

# Effect of Pd-photodeposition over TiO<sub>2</sub> on product selectivity in photocatalytic degradation of vinyl chloride monomer

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## Abstract

Effects of metal co-catalysts, Pd and Pt, on photocatalytic degradation of vinyl chloride monomer (VCM) were studied. Pd-photodeposited TiO<sub>2</sub> (Pd-TiO<sub>2</sub>) did not produce any chlorinated organic compounds into the gas phase, while pure TiO<sub>2</sub> produced monochloroacetylchloride and phosgene. The amounts of CO and formic acid formed by Pd-TiO<sub>2</sub> were much smaller than those by TiO<sub>2</sub>, and the CO<sub>2</sub> production proceeded selectively. However, Pd-TiO<sub>2</sub> decomposed VCM more slowly and produced a larger amount of adsorptive chlorinated organic compound, as compared with TiO<sub>2</sub>. Photodeposited Pd is considered to inhibit the VCM decomposition pathway in which the gaseous byproducts are formed by the aid of Cl<sup>-</sup> ion adsorbed on the photocatalyst. The electron spin resonance (ESR) suggested that the photodeposited Pd suppress the formation of active species, such as Ti<sup>3+</sup>, O<sub>2</sub><sup>-</sup> and OH, which are responsible for the formation of gaseous byproducts.

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## 1. Introduction

Vinyl chloride monomer (VCM) is produced on a large scale for raw material of poly(vinyl chloride) (PVC), and a part of VCM is emitted into the atmosphere. As VCM has carcinogenicity, mutagenicity and teratogenicity, the emission of VCM should be reduced for human health [1–3]. Photocatalytic mineralization of VCM may be one of the candidates for its removal method since many organic compounds or chlorinated organic compounds can be decomposed by TiO<sub>2</sub> photocatalyst [4,5].

We have reported photocatalytic mineralization of ethylene and VCM on TiO<sub>2</sub> [6]. In an ideal photocatalytic mineralization of chlorinated hydrocarbon, it will be oxidized into CO<sub>2</sub>, H<sub>2</sub>O, and HCl [7]. However, the complete mineralization was not realized as byproducts, such as CO, formic acid, monochloroacetyl chloride (MCAC) and phosgene (COCl<sub>2</sub>), were formed by partial oxidation; some of them are even toxic. It is considered that Cl<sup>-</sup> ions adsorbed on TiO<sub>2</sub> participate in the photocatalytic decomposition of VCM and enhance the formation of byproducts. Modification of the TiO<sub>2</sub> surface will be one of the ways to control the effect of Cl<sup>-</sup> ion and improve the product selectivity. The addition of noble metals, such as Pt or Pd, is a conventional method to modify surface of thermocatalyst. Also,

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the addition of Pt as co-catalyst on TiO<sub>2</sub> can increase the efficiency of photocatalytic water splitting [8]. However, the effect of noble metals on photocatalytic degradation of chlorinated organic compounds is less well understood.

In the present paper, we synthesized metal-loaded TiO<sub>2</sub> photocatalysts and studied the effect of metal co-catalysts on the photocatalytic activities for VCM degradation.

## 2. Experimental

### 2.1. Preparation of photocatalysts

The Pd- and Pt-loaded TiO<sub>2</sub> photocatalysts were synthesized by the photodeposition method [9–12]. PdCl<sub>2</sub> (analytical grade), H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O (analytical grade) and anatase type TiO<sub>2</sub> (Degussa, P25) were used. The amount of Pd loaded was varied between 0.1 and 1.5 wt.% versus TiO<sub>2</sub>. The procedure of photodeposition method is briefly described as follows. A 1.0 g portion of TiO<sub>2</sub> was dispersed into 75 cm<sup>3</sup> of PdCl<sub>2</sub> or H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O solution ( $1.25 \times 10^{-4}$  to  $1.88 \times 10^{-3}$  mol dm<sup>-3</sup>). The pH of the suspension was adjusted to 6.8 by addition of KOH solution (0.01–0.1 mol dm<sup>-3</sup>) while the suspension was stirred vigorously by a magnetic stirrer. The suspension was poured into a quartz cell for photodeposition and was aged for 30 min at room temperature. UV light from a high pressure Hg lamp (Ushio, USH-500D, 500 W) was irradiated to the suspension through a longpass filter (cut-off wavelength, 295 nm) for 30 min while purified air was passed through the suspension (photodeposition process). The product was collected by the aid of centrifugation, washed with distilled water four times. A 0.3 g portion of photocatalyst was spread on a glass plate (80 cm<sup>2</sup>) and dried at 383 K for 12 h to fix the photocatalyst.

The solid phases were identified by powder X-ray diffractometry (XRD) with Cu K $\alpha$  radiation (Rigaku, model RU-300) and X-ray photoelectron spectroscopy (XPS) with Al K $\alpha$  radiation (Fisons instruments, Escalab220i-XL). The amount of deposited Pd was determined by X-ray fluorescence analysis (XRF; Philips, PW2404). Electron spin resonance (ESR) spectra were obtained at 77 K (JEOL, JES-TE300 ESR spectrometer). A 0.10 g portion of the photocatalyst

was placed in a sample tube of Suprasil quartz-glass, and the tube was sealed at atmospheric pressure and room temperature. The *g* value was corrected by a Mn<sup>2+</sup> marker.

### 2.2. Photocatalytic decomposition of VCM

The glass plate with photocatalyst was placed in the reaction vessel ( $1.83 \times 10^3$  cm<sup>3</sup>) with a cover window of Tempax glass (8 mm thickness, cut-off wavelength 300 nm) [6]. The surface of photocatalyst was cleaned by UV-irradiation in dry air for 30 min to remove organic impurities. The photocatalytic decomposition was carried out in a closed gas circulation system (total volume  $2.54 \times 10^3$  cm<sup>3</sup>) with a multireflection gas cell (path length 3 m) for Fourier transform infrared spectroscopy (FT-IR, JASCO, FT-IR 610). After the reaction vessel was evacuated, required volume of VCM gas (5200 ppm, N<sub>2</sub> balance, from Takachiho Chemicals) was introduced into the vessel (VCM 0.22 kPa, 240  $\mu$ mol), and then dry air (in a cylinder) was added until the inner pressure became the atmospheric pressure.

In the photocatalytic decomposition of VCM, the photocatalyst was irradiated with UV light (0.63 mW cm<sup>-2</sup>) from three black light lamps (Toshiba FL10BL, 10 W) through the Tempax glass window at room temperature (298 K). The partial pressures of gasses were calculated from the absorbance areas of FT-IR spectra, which had been calibrated with standard gasses. The amount of Cl<sup>-</sup> ion adsorbed on TiO<sub>2</sub> was determined by washing the photocatalyst with purified water (Millipore, Milli-Q system) and analyzing the washings by an ion chromatograph (Shimadzu, HIC-6A with CDD-6A).

## 3. Results and discussion

### 3.1. Characterization of the Pd-photodeposited TiO<sub>2</sub> (Pd-TiO<sub>2</sub>)

The relation between the amounts of Pd in the preparation suspension and on the TiO<sub>2</sub> photocatalyst determined by XRF was shown in Fig. 1. When the Pd content in suspension was less than 1 wt.% against TiO<sub>2</sub>, the amount of Pd deposited on TiO<sub>2</sub> increased with increasing Pd content in suspension. However,

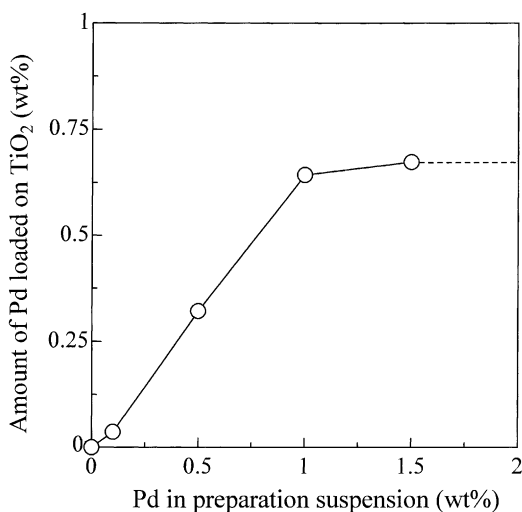


Fig. 1. Relation between amounts of Pd contained in preparation suspension and deposited on TiO<sub>2</sub>. Photodeposition time: 30 min.

the amount of Pd loaded was lower than that contained in the preparation suspension; approximately 60% of Pd<sup>2+</sup> ions in the suspension was loaded. This indicates that the Pd<sup>2+</sup> ion in the preparation suspension was not completely deposited on TiO<sub>2</sub> during the UV-irradiation for 30 min. The Pd<sup>2+</sup> ion that had not been deposited on TiO<sub>2</sub> was present in the solution. When the Pd content in suspension was over 1 wt.%, the amount of Pd on TiO<sub>2</sub> did not increase with increasing Pd content in the suspension. In the present study, UV-irradiation time for photodeposition was set to be constant (30 min), regardless of the amount of Pd content. It is considered that the UV-irradiation time was not enough for the photodeposition of the larger amount of Pd and that all of Pd<sup>2+</sup> ion in the suspension was not photodeposited. In the following text, an amount of Pd denotes a deposited amount determined by XRF, which is not a content in preparation suspension. The amount of Pt photodeposited on TiO<sub>2</sub> was almost same as that contained in the suspension.

In the XRD patterns of all photocatalysts, only the peaks of TiO<sub>2</sub>, anatase and rutile, appeared and those of Pd or Pd-related compounds were not detected. This indicates that the Pd was loaded in the state of ions or undetectably small particles. The *d*-spacing of the anatase or rutile in the photocatalysts was identical to

that of the raw material. The surface characteristics of photocatalyst analyzed by XPS will be discussed later.

### 3.2. Photocatalytic degradation of VCM with Pd-TiO<sub>2</sub>

The gaseous products formed in the photocatalytic degradation of VCM with pure TiO<sub>2</sub> and Pd-TiO<sub>2</sub> were analyzed by FT-IR. In the degradation by pure TiO<sub>2</sub>, HCl, CO<sub>2</sub>, CO, MCAC, formic acid, H<sub>2</sub>O and phosgene (COCl<sub>2</sub>) were detected (Fig. 2(a)). The formation of COCl<sub>2</sub> and MCAC, which contain two Cl atoms in a molecule, indicates that Cl<sup>-</sup> ion or chlorine containing species participated in the VCM decomposition, since a VCM molecule contains only one Cl atom. On the other hand, Pd-TiO<sub>2</sub> did not produce any chlorinated organic compounds into the gas phase (Fig. 2(b)). This suggests that Cl<sup>-</sup> ion or chlorine containing species on Pd-TiO<sub>2</sub> do not participate in the VCM decomposition. Table 1 shows the maximal partial pressures of byproducts formed in the course of VCM degradation. By adding Pd co-catalyst, the production of MCAC and COCl<sub>2</sub> were completely inhibited. The partial pressure of formic acid was 5 Pa at

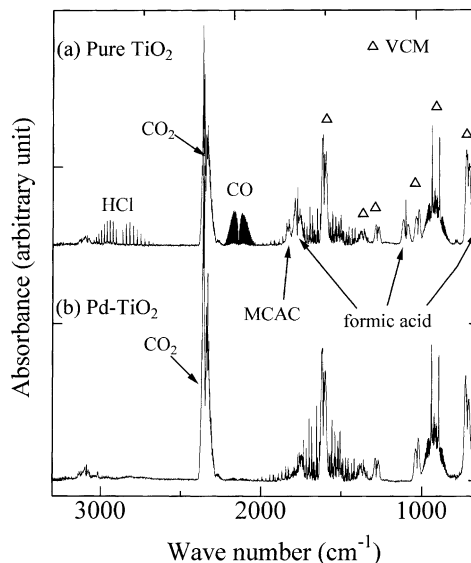


Fig. 2. Gas phase FT-IR spectra taken in VCM degradation by pure TiO<sub>2</sub> at 20 min (a); and by Pd-TiO<sub>2</sub> at 90 min (b). In both the cases, approximately half of VCM introduced into the reaction vessel was removed.

Table 1  
Effect of metal co-catalyst on the maximal partial pressures of byproducts detected in the course of VCM degradation

Co-catalyst	Deposition amount (wt.%)	Byproducts ( $\mu\text{mol}$ )			
		Formic acid	MCAC	$\text{COCl}_2$	$C_{\text{ads}}$
None	–	17	4.8	0.4	91
Pd	0.63	4.4	nd	nd	214
Pt	1.1	12	3.0	0.7	158

maximum, which was much lower than that produced by pure  $\text{TiO}_2$ . The properties of Pt-loaded  $\text{TiO}_2$  were intermediate between those of pure  $\text{TiO}_2$  and Pd- $\text{TiO}_2$ .

The time-courses of the partial pressures of VCM and products in the photocatalytic VCM degradation by Pd- $\text{TiO}_2$  (Pd 0.63 wt.%) were shown in Fig. 3. The partial pressure of VCM in the reaction vessel decreased linearly with irradiation time when the photocatalyst was irradiated by UV light. The VCM introduced into the reactor ( $240 \mu\text{mol}$ ) was completely removed in 300 min by Pd- $\text{TiO}_2$ . Since pure  $\text{TiO}_2$  removed the same amount of VCM in 60 min [6], the VCM decomposition rate by Pd- $\text{TiO}_2$  was smaller than that by pure  $\text{TiO}_2$ .  $C_{\text{ads}}$  denotes the part of carbon compounds that were not detected by FT-IR

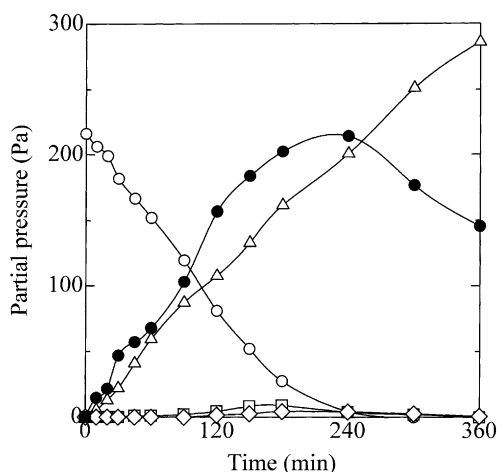


Fig. 3. Time-courses of partial pressures of VCM and products in photocatalytic VCM degradation by Pd- $\text{TiO}_2$  (Pd 0.63 wt.%). Photocatalyst 0.3 g, initial VCM pressure 0.22 kPa, UV-A irradiance was  $0.63 \text{ mW cm}^{-2}$ . (○) VCM, (△)  $\text{CO}_2$ , (□) CO, (◇) HCOOH, (■) HCl, and (●)  $C_{\text{ads}}$ .

measurements and that may be adsorbed on  $\text{TiO}_2$  or the reactor wall. The amount of  $C_{\text{ads}}$  was determined from the mass balance of removed VCM, formed  $\text{CO}_2$ , CO and the observed organic compounds, and was plotted by converting to partial pressure of  $C_1$  compound. The maximal amount of  $C_{\text{ads}}$  produced by Pd- $\text{TiO}_2$  was about twice as that by pure  $\text{TiO}_2$ , suggesting that the Pd- $\text{TiO}_2$  produced a larger amount of adsorptive substances by partial oxidation or polymerization of VCM. Pure  $\text{TiO}_2$  mineralized all  $C_{\text{ads}}$  into  $\text{CO}_2$  by further UV-irradiation for 6 h. However, Pd- $\text{TiO}_2$  did not oxidize all  $C_{\text{ads}}$  into CO or  $\text{CO}_2$  until 18 h UV-irradiation, and 71 Pa (16% of carbon atom in VCM) of  $C_{\text{ads}}$  was not mineralized.

The Pd co-catalyst also reduced the production of CO in the VCM degradation and improved  $\text{CO}_2$ -CO selectivity ( $[\text{CO}_2]/([\text{CO}_2]+[\text{CO}])$ ). Pure  $\text{TiO}_2$  produced  $193 \mu\text{mol}$  of CO and  $289 \mu\text{mol}$  of  $\text{CO}_2$ , during 6 h UV-irradiation; therefore the  $\text{CO}_2$ -CO selectivity was 0.60. On the other hand, Pd- $\text{TiO}_2$  produced  $312 \mu\text{mol}$  of  $\text{CO}_2$  without CO production; the selectivity was 1. Pt- $\text{TiO}_2$  produced  $112 \mu\text{mol}$  of CO and  $333 \mu\text{mol}$  of  $\text{CO}_2$ , and the selectivity was 0.85, which was lower than that by Pd- $\text{TiO}_2$ . The  $\text{CO}_2$ -CO selectivity increased with increasing amount of loaded Pd (Fig. 4). Also, the amount of  $C_{\text{ads}}$  increased with Pd amount. The reason was that the amount of CO formed decreased with increasing amount of loaded Pd while the amount of  $\text{CO}_2$  did not change.

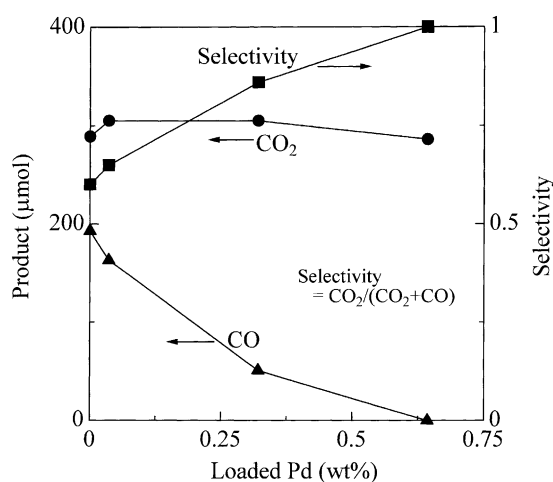


Fig. 4. Relation between the amounts of loaded Pd on  $\text{TiO}_2$  and  $\text{CO}_2$ -CO selectivity.

Because the rate of CO oxidation into CO<sub>2</sub> by Pd-TiO<sub>2</sub> (Pd 0.63 wt.%) was only 7 μmol/h, which was much lower than the CO formation rate by pure TiO<sub>2</sub> (ca. 220 μmol/h), the CO oxidation by Pd-TiO<sub>2</sub> did not make a substantial contribution to the decrease of CO. These results suggest that loaded Pd inhibits the direct CO formation from VCM.

The amounts of Cl<sup>-</sup> ion adsorbed on the photocatalysts were determined with an ion chromatograph and the mass balance of Cl atom in VCM degradation was analyzed. Pd-TiO<sub>2</sub> (Pd 0.63 wt.%) used for 18 h UV-irradiation released 40 μmol of Cl<sup>-</sup> ion into water, which was not so different from the amount of Cl<sup>-</sup> on pure TiO<sub>2</sub> (34 μmol). These amounts correspond to only 14 and 17% of decomposed VCM, respectively. The amounts of HCl detected by FT-IR were 0 μmol for Pd-TiO<sub>2</sub> and 43 μmol for pure TiO<sub>2</sub>. For the degradation by TiO<sub>2</sub>, the residual Cl atom in decomposed VCM may be adsorbed on the reactor wall as Cl<sup>-</sup>, since the entire carbon atom from VCM was oxidized into CO or CO<sub>2</sub> and no chlorinated organic compounds should be present. In the degradation by Pd-TiO<sub>2</sub>, HCl was not observed in the gas phase, so the amount of Cl<sup>-</sup> adsorbed on the reactor wall should be smaller. It is considered that Cl<sup>-</sup> was trapped on Pd-TiO<sub>2</sub> as chlorinated organic compounds, since all C<sub>ads</sub> was not mineralized.

### 3.3. ESR and XPS studies of Pd-TiO<sub>2</sub>

ESR measurements of the photocatalysts were performed to investigate the differences in the VCM degradation activities between Pd-TiO<sub>2</sub> and pure TiO<sub>2</sub>. Fig. 5(a)–(c) show the ESR spectra of the pure TiO<sub>2</sub>, Pd-TiO<sub>2</sub>, and Cl<sup>-</sup> adsorbed TiO<sub>2</sub> under UV-irradiation recorded at 77 K. In the ESR spectrum for the pure TiO<sub>2</sub> (Fig. 5(a)), simple signals at  $g = 1.979$ ,  $1.992$  and  $2.004$ , and complex signals at  $g = 2.007$ – $2.025$  were observed. The signals were not ascribed completely, however, they seem to be a combination of signals for Ti<sup>3+</sup> ( $g = 1.979$  and  $1.992$ ) and O<sub>2</sub><sup>-</sup> ( $g = 2.004$  and  $2.007$ – $2.025$ ) [13–15]. Since the TiO<sub>2</sub> used in this study (P25) contains two types of TiO<sub>2</sub> crystal, rutile and anatase, the ESR spectrum for P25 should be a complex pattern.

In the ESR spectrum for Pd-TiO<sub>2</sub> (Fig. 5(b)), weak signals appeared at the same  $g$  values observed in the spectrum for pure TiO<sub>2</sub>. However, all the signal in-

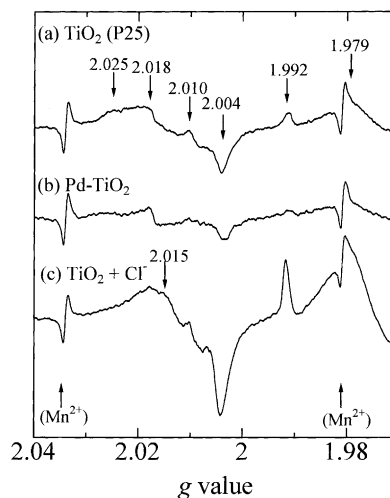


Fig. 5. ESR spectra for pure TiO<sub>2</sub> (a), Pd-TiO<sub>2</sub> (Pd 0.63 wt.%) (b), and Cl<sup>-</sup> adsorbed TiO<sub>2</sub> (c) recorded at 77 K under UV-irradiation.

tensities were much smaller. Additionally, weak signals appeared at around  $g = 2.25$  and  $4.54$ , which could be assigned to electrons in Pd co-catalysis [16]. These results suggest that electrons formed in Pd-TiO<sub>2</sub> and pure TiO<sub>2</sub> by UV absorption transfer to different pathways; to deposited Pd as conduction electron (Pd-TiO<sub>2</sub>) and to adsorbed O<sub>2</sub> to produce O<sub>2</sub><sup>-</sup> (pure TiO<sub>2</sub>). This may cause the differences in the photocatalytic activities and in the product selectivity during the VCM degradation.

Fig. 5(c) shows the ESR spectrum of TiO<sub>2</sub> with Cl<sup>-</sup> ion, which was prepared by VCM mineralization on pure TiO<sub>2</sub> for 6 h. Larger signals of Ti<sup>3+</sup> and O<sub>2</sub><sup>-</sup> were detected at the same  $g$  values observed in the spectrum for pure TiO<sub>2</sub>. Additionally, an unidentifiable signal was observed at  $g = 2.015$ , which may be due to the presence of Cl<sup>-</sup> ion. The increase in the signal intensity of Ti<sup>3+</sup> and O<sub>2</sub><sup>-</sup> suggests that the adsorbed Cl<sup>-</sup> enhances the formation of those active species or extends their lifetime. In our foregoing paper [6], we mentioned that the adsorption of Cl<sup>-</sup> ion on TiO<sub>2</sub> enhances the formation of CO and formic acid. The adsorbed Cl<sup>-</sup> ion increased the ESR signals of Ti<sup>3+</sup> and O<sub>2</sub><sup>-</sup>, and enhanced the formation of CO and formic acid, while the deposited Pd decreased the signals and inhibits the formation of CO and formic acid. From these observations, it is inferred that the active species (Ti<sup>3+</sup> and O<sub>2</sub><sup>-</sup>) formed on TiO<sub>2</sub> are

responsible for the formation of CO and formic acid, and that Pd co-catalyst inhibits the formation of these active species to reduce the formation of CO and formic acid. As mentioned above, pure TiO<sub>2</sub> decomposed VCM faster than Pd-TiO<sub>2</sub>. This is probably due to the effect of Pd co-catalyst that reduces the formation of active species and that inhibits one of the VCM decomposition pathways in which formic acid and CO are formed.

The surface characteristics of Pd-TiO<sub>2</sub> were analyzed by XPS. Fig. 6(a) shows the C 1s spectra for the Pd-TiO<sub>2</sub> as prepared (Pd loading 0.63 wt.%) and the Pd-TiO<sub>2</sub> used for VCM degradation for 18 h. The intensity of C 1s slightly increased in the VCM degra-

dition. Based on the difference of two spectra, signals around 284.6, 286.3 and 284.6 eV increased. These signals could be assigned to C–C, C–O and C=O, respectively [17,18]. In the Cl 2p region (Fig. 6(b)), no peak appeared in the spectrum for Pd-TiO<sub>2</sub> as prepared, on the other hand, a peak of Cl<sup>-</sup> appeared in the spectrum for the used Pd-TiO<sub>2</sub>. The peak at around 199.9 eV may be ascribed to Cl atom in chlorinated organic compound [18]. Since the signal of C 1s and Cl 2p increased, it is considered that a part of VCM was polymerized on the photocatalyst as chlorinated organic compounds, which worked as a chlorine concentrator. The peak of Pd 3d<sub>5/2</sub> shifted from 335.5 eV (as prepared) to 334.8 eV (after VCM degradation)

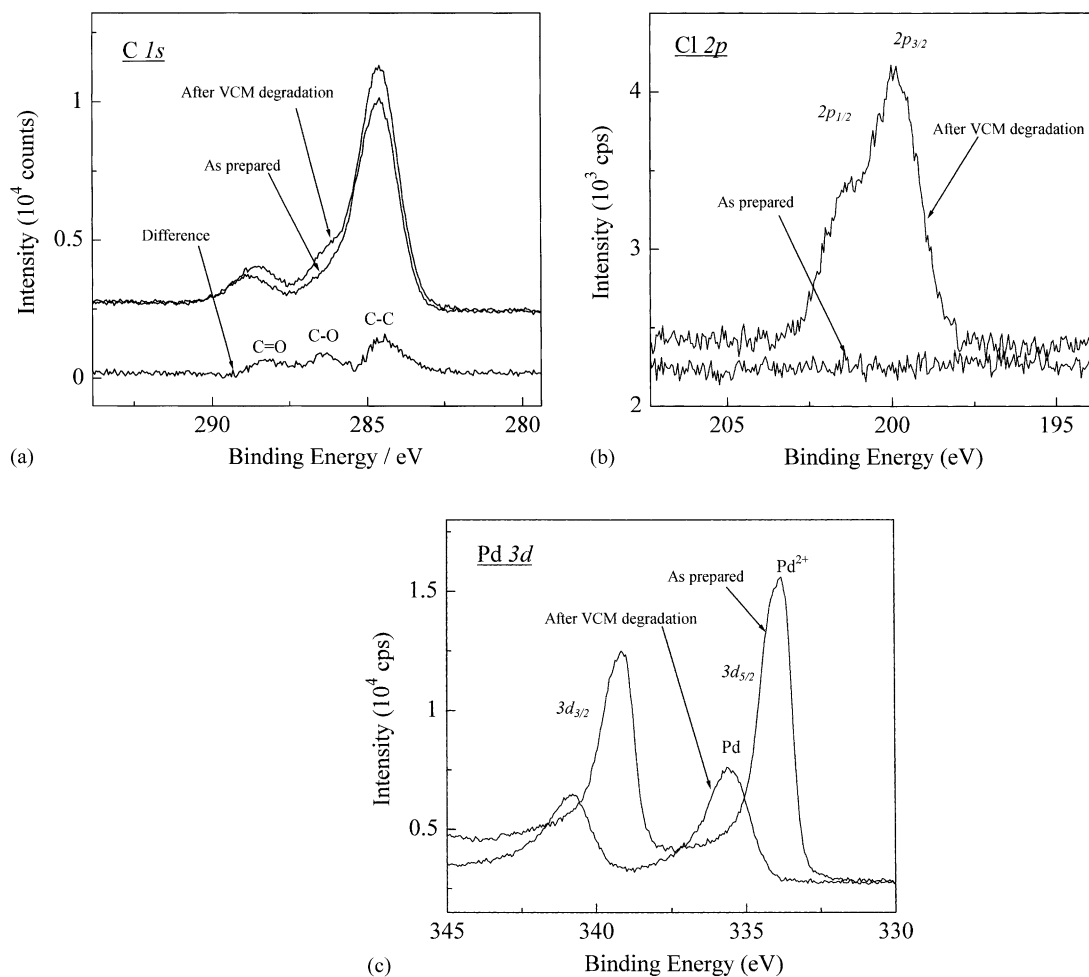


Fig. 6. XPS spectra for Pd-TiO<sub>2</sub> before and after photocatalytic VCM degradation; (a) C 1s, (b) Cl 2p and (c) Pd 3d.

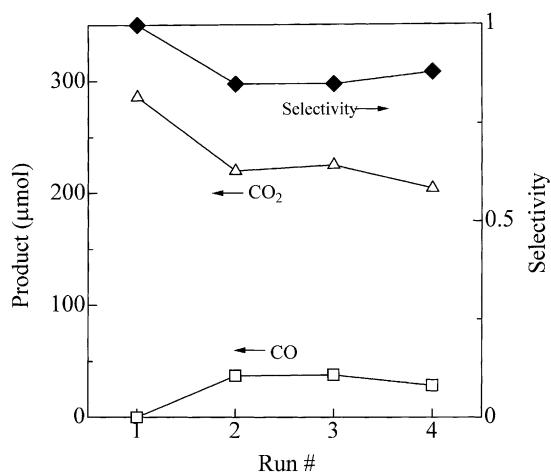


Fig. 7. Change in CO<sub>2</sub>-CO selectivity with repeated use of Pd-TiO<sub>2</sub>.

(Fig. 6(c)). This suggests that the surface of loaded Pd was reduced from Pd<sup>2+</sup> (PdO) to metal Pd during the degradation [18].

The VCM degradation by Pd-TiO<sub>2</sub> was performed repeatedly. The amount of CO and CO<sub>2</sub> produced within 6 h UV-irradiation and the CO-CO<sub>2</sub> selectivity were indicated in Fig. 7. After each run, UV light was irradiated to the photocatalyst for 12 h and then the reaction vessel was evacuated for 15 min. As mentioned, Pd-TiO<sub>2</sub> did not produce CO and the selectivity was 1.0 at the first run. In the second run, the CO-CO<sub>2</sub> selectivity was 0.85, which is lower than that of first run, but is higher than pure TiO<sub>2</sub> (0.60). After the second run, the selectivity did not change. Based on XPS study, the Pd<sup>2+</sup> on Pd-TiO<sub>2</sub> was reduced to metal Pd during the first run. These results suggest that Pd<sup>2+</sup> (PdO) is strongly responsible for the selectivity and that metal Pd also affects the selectivity weakly. The amount of Pd deposited on Pd-TiO<sub>2</sub> (Pd 0.63 wt.%) was 18 μmol. Assuming that all the reduction of Pd<sup>2+</sup> into metal Pd is due to the non-catalytic oxidation of CO into CO<sub>2</sub>, only 18 μmol of CO is oxidized. Since this value is quite smaller than the amount of CO produced by pure TiO<sub>2</sub> (193 μmol), non-catalytic oxidation of CO by Pd<sup>2+</sup> is not effective on high CO-CO<sub>2</sub> selectivity of Pd-TiO<sub>2</sub>. The catalytic cycle between Pd<sup>2+</sup> and metal Pd may contribute to the repression of the formation CO and byproducts.

## 4. Conclusion

The Pd-photodeposited TiO<sub>2</sub> inhibited the production of chlorinated organic compounds into the gas phase and concentrated chlorine atom on the photocatalyst in the photocatalytic degradation of VCM. Additionally, the Pd co-catalyst improved the CO<sub>2</sub>-CO selectivity. This may be due to two effects of photodeposited Pd: (i) participants of Cl<sup>-</sup> ion and chlorine-containing species on Pd-TiO<sub>2</sub> in the VCM degradation are inhibited; (ii) formation of the active species (Ti<sup>3+</sup> and O<sub>2</sub><sup>-</sup>), which are responsible for the production of CO and formic acid, are suppressed. The formation of adsorptive chlorinated organic compounds on Pd-TiO<sub>2</sub> was confirmed by XPS, however, the chemical composition and the formation mechanism of the adsorptive compounds were not clarified at this stage. Since Pd-TiO<sub>2</sub> is substantially superior in the product selectivity while its VCM removal rate is lower than that of pure TiO<sub>2</sub>, the combination of pure TiO<sub>2</sub> and Pd-TiO<sub>2</sub> would realize a fast and safe method to remove VCM or chlorinated organic compounds in a practical use.

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