Anchoring and reactivation of single-site Co–porphyrin over TiO₂ for the efficient photocatalytic CO₂ reduction

Keisuke Hara, Chao Zhang, Jiwon Yang, 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 renewable energy sources completes a new C-neutral cycle in sustainable society. Semiconductors have been extensively studied for the catalysts. Metal complexes are usually employed for CO₂ photoreduction allowing precise control of catalytic properties. Accurate molecular design of metal complexes and further combination with semiconductors enable higher catalytic activity over stable photocatalyst. In this study, a photocatalyst consisting of Co–tetakis(4-carboxyphenyl)porphyrin (TCPP) metal complex and TiO₂ was designed. The site coordination and electronic structure of active Co sites were monitored by EXAFS.

2. Experimental section H–TCPP and CoCl₂·6H₂O were dissolved into dimethylformamide and refluxed at 433 K. The red precipitate was washed with deionized water, and dried in vacuum at 333 K. Co–TCPP was added into suspended TiO₂ in ethanol and stirred. The precipitate was filtered, washed, and dried in vacuum at 298 K.

The photocatalysts Co–TCPP–TiO₂ that was used for a photocatalytic test was reactivated under ethanol (2.7 kPa) and the irradiation of UV–visible light [1].

3. Results and Discussion Using $^{13}\text{CO}_2$, H₂, UV–visible light, and Co–TCPP–TiO₂ composites, $^{13}$CO formation rate reached a maximum: 5.6 μmol h⁻¹ g⁻¹. When reactivated with ethanol, $^{13}$CO formation rate was 63.0 μmol h⁻¹ g⁻¹.

The reason of reactivation was investigated using Co K-edge EXAFS (Figure 1A). The coordination at Co site retained during the reaction using ethanol and UV–visible light. Co–N coordination number (N; the value was 4) for fresh catalyst decreased to 3.5 after the photocatalytic test (a peak at 0.14 nm, phase shift uncorrected, Figure 1B-b) mostly due to the deformation and/or partial/reductive decomposition of Co–TCPP. The N value further decreased to 3.1 after the reactivation using ethanol and UV–visible light (a peak at 0.14 nm, phase shift uncorrected, Figure 1B-c) due to the formation of unsaturated Co site by the removal of hydroxy group by ethanol enabling the highest $^{13}$CO formation rate: 63 μmol h⁻¹ g⁻¹.

The Co K-edge XANES spectra were also compared for fresh Co–TCPP–TiO₂ (Figure 1C-a), the catalyst under CO₂ and H₂ before, and after UV–visible light irradiation (Figure 1C-b), and the catalyst of Figure 1C-b reactivated under ethanol and UV–visible light (Figure 1C-c). These XANES pattern retained very similar pattern, demonstrating the intact single Co site coordinated by TCPP ligand. The intensity of pre-edge peak at 7712 eV progressively decreased by CO₂ photoreduction test (Figure 1C-b), then reactivation under ethanol and UV–visible light (Figure 1C-c), suggesting gradual reduction of Co ion site. The reductive decomposition of TCPP was still minor under CO₂, H₂, and light and/or under ethanol and light.

Figure 1. (A) $k^1\chi$ and (B) its associated Fourier transform of Co K-edge EXAFS of Co–TCPP (2.5 wt %)–TiO₂ as fresh, evacuated (a), after photoreduction test using CO₂ (2.7 kPa), H₂ (20.7 kPa), and UV–visible light (b), and after subsequent treatment using C₃H₇OH (2.7 kPa) and UV–visible light (c).

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* yizumi@faculty.chiba-u.jp