

Efficient Volcano-type Dependence of Photocatalytic CO₂ Conversion into Methane Using Hydrogen on Reaction Pressure up to 0.80 MPa

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1 Introduction

The photoreduction of CO₂ to fuels using natural light can contribute simultaneously to reduction of the major greenhouse gas and the development of sustainable energy [1]. Efficient photoreduction of CO₂ into methanol (or CO) was reported using layered double oxides (LDHs) [2–4] while various studies reported efficient photoconversion of CO₂ into fuels using TiO₂-based catalysts [1,5]. However, the reaction pressure dependence has not been systematically investigated. In this study, the amount of semiconductors and reaction pressure were optimized in CO₂ and H₂ using Pd/TiO₂ as a photocatalyst irradiated by UV–visible light [9].

2 Experimental Section

1.0 mM of sodium tetrachloropalladate (>98%, Sigma Aldrich) solution was stirred with TiO₂ (P25, Degussa; anatase phase/rutile phase = 8/2, specific SA 60 m² g⁻¹) at 290 K for 24 h and 40 mM of NaBH₄ aqueous solution was added to be the molar ratio of Pd/NaBH₄ = 1/8 and stirred at 290 K for 1 h. The solution was filtered and the collected yellow precipitate was washed with deionized water. The powder was dried under vacuum at 290 K for 24 h. The obtained gray powder was denoted as Pd/TiO₂. The loading of Pd was 0.5 wt%. Palladium K-edge XAFS spectra and titanium K-edge XAFS spectra were measured at 290 K at beamline NW10A, 9A, and 12C.

3 Results and Discussion

First, Pd K-edge XAFS spectra were measured for fresh Pd/TiO₂ (100 mg) and used one under CO₂ (2.3 kPa) + H₂ (22 kPa) and UV–visible light for 5 h. The X-ray absorption near-edge structure (XANES) spectra are depicted in Figure 1A-c and d, respectively. The energy values at the tops and the bottoms in post-edge oscillation for normalized oscillation μt coincided with those for Pd metal (Figure 1A-b), however, the pattern was quite different from that for PdO (Figure 1A-a), demonstrating dominant metallic Pd⁰ state for fresh Pd/TiO₂ sample and one after CO₂ photoconversion test at 24 kPa. The amplitude of post-edge oscillation was apparently weaker for Pd/TiO₂ (Figure 1A-c, d) compared to that for Pd foil (spectrum b), indicating the Pd particle size of a few nanometers.

Best-fit results and the fit errors of Pd K-edge EXAFS for Pd/TiO₂ photocatalysts were summarized in Table 1A. The data was well fit with two shells: Pd–O and Pd–Pd for fresh Pd/TiO₂ (Figure 1B-c3, c4 and Table 1A-c). The

coordination of Pd–Pd interatomic pair at 0.276 nm (Figure 1B-c2) was predominant ($N = 5.9$) in consistent with the assignment of predominant Pd⁰ based on XANES above (Figure 1A-c). The minor coordination of Pd–O ($N = 1.9$) would be the interfacial bonding between metallic Pd nanoparticles and the TiO₂ surface. The N value for Pd–Pd (5.9) corresponds to mean nanoparticle size of 1.1 ± 0.1 nm (Table 1d).

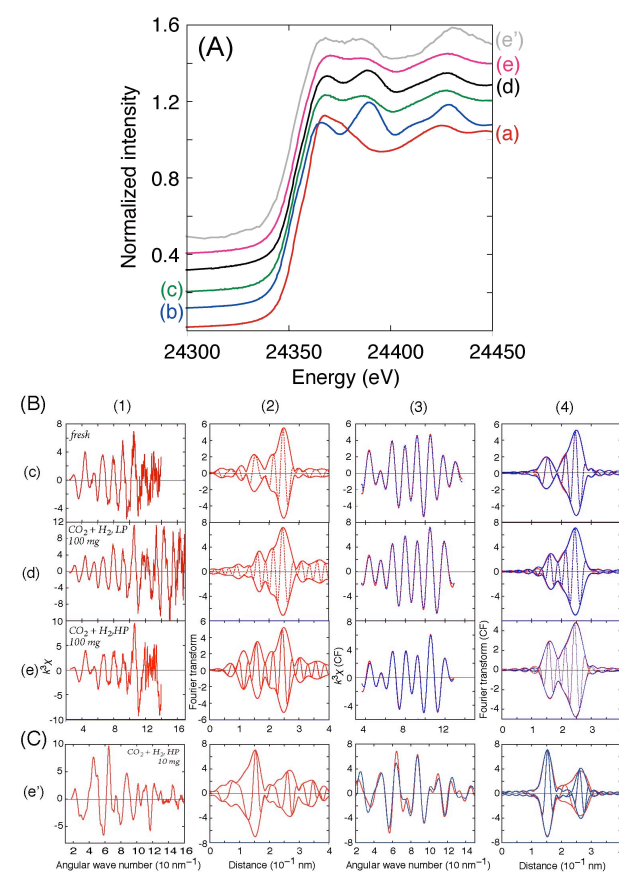


Figure 1. Pd K-edge XANES (A), EXAFS (B), and Ti K-edge EXAFS (C) for PdO (a), Pd foil (thickness 12.5 μm ; b), Pd/TiO₂ as fresh (c), after 5-h photocatalytic test under CO₂ (2.3 kPa) + H₂ (22 kPa) using 100 mg of Pd/TiO₂ (d), and CO₂ (0.12 MPa) + H₂ (0.28 MPa) using 100 mg (e) or 10 mg of Pd/TiO₂ (e'). Spectra were measured in transmission mode except that the Pd K-edge of sample e' was taken in fluorescence mode. Panels in B and C: k^3 -weighted EXAFS oscillation (1), its associated Fourier transform (2), and best-fit results in k -space (3) and R -space (4).

Table 1. Best-fit Results of (A) Pd K-edge and (B) Ti K-edge EXAFS Spectra for Pd/TiO₂ photocatalysts

Entry	Samples	Pd–O	Pd–Pd	Goodness of fit
		R (nm) N $\Delta(\sigma^2)$ (10 ⁻⁵ nm ²)	R (nm) N $\Delta(\sigma^2)$ (10 ⁻⁵ nm ²)	
c	Fresh	0.199 (±0.006) 1.9 (±0.4) -4.8 (±1.7)	0.276 (±0.001) 5.9 (±0.5) 5.0 (±0.6)	1.2 × 10 ³
d	5-h photocatalytic test under CO ₂ (2.3 kPa) + H ₂ (22 kPa), 100 mg	0.21 (±0.04) 0.57 (±0.2) -7.9 (±1.7)	0.276 (±0.002) 8.9 (±0.4) 3.3 (±0.3)	2.0 × 10 ²
e	5-h photocatalytic test under CO ₂ (0.12 MPa) + H ₂ (0.28 MPa), 100 mg	0.2018 (±0.0004) 0.9 (±0.3) -6 (±2)	0.2748 (±0.0003) 5.0 (±0.4) 2.6 (±0.3)	1.1 × 10 ³

(B)

Entry	Samples	Ti–O	Ti(–O–)Ti	Goodness of fit
		R (nm) N $\Delta(\sigma^2)$ (10 ⁻⁵ nm ²)	R (nm) N $\Delta(\sigma^2)$ (10 ⁻⁵ nm ²)	
e'	5-h photocatalytic test under CO ₂ (0.12 MPa) + H ₂ (0.28 MPa), 10 mg	0.1977 (±0.0002) 6.1 (±0.4) 1.6 (±0.4)	0.313 (±0.002) 11 (±2) -2 (±1)	9.9 × 10 ⁴

For used samples for photoconversion under 24 kPa and light, the major Pd–Pd interatomic distance was also 0.276 nm (Table 1A-d and Figure 1B-d2, d4). The *N* value slightly increased by 3.0 starting from one for fresh sample (Table 1A-c, d). The values corresponded to mean particle size of 2.3±0.1 nm that was greater by 1.2 nm for fresh sample. Pd–O interatomic distance increased by 0.01 nm to 0.21 nm while the *N* value significantly decreased from 1.9 to 0.57. The reason was not clear whether the oxygen vacancy (O_v) sites increased at the interface between Pd and TiO₂ surface and/or the relative number of interface Pd sites in contact with TiO₂ surface decreased due to partial growth of Pd particles by 1 nm.

After 0.40 MPa of photoconversion test of CO₂ using 100 mg of Pd/TiO₂, the peak energy and intensity in XANES was quite similar to that of fresh one (Figure 1A-c, e). The *N* value of Pd–Pd pair was 5.0 that did not significantly change from 5.9 for fresh sample based on fit errors (Table 1A-c, e and Figure 1B-e3, e4) while the *N* value for Pd–O pair decreased from 1.9 to 0.9 (Table 1A-c, e). Thus, the increase of O_v sites for nearly constant mean size of Pd particles during photoconversion test was suggested after photoconversion test at 0.40 MPa. The

reason why mean Pd particle size partially became greater only at lower pressure condition versus remained unchanged at higher pressure condition (Table 1A-d, e) is unknown, however, the strong adsorption of H on Pd may prevented to coalesce to greater Pd nanoparticles. The XANES spectrum (Figure 1A-e) resembled that of fresh Pd/TiO₂ (c), supporting the interpretation based on EXAFS.

XANES spectrum was also taken for 10 mg of Pd/TiO₂ film (Figure 1C) after a photoconversion test at 0.40 MPa (Figure 1A-e') was quite similar to spectra Figure 1A-c for fresh one. In summary, Pd sites in 10–100 mg of Pd/TiO₂ photocatalyst remained at Pd⁰ sites before and after photoreduction tests at 24 kPa–0.40 MPa of CO₂ + H₂.

Complimentary to Pd K-edge XAFS, Ti K-edge EXAFS was measured for 10 mg of Pd/TiO₂ photocatalyst after the photoconversion test at 0.40 MPa. The *N*(Ti–O) and *N*(Ti(–O–)Ti) values were 6.1 and 11 (Table 1B-e' and Figure 1C-e'3, e'4), similar to values for untreated rutile- or anatase-phase TiO₂; 6 and 12, respectively. Thus, while the decrease of O_v sites at the interface between Pd and TiO₂ surface sites under the condition was significant based on *N*(Pd–O) decrease (Table 1A-c, e), the O_v sites were negligible as in the TiO₂ bulk and should be populated only at the interface with Pd nanoparticles after the photoconversion test [9].

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