Why Is Water More Reactive than Hydrogen in Photocatalytic CO₂ Conversion? – Elucidation by Means of X-Ray Absorption Fine Structure

Photocatalytic conversion of CO_2 into mainly methane using Pd/TiO_2 proceeds faster using water than hydrogen as a reductant. This is contradictory because the former reaction consists of water photosplitting and the latter reaction (CO_2 + hydrogen). To elucidate the reason, Pd and Ti K-edge X-ray absorption fine structure was monitored during CO_2 photoconversion using H_2 or moisture. As a result, the coordination number N(Ti–O) and N(Ti(–O–)Ti) values decreased from the original values for crystalline TiO_2 (6 and 12) to 4.9–5.7 and 9.7–10.6 under CO_2 and moisture in contrast to smaller decreases under CO_2 and H_2 and under Ar.

Photocatalytic conversion of CO_2 into fuels is one of the routes to producing C neutral fuels without a net increase in atmospheric CO_2 concentration associated with fossil-derived alternatives [1]. The reaction includes two steps: water oxidation to O_2 followed by CO_2 photoconversion to form methane, etc.:

$$2H_2O \text{ (g)} \rightarrow O_2 \text{ (g)} + 4H^+ \text{ (surface)} + 4e^- \qquad (1)$$
$$CO_2 \text{ (g)} + 8H^+ \text{ (surface)} + 8e^- \rightarrow CH_4 \text{ (g)} + 2H_2O \text{ (g)} \qquad (2)$$
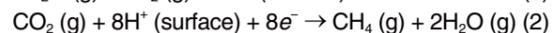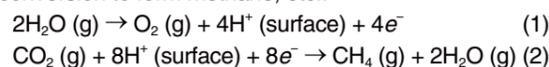
We systematically tested photocatalytic reaction under CO_2 + H_2 (**Table 1a**), essentially identical to equation 2, for photocatalytic conversion of CO_2 into fuels if it is combined with the water photo-oxidation step (equation 1) [2]. Based on the total formation rates of CH_4, CO, and methanol, water was evidently more reactive than H_2 for CO_2 photoconversion (**Table 1a, b**).

The Pd/TiO_2 sample was prepared via liquid phase reduction from an aqueous solution of Na_2PdCl_4 and TiO_2 (P25, Degussa) [2]. Pd K-edge XAFS spectra were measured on beamline AR-NW10A. Ti K-edge XAFS spectra were measured on beamlines 9A, 9C, and 12C. Spectra for the Pd/TiO_2 sample (10 mg) diluted by boron nitride were measured in the presence or absence of UV–visible light irradiation provided by a 500-W Xe arc lamp (81.6 mW cm⁻²) at the beamline. The obtained

Table 1. Results of photocatalytic tests for 5 h using 10 mg of Pd(0.5 wt%)/TiO_2 photocatalysts at 0.80 MPa.

Entry	Reactants (MPa)			Formation rates (µmol h⁻¹ g$_{cat}$⁻¹)			
	CO_2	H_2	H_2O	CO	CH_3OH	CH_4	Σ(C-products)*1
a	0.24	0.56		< 0.08	< 0.004	8.6	8.6
b	0.80		0.002 3	6.3	0.52	30	37

*1 Total rates for C-containing products.

XAFS data were analyzed using the XDAP software package.

The X-ray absorption near-edge structure (XANES) at the Pd K-edge suggested metallic Pd nanoparticles (mean particle size ~3 nm) on TiO_2. The extended X-ray absorption fine structure (EXAFS) also did not show significant change during photoreactions under CO_2 + H_2 or CO_2 + moisture based on the Pd–Pd shell, but the coordination number N(Pd–O) decreased from 1.9 for fresh sample to 0.6–0.9 after the photocatalytic tests under CO_2 + H_2 at 0.024–0.40 MPa [2] and to 0.8–1.0 under CO_2 + moisture at 0.0046–0.40 MPa [3]. The decrease of N(Pd–O) values suggested the formation of oxygen vacancy (O_v) sites on/in TiO_2 near Pd nanoparticles under the reaction conditions of CO_2 photoconversion.

Figure 1: Time course of Ti K-edge EXAFS for Pd/TiO_2 photocatalyst (10 mg) under CO_2 (100 kPa) and moisture (2.2 kPa) for 3.5 h irradiated by UV–visible light and subsequently for 0.5 h under dark. The changes of **(A)** N(Ti–O) values, **(B)** N(Ti(–O–)Ti) values, and **(C)** Fourier transform of angular wavenumber k^3-weighted EXAFS χ function.
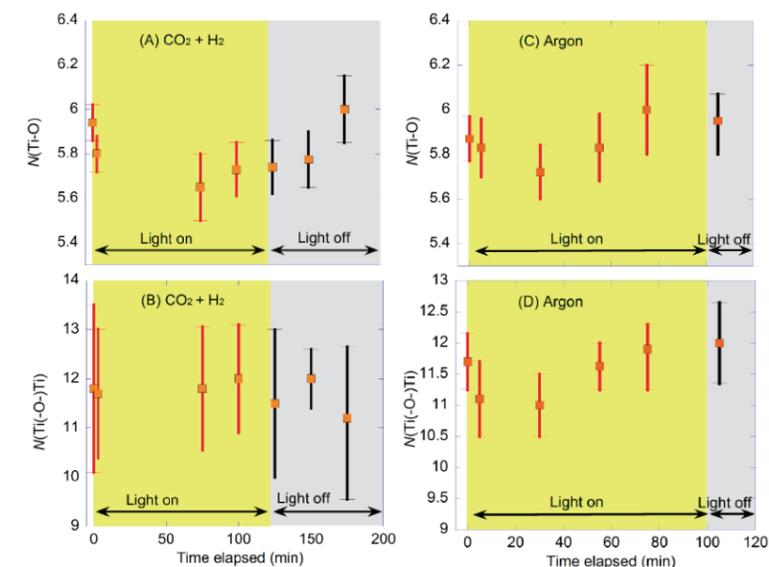
Figure 2: Time course of Ti K-edge **(A–D)** EXAFS for Pd/TiO_2 photocatalyst (10 mg). **(A, B)** under CO_2 (70 kPa) and H_2 (30 kPa) for 125 min irradiated by UV–visible light and subsequently for 75 min under dark. **(C, D)** under Ar (100 kPa) for 100 min irradiated by UV–visible light and subsequently for 20 min under dark. The changes of **(A)** and **(C)** N(Ti–O) values and **(B)** and **(D)** N(Ti(–O–)Ti) values.

The change in Ti K-edge XAFS during CO_2 photoconversion was the key to answer the question: *why is water more reactive than hydrogen in photocatalytic CO_2 conversion (Table 1)?* Under CO_2 (100 kPa), moisture (2.2 kPa), and UV–visible light, the change in N(Ti–O) values was monitored (**Figs. 1A** and **C**). In comparison to the initial value (6.0) under CO_2, moisture, and dark, the value significantly decreased to 4.9–5.7 during light irradiation for 3.5 h. At 0.5 h after the light was turned off, the N(Ti–O) value increased to the original value (6.0). N(Ti(–O–)Ti) values followed a similar trend: decrease from the initial 11.3 to 9.7–10.6 during the irradiation of UV–visible light (**Fig. 1B**). Taking the experimental and fitting errors into account (**Figs. 1A** and **B**), the N(Ti–O) and N(Ti(–O–)Ti) values are good indicators to evaluate the concentration of O_v sites in/on TiO_2 [3].

Two control tests were also performed: (i) using H_2 instead of moisture as reductant and (ii) using only Ar. Under CO_2 (70 kPa) and H_2 (30 kPa), and UV–visible light, the change in N(Ti–O) and N(Ti(–O–)Ti) values was monitored (**Figs. 2A** and **B**). In comparison to the initial value (5.9) under CO_2, H_2, and dark, the N(Ti–O) value varied, but within a small range of 5.6–5.8 during light irradiation for 125 min. At 50 min after the light was turned off, the N(Ti–O) value increased to the original value (6.0). In comparison to the reaction of CO_2 and moisture (starting from 6.0 to 4.9–5.7; **Fig. 1A**), the decrease in N(Ti–O) value was effectively smaller under CO_2 and H_2 (starting from 5.9 to 5.6–5.8) during photoirradiation. The N(Ti(–O–)Ti) value remained between 12 and 11.7 under the irradiation of UV–visible light and negligibly changed after the light was turned off: 12–11.2 (**Fig. 2B**). Under CO_2 and moisture, the decrease was from 11.3 to 9.7–10.6 by the effect of light (**Fig. 1B**).

These differences in N(Ti–O) and N(Ti(–O–)Ti) values occurred because more O_v sites were formed under the photoreduction of CO_2 using moisture rather than H_2 or Ar.

Under Ar (100 kPa) and UV-visible light, the N(Ti–O) value changed between 5.7 and 6.0 during light irradiation for 100 min. At 5 min after the light was turned off, the N(Ti–O) value remained at 5.9 (**Fig. 2C**). The changes in N(Ti(–O–)Ti) values were also minimal under Ar: 12–11 throughout the study under light/dark (**Fig. 2D**).

Thus, the answer to the above question is that water forms hydroxy radicals under the irradiation of UV–visible light (equation 3) and then O_v sites are formed but not using H_2 (equation 4):

$$H_2O + h^+ \rightarrow H^+ + \cdot OH \qquad (3)$$
$$\cdot OH + O \text{ (surface)} + 3h^+ \rightarrow O_2 \text{ (g)} + O_v + H^+ \text{ (surface)} \qquad (4)$$
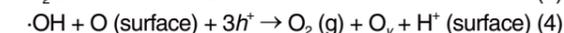
Reactions 3 and 4 proceeded over TiO_2 spatially separated from CO_2 reduction sites on Pd for equation 2. Thus, the effective redox reaction of equations 1 and 2 proceeded using water. Both reactions 1 and 2 would proceed competitively on Pd under CO_2 + H_2 and the efficiency followed a volcano-like dependence as a function of partial pressures of reactants [2].

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