A, 0 min). This oxidation is attributed to the formation of an M-shaped Fe²⁺–O–C(=Fe⁰)–O–Fe²⁺ species upon CO₂ adsorption on Fe. At this stage, CO did not desorb spontaneously from Fe surface. Upon UV–visible light irradiation, the Fourier transform of EXAFS spectra (Fig. 1A, 0 min) showed that the Fe–O and Fe···Fe peaks corresponding to Fe–O were rapidly replaced by a metallic Fe–Fe peak at 0.21 nm (phase shift uncorrected; Fig. 1A, 12 min). This transformation indicates the reduction of Fe²⁺ in the M-shaped Fe²⁺–O–C(=Fe⁰)–O–Fe²⁺ species.

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

Thus, metallic Fe⁰ sites were proved to be responsible for C₁₋₃ hydrocarbon synthesis from CO₂ based on EXAFS.

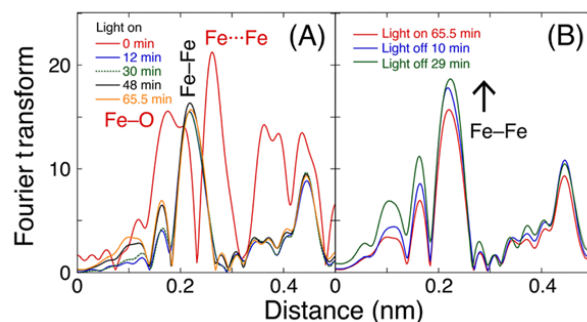


Figure 1. Time-course change of the Fourier transform of the angular wave number k^3 -weighted EXAFS χ -uncorrection for the Fe (7.5 wt %)-ZrO₂ photocatalyst reduced in H₂ at 973 K under CO₂ (2.3 kPa), and H₂ (21.7 kPa) (A) during irradiation under UV–visible light and (B) under dark.

References

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- [2] Vaarkamp, M.; Linders, H.; Koningsberger, D. XDAP Version 3.2.9.; XAFS Services International: Woudenberg, The Netherlands, 2022.

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