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

Shogo Kawamuraqa, Hongwei Zhanga, Masayuki Tambab, Takashi Kojimab, Masaya Miyanoa, Yusuke Yoshidaa,1, Mao Yoshiba, Yasuo Izumia,

⇑

a Department of Chemistry, Graduate School of Science, Chiba University, Yayoi 1-33, Inage-ku, Chiba 263-8522, Japan
b Department of Applied Chemistry and Biotechnology, Graduate School of Engineering, Chiba University, Yayoi 1-33, Inage-ku, Chiba 263-8522, Japan

Article info

Article history:
Received 30 August 2016
Revised 20 October 2016
Accepted 22 October 2016

Keywords:
CO₂ conversion
Pressure dependence
Pd/TiO₂
Electron trap
Oxygen vacancy
Interface site
Surface plasmon resonance
Contour plot

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/C₂₉Ag/ZrO₂/C₂₄g-C₃N₄ > Ag/Zn₃Ga-layered double hydroxide/C₂₄BiOCl. 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.

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 photocconversion 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,

\[
2H₂O → O₂ + 4H^+ + 4e^-.
\] (1)

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

\[
\text{NADP}^+ + H^+ + 2e^- → \text{NADPH}.
\] (2)

Our analogue of Photosystem I in heterogeneous catalysis is CO₂ photocoonsversion using LDH and Pd/TiO₂ to form methanol and methane [6–8]:

\[
\text{CO}_2 + 6\text{H}^+ + 6e^- → \text{CH}_3\text{OH} + \text{H}_2\text{O}
\] (3)

\[
\text{CO}_2 + 8\text{H}^+ + 8e^- → \text{CH}_4 + 2\text{H}_2\text{O}
\] (4)

\[
2\text{H}_2\text{O} + 2\text{NADP}^+ → \text{O}_2 + 2\text{NADPH} + 2\text{H}^+ (1 + 2)
\]

\[
4\text{H}_2\text{O} + 2\text{CO}_2 → 3\text{O}_2 + 2\text{CH}_3\text{OH} (1 + 3)
\]

\[
2\text{H}_2\text{O} + \text{CO}_2 → 2\text{O}_2 + \text{CH}_4 (1 + 4)
\]

Although significant progress has been achieved by many researchers in the photocconversion of CO₂ into fuels [1–3], most studies have evaluated the photocconversion of dissolved CO₂ in aqueous solution, namely Eqs. (1) and (3) or (1) and (4). For example, the critical role of oxygen vacancy (O₉) sites in CO₂/H₂O was suggested [10–13], and enhanced photocconversion of CO₂ was reported at ele-
vated reaction pressure of CO₂ and moisture [10,11] or liquid water [11,14–19]; however, most of the mechanisms are unknown. Thus, the systematic dependence of CO₂ photocatalysis on reaction pressure and an independent understanding of the reduction sites and mechanism for CO₂ 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 (Eg) 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·mH₂O LDH while keeping the conduction band (CB) minimum more negative than the reduction potential (E°C) 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 CO₂ conversion using H₂ 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⁻¹ catalyst [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 H₂ to form Ni–H species followed by thermal hydrogenation of CO₂ 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 CO₂ photocatalysis 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 concentrations of O₂ sites in TiO₂ by X-ray absorption fine structure (XAFS). This paper is the first of several in which the mechanism for reaction in CO₂ + H₂ is compared with those for reaction in CO₂ + H₂O. As site separation between photo-oxidation (H₂ or moisture) and photoreduction (CO₂), and the concentrations and roles of O₂ sites on the catalysis are complicated issues, the photoconversion of CO₂ 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 ZrO₂ [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 polytetrafluoroethylene-based membrane filter (Omni Pure JWP04700, 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 RUF4242TA (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-C₃N₄ [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, >95.5%, 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 TiO₂ (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 JWP04700 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 JVP04700 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 [Zn₃Ga(OH)₈]₂CO₃·mH₂O has been described previously [8]. A quantity of 1.0 mM of Ag nitrate solution was stirred with [Zn₃Ga(OH)₈]₂CO₃·mH₂O 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 JGW04700 filter and the collected yellow precipitate was washed with deionized water. The obtained yellow powder was 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) of 2θ = 5.0–60° 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 Kα emission (wavelength λ = 0.15419 nm) [25,26] and a nickel filter. Crystallite sizes (t) were estimated using the Scherrer equation

\[
t = \frac{0.9\lambda}{\text{Peak width} \times \cos\theta_b}
\]

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 Eₗ values were estimated via simple extrapolation of the absorption edge or by fitting to the Davis–Mott equation,

\[
\alpha h\nu \propto (h\nu - E₀)^n
\]

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 E₀ 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
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 molybdenum mica filter. The number of independent data points in the fit range was calculated based on the Nyquist theorem and the XAFS-specific modification by Stern [35].

\[ n = \frac{2\Delta k \Delta R}{\pi} + 2. \]  

(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 ultrasonic (430 W, 38 kHz) for 3 min. The suspension was mounted on a Pyrex glass plate (25 × 25 × 1 mm) and dried at 373 K for 12 h. The area of the obtained films was 20 × 20 mm. Films on plates or as-synthesized fine powder samples in a Pyrex dish (\( \Phi_{\text{external}} = 37 \) 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/
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 $\lambda = 420$ nm [40] or a U-330 filter (2.5 mm thick, Kenko) that filters the light less than $\lambda = 250$ nm and between $\lambda = 390$ 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 H$_2$ 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 H$_2$ and most of the CO$_2$.

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 CO$_2$ only, in 0.28 MPa of H$_2$ 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-C$_3$N$_4$, BiOCl, and Zn$_2$Ga-LDH and the preparation of Ag/ZrO$_2$, Pd/TiO$_2$, Cu/TiO$_2$, and Ag/Zn$_2$Ga-LDH were verified by their XRD patterns (Fig. 3) and UV–visible spectra (Fig. 4). For Ag/ZrO$_2$ (Fig. 3a), the XRD peaks appeared at $2h_B = 17.5^\circ$, $24.3^\circ$, $28.3^\circ$, $31.5^\circ$, $34.3^\circ$, $35.3^\circ$, $38.6^\circ$, $41.0^\circ$, $45.1^\circ$, $50.3^\circ$, $54.2^\circ$, and $55.6^\circ$ and were ascribed to 001, 011, 1 1 1, 1 1 1, 0 2 0, 0 0 2, 120, 112, 2 0 2, 0 2 2, 0 0 3, and 310 reflections of monoclinic ZrO$_2$ [43,44]. No peaks due to Ag metal or Ag$_2$O nanoparticles were observed [28,29].

Broad peaks at $2h_B = 13.3^\circ$ and 27.5$^\circ$ and a weak peak at $2h_B = 44^\circ$ in pattern b appeared essentially at the same position as those reported for g-C$_3$N$_4$ in the literature [22,45] and were assigned to 100, 002, and 200 reflections, respectively. The peak positions and relative intensities for peaks at $12.0^\circ$, $26.0^\circ$, $32.7^\circ$, $33.6^\circ$, $41.0^\circ$, $46.8^\circ$, $49.8^\circ$, $54.3^\circ$, and $58.8^\circ$ in pattern c were in

![Fig. 1. (A, B) High-pressure stainless reactor equipped with quartz windows and a pressure gauge for CO$_2$ photoconversion tests irradiated by UV–visible light from a 500-W Xe arc lamp (A: top view, B: side view). (C) Photocatalyst films (20 × 20 mm) of Ag/ZrO$_2$, g-C$_3$N$_4$, BiOCl, Pd/TiO$_2$, Cu/TiO$_2$, and Ag/Zn$_2$Ga-LDH (top to bottom).](image1)

![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/TiO$_2$ powder (c), and in the presence of the quartz windows and 10 mg of Pd/TiO$_2$ film (d).](image2)
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 \( E_g \) 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). 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 \( \mu \) 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 Pd\( ^0 \) 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. 6B–C3, c4, and Table 2-c). The coordination of the Pd–Pd interatomic

accord with the literature reports for BiOCl and were assigned to 001, 101, 110, 102, 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\( \theta \) = 25.4°, 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\( \theta \) = 27.5°, 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\( \theta \) = 11.7°, 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
pair at 0.276 nm (Fig. 6B-c2) was predominant (N = 5.9), which is consistent with the assignment of the predominant Pd\(^0\) 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 TiO\(_2\) 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\(_{\mathrm{V}}\) sites increased at the interface between Pd and the TiO\(_2\) surface and/or the relative number of interface Pd sites in contact with the TiO\(_2\) 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/TiO\(_2\), 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\(_{\mathrm{V}}\) 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/TiO\(_2\) (c), supporting the interpretation based on EXAFS. The XANES spectrum taken for 10 mg of Pd/TiO\(_2\) 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/TiO\(_2\) photocatalyst remained Pd\(^0\) before and after photoreduction tests in CO\(_2\) and H\(_2\) 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/TiO\(_2\) 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-e3, e4), similar to the values of 6 and 12 for the untreated rutile or anatase phase TiO\(_2\), respectively [33,36,37]. In contrast, the decrease in O\(_{\mathrm{V}}\) sites at the interface between Pd and TiO\(_2\) surface sites under these conditions was sig-

**Fig. 5.** TEM images of Pd/TiO\(_2\) as prepared (A) and after CO\(_2\) photoreduction tests in CO\(_2\) (0.09 MPa) and H\(_2\) (0.21 MPa) (B), and cross-sectional SEM images of fresh Pd/TiO\(_2\) (C1, C2).
Fig. 6. Pd K-edge XANES (A) and EXAFS (B) and Ti K-edge EXAFS (C) for PdO (a), Pd foil (thickness 12.5 μm; 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: k³-weighted EXAFS oscillation (1), its associated Fourier transform (2), and best-fit results in k-space (3) and R-space (4).
significant based on the \(N(\text{Pd–O})\) decrease (Table 2-c, e) and should be populated only at the interface with Pd nanoparticles after the photocatalysis test. The \(O_v\) sites were negligible in/on TiO\(_2\) apart from Pd nanoparticles.

### 3.4. Photoconversion in \(CO_2\) and \(H_2\) at 0.20–0.80 MPa

\(CO_2\) photoreduction using \(H_2\) and 100 mg of Pd/TiO\(_2\) or Ag/Zn\(_3\)Ga-LDH powder at a reaction pressure of 24 kPa \([6–8]\) irradiated with UV–visible light produced methane, CO, and/or methanol, with \(UV–\text{visible}\) light produced methane, CO, and/or methanol, whereas Pd/TiO\(_2\), Cu/TiO\(_2\), and Ag/Zn\(_3\)Ga-LDH favored methane formation for the photocatalysts. If compared with the maximum evaluation error of \(H_2O\) by GC (26%).

Conversely, the observed water formation rate using BiOCl was a factor of 3.7 than the \(r(H_2O)\) value (3.5 \(\mu\)mol h\(^{-1}\) g\(_{\text{cat}}\)) in good agreement with the experimental values of 0.64, 0.57, 6.3, and 0.65 \(\mu\)mol-H\(_2\)O h\(^{-1}\) g\(_{\text{cat}}\), respectively (Table 4c, d, g, h) if compared with the maximum evaluation error of \(H_2O\) by GC (26%).

CO\(_2\) photoreduction using \(H_2\) and 100 mg of Pd/TiO\(_2\) or Ag/Zn\(_3\)Ga-LDH powder at a reaction pressure of 24 kPa \([6–8]\) irradiated with UV–visible light produced methane, CO, and/or methanol, with \(UV–\text{visible}\) light produced methane, CO, and/or methanol, whereas Pd/TiO\(_2\), Cu/TiO\(_2\), and Ag/Zn\(_3\)Ga-LDH favored methane formation for the photocatalysts. If compared with the maximum evaluation error of \(H_2O\) by GC (26%).

Conversely, the observed water formation rate using BiOCl was a factor of 3.7 than the \(r(H_2O)\) value (3.5 \(\mu\)mol h\(^{-1}\) g\(_{\text{cat}}\)) in good agreement with the experimental values of 0.64, 0.57, 6.3, and 0.65 \(\mu\)mol-H\(_2\)O h\(^{-1}\) g\(_{\text{cat}}\), respectively (Table 4c, d, g, h) if compared with the maximum evaluation error of \(H_2O\) by GC (26%).

\(CO_2\) photoreduction using \(H_2\) and 100 mg of Pd/TiO\(_2\) or Ag/Zn\(_3\)Ga-LDH powder at a reaction pressure of 24 kPa \([6–8]\) irradiated with UV–visible light produced methane, CO, and/or methanol, with \(UV–\text{visible}\) light produced methane, CO, and/or methanol, whereas Pd/TiO\(_2\), Cu/TiO\(_2\), and Ag/Zn\(_3\)Ga-LDH favored methane formation for the photocatalysts. If compared with the maximum evaluation error of \(H_2O\) by GC (26%).

Conversely, the observed water formation rate using BiOCl was a factor of 3.7 than the \(r(H_2O)\) value (3.5 \(\mu\)mol h\(^{-1}\) g\(_{\text{cat}}\)) in good agreement with the experimental values of 0.64, 0.57, 6.3, and 0.65 \(\mu\)mol-H\(_2\)O h\(^{-1}\) g\(_{\text{cat}}\), respectively (Table 4c, d, g, h) if compared with the maximum evaluation error of \(H_2O\) by GC (26%).

Conversely, the observed water formation rate using BiOCl was a factor of 3.7 than the \(r(H_2O)\) value (3.5 \(\mu\)mol h\(^{-1}\) g\(_{\text{cat}}\)) in good agreement with the experimental values of 0.64, 0.57, 6.3, and 0.65 \(\mu\)mol-H\(_2\)O h\(^{-1}\) g\(_{\text{cat}}\), respectively (Table 4c, d, g, h) if compared with the maximum evaluation error of \(H_2O\) by GC (26%).

Conversely, the observed water formation rate using BiOCl was a factor of 3.7 than the \(r(H_2O)\) value (3.5 \(\mu\)mol h\(^{-1}\) g\(_{\text{cat}}\)) in good agreement with the experimental values of 0.64, 0.57, 6.3, and 0.65 \(\mu\)mol-H\(_2\)O h\(^{-1}\) g\(_{\text{cat}}\), respectively (Table 4c, d, g, h) if compared with the maximum evaluation error of \(H_2O\) by GC (26%).
It seems contradictory that this effect of O uptake derived from CO₂ on O₅ sites on TiO₂ was not confirmed using Cu/TiO₂ (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 \( \mu \text{mol h}^{-1} \text{g}^{-1} \text{cat} \), 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, 6.3, 0.044 \( \text{mol h}^{-1} \text{g}^{-1} \text{cat} \), 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, j, v) or preferably (Table 4x) at rates of 4.3, 3.8, 19, and 22 \( \mu \text{mol h}^{-1} \text{g}^{-1} \text{cat} \). A quantity of 10 mg of BiOCl film formed CO (64% selectivity) at a total formation rate of 3.0 \( \mu \text{mol h}^{-1} \text{g}^{-1} \text{cat} \) (Table 4k), higher by a factor of 12 than when 100 mg of BiOCl was used (Table 4k).

The total photofomration rates on a C basis using 10 mg of photocatalyst at 0.40 MPa of CO₂ and H₂ (Table 4j, k, n, v, x, and Table S1) were in the order

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

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 μm for the Fischer–Tropsch reaction [59]. A mean 0.7 μm-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 μm 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 μm, Fig. 5C2) and would not be significant in 100 mg of powder (~100 μm).

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

### 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.

<table>
<thead>
<tr>
<th>Ent.</th>
<th>Photocatalyst</th>
<th>Reactants (MPa)</th>
<th>Formation rates ((\mu\text{mol h}^{-1} \text{g}^{-1} \text{cat}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Pd/TiO₂</td>
<td>100 0.0023 0.022</td>
<td>&lt;0.008 0.0004 1.0 5.0 0 1.0</td>
</tr>
<tr>
<td>b</td>
<td>Ag/Zn₃Ga-LDH</td>
<td>0.11 0.028 &lt;0.012 0.64</td>
<td>0.64</td>
</tr>
<tr>
<td>c</td>
<td>Ag/ZrO₂</td>
<td>0.12 0.28 0.64 0.0021 &lt;0.012</td>
<td>0.012 0.57</td>
</tr>
<tr>
<td>d</td>
<td>g-C₃N₄</td>
<td>0.53 0.0021 &lt;0.012</td>
<td>0.012 0.53</td>
</tr>
<tr>
<td>e</td>
<td>BiOCl</td>
<td>0.15 &lt;0.0004 0.10</td>
<td>0.10 0.25</td>
</tr>
<tr>
<td>f</td>
<td>Pd/TiO₂</td>
<td>0.057 &lt;0.0004 1.7</td>
<td>1.7 2.2</td>
</tr>
<tr>
<td>g</td>
<td>Cu/TiO₂</td>
<td>&lt;0.008 0.0030 2.8</td>
<td>2.8 6.3</td>
</tr>
<tr>
<td>h</td>
<td>Ag/Zn₃Ga-LDH</td>
<td>0.044 &lt;0.0004 0.32</td>
<td>0.32 0.65</td>
</tr>
<tr>
<td>i</td>
<td>Ag/ZrO₂</td>
<td>10 &lt;0.004 4.3</td>
<td>4.3 6.5</td>
</tr>
<tr>
<td>j</td>
<td>g-C₃N₄</td>
<td>0.08 &lt;0.004 3.8</td>
<td>3.8 4.1</td>
</tr>
<tr>
<td>k</td>
<td>BiOCl</td>
<td>0.019 &lt;0.004 1.1</td>
<td>1.1 3.7</td>
</tr>
<tr>
<td>l</td>
<td>Pd/TiO₂</td>
<td>0.06 0.14 &lt;0.004</td>
<td>0.014 1.3</td>
</tr>
<tr>
<td>m</td>
<td>0.09 0.21 0.18</td>
<td>23 43 23</td>
<td></td>
</tr>
<tr>
<td>n</td>
<td>0.12 0.28 &lt;0.004</td>
<td>38 68 38</td>
<td></td>
</tr>
<tr>
<td>n⁰</td>
<td>&lt;0.08 0.018 8.8</td>
<td>8.8 11</td>
<td></td>
</tr>
<tr>
<td>n⁰¹</td>
<td>&lt;0.009 &lt;0.12 7.2</td>
<td>7.2 &lt;0.21</td>
<td></td>
</tr>
<tr>
<td>n⁰¹²</td>
<td>&lt;0.004 3.0</td>
<td>3.0 5.1</td>
<td></td>
</tr>
<tr>
<td>n⁰²²</td>
<td>&lt;0.016 1.3</td>
<td>1.3 9.8</td>
<td></td>
</tr>
<tr>
<td>n⁰³³</td>
<td>0.012 0.008 &lt;0.012</td>
<td>0.12 11 &lt;0.20</td>
<td></td>
</tr>
<tr>
<td>n⁰³⁴</td>
<td>0.008 &lt;0.12 8.2</td>
<td>8.2 &lt;0.20</td>
<td></td>
</tr>
<tr>
<td>n⁰⁴⁴</td>
<td>0.15 0.17 20</td>
<td>20 28</td>
<td></td>
</tr>
<tr>
<td>o</td>
<td>0.18 0.42 &lt;0.004</td>
<td>14 12 14</td>
<td></td>
</tr>
<tr>
<td>q</td>
<td>0.24 0.56 &lt;0.004</td>
<td>8.6 9.6 8.6</td>
<td></td>
</tr>
<tr>
<td>r</td>
<td>0.12 0.013 12</td>
<td>12 25 12</td>
<td></td>
</tr>
<tr>
<td>s</td>
<td>0.28 0.026 22</td>
<td>22 58 22</td>
<td></td>
</tr>
<tr>
<td>t</td>
<td>0.07 0.14 27</td>
<td>27 44 27</td>
<td></td>
</tr>
<tr>
<td>u</td>
<td>0.19 0.08 26</td>
<td>26 39 26</td>
<td></td>
</tr>
<tr>
<td>v</td>
<td>Cu/TiO₂</td>
<td>0.12 0.056 19</td>
<td>19 33 19</td>
</tr>
<tr>
<td>w</td>
<td>TiO₂</td>
<td>&lt;0.008 0.027 4.0</td>
<td>4.0 56</td>
</tr>
<tr>
<td>x</td>
<td>Ag/Zn₃Ga-LDH</td>
<td>0.95 0.10 2.1</td>
<td>2.1 5.3 3.2</td>
</tr>
<tr>
<td>y</td>
<td>No catalyst</td>
<td>&lt;0.0008 &lt;0.00004</td>
<td>&lt;0.0012 &lt;0.0012 &lt;0.0020</td>
</tr>
</tbody>
</table>

### Notes

- Total molar amount of C-containing products.
- Using U₃30 filter at the light exit (Fig. 1B).
- Using L₄2 filter at the light exit (Fig. 1B).
- In units of \(\mu\text{mol h}^{-1} \text{g}^{-1} \text{cat}\).
- In the absence of UV–visible light at 298 K.
- In the absence of UV–visible light at 353 K.
- In 0.40 MPa of helium.
- In units of \(\mu\text{mol h}^{-1} \text{g}^{-1} \text{cat}\).
XRD pattern for 10 mg of Pd/TiO2 film in comparison to ones for Pd/TiO2 powder ([Figs. 51 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(H2O), formation rates were predicted to be 8.6, 7.6, 4.1, 76, 38, and 5.3 μmol h\(^{-1}\) g\(_{\text{cat}}\) based on Eq. (10), and experimental values were 6.5, 4.1, 37, 68, 33, and 5.3 μmol h\(^{-1}\) g\(_{\text{cat}}\), respectively (Table 4k–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 Pd\(_l\) 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 μmol (Table 4n), whereas the number of surface Pd atoms in 10 mg of Pd/TiO2 catalyst was 0.19 μmol if we assume the Pd dispersion is 0.10 for a mean nanoparticle size of 3.1 nm (Table 1d) [62], indicating a turnover of 10 and thus demonstrating catalytically phenomena.

Using g-C3N4, the observed water formation rate was 0.54 times lower than the calculated r(H2O) value; thus, approximately 50% of O originating from CO2 would remain, or formed water readsorbed during the adsorption/desorption equilibrium with adsorbed water molecules in the TiO2 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\(_{\text{cat}}\) × 5 h = 0.010 g\(_{\text{cat}}\) = 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\(_{\text{cat}}\) [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\(_{\text{cat}}\) 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\(_{\text{cat}}\) (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.

Conversely, using a filter of L42 that totally cuts UV light, methanol was formed very slowly (0.009 μmol h\(^{-1}\) g\(_{\text{cat}}\); 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 pressure 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\(_{\text{cat}}\) at 0.40 MPa and then suddenly dropped above 0.40 MPa and finally decreased to 8.6 μmol h\(^{-1}\) g\(_{\text{cat}}\) 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 μmol h\(^{-1}\) g\(_{\text{cat}}\), and the observed formation rates were 38, 43, 68, 28, 12, and 9.6 μmol h\(^{-1}\) g\(_{\text{cat}}\), 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 K-edge and Ti K-edge XAFS results at 0.40 MPa of CO2 and H2 for Pd/TiO2, Pd nanoparticles remained metallic and O\(_2\) 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\(_2\), 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 0.3–0.80 μmol after the photocatalytic tests at 0.50–0.80 MPa. The hydroxyl 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 hydroxyl groups desorb as water to leave O\(_2\) 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 two-dimensional 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 \(P_{\text{CO2}} = (3/7)P_{\text{H2}}\) in [Fig. 8]. Photocatalytic tests were also performed on three straight lines of \(P_{\text{CO2}} = P_{\text{H2}}\), \(P_{\text{H2}} = 0.28\) MPa, and \(P_{\text{CO2}} = 0.12\) MPa (Table 4r, s; Table 4n, n‘, s, t, u; Table 4n, n‘‘, n‘‘‘, r, respectively). The exclusive methane formation rates primarily depended on \(P_{\text{H2}}\); the rates increased until \(P_{\text{H2}}\) reached 0.28 MPa and then gradually dropped until \(P_{\text{H2}}\) increased to 0.56 MPa, whereas they depended negligibly on \(P_{\text{CO2}}\). However, within the zone \(P_{\text{H2}} = 0.20–0.35\) MPa, the rates critically increased until a \(P_{\text{CO2}}\) of 0.12 MPa was reached and then gradually decreased until \(P_{\text{CO2}}\) 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 photocatalysis 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 μmol h\(^{-1}\) g\(_{\text{cat}}\) 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 μmol h\(^{-1}\) g\(_{\text{cat}}\); Table 4n‘‘‘‘ and [Fig. 8]). As the rate was negligible compared with the methane formation rate in the presence of CO2 + H2 (38 μmol h\(^{-1}\) g\(_{\text{cat}}\)), 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.
Table 4n, demonstrating that most of the CO₂ conversion from CO₂ and H₂ using a Pd/TiO₂ photocatalyst as a function of the partial pressures of H₂ and CO₂, the activity order Eqns. (9) and (14) for formation of all C-containing compounds (methane, CO, and methanol) can be summarized as

\[ \text{Pd or Cu on TiO}_2 > Ag/ZrO_2 \sim g - C_3N_4 \]
\[ > Ag/Zn_3Ga-LDH \sim BiOCl. \] (15)

This order was not correlated to the \( E_v \) 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 more negative than the CB of TiO₂ (−0.1 V; Scheme 1B). The O₂ 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, and ~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 \( \lambda > 420 \text{ nm} \) (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).
The dependence of CO$_2$ conversion rates for the most active Pd/TiO$_2$ catalyst on the partial pressures of CO$_2$ and H$_2$ was investigated. The rates reached a maximum at P$_{CO_2} = 0.12$ MPa and P$_{H_2} = 0.28$ MPa. In the zone P$_{CO_2} \lesssim 0.12$ MPa and P$_{H_2} \lesssim 0.28$ 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 CO$_2$-derived species and electrons due to the SPR effects of Pd (Scheme 1B), finally forming methane and water. If the protons do not encounter CO$_2$-derived species, they can react with lattice oxygen at the interface between Pd and the TiO$_2$ surface to form water and O$_2$ sites.

Conversely, in the zone P$_{CO_2} \geq 0.12$ MPa and P$_{H_2} \geq 0.28$ MPa, exclusive methane formation rates drastically decreased (Fig. 8), and deviations from the mass balance of Eq. (11) became more significant (Table 4o–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$_2$ sites at the interface with TiO$_2$ surface increased after the CO$_2$ 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 CO$_2$ (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 CO$_2$ onto Pd sites became difficult, the conversion of CO$_2$ to methane and O$_2$ decreased (Fig. 7), and intermediates and/or water would remain on the TiO$_2$ surface, e.g., on O$_2$ 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 H$_2$ on the Pd surface at 298 K would also combine with CO$_2$-derived species. In fact, 7.9% of the methane formed under UV–visible illumination was produced from H$_2$ on the Pd surface at 298 K (Table 4n, o) was higher than those into methane (0.15–17 $\mathrm{mol}^{-1}$) or H$_2$ [11, 12, 56, 72, 77–80] by 1–2 orders of magnitude, suggesting the importance of Pd sites for CO$_2$ reduction. However, CO$_2$ activation via Eq. (16) and/or (17) is, at most, only partial in this study (Scheme 1A).

Recently, CO$_2$ activation at O$_2$ sites on TiO$_2$ has often been suggested experimentally [10–13] and theoretically [75, 76], in most cases using water as a reductant via

\[
\begin{align*}
\text{CO}_2 + \text{O}_2 & \rightarrow \text{CO} + \text{O} \text{(surface)} \quad (16) \\
\text{and/or} \\
\text{CO}_2 + \text{Ti}^{3+} & \rightarrow \text{Ti}^{4+} - \text{CO}_2 \quad (17) \\
\text{CO}_2 + \text{H}^+ + e^- & \rightarrow \text{CO} + \text{OH}^- \quad (18)
\end{align*}
\]

The rate of CO$_2$ photoconversion into methane using Pd/TiO$_2$ (38 $\mu$mol h$^{-1}$ g$_{\text{cat}}^{-1}$; Table 4n) was higher than those into methane and methanol using undoped TiO$_2$ (4.0 $\mu$mol h$^{-1}$ g$_{\text{cat}}^{-1}$; Table 4w) or reported in the literature (0.15–17 $\mu$mol h$^{-1}$ g$_{\text{cat}}^{-1}$) [11, 12, 56, 72, 77–80] by 1–2 orders of magnitude, suggesting the importance of Pd sites for CO$_2$ reduction. However, CO$_2$ activation via Eq. (16) and/or (17) is, at most, only partial in this study (Scheme 1A).

The negligible activity using Pd/TiO$_2$ irradiated by visible light only (0.009 $\mu$mol CH$_3$OH h$^{-1}$ g$_{\text{cat}}^{-1}$ Table 4n$'$), which was even lower than that in the absence of light at 298 K (3.0 $\mu$mol CH$_3$OH h$^{-1}$ g$_{\text{cat}}^{-1}$).
produced in the absence of UV–visible irradiation (Table 4n), 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 μmol h−1 gcat−1 under 0.40 MPa of CO2 and H2 (Table 4n) is as small as 93 Pa. As the critical pressures for CO2 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 TiO2 photocatalyst (Table 4w), the thermal-equilibrium 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 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 H2 in this study.

In summary, no reactions proceeded in the absence of reactants (Table 4nn′′′) or catalyst (Table 4y). 7.9–3.4% of the methane was produced in the absence of UV–visible irradiation (Table 4nn′, 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/ZnGa2LDH, and BiOC. The catalytic activities were in the order Pd or Cu on TiO2 \(\gg\) Ag/ZrO2 \(\sim\) g-C3N4 \(\sim\) Ag/ZnGa2-LDH \(\sim\) BiOC. A two-step 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 CO2 to methane or CO (\(-0.12\) to 0.30 V), and the remaining positive charge should combine with excited electrons that have diversified from the semiconductor. Therefore, as the levels of hot/excited electrons became more negative, the catalysts basically became more active except for intrinsic semiconductor (ZrO2) 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\(_2\) 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 \(P_{\text{in}}\). The methane formation rate reached a maximum \(38 \mu\text{mol h}^{-1} \text{gcat}^{-1}\) at \(P_{\text{in}} = 0.12\) MPa and \(P_{\text{in}} = 0.28\) MPa, but the rate dropped at higher pressures due to hindrance of CO2 adsorption by H.

Acknowledgments

The authors are grateful for financial support from Grant-in-Aid for Scientific Research C (26410204) from the Japan Society for the Promotion of Science and the Leading Research Promotion Program (2015) from the Institute for Global Prominent Research, Chiba University. X-ray absorption experiments were conducted under the approval of the Photon Factory Proposal Review Committee (2015G586 and 2014G631). The authors thank Sakino Oshiro for sample preparation and kinetic measurements. The authors thank Enago (www.enago.jp) for the English language review.

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.

References
