ACS APPLIED MATERIALS & INTERFACES

RESEARCH ARTICLE

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Photochemical Reduction of CO_2 Using TiO_2: Effects of Organic Adsorbates on TiO_2 and Deposition of Pd onto TiO_2

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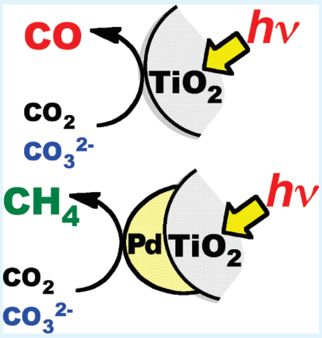

ABSTRACT: Reduction of CO_2 using semiconductors as photocatalysts has recently attracted a great deal of attention again. The effects of organic adsorbates on semiconductors on the photocatalytic products are noteworthy. On untreated TiO_2 (P-25) particles a considerable number of organic molecules such as acetic acid were adsorbed. Although irradiation of an aqueous suspension of this TiO_2 resulted in the formation of a significant amount of CH_4 as a major product, it was strongly suggested that its formation mainly proceeded via the photo-Kolbe reaction of acetic acid. Using TiO_2 treated by calcination and washing procedures for removal of the organic adsorbates, CO was photocatalytically generated as a major product, along with a very small amount of CH_4, from an aqueous suspension under a CO_2 atmosphere. In contrast, by using Pd (>0.5 wt %) deposited on TiO_2 (Pd−TiO_2) on which organic adsorbates were not detected, CH_4 was the main product, but CO formation was drastically reduced compared with that on the pretreated TiO_2. Experimental data, including isotope labeling, indicated that CO_2 and CO_3^{2-} are the main carbon sources of the CH_4 formation, which proceeds on the Pd site of Pd−TiO_2. Prolonged irradiation caused deactivation of the photocatalysis of Pd−TiO_2 because of the partial oxidation of the deposited Pd to PdO.

KEYWORDS: CO_2 reduction, methane formation, organic adsorbate, Pd−TiO_2, photocatalyst

INTRODUCTION

Ever since photocatalysis by semiconductors was reported by Honda and Fujishima's group,[1] its application in converting solar light to chemical energy has been an attractive research field.[2−11] In particular, photocatalysts for stoichiometric water splitting to make hydrogen have been the subject of a lot of attention[12−20] because of the serious problem of the shortage of fossil fuels. Although the reduction of CO_2 using semiconductors such as TiO_2 as a photocatalyst was also reported by Fujishima and his co-workers in 1979,[21] the progress achieved in this field had not been as dramatic as that in hydrogen evolution for a few decades because of the low reaction efficiencies.[3,22−25] Recently, however, photocatalytic reduction of CO_2 has attracted considerable attention again because this is a potentially applicable technology to utilization of CO_2 using solar light.[26−59]

It has been well-known that semiconductors such as metal-oxides show a tendency to absorb organic contaminations on their surfaces. Especially, semiconductor particles with large surface areas can easily absorb a considerable amount of organic compounds on the surface, and the adsorbed organic compounds might act as both a carbon source for the products and an electron donor. However, the carbon source of the photocatalytic reduction products of CO_2 has not been identified, and removal and evaluation methods of the organic contaminations on the surface have not been precisely described even in many recent papers.[50−59] Although metal particles deposited on the semiconductor photocatalyst have been often used as cocatalysts for CO_2 reduction,[28] they have potential for working as an electron donor. However, the oxidation state of the cocatalysts on semiconductor particles has not been described in many papars.[41,46,50,56,60−65] Lack of this verification should also be a problem for evaluating the photocatalyses.

Very recently, Mul and his co-workers have carefully investigated carbon sources in the photocatalytic CO_2 reduction with copper oxide promoted TiO_2 (Cu(I)/TiO_2) by the combined use of diffuse reflectance IR (DRIFT) spectroscopy and ^{13}C labeled CO_2.[66] This clearly showed that organic contaminations on the photocatalyst largely participate in formation of CO as a reaction product. Although the DRIFT spectroscopy is a magnificent method to detect organic compounds attached on the surface, released products into the gas phase have not been discussed in this paper because of limitation of this method.

In the first part of this paper, the effects of adsorbed organic molecules on TiO_2 particles on the photocatalytic reduction of CO_2 are clarified on the basis of the products in the gas phase, and methods for removing them from the surface of TiO_2 are reported. We have briefly reported that various metals deposited on TiO_2 accelerate the reduction of CO_2, and that Pd-deposited on TiO_2 (Pd−TiO_2) worked as the most efficient photocatalyst for producing CH_4 from CO_2 compared with other metals

Received: April 7, 2011
Accepted: June 10, 2011
Published: June 10, 2011

deposited on TiO_2.[67] The detail of the photocatalytic reduction of CO_2 to CH_4 using Pd−TiO_2 will be discussed in the latter part of the paper, that is, oxidation of Pd proceeded during photocatalytic reduction of CO_2, and this strongly affected the photocatalysis.

EXPERIMENTAL SECTION

General Methods, Materials, and Equipment. Before starting the photocatalytic reactions, all the equipment and materials (such as the reaction vessel, vacuum line, membrane filter, spatula, deionized water, and CO_2 gas) were checked by gas and ion exclusion chromatographies (GC and IEC) to ensure that there was no contamination by organic compounds (methane, organic acids, aldehydes, alcohols, and CO). Deionized water and CO_2 were introduced into the reaction vessel and irradiated for several hours by the same method used for the photocatalytic reactions except for the absence of the semiconductor photocatalyst. Neither CH_4 nor CO was detected. The other instruments were washed with water until alcohols, aldehydes, and organic acids were not detected in the washing water by GC and IEC. To avoid contamination from the experimenter, polyethylene gloves and a surgical mask were used when the sample was prepared. Freshly prepared deionized water was used as the solvent, and the absence of contamination of organic compounds was confirmed by GC and IEC analyses before every experiment. Degussa P-25 TiO_2 particles provided by AEROSIL and Na_2PdCl_4 (Mitsuwa Chemical Co. Ltd.) were used as the photocatalyst and the palladium source, respectively. Carbon dioxide and argon of the highest purities (>99.99%) were supplied by Nihon-sanso Co. Ltd.

Gas chromatographic analyses of both CO and hydrocarbons were simultaneously performed using a YANACO G2800 (Yanagimoto) with a methanizer, a flame ionization detector (FID), sequentially attached columns (3 $\phi \times 1.5$ m) of MS5A (80−100 mesh) and MS13X-S (60−80 mesh), and an He carrier (1.1 kg cm^{-2}). Because the introduction of an excess amount of CO_2 into the methanizer causes oxidative deactivation of the Ni catalyst in the methanizer, the MS13X-S column was used as an absorber of CO_2. The gas samples could be analyzed by this method only three times because after that there was an overflow of CO_2 from the column into the methanizer. An aging treatment at 330 °C for 8 h was necessary for the desorption of CO_2 from the column. In the cases where only CH_4 was measured, a single column of MS5A without the methanizer was used for GC analyses.

Alcohols (CH_3OH, C_2H_5OH) and aldehydes (H_2CO, CH_3CHO) in the solution phase were measured by HP5890 GC with FID, a DB-WAX column (0.53 $\phi \times 30$ m, film thickness 1.0 μm) with an He carrier (20 mL min^{-1}) at 50 °C. Organic acids (HCO_2H, CH_3CO_2H) were analyzed by IEC using a SYSTEM14 (DIONEX) ion chromatographic analyzer with a conductive detector, a TSK gel SCX (5 μm × 30 cm) column, and an eluent that was a benzoic acid aqueous solution containing 5% acetonitrile.[68] The detection limits for the organic compounds by the methods described above were as follows: CH_3OH (3.4×10^{-6} M), C_2H_5OH (6.2×10^{-6} M), HCO_2H (0.1×10^{-6} M), CH_3CO_2H (6.7×10^{-6} M), and CH_3CHO (8.7×10^{-6} M). Formaldehyde could only be detected at a concentration higher than 6.25×10^{-4} M.

A 500 W high-pressure mercury arc lamp with a 310 nm sharp cutoff filter was used as the light source. X-ray photoelectron spectroscopy (XPS) was measured with an ESCA750 system (Shimadzu), and the signals were calibrated using Au and pure TiO_2 as external standards.

Sample Preparation. TiO_2 powder was heated at 350 °C under air for 12 h. After the powder was cooled to room temperature, it was washed several times with deionized water, which was prepared just before use, until no organic contaminants were detected by GC and IEC. However, carbonate species (CO_3^{2+}, HCO_3^{+}, and/or H_2CO_3) could not be completely removed by the washing procedures probably because reabsorption of CO_2 proceeded from the air after drying the photocatalysts.

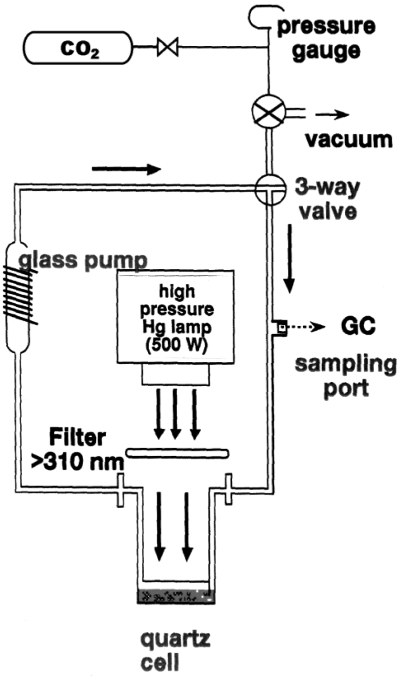

Figure 1. Schematic diagram of the photocatalytic reaction apparatus.

Pd−TiO_2 was made by the photochemical deposition method using methanol as a reductant.[69] The amount of Pd deposited on the TiO_2 was controlled by how much Na_2PdCl_4 was added to the solution. As a typical example, Pd−TiO_2 with 1 wt % of Pd (Pd(1%)−TiO_2) was made as follows: TiO_2 (750 mg) was dispersed in water (100 mL) by sonication, and 20.8 mg of Na_2PdCl_4 and 5 mL of methanol were added. The suspension was irradiated with >310 nm light for 1 h. During the irradiation, the white color of the powder changed to gray. The powder was washed with water several times, dried at room temperature under vacuo for 12 h, and then kept under a N_2 atmosphere. No organic contaminations were detected in the filtrate solution. The XPS spectrum of Pd−TiO_2 exhibited two characteristic signals at 340.0 and 334.7 eV, which corresponded to metallic Pd atom,[70,71] while XPS signals for neither Cl nor Cl$^-$ atoms were observed. This clearly indicates that the deposited Pd existed as metal on the TiO_2 surface.

Photocatalytic Reaction. The pretreated TiO_2 or Pd−TiO_2 (150 mg) was dispersed in 1.5 mL water by the sonicator and then filtered using a membrane filter (GBWP04700, Japan Mili-pore). The filtrate was analyzed by GC and IEC as described above. Especially, washing of the Pd−TiO_2 particles was done with care because they could not be calcinated in the air due to avoiding oxidation of Pd. When some organic compounds were detected in the filtrate, the same washing procedures were repeated again. Once no organic compounds were detectable; the sample (typically 150 mg of TiO_2 dispersed in 1.5 mL of water) was placed in a round-shaped quartz vessel (ϕ = 6 cm) and degassed three times with the freeze−pump−thaw method. This was followed by the introduction of CO_2 through a Deoxidizer (GL-Science) at up to 650 Torr. The pH of the solutions before irradiation was 4.1. The suspension was irradiated with >310 nm light. During the irradiation, the reaction vessel was kept at ∼5 °C using iced water, and CO_2 was circulated with a glass pump (Figure 1).[67] A total of 1.66 mL of the gas phase was introduced to the gas chromatograph through a four-way sampling port. As soon as the irradiation was halted, the liquid phase was analyzed by GC and IEC.

Table 1. Organic Adsorbates on TiO_2 with or without the Pretreatments and Photochemical Formation of CH_4 by TiO_2

	pretreatment		organic adsorbates on TiO_2[a] (10^{-8} mol/150 mg)			formation of CH_4 (10^{-8} mol/150 mg)[b]
run	calcination	rinse	CH_3OH	HCO_2H	CH_3CO_2H	
1	no	no	<1	1.2	10.9	11
2	yes	no	<1	<0.5	<1	3
3	yes	yes	~ 0	~ 0	~ 0	0.7

[a] The filtrate was analyzed by GC and IEC after 150 mg of TiO_2 was dispersed in 1.5 mL of water and filtered. [b] Irradiation of a dispersion (150 mg TiO_2 in 1.5 mL of water) with >310 nm light for 5 h.

■ RESULTS AND DISCUSSION

Adsorbates and Effect of the Pretreatment of TiO_2. The presence of organic adsorbates on the surface of the TiO_2 particles was confirmed by the following procedures. The TiO_2 powder (150 mg) was dispersed in 1.5 mL deionized water and sonicated for 10 min. This dispersion was filtered with a membrane filter, and the filtrate was analyzed by GC and IEC. The chromatographic analysis data clearly showed that considerable amounts of organic compounds were adsorbed on TiO_2 without the pretreatment (run 1 in Table 1): in particular, CH_3CO_2H was a major component. Small amounts of CH_3OH and HCO_2H were also detected, while the concentrations of CH_3CHO and HCHO were less than the detection limits. To remove the organic adsorbates, the TiO_2 powders were heated at 350 °C under air for 12 h. Although the organic adsorbates were drastically reduced, small amounts were still detected (run 2 in Table 1). The residual organic compounds could be removed by washing with deionized water several times (run 3 in Table 3).

Three kinds of TiO_2 (150 mg), with and without the treatments, were dispersed in 1.5 mL of deionized water and irradiated with >310 nm light for 5 h. The amounts of CH_4 formation are summarized in Table 1. Without the treatment, a considerable amount of CH_4 (11×10^{-8} mol) was formed, which was similar to the amount of CH_3CO_2H adsorbed on TiO_2. Although the amounts of adsorbates were drastically reduced by using the TiO_2 particles calcined at 350 °C before use, a small amount of CH_3CO_2H was still detected in the filtrate, and a smaller amount of CH_4 (3×10^{-8} mol) was formed compared with TiO_2 without the treatment. On the other hand, the organic adsorbates were not detected at all in the filtrate obtained from the TiO_2 particles that were pretreated by both calcination and washing. By using this TiO_2, only a very small amount of CH_4 (0.7×10^{-8} mol) formed even with 5 h irradiation.

These results clearly indicate that the organic adsorbates, especially CH_3CO_2H, have a crucial effect on the photochemical formation of CH_4 by TiO_2. The photocatalytic formation of CH_4 from CH_3CO_2H by TiO_2 has been reported, which is called the photo-Kolbe reaction (eqs 1 and 2).[72−75] The photochemical formation of CH_4 described above probably proceeded via the photo-Kolbe reaction. These results also show that the calcination of TiO_2 can effectively reduce the organic adsorbates on the surface of TiO_2, but this procedure is not enough on its own to prepare TiO_2 without organic adsorbates, probably because of the readsorption of organic compounds from the air when the sample was cooled to room temperature. Addition of the rinsing treatment with deionized water reduced the organic adsorbates to less than each of their detection limits. It is noteworthy that a considerable amount of carbonate ion was even detected in the filtrate just after calcination and rinsing. Carbon dioxide in the air is probably converted to the carbonate ion on the TiO_2 surface during the filtration.

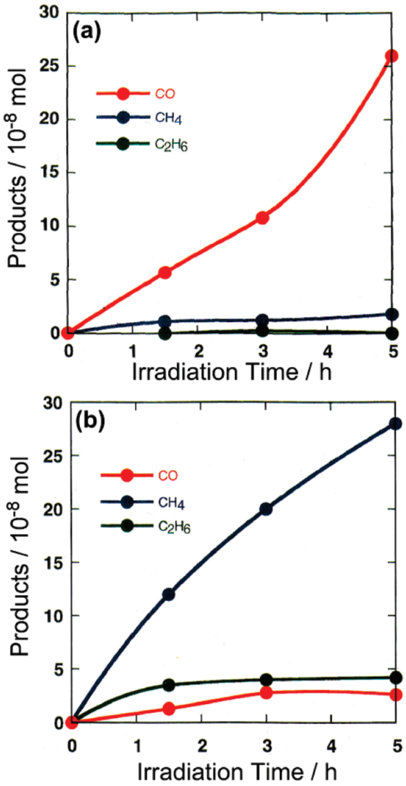

Figure 2. Photocatalytic reduction of CO_2 (650 Torr) by TiO_2 (a) and Pd(1%)−TiO_2 (b).

$$CH_3COOH + h^+ \rightarrow {}^{\bullet}CH_3 + CO_2 + H^+ \quad (1)$$

$$^{\bullet}CH_3 + CH_3COOH \rightarrow {}^{\bullet}CH_2COOH + CH_4 \quad (2)$$

Photocatalysis of TiO_2 and Pd−TiO_2. The TiO_2 or Pd(1%)−TiO_2 particles were rinsed again with deionized water several times until the organic compounds were not detectable in the filtrate just before use and were dispersed in 1.5 mL of deionized water. The dispersion was irradiated under CO_2 (650 Torr) at ~5 °C with >310 nm light. Time courses of products are shown in Figure 2. In the case of TiO_2 as photocatalyst, CO was observed as a major product, with a small amount of CH_4, while C_2H_6 was not detected. On the other hand, in the case of Pd−TiO_2, CH_4 was a major product, and a considerable amount of C_2H_6 formed. However, the amount of CO produced was

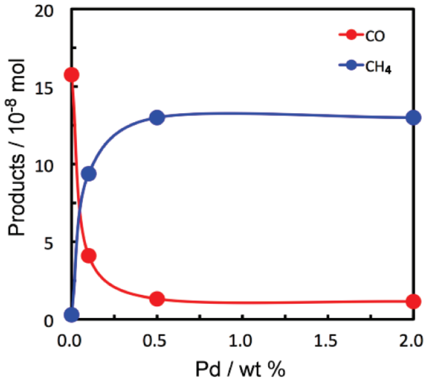

Figure 3. Photocatalytic CH_4 and CO formation by Pd–TiO_2 with various amounts of Pd after 1.5 h irradiation (>310 nm) under CO_2 (650 Torr).

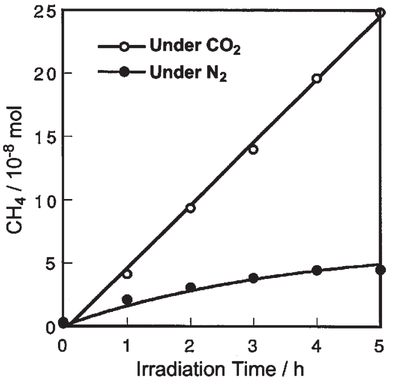

Figure 4. Photocatalytic CH_4 formation by Pd(2%)–TiO_2 under CO_2 and N_2 atmospheres.

drastically reduced compared with that obtained using TiO_2.[76] Although the pH of the reaction solution was adjusted to 6.0 using $NaHCO_3$ (50 mM) and HCl (35 mM), drastic changes of CH_4 formation and product distribution were not observed.

The ratio between the CO and CH_4 produced was strongly dependent on the amount of deposited Pd on TiO_2 (Figure 3): an increase of the amount of Pd caused both a decrease in the CO formation and an increase in the CH_4 formation.[77] For amounts of Pd higher than 0.5%, the product ratio was almost stable (CO:CH_4 ~ 1:10). On the basis of these results, we chose Pd(1%)–TiO_2 or Pd(2%)–TiO_2 as the photocatalyst for the following experiments.

A comparison of photocatalytic formation of CH_4 using Pd(2%)–TiO_2 under nitrogen and CO_2 atmospheres is shown in Figure 4. Although CH_4 formed even under a N_2 atmosphere, the formation of CH_4 stopped after 4 h irradiation, and the amount of CH_4 produced for 5 h irradiation was ~5 times less than that under a CO_2 atmosphere. Even under a N_2 atmosphere, the addition of $NaHCO_3$ (0.3 mmol) to the reaction solution caused a drastic increase in the photocatalytic formation of CH_4 (14×10^{-8} mol for 5 h irradiation). Because IEC analysis clearly showed that the CO_3^{2-} species were adsorbed on the Pd–TiO_2 surface even after the rinsing as described above, these results indicate that the carbon sources of the photocatalytic CH_4 formation were CO_2 and the CO_3^{2-} species.[78,79]

To confirm this, photocatalytic reactions under $^{13}CO_2$ were carried out and, consequently, a signal at $m/e = 17$ attributed to $^{13}CH_4$ was detected on the GC-MS spectra (Figure 5) as well as a $^{12}CH_4$ signal ($m/e = 16$) that was probably produced from the CO_3^{2-} species adsorbed on the photocatalyst.[78]

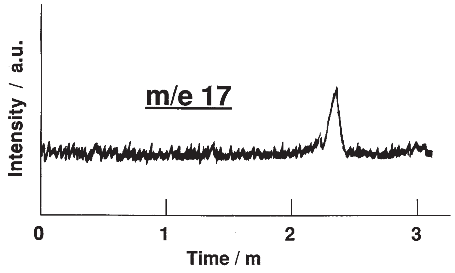

Figure 5. GC-MS chromatogram at $m/e = 17$ attributable to $^{13}CH_4$ of the gas sample produced by the photocatalytic reaction using Pd(2%)–TiO_2 under a $^{13}CO_2$ atmosphere.

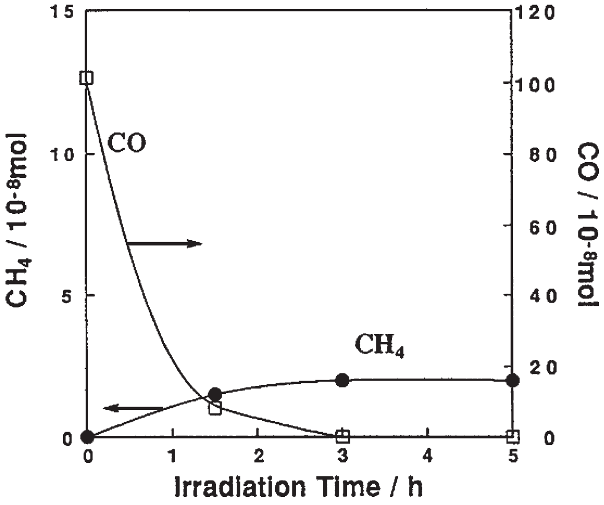

Figure 6. Photochemical reaction with Pd(2%)–TiO_2 under Ar containing CO (1.1×10^{-6} mol).

As described above, TiO_2 can photocatalyze the formation of a two-electron reduced product of CO_2, i.e., CO. In the case of photocatalytic reduction of CO_2 by Pd(1%)–TiO_2, CH_4 (an 8-electron reduced species of CO_2) was the main product, and CO formation was drastically decreased compared with TiO_2. One possible mechanism of the CH_4 formation is as follows: at first, CO_2 is photochemically reduced to CO on the TiO_2 site of Pd–TiO_2 (2-electron process), and then the produced CO is reductively converted to CH_4 on the Pd site (6-electron process). To check this possibility, a photochemical reaction with Pd(2%)-TiO_2 was carried out under an Ar atmosphere containing CO (1.1 μmol) (Figure 6). Although a small amount of CH_4 was generated in the initial stage, the CH_4 formation stopped after 3 h irradiation, and the amount of CH_4 produced was about 10 times less than that for the photocatalytic reaction under a CO_2 atmosphere. At the same time, a rapid decrease of CO during the photochemical reaction occurred; however, there was no correlation in quantity between the CO consumption and the CH_4 production. After 5 h irradiation, the amount of the CH_4 formation (~2×10^{-8} mol) under an Ar atmosphere containing CO was less than that under a N_2 atmosphere (Figure 4). These results indicated that CO_2 was reduced on the Pd site of Pd–TiO_2 to CH_4 (8-electron process) during the photocatalytic

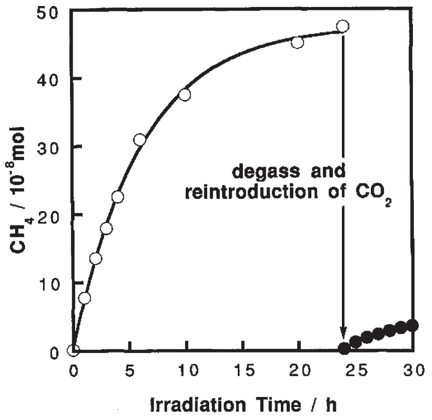

Figure 7. Photocatalytic formation of CH_4 by Pd(2%)−TiO_2 (150 mg in 1.5 mL of deionized water) under CO_2 with prolonged irradiation. The reaction sample was degassed after 24 h irradiation, CO_2 (650 Torr) was introduced to it, and then the vessel was irradiated again (solid circle).

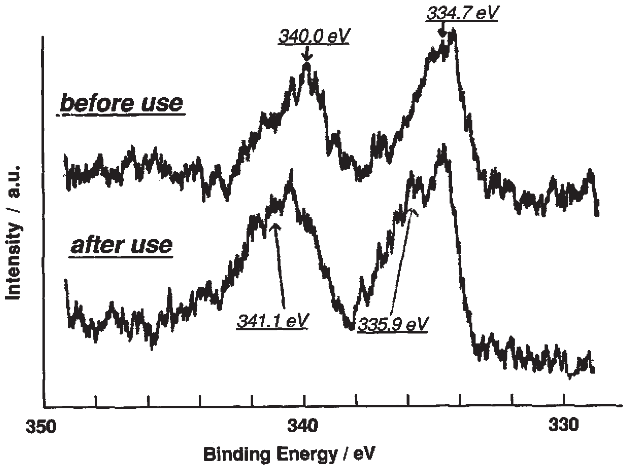

Figure 8. XPS spectra of Pd(2%)−TiO_2 before and after 24 h irradiation under the photocatalytic reaction conditions.

reaction. Although we have not clarified what is produced from CO during the photochemical reaction, the photochemical water−gas shift reaction might occur on Pd−TiO_2 to produce H_2 and CO_2 from CO and water.[80−84] Unfortunately, we could not analyze H_2 evolution in this system because of technical limitations.

Deactivation of Pd−TiO_2 and Oxidation of Pd Co-catalyst. We checked the durability of Pd−TiO_2 as a photocatalyst. Figure 7 shows CH_4 formation by Pd(2%)−TiO_2 during prolonged irradiation. Formation of CH_4 increased linearly up to 8 h irradiation, and then the formation rate of CH_4 decreased. After 24 h irradiation, the reaction vessel was degassed by the freeze−pump−thaw procedure, and CO_2 (650 Torr) was introduced to it again. However, the photocatalytic activity was not restored to its former state, as shown in Figure 6. This clearly indicates that deactivation of Pd(2%)−TiO_2 as a photocatalyst proceeded during the long irradiation.

Although the filtrate obtained from the reaction suspension after 24 h irradiation was analyzed by inductively coupled plasma (ICP) and electron paramagnetic resonance (EPR) spectroscopies, no peaks corresponding to Pd^{2+} or Pd^+ were observed. XPS spectra of Pd(2%)−TiO_2 both before and after 24 h irradiation under a CO_2 atmosphere were shown in Figure 8. The sample before irradiation showed two characteristic signals attributed to metallic Pd at 340.0 and 334.7 eV.[70,71] After 24 h irradiation, on the other hand, new signals attributable to PdO were observed at around 342.1 and 336.6 eV as shoulders of the peaks of Pd.[70] This clearly indicated that Pd on TiO_2 was oxidized during the photocatalytic reaction, and probably because of this, photocatalysis by Pd−TiO_2 reduced. As shown in Figure 7, Pd(2%) -TiO_2 produced 4.5×10^{-7} mol of CH_4 in the final stage; thus, 3.6×10^{-6} mol of electrons were consumed during the photocatalytic reduction of CO_2 and/or CO_3^{2-} species. On the other hand, the Pd(2%)−TiO_2 (150 mg) contained 2.8×10^{-5} mol of Pd. Although XPS can analyze only a surface of a sample and only a small portion of the irradiated Pd−TiO_2 particles was oxidized, as shown in Figure 8, Pd should work not only as cocatalyst but also partially as oxygen acceptor from CO_2, and/or electron donor. Probably oxidation of the surface of the Pd particle on TiO_2 caused the deactivation of the photocatalysis of Pd-TiO_2.

■ CONCLUSION

Photocatalytic reduction of CO_2 using TiO_2 and Pd−TiO_2, from which adsorbates were removed, was investigated. Treatments to remove organic adsorbates from the semiconductor, especially the washing procedure, are essential for the evaluation of how the semiconductor works as a photocatalyst for CO_2 reduction. TiO_2 can photocatalyze this reduction, with the formation of CO as a major product. Deposition of Pd onto TiO_2 caused a decrease in CO generation and an increase in CH_4 formation instead. As the CH_4 formation progressed, Pd on TiO_2 was partially oxidized to become PdO, which deactivated the photocatalytic behavior of Pd−TiO_2. These results clearly show that removal of organic adsorbates from semiconductors and careful analysis of used photocatalysts and cocatalyst are essential for estimating photocatalysis of the semiconductors for CO_2 reduction.[66]

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■ ACKNOWLEDGMENT

This work was partly supported by the Next Generation World-Leading Researchers Funding Program of JSPS. T.Y. thanks for the valuable support.

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