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Efficient volcano-type dependence of photocatalytic CO₂ conversion into methane using hydrogen at reaction pressures up to 0.80 MPa



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1. Introduction

Photocatalytic conversion of CO₂ into fuels is one of the routes to carbon-neutral fuels, avoiding the net increase in atmospheric CO₂ concentrations associated with fossil fuel-derived alternatives [1–3]. TiO₂ has been investigated most intensively for this purpose and is known to produce methane and/or CO. CuO supported on TiO₂ photoreduced CO₂ into methanol [2,3] or methane [1–3]. However, when isotope-labeled ¹³CO₂ was used, C-containing impurities at the TiO₂ surface were likely to be reduced to CO [3,4]. The product using Pd/TiO₂ was carefully confirmed to be ¹³CH₄ [3,5].

We recently reported CO₂ photoconversion into methanol using H₂ and layered double hydroxides (LDHs) [6–8]. Industrially, H₂ is produced via cracking and reforming fossil fuels. H₂ can instead be produced sustainably from water utilizing natural light, in a way similar to Photosystem II,

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-,$$
 (1)

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ABSTRACT

Photocatalytic conversion of CO₂ into fuels could mitigate global warming and energy shortage simultaneously. In this study, the reaction pressure was optimized for CO₂ reduction by H₂. The major products were methane, CO, and methanol, and the observed catalytic activity order was Cu or Pd on TiO₂ \gg Ag/ZrO₂ \sim g-C₃N₄ > Ag/Zn₃Ga-layered double hydroxide \sim BiOCl. Hot/excited electrons due to surface plasmon resonance could be transferred to CO₂-derived species and the remaining positive charge could combine with excited electrons in the semiconductor. As the levels of hot/excited electrons became more negative, the catalysts became more active, except for Ag/ZrO₂ and Ag/Zn₃Ga-LDH, probably due to lower charge separation efficiency for intrinsic semiconductors or hydroxides. The reaction order was controlled by the partial pressure of H₂, demonstrating preferable adsorption of H on Pd. The photoconversion of CO₂ into methane was optimum at P_{H2} = 0.28 MPa and P_{CO2} = 0.12 MPa, but the rates gradually dropped at higher partial pressures due to adsorption of CO₂ being hindered by H.

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followed by the production of nicotinamide adenine dinucleotide phosphate (NADPH) by Photosystem I [9],

$$NADP^{+} + H^{+} + 2e^{-} \rightarrow NADPH.$$
(2)

Our analogue of Photosystem I in heterogeneous catalysis is CO_2 photoconversion using LDH and Pd/TiO₂ to form methanol and methane [6–8]:

$$\mathrm{CO}_2 + 6\mathrm{H}^+ + 6\mathrm{e}^- \to \mathrm{CH}_3\mathrm{OH} + \mathrm{H}_2\mathrm{O} \tag{3}$$

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$$
 (4)

$$2H_2O + 2NADP^+ \rightarrow O_2 + 2NADPH + 2H^+ \tag{1+2}$$

$$4H_2O+2CO_2 \rightarrow 3O_2+2CH_3OH \tag{1+3}$$

$$2H_2O+\ CO_2\rightarrow 2O_2+\ CH_4 \tag{1+4}$$

Although significant progress has been achieved by many researchers in the photoconversion of CO_2 into fuels [1–3], most studies have evaluated the photoconversion of dissolved CO_2 in aqueous solution, namely Eqs. (1) and (3) or (1) and (4). For example, the critical role of oxygen vacancy (O_V) sites in CO_2/H_2O was suggested [10–13], and enhanced photoconversion of CO_2 was reported at ele-



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vated reaction pressure of CO_2 and moisture [10,11] or liquid water [11,14–19]; however, most of the mechanisms are unknown. Thus, the systematic dependence of CO_2 photoconversion on reaction pressure and an independent understanding of the reduction sites and mechanism for CO_2 conversion (Eqs. (3) and (4)) are still open for discussion.

The present study screened semiconductor photocatalysts for efficient photoreduction of CO₂ into fuels using H₂ as a reductant at 0.12–0.80 MPa in order to clarify the role of Eq. (3) and/or (4). The band gap (E_g) values of the semiconductors were varied between 2.6 and 5.6 eV by employing ZrO₂, g-C₃N₄, BiOCl, TiO₂, and [Zn₃Ga(OH)₈]₂CO₃·*m*H₂O LDH while keeping the conduction band (CB) minimum more negative than the reduction potential (E°) for CO₂ to methane, CO, or methanol (–0.32 to –0.11 V against the standard hydrogen electrode (SHE)) [3,8]. The reaction pressure dependence for Reaction (3) and/or (4) was carefully investigated.

Sastre et al. reported CO_2 conversion using H_2 and Ni-based catalysts irradiated by a solar simulator, and the rates were surprisingly as high as those using a photocatalyst: 55 mmol h⁻¹ g_{cat} [20]. The temperature and gas pressure reached 423 K and some hundreds of kPa due to the exothermic nature of Eq. (4). On the basis of blank tests below 453 K in the absence of light, photocatalytic activation of H_2 to form Ni–H species followed by thermal hydrogenation of CO_2 to formate on metallic Ni was suggested [2,20]. The possibility of a thermal assist for activation is also discussed in this study.

The reason that a volcano-type dependence of CO_2 photoconversion on reaction pressure is obtained using the most active Pd/TiO₂ photocatalyst was investigated by monitoring the mass balance of reactions, the oxidation state of Pd, and the concentration of O_V sites in TiO₂ by X-ray absorption fine structure (XAFS). This paper is the first of several in which the sites and mechanism for reaction in $CO_2 + H_2$ are compared with those for reaction in $CO_2 + H_2O$. As site separation between photo-oxidation (H_2 or moisture) and photoreduction (CO_2), and the concentrations and roles of O_V sites on the catalysis are complicated issues, the photoconversion of CO_2 using moisture is reported separately [21].

2. Experimental

2.1. Catalyst synthesis

An aqueous solution (1.0 mM) of Ag nitrate (>99.8%, Wako Pure Chemical) was stirred with ZrO_2 {JRC-ZRO-3, Catalysis Society of Japan, specific surface area (SA) 94 m² g⁻¹} for 24 h. An aqueous solution of 40 mM of NaBH₄ (>95%, Wako Pure Chemical) was then added in the molar ratio Ag:NaBH₄ = 1:4 and the solution was stirred for 1 h. The solution was filtered using a polytetrafluoroethene-based membrane filter (Omnipore JVWP04700, Millipore; pore size 0.1 µm) and the collected yellow precipitate was washed with deionized water (<0.055 µS cm⁻¹) supplied by a model RFU424TA (Advantec). The powder was dried under vacuum at 290 K for 24 h. The obtained yellow powder is denoted as Ag/ZrO₂. The loading of Ag was 0.5 wt.% (Table 1a).

Ten grams of urea (>99%, Wako Pure Chemical) was heated at 823 K for 3 h and the resultant yellow powder was washed with 0.1 M of nitric acid (Wako Pure Chemical) and deionized water to obtain g- C_3N_4 [22].

BiOCl was synthesized via a solvothermal procedure described in Ref. [23]. Briefly, 2.0 g of Bi nitrate pentahydrate (>99.5%, Wako Pure Chemical) and 1.3 g of cetyltrimethylammonium chloride (>95%, Wako Pure Chemical) were dissolved in 80 mL of ethylene glycol (EG, >99.5%, Wako Pure Chemical). The solution was stirred for 1 h and 1.0 M of KOH (85%, Wako Pure Chemical) in EG was added. The reaction solution was maintained at 433 K for 12 h. The solution was filtered and the collected white powder was washed with deionized water and ethanol.

Sodium tetrachloropalladate (>98%, Sigma Aldrich) solution (1.0 mM) was stirred with TiO_2 (P25, Degussa; anatase phase:rutile phase = 8:2, specific SA 60 m² g⁻¹) at 290 K for 24 h. Then 40 mM of NaBH₄ aqueous solution was added in the molar ratio Pd: NaBH₄ = 1:8 and the suspension was stirred at 290 K for 1 h. The solution was filtered using a JVWP04700 filter and the collected yellow precipitate was washed with deionized water before drying 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.% (Table 1d).

Cu(NO₃)₂·3H₂O (0.078 g; >99.9%, Wako Pure Chemical) and urea (2.5 g) were dissolved in 50 mL of deionized water. A quantity of 1.0 g of TiO₂ (P25) was added to this solution. Thereafter, the temperature of the suspension was increased to 353 K and kept constant for 4 h while stirring as a deposition–precipitation step. The sample was then washed with deionized water (50 mL each) and filtered five times using a JVWP04700 filter. After drying, the sample temperature was elevated at a rate of 1.25 K min⁻¹ and kept at 673 K in air for 2 h [24]. The loading of Cu was 3.2 wt.% (Table 1e).

The synthetic procedure for preparing LDH $[Zn_3Ga(OH)_8]_2CO_3$ - mH_2O has been described previously [8]. A quantity of 1.0 mM of Ag nitrate solution was stirred with $[Zn_3Ga(OH)_8]_2CO_3 \cdot mH_2O$ powder at 290 K for 24 h and then 40 mM NaBH₄ aqueous solution was added in the molar ratio Ag:NaBH₄ = 1:4 and stirred for 1 h. The solution was filtered using a JGWP04700 filter and the collected yellow precipitate was washed with deionized water. The obtained yellow powder is denoted Ag/Zn₃Ga-LDH. The loading of Ag was 0.5 wt.% (Table 1f).

2.2. Characterization

X-ray diffraction (XRD) patterns were observed using a D8 ADVANCE diffractometer (Bruker) at the Center for Analytical Instrumentation, Chiba University, at a Bragg angle (θ_B) of $2\theta_B = 5.0-60^\circ$ with a scan step of 0.02° and a scan rate of 3 s per step. The measurements were performed at 40 kV and 40 mA using Cu K α emission (wavelength $\lambda = 0.15419$ nm) [25,26] and a nickel filter. Crystallite sizes (*t*) were estimated using the Scherrer equation

$$t = \frac{0.9\lambda}{\text{Peak width} \times \cos\theta_{\text{B}}}.$$
(5)

Ultraviolet (UV)–visible spectra were measured using a Model V-650 (JASCO) spectrophotometer equipped with an integrating sphere (ISV-469, JASCO) for diffuse reflectance measurements in the wavelength range 200–800 nm. The E_g values were estimated via simple extrapolation of the absorption edge or by fitting to the Davis–Mott equation,

$$\alpha h \nu \propto \left(h \nu - E_{\rm g} \right)^n,\tag{6}$$

where α , h, and ν are the absorption coefficient, Planck's constant, and the frequency of light, respectively, and n is 1/2, 3/2, 2, or 3 for allowed direct, forbidden direct, allowed indirect, and forbidden indirect electronic transitions, respectively [8,27,28]. Fits to Eq. (6) were performed assuming each n value, or using the n value evaluated based on fits to the log–log form of Eq. (6) using the E_g value obtained by simple extrapolation of the absorption edge to the wavelength axis in the UV–visible spectra.

Transmission electron microscopy (TEM) images were observed using a Model H-7650 transmission electron microscope (Hitachi) at an accelerating voltage of 100 kV. A tungsten filament was used in the electron gun and samples were mounted on conducting carbon with a Cu grid mesh (150 mesh per inch). The magnification

Table 1				
Basic physicochemical pro	perties of the	photocatalysts	s screened	in this study.

Entry	Photocatalyst	Metal loading (wt.%)	Color	Peak due to SPR (nm)	Pd mean particle size E_s (nm)TEMEXAFSExamples		$E_{\rm g}({ m eV})$		<i>n</i> obtained from log-log form	
							Extrapolated	Based on Eq. (6) (associated n)	of Eq. (6)	
a	Ag/ZrO_2	0.5	Yellow	428			5.1	5.2 $(n = 1/2)$ 5.0 $(n = 3/2)$	1.25	
b	$g-C_3N_4$	-	Lime yellow				2.9	3.0 (n = 1/2) 2.8 (n = 3/2)	0.99	
с	BiOCl	-	White				3.6	3.8 $(n = 1/2)$ 3.4 $(n = 3/2)$	1.06	
d	Pd/TiO ₂	0.5	Gray	(Too broad)	$3.1(\pm 0.9)$ {3.9 $(\pm 1.3)^{a}$ }	$1.1(\pm 0.1)$ {2.3 $(\pm 0.1)^{b}$ }	3.1	3.4 (n = 1/2) 2.9 (n = 3/2)	1.05	
e	Cu/TiO ₂	3.2	Light gray	$\sim \! 440$			3.2	3.4 (n = 1/2) 3.0 (n = 3/2)	0.98	
f	Ag/Zn₃Ga- LDH	0.5	Yellow	395			5.2	5.6 $(n = 1/2)$ 5.0 $(n = 3/2)$	1.32	

^a After photocatalytic tests under CO_2 (0.09 MPa) and H_2 (0.21 MPa) for 5 h.

^b After photocatalytic tests under CO_2 (2.3 kPa) and H_2 (22 kPa) for 5 h.

was between 60,000 and 200,000 times. Cross-sectional scanning electron microscopy (SEM) images were also observed using a Model JSM-6510 scanning electron microscope (JEOL) at an accelerating voltage of 20 kV. A tungsten filament was used in the electron gun. The photocatalyst film on a Pyrex glass plate was cut and mounted on the Al sample holder by an adhesive. The incident angle of electrons with reference to the normal of the sample surface was between 75° and 85°. The magnification was between 200 and 3000 times.

Palladium K-edge XAFS spectra were measured at 290 K in transmission mode in the Photon Factory Advanced Ring at the High Energy Accelerator Research Organization (KEK, Tsukuba) on beamline NW10A [23,28,29]. The storage ring energy was 6.5 GeV and the ring current was 52.1-20.7 mA. A Si (311) double-crystal monochromator and a Pt-coated cylindrical focusing mirror were inserted into the X-ray beam path. The X-ray intensity was maintained at 67% of the maximum flux using a piezo translator applied to the crystal to suppress higher harmonics. The slit opening was 1.0 mm (vertical) \times 2.0 mm (horizontal) in front of the I_0 ionization chamber. Samples (10 mg of film) mounted on Pyrex glass plates for photoconversion tests in 0.12 MPa CO₂ and 0.28 MPa H₂ were measured at 290 K in the fluorescence mode using a Lytle detector and a 3 µm thick RuO₂ filter between the sample and the $I_{\rm f}$ ion chamber [30–32]. The Pd K-edge absorption energy was calibrated to 24,348 eV using the spectrum of 12.5 µm thick Pd foil [25].

Titanium *K*-edge XAFS spectra were measured in transmission mode in the Photon Factory at KEK on beamline 9A [33,34]. The storage ring energy was 2.5 GeV and the ring current was 447.7– 342.7 mA. A Si (111) double-crystal monochromator and a pair of bent conical mirrors were inserted into the X-ray beam path. Spectra for the Pd/TiO₂ sample (10 mg) diluted by boron nitride were measured under argon. The Ti *K*-edge absorption energy was calibrated to 4964.5 eV using the spectrum of 5 μ m thick Ti foil [25].

XAFS data were analyzed using the XDAP software package [35]. The pre-edge background was approximated by a modified Victoreen function $C_2/E^2 + C_1/E + C_0$. The background of the postedge oscillation was approximated by a smoothing spline function and was calculated for the particular number of data points, using

$$\sum_{i=1}^{\text{Data Points}} \frac{(\mu x_i - BG_i)^2}{\exp(-0.075k_i^2)} \leq \text{smoothing factor},$$
(7)

where *k* is the angular wavenumber of the photoelectrons.

Multiple-shell curve-fit analyses were performed [23,28,29,33] for the Fourier-filtered k^3 -weighted extended XAFS (EXAFS) data in k- and R-space using empirical amplitudes extracted from the EXAFS data for Pd foil, PdO powder, and rutile-type TiO₂ powder. The interatomic distance (R) and its associated coordination number (N) for the Pd–Pd, Pd–O, Ti–O, and Ti(–O–)Ti pairs were set to 0.27509 nm with an N value of 12 [36], 0.2026 nm with an N value of 4 [37], 0.1959 nm with an N value of 6, and 0.3058 nm with an N value of 12 [33,38,39], respectively. The many-body reduction factor S_0^2 was assumed to be equal for the sample and the reference.

The number of independent data points in the fit range was calculated based on the Nyquist theorem and the EXAFS-specific modification by Stern [35],

$$v = \frac{2\Delta k \Delta R}{\pi} + 2. \tag{8}$$

The number was 10.8–13.1 for Pd *K*-edge EXAFS data and 14.4–15.8 for Ti *K*-edge EXAFS data. Three-shell fits were also tried for Ti EXAFS; however, the fit errors were significantly greater than those obtained in two-shell fits. Thus, two-shell fits (four variables in a shell) were chosen for both Pd and Ti *K*-edge EXAFS analyses.

2.3. High-pressure photoconversion tests of CO₂

The synthesized/prepared catalysts (Table 1a–f) were immersed in deionized water and agitated by ultrasound (430 W, 38 kHz) for 3 min. The suspension was mounted on a Pyrex glass plate ($25 \times 25 \times 1$ mm) and dried at 373 K for 12 h. The area of the obtained films was 20×20 mm. Films on plates or assynthesized fine powder samples in a Pyrex dish ($\Phi_{internal} = 37$ mm) were introduced into a homemade high-pressure stainless steel reactor equipped with quartz double windows, a pressure gauge, and Swagelok valves (Fig. 1A, B) for photoconversion tests. The effective internal volume of the reactor was 98.4 mL.

A mixed CO_2/H_2 gas (0.20–0.80 MPa in a ratio of 2:8, 3:7, 4:6, or 5:5) was introduced into the reactor. The photocatalyst was irradiated with UV–visible light provided by a 500-W Xe arc lamp (Model OPM2-502, Ushio) through quartz windows in the reactor chamber for 5 h (Fig. 1A, B). The distance between the light exit and the photocatalyst surface was 82.7 mm. Light transmission was checked using a photosensor and a counter (Model PCM-01, Prede and Model KADEC-UP, North One, respectively). The light intensity at the center of the photocatalyst was 90.2 mW cm⁻² (Fig. 2a). The quartz windows of the high-pressure reactor absorbed/reflected 9.5% of the light (Fig. 2b), and 100 mg of Pd/



Fig. 1. (A, B) High-pressure stainless reactor equipped with quartz windows and a pressure gauge for CO₂ photoconversion tests irradiated by UV-visible light from a 500-W Xe arc lamp (A: top view, B: side view). (C) Photocatalyst films $(20 \times 20 \text{ mm})$ of Ag/ZrO₂, g-C₃N₄, BiOCl, Pd/TiO₂, Cu/TiO₂, and Ag/Zn₃Ga-LDH (top to bottom).

TiO₂ powder on a Pyrex dish and 10 mg of Pd/TiO₂ film on Pyrex glass plate absorbed/reflected/scattered 40% and 49% of the light, respectively (Fig. 2c, d). Densely mounted films were advantageous for light absorption efficiency compared with fine powders based on the difference of their mean areal densities of 2.5 versus 9.3 mg cm^{-2} , respectively, and the exposed ratio of particles. Fine powders should reflect/scatter more at exposed faces and less light reach at the lower part of layers (Fig. 2c) compared with densely mounted films (Fig. 2d).

As comparisons, photocatalytic tests were also performed using an L42 filter (2.5 mm thick, Kenko) that filters the light less than $\lambda = 420 \text{ nm } [40]$ or a U-330 filter (2.5 mm thick, Kenko) that filters the light less than $\lambda = 250 \text{ nm}$ and between $\lambda = 390 \text{ nm}$ and 695 nm [41], set between the light exit and the high-pressure reactor (Fig. 1A, B). After 5 h of irradiation, the reaction gas was analyzed using packed columns of 13X-S molecular sieves and polyethylene glycol (PEG-6000) supported on Flusin P (GL Sciences) set in a gas chromatograph equipped with a thermal conductivity detector (Model GC-8A, Shimadzu) [6–8,28,42]. Helium (>99.99995%) was used as a carrier gas for all analytes except H₂, for which argon (>99.998%) was used. The amounts of methanol and moisture were double-checked by concentrating them using a trap made from a mixture of diethyl ether and dry ice (192 K) to separate them from H₂ and most of the CO₂.

The experimental errors of 4 Pa of methanol or moisture were evaluated in this GC analysis procedure. The errors were 7.7% and 8.4%, but increased to 41% and 26% by the adsorption of methanol or moisture onto the surface of the Pyrex glass tube and vacuum grease (Apiezon H). The gas adsorption could be minimized by completely heating the vacuum system using a dryer just before the online GC analysis.

Blank tests were also performed by eliminating one of the three control factors or adding one alternative control factor: (i) UV-visible light, (ii) reactants, (iii) catalyst, and (iv) temperature, i.e., in the absence of any light at 298 or 353 K, in 0.12 MPa of CO₂ only, in 0.28 MPa of H₂ only, or 0.4 MPa of helium (the absence of any reactants) and in the absence of any catalyst.

3. Results

3.1. Characterization by XRD and UV-visible spectroscopy

The syntheses of g-C₃N₄, BiOCl, and Zn₃Ga-LDH and the preparation of Ag/ZrO₂, Pd/TiO₂, Cu/TiO₂, and Ag/Zn₃Ga-LDH were verified by their XRD patterns (Fig. 3) and UV–visible spectra (Fig. 4). For Ag/ZrO₂ (Fig. 3a), the XRD peaks appeared at $2\theta_{\rm B}$ = 17.5°, 24.3°, 28.3°, 31.5°, 34.3°, 35.3°, 38.6°, 41.0°, 45.1°, 50.3°, 54.2°, and 55.6° and were ascribed to 001, 011, $\overline{1}$ 1 1, 111, 020, 002, 120, $\overline{1}$ 1 2, $\overline{2}$ 0 2, 022, 003, and 310 reflections of monoclinic ZrO₂ [43,44]. No peaks due to Ag metal or Ag₂O nanoparticles were observed [28,29].

Broad peaks at $2\theta_B = 13.3^{\circ}$ and 27.5° and a weak peak at $2\theta_B = 44^{\circ}$ in pattern b appeared essentially at the same position as those reported for g-C₃N₄ in the literature [22,45] and were assigned to 100, 002, and 200 reflections, respectively. The peak positions and relative intensities for peaks at 12.0°, 26.0°, 32.7°, 33.6°, 41.0°, 46.8°, 49.8°, 54.3°, and 58.8° in pattern c were in



Fig. 2. The light intensity at the photocatalyst position in the high-pressure stainless-steel reactor (Fig. 1) (a), in the presence of the quartz windows of the reactor (b), in the presence of the quartz windows and 100 mg of Pd/TiO₂ powder (c), and in the presence of the quartz windows and 10 mg of Pd/TiO₂ film (d).



Fig. 3. XRD patterns for Ag/ZrO_2 (a), g-C_3N_4 (b), BiOCl (c), Pd/TiO_2 (d), and Ag/ Zn_3Ga-LDH (e).



Fig. 4. UV-visible spectra for fresh samples of Ag/ZrO₂ (a), g-C₃N₄ (b), BiOCl (c), Pd/TiO₂ (d), Cu/TiO₂ (e), and Ag/Zn₃Ga-LDH (f).

accord with the literature reports for BiOCl and were assigned to 001, 101, 110, 102, 112, 200, 113, 202, and 212 reflections, respectively, of the tetragonal layered structure [23].

In the pattern for Pd/TiO₂ (Fig. 3d), peaks appeared at $2\theta_B = 25.4^\circ$, 37.0°, 38.6°, 48.1°, 54.0°, and 55.1° and were assigned to the 101, 103, 112, 200, 105, and 211 reflections, respectively, of the anatase phase, and the peaks that appeared at $2\theta_B = 27.5^\circ$, 36.1°, 37.9°, 41.3°, 44.1°, and 56.7° were assigned to the 110, 101, 004, 111, 210, and 220 reflections, respectively, of the rutile phase [46,47]. No peaks arising from Pd nanoparticles were observed above the detection limit.

As for pattern e for Ag/Zn₃Ga-LDH, peaks appeared at $2\theta_B = 11.7^\circ$, 23.5° , 33.5° , 34.2° , 36.9° , 38.9° , 43.6° , 46.4° , and 52.6° and were assigned to the 003, 006, 009, 012, 104, 015, 017, 018, and 100 reflections of Zn₃Ga-LDH, respectively, in accord with the literature [7,8].

For Ag/ZrO₂, the UV absorption edge was extrapolated to 242 nm, corresponding to an E_g value of 5.1 eV (Table 1a). A broad

peak centered at 428 nm appeared due to the surface plasmon resonance (SPR) of the Ag nanoparticles (Fig. 4a). An SPR peak at 411 nm was reported for Ag particles with a mean size of 1.6 nm on LDH [28].

The absorption edge shifted from the UV to the visible light region (435 nm) for g-C₃N₄ (Fig. 4b), corresponding to an E_g value of 2.9 eV (Table 1b). The absorption edge in the UV region was extrapolated to 344 nm, corresponding to an E_g value of 3.6 eV for BiOCl, in agreement with the literature value (Table 1c and Fig. 4c) [23].

The absorption edges were extrapolated to 394 and 384 nm, corresponding to $E_{\rm g}$ values of 3.1 and 3.2 eV for Pd/TiO₂ and Cu/TiO₂ (spectra d and e), respectively, in agreement with the literature for TiO₂ [33]. Nearly flat background absorption extended over the entire range of visible light due to various sizes of Pd nanoparticles, and a weak peak appeared at approximately 440 nm due to SPR effects arising from the Cu.

3.2. TEM and cross-sectional SEM observations

TEM images were observed for the Pd/TiO₂ photocatalyst. For the fresh sample, polygonal particles of TiO₂ were observed with sizes distributed between 30 and 50 nm (Fig. 5A). Smaller particles that are clearly darker than the TiO₂ were identified as Pd species and their mean size was 3.1 ± 0.9 nm (Fig. 5A, histogram and Table 1d). The wavelength of the SPR peaks progressively decreased as the metal particle size decreased due to the change in the oscillation frequency of confined free electrons [48]. The size distribution of the Pd species was between 1.0 and 6.0 nm, leading to SPR peaks at various wavelengths with broad absorbance in the wavelength range 400–800 nm (Fig. 4d).

TEM images were also observed for Pd/TiO₂ samples after 5 h of CO₂ photoconversion testing in CO₂ (0.09 MPa) and H₂ (0.21 MPa). The particle size distribution of Pd species slightly widened to 1–9 nm and the mean size increased by 0.8 nm to 3.9 ± 1.3 nm (Fig. 5B, histogram and Table 1d).

SEM images revealed that the surface of fresh Pd/TiO₂ photocatalyst films coated on Pyrex glass was quite flat and smooth (Fig. 5C1). Cross-sectional views were also observed (Fig. 5C2) and the mean thickness of the photocatalyst films was 11 μ m. The mean particle size of the TiO₂ was estimated to be 32 nm, based on analysis of the 101 XRD peak of the anatase phase using Eq. (5), which is in agreement with the size range 30–50 nm observed by TEM (Fig. 5A).

3.3. Monitoring the active sites using Pd and Ti K-edge XAFS

First, Pd *K*-edge XAFS spectra were measured for fresh Pd/TiO₂ (100 mg) and Pd/TiO₂ after testing in CO₂ (2.3 kPa) + H₂ (22 kPa) under UV-visible light irradiation for 5 h. The photocatalytic test conditions were conducted at lower than atmospheric pressure [6–8,28]. The X-ray absorption near-edge structure (XANES) spectra are depicted in Fig. 6A–c and d, respectively. The energy values at the tops and the bottoms of the post-edge oscillation for normalized oscillation μt coincided with those for Pd metal (Fig. 6A-b); however, the pattern was quite different from that of PdO (Fig. 6A-a), demonstrating the dominant metallic Pd⁰ state for fresh Pd/TiO₂ samples and for those after CO₂ photoconversion tests at 24 kPa. The amplitude of the post-edge oscillation was apparently lower for Pd/TiO₂ (Fig. 6A-c, d) than that for Pd foil (spectrum b), indicating a Pd particle size of a few nanometers, as already shown by TEM (Fig. 5A, B).

The best-fit results and fit errors of the Pd *K*-edge EXAFS for Pd/ TiO₂ photocatalysts are summarized in Table 2. The data were well fitted with two shells: Pd–O and Pd–Pd for fresh Pd/TiO₂ (Fig. 6Bc3, c4, and Table 2-c). The coordination of the Pd–Pd interatomic



Fig. 5. TEM images of Pd/TiO₂ as prepared (A) and after CO₂ photoreduction tests in CO₂ (0.09 MPa) and H₂ (0.21 MPa) (B), and cross-sectional SEM images of fresh Pd/TiO₂ (C1, C2).

pair at 0.276 nm (Fig. 6B-c2) was predominant (N = 5.9), which is consistent with the assignment of the predominant Pd⁰ based on the XANES data above (Fig. 6A-c). The minor coordination of Pd-O (N = 1.9) arises from the interfacial bonding between metallic Pd nanoparticles and the TiO₂ surface [49–53]. The N value for Pd–Pd (5.9) corresponds to a mean nanoparticle size of 1.1 ± 0.1 nm (Table 1d) [53]. The discrepancy compared with the mean particle size based on TEM (3.1 ± 0.9 nm) is found because particles smaller than ~1 nm cannot be observed by TEM.

For the samples measured after undergoing photoconversion under 24 kPa and light irradiation (see *Photoconversion in CO*₂ and H_2 at 0.20–0.80 MPa), the major Pd–Pd interatomic distance was also 0.276 nm (Table 2-d and Fig. 6B-d2, d4). The N value slightly increased by 3.0 relative to the fresh sample (Table 2-c, d). This value corresponds to the mean particle size of 2.3 ± 0.1 nm, which is 1.2 nm larger than for the fresh sample [53]. The particle growth based on EXAFS was consistent with the corresponding value (0.8 nm) derived from TEM (Table 1d). The Pd–O interatomic distance increased by 0.01–0.21 nm and the N value decreased significantly from 1.9 to 0.57. Presumably, the reason for this is that the number of O_V sites increased at the interface between Pd and the TiO₂ surface and/or the relative number of interface Pd sites in contact with the TiO₂ surface decreased due to partial growth of the Pd particles by 1 nm [49–53].

After 0.40 MPa of CO_2 photoconversion testing using 100 mg of Pd/TiO₂, the peak energy and intensity in XANES were quite similar

to those of fresh samples (Fig. 6A–c, e). The *N* value of the Pd–Pd pair was 5.0 and did not significantly change from 5.9 for the fresh sample based on the fit errors (Table 2-c, e and Fig. 6B-e3, e4), whereas the *N* value for the Pd–O pair significantly decreased from 1.9 to 0.9 (Table 2-c, e). Thus, the increase in O_V sites for a nearly constant mean size of Pd particles during the photoconversion test was suggested after the photoconversion test at 0.40 MPa. The reason that the mean Pd particle size increased only under lower pressure conditions but remained unchanged under higher pressure conditions (Table 2-d, e) is unknown; however, the strong adsorption of H on Pd [54] may have prevented the coalescence of Pd nanoparticles. The XANES spectrum (Fig. 6A–e) resembled that of fresh Pd/TiO₂ (c), supporting the interpretation based on EXAFS.

The XANES spectrum taken for 10 mg of Pd/TiO₂ film (Fig. 1C) after a photoconversion test at 0.40 MPa (Fig. 6A–e') was quite similar to the spectrum in Fig. 6A–c for a fresh sample. In summary, Pd sites in 10–100 mg of Pd/TiO₂ photocatalyst remained Pd⁰ sites before and after photoreduction tests in CO₂ and H₂ over a pressure range from 24 kPa to 0.40 MPa.

To compliment 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 3-e' and Fig. 6C–e'3, e'4), similar to the values of 6 and 12 for the untreated rutile or anatase phase TiO₂, respectively [33,36,37]. In contrast, the decrease in O_V sites at the interface between Pd and TiO₂ surface sites under these conditions was sig-



Fig. 6. Pd *K*-edge XANES (A) and EXAFS (B) and Ti *K*-edge EXAFS (C) for PdO (a), Pd foil (thickness 12.5 μ m; b), fresh Pd/TiO₂ (c), and Pd/TiO₂ after 5 h photocatalytic testing in CO₂ (2.3 kPa) and H₂ (22 kPa) using 100 mg of Pd/TiO₂ (d) and in CO₂ (0.12 MPa) and H₂ (0.28 MPa) using 100 mg (e) or 10 mg of Pd/TiO₂ (e'). Spectra were measured in the transmission mode except that the Pd *K*-edge of sample e' was taken in the 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 2

Best-fit results of Pd K-edge and EXAFS spectra for Pd/TiO₂ photocatalysts.

Entry	Samples	Pd-O R (nm) N $\Delta(\sigma^2)$ (10 ⁻⁵ nm ²)	Pd-Pd R (nm) N $\Delta(\sigma^2)$ (10 ⁻⁵ nm ²)	Goodness of fit
с	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 ^a	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 ^b	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

^a After photocatalytic test listed in Table 4a.

^b After photocatalytic test listed in Table 4f.

Table 3

Best-fit results of Ti K-edge EXAFS spectra for Pd/TiO₂ photocatalysts.

Entry	Samples	Ti-O R (nm) N $\Delta(\sigma^2)$ $(10^{-5} nm^2)$	$Ti(-O-)TiR (nm)N\Delta(\sigma^2)(10^{-5} nm^2)$	Goodness of fit
e' ^a	5-h photocatalytic test under $\rm CO_2$ (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

^a After photocatalytic test listed in Table 4n.

nificant based on the N(Pd-O) decrease (Table 2-c, e) and should be populated only at the interface with Pd nanoparticles after the photoconversion test. The O_v sites were negligible in/on TiO₂ apart from Pd nanoparticles.

3.4. Photoconversion in CO₂ and H₂ at 0.20–0.80 MPa

CO₂ photoreduction using H₂ and 100 mg of Pd/TiO₂ or Ag/Zn₃-Ga-LDH powder at a reaction pressure of 24 kPa [6-8] irradiated with UV-visible light produced methane, CO, and/or methanol, and the rates on a C basis were 0.14–1.0 μ mol h⁻¹ g_{cat}⁻¹ (Table 4a, b). Table 4 lists normalized formation rates per photocatalyst weight for the practical comparisons to some of the literature, e.g., Refs. [10-12,14-17,55,56], but real formation rates in the unit μ mol h⁻¹ are also listed in Table S1 in the Supplementary Information for the comparisons with the other part of the literature because photocatalyst weight had a critical influence on the photocatalytic activities in this section. If the reaction pressures were elevated to 0.12 MPa of CO₂ and 0.28 MPa of H₂, the total rates increased by a factor of 1.8–2.6 times (0.36–1.8 μ mol h⁻¹ g_{cat}⁻¹; Table 4f, h). At a total reaction pressure of 0.40 MPa, the order of the total photoformation rates using 100 mg of powder samples on a C basis was as follows (Tables 4 and S1):

$$\begin{split} Cu/TiO_2(2.8) > & Pd/TiO_2(1.8) >> Ag/ZrO_2(0.64) \\ &\sim g - C_3N_4(0.53) > & Ag/Zn_3Ga - LDH(0.36) \\ &> & BiOCl(0.25). \end{split} \tag{9}$$

Ag/ZrO₂, g-C₃N₄, and BiOCl mostly produced CO at formation rates of 0.64, 0.53, and 0.15 µmol h⁻¹ g⁻¹_{cat}, respectively (Table 4c-e), whereas Pd/TiO₂, Cu/TiO₂, and Ag/Zn₃Ga-LDH favored methane formation at rates of 1.7, 2.8, and 0.32 µmol h⁻¹ g⁻¹_{cat}, respectively (Table 4f–h). A minor product was methanol, which was formed at a rate of up to 0.003 µmol h⁻¹ g⁻¹_{cat} using these photocatalysts.

The theoretical formation rate of water, $r(H_2O)$, is given by the equation

$$r(H_2O) = 2r(CH_4) + r(CO) + r(CH_3OH)$$
(10)

based on the stoichiometry of the equations

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \tag{11}$$

$$CO_2 + H_2 \rightarrow CO + H_2O \tag{12}$$

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \tag{13}$$

which account for the formation of methane, CO, and methanol.

For Ag/ZrO₂, g-C₃N₄, Cu/TiO₂, and Ag/Zn₃Ga-LDH, the $r(H_2O)$ values were calculated to be 0.64, 0.53, 5.6, and 0.68 µmol-H₂O h⁻¹ g⁻¹_{cat}, which are in good agreement with the experimental values of 0.64, 0.57, 6.3, and 0.65 µmol-H₂O h⁻¹ g⁻¹_{cat}, respectively (Table 4c, d, g, h) if compared with the maximum evaluation error of H₂O by GC (26%).

Conversely, the observed water formation rate using BiOCl $(1.3 \,\mu\text{mol}\,h^{-1}\,g_{cat}^{-1},\,\text{Table 4e})$ was larger by a factor of 3.7 than the $r(H_2O)$ value based on Eq. (10) (0.35 μ mol h⁻¹ g_{cat}⁻¹), suggesting concurrent noncatalytic hydrogenation of reactive lattice O atoms at the BiOCl surface [23,57]. Using Pd/TiO₂, the observed water formation rate was 2.2 μ mol h⁻¹ g_{cat}⁻¹ (Table 4f), which is a factor of 0.63 times lower than the $r(H_2O)$ value (3.5 µmol h⁻¹ g_{cat}) that was a significant difference in comparison to maximum evaluation error by GC (26%). Because Pd nanoparticles remained metallic and the number of O_V sites at the interface with the TiO₂ surface increased under the photocatalytic conditions (Table 2-e and Fig. 6B–e), approximately 40% of O originating from CO₂ should be adsorbed onto the TiO₂ surface away from Pd nanoparticles. The quantity of missing O atoms based on the stoichiometry of Eqs. (11) and (12) was 0.65 μ mol. The quantity of hydroxy groups in the untreated Pd/TiO₂ catalyst (7 species nm⁻²) [58] amounted to 69 µmol in 100 mg of Pd/TiO₂ powder. These hydroxy groups are plausible adsorption sites under the photocatalytic conditions if 0.94% of them desorb as water, leaving behind O_V sites during the pretreatment of Pd/TiO₂.

Table 4

Dependence of CO₂ photoconversion on the amount of photocatalyst and reactant pressure, and control conversion results in the absence of UV-visible light, catalyst, or reactant.

Ent.	Photocatalyst		Reactants (MPa)Formation rates $(\mu mol h^{-1} g_{cat}^{-1})$							
	Туре	Wt (mg)	CO2	H ₂	СО	CH₃OH	CH ₄	H ₂ O	02	$\sum c^{a}$
a	Pd/TiO ₂	100	0.0023	0.022	<0.008	< 0.0004	1.0	5.0	0	1.0
b	Ag/Zn₃Ga-LDH				0.11	0.028	< 0.012	-		0.14
с	Ag/ZrO_2		0.12	0.28	0.64	0.0021	< 0.012	0.64		0.64
d	g-C ₃ N ₄				0.53	0.0021	< 0.012	0.57		0.53
e	BiOCl				0.15	< 0.0004	0.10	1.3		0.25
f	Pd/TiO ₂				0.057	< 0.0004	1.7	2.2		1.8
g	Cu/TiO ₂				< 0.008	0.0030	2.8	6.3		2.8
ĥ	Ag/Zn ₃ Ga-LDH				0.044	< 0.0004	0.32	0.65		0.36
i	Ag/ZrO_2	10			< 0.08	< 0.004	4.3	6.5		4.3
j	g-C ₃ N ₄				< 0.08	< 0.004	3.8	4.1		3.8
k	BiOCl				1.9	< 0.004	1.1	37		3.0
1	Pd/TiO ₂		0.06	0.14	< 0.08	< 0.004	13	38		13
m			0.09	0.21	< 0.08	0.18	23	43		23
n			0.12	0.28	< 0.08	< 0.004	38	68		38
n′ ^b					< 0.08	0.018	8.8	11		8.8
n″ ^c					< 0.08	0.009	<0.12	7.2		<0.21
n′″ ^d					< 0.08	< 0.004	3.0	5.1		3.1
n″″e					< 0.08	0.016	1.3	9.8		1.3
n'''''			0	0.28	< 0.08	< 0.004	<0.12	11		<0.20
n″″″			0.12	0	< 0.08	0.008	<0.12	19		<0.20
n″″″′f			0	0	<0.08	< 0.004	<0.12	8.2		<0.20
0			0.15	0.35	< 0.08	0.17	20	28		20
р			0.18	0.42	<0.08	< 0.004	14	12		14
q			0.24	0.56	<0.08	< 0.004	8.6	9.6		8.6
r			0.12	0.12	< 0.08	0.013	12	25		12
S			0.28	0.28	< 0.08	0.020	22	58		22
t			0.07	0.28	< 0.08	0.14	27	44		27
u			0.19	0.28	< 0.08	0.08	26	39		26
v	Cu/TiO ₂		0.12	0.28	<0.08	0.056	19	33		19
w	TiO ₂				< 0.08	0.027	4.0	56		4.0
х	Ag/Zn ₃ Ga-LDH				0.95	0.10	2.1	5.3		3.2
У	No catalyst	0			<0.0008 ^g	<0.00004 ^g	< 0.0012 ^g	<0.03 ^g		< 0.0020 ^g

^a Total molar amount of C-containing products.

^b Using U330 filter at the light exit (Fig. 1B).

^c Using L42 filter at the light exit (Fig. 1B).

^d In the absence of UV-visible light at 298 K.

^e In the absence of UV-visible light at 353 K.

^f In 0.40 MPa of helium.

^g In units of μ mol h⁻¹.

It seems contradictory that this effect of O uptake derived from CO_2 on O_V sites on TiO_2 was not confirmed using Cu/TiO_2 (Table 4g). One of the reasons for the difference is the different final treatment temperature: 290 K under vacuum (Pd/TiO₂) versus 673 K in air (Cu/TiO₂) leading to fewer hydroxy groups for Cu/TiO₂ [58].

Next, at the same reaction pressure (0.40 MPa), the amount of photocatalyst was decreased to 10 mg. Using 10 mg of Pd/TiO₂ film, methane was exclusively formed at a rate of 38 µmol h⁻¹ g_{cat}⁻¹, higher by a factor of 22 times than when 100 mg of Pd/TiO₂ powder was used (Table 4f, n). Samples of 10 mg of Ag/ZrO₂, g-C₃N₄, Cu/TiO₂, and Ag/Zn₃Ga-LDH films exclusively (Table 4i, j, v) or preferentially (Table 4x) formed methane at rates of 4.3, 3.8, 19, and 2.1 µmol h⁻¹ g_{cat}⁻¹, factors of 6.7, 7.2, 6.8, and 8.9 times higher, respectively, on a total C basis than when 100 mg of the corresponding catalyst was used (Table 4c, d, g, h). A quantity of 10 mg of BiOCl film formed CO (64% selectivity) at a total formation rate of 3.0 µmol h⁻¹ g_{cat}⁻¹ (Table 4k), higher by a factor of 12 than when 100 mg of BiOCl was used (Table 4e).

The total photoformation rates on a C basis using 10 mg of photocatalyst at 0.40 MPa of CO_2 and H_2 (Table 4j, k, n, v, x and Table S1) were in the order

$$\begin{split} \text{Pd}/\text{TiO}_2(38) > & \text{Cu}/\text{TiO}_2(19) \gg \text{Ag}/\text{ZrO}_2(4.3) \\ & \sim & \text{g}-\text{C}_3\text{N}_4(3.8) > & \text{Ag}/\text{Zn}_3\text{Ga}-\text{LDH}(3.2) \\ & \sim & \text{BiOCl}(3.0). \end{split}$$

Formation rates were boosted by a factor of 22-6.7 times when 10 mg of photocatalyst films was used; however, the activity order did not change compared with Eq. (9) using 100 mg of catalyst, except for a reversal of the order of the top two TiO₂-based catalysts.

One of the reasons for these rate increases was the improvement of light absorption efficiency for the photocatalyst film compared with that for powders: 49% versus 40% (Fig. 2c, d) due to the difference in the exposed ratio of particles. As noted in Section 2.3, the film of areal density of 2.5 mg cm⁻² absorbed more light compared to the powders of 9.3 mg cm⁻² due to the relatively greater reflection/scattering by the powders. Furthermore, the activity increase by a factor of 22–6.7 times using six kinds of photocatalysts suggested that the other control factor(s) also exist.

Mass transfer limitation was suggested for catalyst pellets greater than 250 μ m for the Fischer–Tropsch reaction [59]. A mean 0.7 μ m-thick TiO₂ catalyst film was not controlled by mass transfer limitation for photocatalytic decomposition of formic acid [60]. No mass transport effect was observed for 2–5 μ m of Pt/Al₂O₃ catalyst film for the CO preferential oxidation reaction [61]. Taking the lower reaction rates for photocatalytic CO₂ conversion compared with these thermodynamically easier reactions [59–61], the mass transfer limitation seems negligible in the thin 10 mg films (thickness ~11 μ m, Fig. 5C2) and would not be significant in 100 mg of powder (~100 μ m).

Instead, the anatase 1 0 1 and rutile 1 1 0 diffraction peaks, especially the anatase 1 0 1 peak, were relatively weak in the

XRD pattern for 10 mg of Pd/TiO₂ film in comparison to ones for Pd/TiO₂ powder (Figs. S1 and 3d and Table S2). The population of these planes in parallel with the sample holder of the XRD apparatus would be smaller and the other plane(s) favorable for CO₂ photoreduction may be preferably exposed on Pd/TiO₂ film (see Supplementary Material).

Using 10 mg of Ag/ZrO₂, g-C₃N₄, BiOCl, Pd/TiO₂, Cu/TiO₂, and Ag/Zn₃Ga-LDH, $r(H_2O)$, formation rates were predicted to be 8.6, 7.6, 4.1, 76, 38, and 5.3 µmol h⁻¹ g⁻¹_{cat} based on Eq. (10), and experimental values were 6.5, 4.1, 37, 68, 33, and 5.3 µmol h⁻¹ g⁻¹_{cat}, respectively (Table 4i–k, n, v, x). Thus, CO₂ conversion using Ag/ZrO₂, Pd/TiO₂, Cu/TiO₂, and Ag/Zn₃Ga-LDH almost/exactly followed the stoichiometry of Eqs. (11-13) because the deviation between predicted and experimental values was 11–24% smaller than the maximum evaluation error for 4 Pa of water using GC (see Section 2). This result is consistent with the exclusive Pd⁰ sites of Pd/TiO₂ (10 mg) before and after the photoreduction tests in CO₂ and H₂ at 0.40 MPa (Fig. 6A–e').

Using Pd/TiO₂, the amount of methane formed at 0.40 MPa in 5 h was 1.9 μ mol (Table 4n), whereas the number of surface Pd atoms in 10 mg of Pd/TiO₂ catalyst was 0.19 μ mol if we assume the Pd dispersion is 0.40 for a mean nanoparticle size of 3.1 nm (Table 1d) [62], indicating a turnover of 10 and thus demonstrating catalytic phenomena.

Using $g-C_3N_4$, the observed water formation rate was 0.54 times lower than the calculated $r(H_2O)$ value; thus, approximately 50% of O originating from CO₂ would remain, or formed water readsorbed on the $g-C_3N_4$ surface. The water formation rate using BiOCl was a factor of 9.0 times higher than the $r(H_2O)$ value, suggesting concurrent noncatalytic hydrogenation of reactive lattice O atoms at the BiOCl surface [23,57].

The possibility of reaction of CO₂ with the product H₂O was also considered. At the end of the photocatalytic test under 0.12 MPa of CO₂ + 0.28 MPa of H₂ for 5 h using the most active Pd/TiO₂, the amount of formed water was 68 µmol h⁻¹ $g_{cat}^{-1} \times 5 h \times 0.010 g_{cat} = 3.4 µmol (Table 4n)$. In our preliminary photocatalytic test under 0.12 MPa of CO₂ + 2.3 kPa (94 µmol) of moisture using the same catalyst (10 mg), the predominant methane formation rate was 14 µmol h⁻¹ g_{cat}^{-1} [21]. If the reaction for methane formation is assumed to be first-order in moisture, the rate under 0.12 MPa of CO₂ + 3.4 µmol of moisture would be 0.51 µmol h⁻¹ g_{cat}^{-1} at the final stage of the photocatalytic test under CO₂ + H₂, which is negligible compared with the observed methane formation rate 38 µmol h⁻¹ g_{cat}^{-1} (Table 4n). Thus, the contribution of the reaction with the product H₂O was negligible in the photocatalytic tests under high-pressure CO₂ + H₂.

Wavelength dependence of irradiation [6,28,63–65] for the Pd/ TiO₂ photocatalyst was also studied using filters between the light source and the high-pressure reactor (Fig. 1A, B). Using a filter of U330 that cuts visible light and part of infrared light, the methane formation rate was decreased to 23% of that under full irradiation from the Xe arc lamp (Table 4n'). Conversely, using a filter of L42 that totally cuts UV light, methane was not detected above the detection limit of GC but methanol was formed very slowly (0.009 µmol h⁻¹ g_{cat}⁻¹; Table 4n''). Thus, the methane formation rate under UV-visible light (Table 4n) was not the summation of that under UV light and that under visible light, but a synergetic effect of UV and visible light was suggested.

Furthermore, the dependence of reaction rates on total pressure was studied using the most active Pd/TiO₂ film in Eq. (14) at pressures in the range 0.20–0.80 MPa (Table 4l–q). The product was exclusively methane (Fig. 7). The reaction order of methane formation was 1.53, as determined by a log–log plot in the pressure range 0–0.40 MPa. Methane formation rates reached a maximum of 38 µmol h⁻¹ g_{cat}⁻¹ at 0.40 MPa and then suddenly dropped above

0.40 MPa and finally decreased to 8.6 μ mol h⁻¹ g⁻¹_{cat} at 0.80 MPa (Table 4n, q and Fig. 7).

At total reactant pressures of 0.20, 0.30, 0.40, 0.50, 0.60, and 0.80 MPa, r(H₂O) values based on Eq. (10) were 26, 46, 76, 40, 28, and 17 μ mol h⁻¹ g_{cat}⁻¹, and the observed formation rates were 38, 43, 68, 28, 12, and 9.6 μ mol h⁻¹ g_{cat}⁻¹, respectively (Table 4l-q). Thus, the photocatalytic tests nicely followed the stoichiometry at total reaction pressures of 0.30 and 0.40 MPa. Based on Pd Kedge and Ti K-edge XAFS results at 0.40 MPa of CO₂ and H₂ for Pd/TiO_2 , Pd nanoparticles remained metallic and O_V sites were only plausible at the interface between Pd and the TiO₂ surface, but were not widely distributed over the TiO₂ surface (Fig. 6A-e, e', B-e, C-e' and Tables 2-e and 3-e'). Hence, at 0.20, 0.50, 0.60, and 0.80 MPa, approximately 32%, 30%, 57%, and 44% of O, respectively, originating from CO₂ would be adsorbed onto the TiO₂ surface away from Pd nanoparticles. The number of O atoms lacking based on the stoichiometry of Eqs. (11) and (13) was 0.37–0.80 umol after the photoconversion tests at 0.50-0.80 MPa. The hydroxy groups of the untreated Pd/TiO₂ catalyst (7 species nm⁻²) [58] corresponded to 6.9 µmol in 10 mg of Pd/TiO₂ film and are plausible adsorption sites under the photocatalytic conditions if 5.4-12% of hydroxy groups desorb as water to leave O_V sites during the pretreatment of Pd/TiO₂. The adsorption of O originating from CO₂ on the TiO₂ surface would be more pronounced at relatively lower photocatalytic activity at 0.20, 0.50, 0.60, and 0.80 MPa.

Next, the pressure dependence was extended to create a twodimensional contour plot of total C formation rates, which were essentially equivalent to the methane formation rates, as a function of H₂ and CO₂ partial pressures (Table 4l-s and Fig. 8). The methane formation curve in Fig. 7 corresponds to a straight line following $P_{CO_2} = (3/7)P_{H_2}$ in Fig. 8. Photocatalytic tests were also performed on three straight lines of $P_{CO_2} = P_{H_2}$, $P_{H_2} = 0.28$ MPa, and $P_{CO_2} = 0.12$ MPa (Table 4r, s; Table 4n, n''', s, t, u; Table 4n, n'''', r, respectively). The exclusive methane formation rates primarily depended on P_{H_2} ; the rates increased until P_{H_2} reached 0.28 MPa and then gradually dropped until P_{H_2} increased to 0.56 MPa, whereas they depended negligibly on P_{CO_2} . However, within the zone $P_{\rm H_2}$ = 0.20–0.35 MPa, the rates critically increased until a P_{CO_2} of 0.12 MPa was reached and then gradually decreased until P_{CO_2} increased to 0.28 MPa (Fig. 8). In this addition of data under both CO2 and H2 (Table 4r-u), predicted and observed amounts of water were in agreement within the maximum evaluation error (26%).

Blank tests were performed by controlling four factors (see Section 2) to compare with the photoconversion tests, as listed in Table 4n using 10 mg of Pd/TiO₂. In the absence of reactants or in the absence of catalyst (Table 4n""", y), no carbon-containing products were detected after 5 h of irradiation under UV–visible light. Water formation at a rate of 8.2 μ mol h⁻¹ g⁻¹_{cat} in the absence of reactants was merely a desorption from Pd/TiO₂ that was in adsorption/desorption equilibrium with adsorbed water molecules, as confirmed by FTIR [21].

In the presence of 0.28 MPa of H₂ only, no C-containing products were detected above he detection limit (Table 4n""' and Fig. 8), demonstrating that CO₂ was the only C source in this study. Conversely, in the presence of 0.12 kPa of CO₂ only, methanol was produced very slowly (0.008 μ mol h⁻¹ g⁻¹_{cat}; Table 4n""" and Fig. 8). As the rate was negligible compared with the methane formation rate in the presence of CO₂ + H₂ (38 μ mol h⁻¹ g⁻¹_{cat}), hydrogen was the predominant reductant for CO₂ compared with adsorbed water or surface hydroxy in this study.

In the absence of light at 298 K (the initial temperature 290 K in the cell increased to 298 K after 10 min of UV–visible light irradiation; Table 4n^{'''}), thermal methane formation proceeded as in Eq. (11), but it was only 7.9% of that under UV–visible light irradiation



Fig. 7. The dependence of formation rates for CH₄, CO, methanol, and water on total reaction pressure using a Pd/TiO₂ photocatalyst, where $P_{CO_2}/P_{H_2} = 3/7$.



Fig. 8. Contour diagram for the total photoformation rates of C-containing products from CO_2 and H_2 using a Pd/TiO₂ photocatalyst as a function of the partial pressures of H_2 and CO_2 .

(Table 4n), demonstrating that most of the CO_2 conversion from CO_2 and H_2 in Table 4 proceeded photocatalytically.

To verify the thermal effects, blank tests in the absence of light were also carried out at 353 K (Table 4n""). The methane formation rate decreased by a factor of 0.43 times compared with that at 298 K. Moreover, 73% of the water formed among 9.8 μ mol h⁻¹ g⁻¹_{cat} (Table 4n"") was not stoichiometric according to Eq. (11), but wass merely simple desorption of adsorbed water from the TiO₂ surface at 353 K.

4. Discussion

4.1. Energetics of the photoconversion of CO₂ and H₂

The dependence of CO₂ photoconversion using H₂ on the type and amount of photocatalyst and the reaction pressure was studied. For 10–100 mg of photocatalyst in 0.40 MPa of CO₂ and H₂, the activity order Eqs. (9) and (14) for formation of all Ccontaining compounds (methane, CO, and methanol) can be summarized as

$$\begin{array}{ll} \mbox{Pd or Cu on TiO}_2 >> \mbox{Ag}/\mbox{ZrO}_2 \sim \ \mbox{g} - \mbox{C}_3 \mbox{N}_4 \\ \\ &> \ \mbox{Ag}/\mbox{Zn}_3 \mbox{Ga} - \mbox{LDH} \ \ \sim \ \mbox{BiOCl.} \eqno(15) \eq$$

This order was not correlated to the E_g values of the metal oxide or hydroxide semiconductors (3.1–3.2, 5.1, 2.9, 5.2, and 3.6 eV; Table 1) and was almost in the opposite direction to the CB minimum potentials for the semiconductors (-0.1, -1.0, -1.3, -1.3, and -0.6 V at pH 0) [8,23,33,45] because more negative voltages are advantageous for CO₂ reduction based on equilibrium control (Scheme 1B). Thus, the (excited) energy level of metal nanoparticles (Pd, Cu, or Ag) for the electron trap and the efficiency of electron injection into CO₂-derived species were the major factors that determined the reaction order of Eq. (15), as discussed below.

Electron traps that decrease the recombination of photogenerated charges were proposed for metal-doped TiO₂ [11]. The work functions (WFs) for Pd. Cu. and Ag are 5.22-5.6, 4.48-5.10, and 4.52–4.74 eV versus the vacuum level [66], corresponding to potentials of 0.78-1.16, 0.04-0.66, and 0.08-0.30 V versus SHE (pH 0), respectively, which are slightly positive compared with the CB of TiO₂ (-0.1 V; Scheme 1B). The O_V sites for BiOCl are reported to exist at ~ 0 V at pH 2 [23,67]. Thus, the potentials for electron trapping levels for Pd/TiO₂, Cu/TiO₂, Ag/ZrO₂, g-C₃N₄, Ag/ Zn₃Ga-LDH, and BiOCl are 0.78–1.16, 0.04–0.66, 0.08–0.30, –1.3, 0.08–0.30, and \sim 0 V, respectively. Except for g-C₃N₄, the electron trapping level was very close to or a little more positive than the reduction potentials of methane (0.17 V at pH 0) or CO (0.30 or -0.12 V at pH 0) [14,68]. In general, the electron trapping level became progressively more positive as the CO₂ photoformation rates increased (Eq. (15)). Thus, the probability of direct electron transfer from the trapping levels to CO₂-derived species seems low.

Xie et al. reported a similar correlation between the potential of electron trapping sites and the photoformation rates of CO₂ to methane and CO using noble-metal-supported TiO₂, which followed the order of the metal WFs: Pt > Pd > Au > Rh > Ag [11]. Thus, we propose that the electron transfer to CO₂-derived species was a combination of excited electron traps at Pd from TiO₂ followed by transfer of hot/excited electrons produced by SPR to CO₂-derived species (Scheme 1B). Thus the proposed reaction mechanism in the energetic diagram was in accord with the wavelength dependence of irradiation for Pd/TiO₂ (Table 4n, n', n"). The summation of rates under UV light and under visible light did not account for the rate under UV-visible light, implying a synergetic effect, e.g., of UV for the band-gap excitation of TiO₂ and of visible light for the hot electrons by SPR. The SPR peak(s) were centered at 3.1–1.5, 2.8, 2.9, and 3.1 eV for Pd/TiO₂, Cu/TiO₂, Ag/ZrO₂, and Ag/ Zn₃Ga-LDH (Table 1a, d, e, f), respectively. Thus, the levels of hot/ excited electrons due to SPR were estimated to be -2.3 to -0.3, -2.8 to -2.1, -2.8 to -2.6, -1.3, -3.0 to -2.8, and ~ 0 V for Pd/ TiO₂, Cu/TiO₂, Ag/ZrO₂, g-C₃N₄, Ag/Zn₃Ga-LDH, and BiOCl, respectively, if we assume that the Fermi level for metal nanoparticles does not shift.

In summary, as the levels of hot/excited electrons became more negative, the catalysts became more active, except for Ag/ZrO₂ and Ag/Zn₃Ga-LDH, probably due to lower charge separation efficiency for intrinsic semiconductor (ZrO₂) [69] or hydroxide (Zn₃Ga-LDH) [70,71]. Essentially, the hot/excited electrons could be transferred easily to CO₂-derived species based on the energy difference, and then the positive charge remaining in the metal nanoparticles recombined with electrons that diffused from the semiconductors (Scheme 1B). However, hot/excited electron transfer by SPR was not enough to complete the reactions (11)–(13), as confirmed by quite poor activity in the photocatalytic test irradiated by light of $\lambda > 420$ nm (Table 4n"). Thus, oxidation site of H₂ to protons should be on TiO₂, close to the interface with Pd, but not on Pd (Scheme 1A).



Scheme 1. Proposed reaction mechanism of CO_2 photoconversion using H_2 (A) and the corresponding energetic diagram (B; pH 0).

Ag/Zn₃Ga-LDH and Cu phthalocyanine(CuPc)/Zn₃Ga-LDH also collected electrons due to SPR of Ag [28] or HOMO–LUMO excitation of the CuPc and BG excitation of the LDH [6,28]. Zhang et al. proposed a similar electron transfer to CO₂ using TiO₂ nanofibers doped with Au/Pt [72]. The efficiency of trapping electrons in metal nanoparticles that had diffused from the semiconductor was suggested to control the activity order in Eq. (15). Wang et al. proposed a similar CO₂ photoconversion mechanism using small Pt nanoparticles on approximately 2 μ m of single-crystal TiO₂ film prepared by metal sputtering for 5–60 s [55]. Ultimately, small Pt nanoparticles approach the WF level of –2.128 V for Pt₁ and would reduce CO₂ directly. On the other hand, similar electron transfers from CB or O_V sites to CO₂ resulting in methane and/or CO formation were already reported for g-C₃N₄ [73] and BiOCI [53,74].

The total formation rates of all C-containing compounds using 100 mg of photocatalyst powder ($0.28-0.025 \mu$ mol-C h⁻¹; Table 4c-h) were clearly lower than those using 10 mg of photocatalyst film ($0.38-0.030 \mu$ mol-C h⁻¹; Table 4i-k, n, v, w). Plausible reasons for this are more effective absorption of UV-visible light in comparison to reflectance/diffraction (Fig. 2c, d) and possibly preferable orientation of TiO₂ crystallites for the 10 mg films compared with the 100 mg powders.

In summary, photoconversion rates of CO_2 were controlled by the energy of hot/excited electrons produced by SPR in metals, the CB minimum of g-C₃N₄, and O_V sites in BiOCl. Cu or Pd on TiO₂, especially as 10 mg films, was the most effective for photoconversion of CO₂ and H₂.

4.2. Reaction mechanism for photoconversion of CO_2 and H_2 using the most active Pd/TiO₂ catalyst

The dependence of CO₂ conversion rates for the most active Pd/ TiO₂ photocatalyst on the partial pressures of CO₂ and H₂ was specific; the top of the volcano was searched for by following the methane formation rates along four straight lines following $P_{CO_2} = (3/7)P_{H_2}$, $P_{CO_2} = P_{H_2}$, $P_{H_2} = 0.28$ MPa, and $P_{CO_2} = 0.12$ MPa and a steep volcano-like contour diagram could be drawn (Fig. 8). The rates reached a maximum at $P_{CO_2} = 0.12$ MPa and $P_{H_2} = 0.28$ MPa. In the zone $P_{CO_2} \leq 0.12$ MPa and $P_{H_2} \leq 0.28$ MPa, the reaction order for methane formation was 1.53 and the dependence was primarily determined by P_{H_2} , suggesting that the Pd surface was preferentially covered with H and the reaction order should be mostly dependent on P_{H_2} . In the partial-pressure zone at 0.30–0.40 MPa, the mass balance of Eq. (11) was preserved (Table 4m, n).

In the proposed mechanism (Scheme 1A), hydrogen dissociates and is oxidized by holes at the interface between Pd and the TiO_2 surface. The protons that form progressively combine with CO₂derived species and electrons due to the SPR effects of Pd (Scheme 1B), finally forming methane and water. If the protons do not encounter CO₂-derived species, they can react with lattice oxygen at the interface between Pd and the TiO₂ surface to form water and O_V sites.

Conversely, in the zone $P_{CO_2} \ge 0.12$ MPa and $P_{H_2} \ge 0.28$ MPa, exclusive methane formation rates progressively dropped (Fig. 8), and deviations from the mass balance of Eq. (11) became more significant (Table 40-q and Fig. 7). These trends were not due to the change of Pd valence states. The Pd sites should be exclusively metallic or even the O_V sites at the interface with TiO₂ surface increased after the CO₂ photoconversion tests, as confirmed by Pd K-edge XAFS (Table 2A-d, e and Fig. 6A-d, e, e' and B-d, e). One of the reasons for the decrease in activity in this pressure zone is that the Pd surface was predominantly covered with H, inhibiting the approach of CO₂ (Scheme 1A). This difference is supported by the difference in binding energies of CO_2 (-0.33 eV) and H (-2.95 eV) on the Pd (111) surface [54]. Once the adsorption of CO₂ onto Pd sites became difficult, the conversion of CO₂ to methane and O₂ decreased (Fig. 7), and intermediates and/or water would remain on the TiO₂ surface, e.g., on O_V sites formed during pretreatment.

In the proposed reaction mechanism, the reaction of CO_2 derived species, protons, and SPR electrons was plausible, but we suspect that the thermally dissociated H species from H₂ on the Pd surface at 298 K would also combine with CO₂-derived species. In fact, 7.9% of the methane formed under UV–visible illumination (Table 4n) could be formed under 0.40 MPa of CO₂ and H₂ after 5 h in the absence of light at 298 K (Table 4n^{'''}). Hence, dissociated H from H₂ on the Pd surface would be incorporated as a minor route among the multiple reduction steps involved in converting CO₂ to methane. Overall, the CO₂ conversion basically proceeded photocatalytically.

Recently, CO_2 activation at O_V sites on TiO_2 has often been suggested experimentally [10–13] and theoretically [75,76], in most cases using water as a reductant via

$$CO_2 + O_V \rightarrow CO + O(surface)$$
 (16)

and/or

$$CO_2 + Ti^{3+} \rightarrow Ti^{4+} - CO_2^-,$$
 (17)

$$CO_2^- + H^+ + e^- \to CO + OH^-.$$
 (18)

The rate of CO₂ photoconversion into methane using Pd/TiO₂ (38 μ mol h⁻¹ g_{cat}⁻¹; Table 4n) was higher than those into methane and methanol using undoped TiO₂ (4.0 μ mol h⁻¹ g_{cat}⁻¹; Table 4w) or reported in the literature (0.15–17 μ mol h⁻¹ g_{cat}⁻¹) [11,12,56,72,77–80] by 1–2 orders of magnitude, suggesting the importance of Pd sites for CO₂ reduction. However, CO₂ activation via Eq. (16) and/ or (17) + (18) is, at most, only partial in this study (Scheme 1A).

The negligible activity using Pd/TiO₂ irradiated by visible light only (0.009 μ mol-CH₃OH h⁻¹ g_{cat}⁻¹ Table 4n"), which was even lower than that in the absence of light at 298 K (3.0 μ mol-CH₄ h⁻¹ g_{cat}⁻¹

Table 4n^m), needs attention. Under the irradiation of visible light only, the formation of protons from H₂ should be negligible and hot electrons by SPR effect diffused in Pd nanoparticles (Scheme 1A). The minor reaction path of CO₂ with thermally formed H on the Pd surface would be suppressed by the electrons because the reaction of CO₂ with negatively charged H should be difficult compared with the coupling of CO₂ with H⁺ or H.

Finally, the possibility of thermal CO₂ conversion is considered. This study employed a similar light source to Ahmed et al. [8] and Yoshida et al. [65,81], in which the maximum temperature reached 313 K. The pressure decrease due to methane formation via Eq. (11) at a rate of 38 $\mu mol \ h^{-1} \ g_{cat}^{-1}$ under 0.40 MPa of CO_2 and H_2 (Table 4n) is as small as 93 Pa. As the critical pressures for CO_2 and H₂ are high (7.38 and 1.30 MPa, respectively) compared with the reaction pressures (0.12 and 0.28 MPa, respectively), the reaction gas can be approximated as an ideal gas. The reaction pressure before the irradiation of UV-visible light (0.400 MPa) gradually increased to 0.412 MPa after approximately 10 min of irradiation and remained constant for 5 h. After the UV-visible light was turned off, the pressure decreased to 0.400 MPa in 30 min. Thus, the initial temperature (290 K) reached thermal equilibrium at 298 K during the test. Under the same reaction conditions but using a white TiO_2 photocatalyst (Table 4w), the thermalequilibrium pressure was 0.406 MPa, corresponding to a reaction temperature of 294 K. Furthermore, partial heating of the catalyst also needs attention. The heat of reaction for Eq. (11) $(165 \text{ kJ mol}^{-1})$ should elevate the Pd/TiO₂ catalyst by 45 K (if the molar heat capacity at constant pressure is assumed to be 55.31 J mol⁻¹ K⁻¹ for anatase-type TiO₂) at a maximum, although part of the heat should diffuse to the Pyrex glass substrate beneath the catalyst film (Fig. 1C). The blank test in the absence of UV-visible light using Pd/TiO₂ in CO₂ and H₂ at 353 K, which is 18 K higher than the theoretical maximum temperature for the Pd/ TiO₂ catalyst, produced only 3.4% methane compared with the UV-visible light irradiated test (Table 4n, n""), reconfirming that UV-visible light was indispensable for the conversion of CO₂ using H_2 in this study.

In summary, no reactions proceeded in the absence of reactants (Table 4n'''''') or catalyst (Table 4y). 7.9–3.4% of the methane was produced in the absence of UV–visible irradiation (Table 4n''', n''''). Thermal processes accounted for a minor fraction of reaction (11), but their rate decreased to 0.43 times the rate at 298 K when the reaction temperature was elevated to 353 K, due to the complex adsorption/reaction steps for reaction (11).

5. Conclusions

Photocatalytic CO₂ conversion was investigated up to 0.80 MPa using H₂ and 10–100 mg of Pd/TiO₂, Cu/TiO₂, Ag/ZrO₂, g-C₃N₄, Ag/ Zn₃Ga-LDH, and BiOCl. The catalytic activities were in the order Pd or Cu on TiO₂ \gg Ag/ZrO₂ \sim g-C₃N₄ > Ag/Zn₃Ga-LDH \sim BiOCl. A twostep electron excitation mechanism was strongly suggested for doped metal nanoparticles, in which hot/excited electrons arising from SPR effects were estimated to exist at -2.8 to -0.3 V vs. SHE, which is more negative than the potentials for the reduction of CO_2 to methane or CO(-0.12 to 0.30 V), and the remaining positive charge should combine with excited electrons that have diffused from the semiconductor. Therefore, as the levels of hot/ excited electrons became more negative, the catalysts basically became more active except, for intrinsic semiconductor (ZrO_2) and hydroxide (LDH) [82]. For the oxidation reaction, H₂ was suggested to couple with photogenerated holes to form protons at the interface between Pd and the TiO₂ surface. The protons would combine progressively with CO₂-derived species and electrons at the Pd to form methane and water, and would also react with lattice O to form O_V sites at the interface between Pd and TiO₂, as confirmed by Pd *K*-edge EXAFS.

Based on blank tests in the absence of UV–visible light at 298– 353 K, thermal CO₂ conversion under H₂ at 0.40 MPa was 7.9–3.4% of that under UV–visible light irradiation. Therefore, the CO₂ conversion in this study is almost exclusively photocatalytic, but thermal H adsorption on Pd from H₂ is also plausible. H was preferably adsorbed on Pd, leading to the CO₂ photoconversion efficiency depending exclusively on P_{H_2} . The methane formation rate reached a maximum (38 µmol h⁻¹ g⁻¹_{cat}) at P_{CO_2} = 0.12 MPa and P_{H_2} = 0.28 MPa, but the rate dropped at higher pressures due to hindrance of CO₂ adsorption by H.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2016.10.024.

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