Photocatalytic Reactivity of Surface Platinized TiO₂: Substrate Specificity and the Effect of Pt Oxidation State

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Surface platinized TiO₂ (Pt/TiO₂) has been frequently studied, but its photocatalytic reactivities reported in the literature are not consistent in some cases. To understand the discrepancies, the effects of Pt speciation on TiO₂ on the photocatalytic degradation (PCD) of a few chlorinated organic compounds (trichloroethylene (TCE), perchloroethylene (PCE), dichloroacetate, etc.) were investigated with several Pt/TiO₂ samples that were prepared differently. The oxidation state of Pt deposits was analyzed by X-ray photoelectron spectroscopy and was found to be the most important factor in determining the initial PCD rates of chlorinated organic compounds. TiO₂ with oxidized Pt species (Pt_{ox}/TiO_2) was less reactive than TiO₂ with metallic Pt (Pt^0/TiO_2) for all substrates tested. In particular, Pt_{ox}/TiO_2 strongly inhibited the PCD of TCE and PCE whereas it was more reactive than pure TiO₂ for the PCD of other compounds. The photocurrents obtained with the Pt_{ox}/TiO_2 electrode were lower than those with the Pt^0/TiO_2 electrode, which was ascribed to the role of Pt_{ox} species as a recombination center. It is proposed that TCE adsorbed on Pt_{ox} chemically mediates the charge recombination through the redox cycle of TCE. The Pt effects in photocatalysis are highly substrate-specific and depend on the Pt−substrate interaction as well as the properties of Pt deposits.

Introduction

TiO₂ has been intensively investigated as a practical photocatalyst for environmental cleanup since the 1980s,[1−6] and many methods have been developed to modify its catalytic performance. The surface platinization of TiO₂ has been a popular photocatalyst modification technique, since Kraeutler and Bard[7] first introduced it, because the platinized TiO₂ (Pt/TiO₂) exhibits enhanced activity for many photocatalytic reactions.[7−10] The presence of Pt deposits on TiO₂ is believed to retard fast charge-pair recombination by serving as an electron sink (Schottky barrier electron trapping) and to facilitate the interfacial electron transfer to dioxygen or other electron acceptors,[3,11] which has been supported by electrochemical and time-resolved spectroscopic investigations.[12−14] However, the reported Pt effects have not been always positive[15−18] and the role of Pt deposits in photocatalytic reaction mechanisms seems to be far more complex than being a simple electron sink. For example, the photocatalytic oxidation of CO was highly enhanced on Pt/TiO₂,[10a,19] but the enhancement effect was not observed at a lower temperature (105 K) at which most thermal effects should be quenched.[20] The thermal catalytic role of Pt is also important in the overall behavior of Pt/TiO₂.[21−23]

On the other hand, the reported Pt effects in photocatalytic degradation (PCD) of a specific substrate are often contradictory. For example, Zhao et al.[24] reported that the PCD of Rhodamine-B (RB) dye on Pt/TiO₂ was 3 times as fast as its PCD on naked TiO₂, whereas Muradov[25] observed that the platinization of TiO₂ did not change the PCD rate of RB significantly. Enhanced PCDs of phenolic compounds on Pt/TiO₂ have not been observed in many studies.[11,17,26] Reported experimental results about the PCD of trichloroethylene (TCE) on Pt/TiO₂ are

contradictory as well. Chen et al.[18] reported that the platinization of TiO₂ drastically reduced the PCD rate of TCE, and Driessen et al.[27] observed a similar phenomenon. On the contrary, Crittenden et al.[28] reported that such a significant retardation in PCD of TCE was not observed with Pt/TiO₂.

This study aims to understand what specific parameters control the photocatalytic reaction when Pt/TiO₂ is used and why reported Pt effects are inconsistent for some substrates. We investigated the platinization effects in the TiO₂-mediated PCD of several chlorinated organic compounds that include trichloroethylene, perchloroethylene, dichloroacetate, trichloroacetate, chloroform, and 4-chlorophenol. The Pt effects in PCD reactions were highly substrate-specific and were sensitively influenced by the condition of Pt deposition. The oxidation state of deposited Pt species was found to be the most important factor in determining the PCD activity.

Experimental Section

Chemicals and Materials. Chemicals that were used as received in this study include trichloroethylene (TCE, Junsei), perchloroethylene (PCE, 98%, Kanto), chloroform (CF, >99%, Matsunoen), 4-chlorophenol (4-CP, extra pure, Junsei), sodium dichloroacetate (DCA, >98% Aldrich), trichloroacetate (TCA, Aldrich), chloroplatinic acid (H₂PtCl₆, 99.995%, Aldrich), phosphotungstic acid (HNa₂PW₁₂O₄₀, or polyoxometalate, Riedel-de Haen). Water used was ultrapure (18 MΩ cm) and prepared by a Barnstead purification system. Titanium dioxide (Degussa P25), a mixture of 80% anatase and 20% rutile, was used as a base photocatalyst. Other chemicals used were of the highest purity available.

Preparation of Platinized TiO₂. Platinization of TiO₂ was carried out using a photodeposition method. An air-equilibrated aqueous suspension of TiO₂ (0.5 g/L) was illuminated with UV

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in the presence of chloroplatinic acid (Pt precursor) and methanol (electron donor). To investigate the effect of deposited Pt speciation, the platinization was carried out under three different conditions: (1) an electron-donor-rich (ED-rich) condition with 1 M methanol and 0.1 mM chloroplatinic acid (illuminated with a 200-W mercury lamp) at pH 3, (2) an electron-donor-deficient (ED-deficient) condition with 0.1 M methanol and 1 mM chloroplatinic acid (illuminated with a 300-W Xe arc lamp) at pH 3, and (3) an electron-donor-free (ED-free) condition with 0.1 mM chloroplatinic acid at pH 10 (illuminated with a 200-W mercury lamp). Note that the ratio of [methanol]/[H_2PtCl_6] in the ED-rich condition is higher by 100 times than that in the ED-deficient condition. After irradiation, the Pt/TiO$_2$ powder was collected by filtration and washed with distilled water. When needed, Pt/TiO$_2$ that was prepared by the photodeposition was further treated by reducing agents such as NaBH$_4$ and reduced polyoxometalate (described later). The concentration of unused chloroplatinic acid remaining in the filtrate solution after the photodeposition was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Thermo Jarrell Ash Corp. IRIS/AP) in order to quantify the amount of deposited Pt. Transmission electron micrographic images of Pt particles loaded on TiO$_2$ were obtained using a JEOL 2100F high-resolution transmission electron microscope (HRTEM).

The oxidation states of Pt deposited on TiO$_2$ catalysts were analyzed by X-ray photoelectron spectroscopy (XPS, Kratos XSAM 800pci) using Mg Kα lines (1253.6 eV) as an excitation source. The spectra were taken for each sample after Ar$^+$ (3 keV) sputter cleaning. Surface charging was minimized by spraying low energy electrons over the sample using a neutralizer gun. Binding energy spectra were recorded in the region of C 1s, Ti 2p, O 1s, and Pt 4f. The binding energies of all peaks were referenced to the Ti 2p line (458.8 eV) in TiO$_2$ and checked against the C 1s line (284.6 eV) originating from surface impurity carbons.

Photolysis and Analysis. All naked or platinized TiO$_2$ suspensions were prepared at a concentration of 0.5 g/L and were dispersed by simultaneous sonication and shaking for 30 s in an ultrasonic cleaning bath. Saturated stock solutions of TCE (8.4 mM), PCE (2.45 mM), and CF (64 mM) were prepared in distilled water containing excess substrates, and desired concentrations were made by dilution. As for 4-CP and DCA, an aliquot of stock solution (10 mM) was added to the TiO$_2$ suspension to make a desired concentration. All photolysis experiments in this work were carried out at initial pH of 4.0.

The photolyses were performed with a 300-W Xe-arc lamp (Oriel). Light passed through a 10-cm IR water filter and a UV cutoff filter ($\lambda > 300$ nm). The filtered light was focused onto a 60-mL Pyrex reactor with a quartz window. The photocatalytic reactor was filled with minimized headspace, sealed with a rubber septum, and stirred magnetically. Sample aliquots of 1 mL were withdrawn from the illuminated reactor with a 1-mL syringe, filtered through a 0.45-μm poly(tetrafluoroethylene) (PTFE) filter (Millipore), and injected into a 2-mL glass vial.

Quantitative analysis of chloride ions generated as a result of PCD of chlorinated substrates was performed by using an ion chromatograph (IC, Dionex DX-120). The IC system was equipped with a Dionex IonPac AS-14 for anions and a conductivity detector. The analysis of 4-CP was done by using a high performance liquid chromatograph (HPLC, Agilent 1100) equipped with a C-18 column (Agilent Zorbax 300SB) and a diode-array detector (DAD). The rates of chloride generation

or substrate degradation were linear during the initial 30 min. The PCD rates were expressed in terms of the initial rate.

Photoelectrochemical Measurements. The photoelectrochemical characteristics of naked TiO$_2$, Pt$_{ox}$/TiO$_2$, and Pt^0/TiO$_2$ electrodes were compared. TiO$_2$ electrodes were prepared as described elsewhere.[29] Degussa P25 TiO$_2$ (0.2 g) was added to 2 g of 50 wt % aqueous Carbowax (poly(ethylene glycol)) solution as a binder and thoroughly mixed. The resulting paste was cast on an indium tin oxide (ITO) glass (1 × 1 cm^2, Samsung) with two tracks of one layer of Scotch Magic Tape and then left at room temperature for 30 min. The dried film was heated at 400 °C for 30 min to burn off any organics on the TiO$_2$ film surface. For Pt deposition onto a TiO$_2$ electrode, the electrode was immersed in an aqueous solution of 1 mM H$_2$PtCl$_6$ and 0.1 M methanol (ED-deficient condition) and irradiated with a 200-W Hg lamp for 30 min. The XPS spectra of Pt (4f band) deposited on the TiO$_2$ electrode showed that the main Pt species was PtO$_2$. The resulting electrode was Pt$_{ox}$/TiO$_2$. The Pt^0/TiO$_2$ electrode could be prepared by chemically reducing PtO$_2$ on the TiO$_2$ electrode using NaBH$_4$ reagent. The oxidation state of Pt^0 was confirmed by the XPS analysis.

The photoelectrochemical reactor was cylindrical and had a working electrode (TiO$_2$, Pt$_{ox}$/TiO$_2$, or Pt^0/TiO$_2$), a reference saturated calomel electrode (SCE), and a graphite rod as a counter electrode. Photocurrents were collected by applying a potential (+0.5 V vs SCE) to the working electrode using a potentiostat (EG&G 263A2) connected to a computer. The photocurrent generation in the presence of chlorinated organic substrates was compared among different TiO$_2$ electrodes (TiO$_2$, Pt$_{ox}$/TiO$_2$, and Pt^0/TiO$_2$). A 300-W Xe arc lamp (Oriel) was used as a UV light source as in PCD experiments.

Results and Discussion

Substrate-Specific Pt Effect in PCD Reactions. The PCD rates of TCE, PCE, DCA, 4-CP, and CF in air-equilibrated aqueous suspensions are compared in Figure 1 when a series of Pt/TiO$_2$ samples prepared with varying Pt photodeposition time (1, 2, 5, 30, and 60 min) were used as a photocatalyst. The platinization was carried out in the ED-rich condition. As for DCA degradation, a volcano-shaped activity curve, which has been frequently observed in other studies,[11,24,26,30] was obtained. In general, the PCD rate increases with Pt loading because of the efficient charge separation at the interface of Pt and TiO$_2$ but too much Pt loading decreases the photoreactivity mainly because active sites on TiO$_2$ are covered by Pt. However, the PCD dependence of TCE and PCE on the Pt loading is drastically different from the general case. TiO$_2$ that was photoplatinized for 1, 2, and 5 min had detrimental effects on the PCD rates of TCE and PCE, while the 30-min photodeposition of Pt recovered the photoactivity to a level similar to that of naked TiO$_2$. Further photodeposition for 60 min decreased the TCE and PCE degradation rate as in the case of DCA. The effect of Pt deposition on the PCD of 4-CP was similar to the case of DCA, whereas the CF case did not show a sign of activity decrease up to 60 min of photodeposition (Figure 1b). This result clearly demonstrates that the Pt loading effects in TiO$_2$ photocatalytic reactions depend on not only the Pt loading but also the kind of substrates, and hence cannot be generalized. This also provides a reasonable explanation of why the Pt loading effects reported in the literature are often inconsistent even for the same substrate (e.g., TCE). The term "platinized TiO$_2$" or simply "Pt/TiO$_2$" may represent very different photocatalysts depending on the preparation conditions. The characteristics of a "Pt/TiO$_2$" catalyst should depend on various
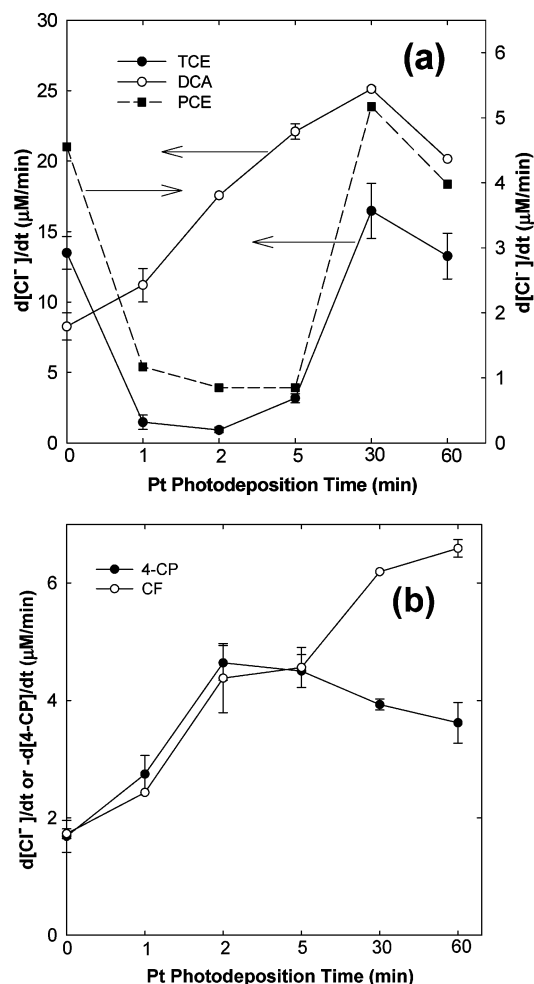
Figure 1. Effects of Pt photodeposition time on the PCD rates of (a) TCE, PCE, DCA and (b) 4-CP, CF. The experimental conditions were [Pt/TiO$_2$] = 0.5 g/L; [TCE]$_0$ = 0.4 mM; [PCE]$_0$ = 0.25 mM; [DCA]$_0$ = 1 mM; [4-CP]$_0$ = 0.25 mM; [CF]$_0$ = 1 mM; pH = 4.0; air-equilibrated [note that the abscissa scale (photodeposition time) is not linear]. The photoplatinization was carried out under the ED-rich condition.

parameters such as the property of substrate TiO$_2$, the loaded Pt amount, the oxidation state of Pt, the particle size and dispersity of Pt, etc.

Effects of Pt Loading and Size. The properties of deposited Pt change with the photodeposition time. The amount of Pt deposited on TiO$_2$ was determined by ICP-AES analysis. The Pt loading was not proportional to the photodeposition time: the loaded Pt was 2.2 and 2.5 wt % for 1- and 2-min photodeposition and remained constant around 3.3 wt % (corresponding to quantitative deposition of all platinic acids) for 5-min photodeposition and beyond. The XPS analysis of surface atomic compositions also showed a minor effect of photodeposition time on the Pt loading: the surface Pt concentration increased only from 1.0 to 1.4 at. % between the photodeposition times of 1 and 60 min. The minor variation of Pt loading on TiO$_2$ in this range of photodeposition time does not seem to be responsible for the sensitive response of the photoreactivity to the photodeposition time (Figure 1). In particular, the drastic retardation in the PCD rates of TCE and PCE observed with Pt/TiO$_2$ (1−5 min of photodeposition) cannot be explained by the shielding effect that Pt coverage blocks reactive surface sites.[24,30]

On the other hand, the size of Pt particles was dependent on the photodeposition time and the electron donor concentration.

Figure 2 compares the TEM images of Pt/TiO$_2$ catalysts that were prepared in the ED-rich (a,b) and ED-deficient conditions (c,d), respectively. The TEM image of Pt/TiO$_2$ (ED-free, image not shown) was similar to that of Pt/TiO$_2$ (ED-deficient). For Pt/TiO$_2$ prepared in the ED-rich condition, Pt particles on Pt/TiO$_2$ (1 min) are too small to be clearly seen but those on Pt/TiO$_2$ (30 min) are well defined with the size of 2−10 nm. The metal particles with different size may differ in their activities for the interfacial electron transfer and catalysis on TiO$_2$. For example, Subramanian et al.[31] observed that the electron transfer to C$_{60}$ on Au/TiO$_2$ increased when the size of Au nanoparticles decreased. However, in the present case of Pt/TiO$_2$, the size of Pt particles does not seem to be a main parameter in determining the photocatalytic activity since smaller Pt particles (Figure 2a) were less active than larger ones (Figure 2b) for the PCD of all substrates tested. As for Pt/TiO$_2$ prepared in the ED-deficient condition, the size of Pt particles does not change with the photodeposition time (compare Figure 2c with Figure 2d) and are smaller than those made in the ED-rich condition (compare Figure 2b with Figure 2d). As discussed later, Pt/TiO$_2$ (ED-deficient) is less active than Pt/TiO$_2$ (ED-rich), which also shows that smaller Pt particles on TiO$_2$ are not more active than larger ones for PCD reactions. The size of Pt particles should not be the main deciding factor in controlling the PCD activity.

Effect of Pt Oxidation State. Photodeposited Pt on a TiO$_2$ surface reportedly exists in various oxidation states such as Pt^{IV}, Pt^{II}, and Pt^0 species.[32] The main effect of photodeposition time might be related to the change in the oxidation state of deposited Pt species, and the Pt oxidation state can be controlled by changing the preparation condition. PtCl$_6$$^{2-}$ in aqueous solution can be hydrolyzed to form Pt(OH)$_x$Cl$_{6-x}$$^{2-}$ ($x = 1-5$), which is pH-dependent.[33] Each Pt(OH)$_x$Cl$_{6-x}$$^{2-}$ species should differ in its reactivity for conduction band (CB) electrons and valence band (VB) holes. For example, it has been reported that PtO$_2$ and PtO (or Pt(OH)$_2$) were deposited in alkaline conditions through the reaction of hydrolyzed Pt complexes with VB holes (e.g., Pt(OH)$_4$Cl$_2$$^{2-}$ + 4h$_{vb}$$^+$ → PtO$_2$ + 4H$^+$ + O$_2$ + 2Cl$^-$) whereas Pt^0 was mainly deposited at acidic pH.[33,34] The degree of the hydrolysis of PtCl$_6$$^{2-}$ increases with pH, and the formation of Pt oxides seems to be favored at basic conditions.[34] Therefore, Pt oxides were deposited in the ED-free condition at pH 10 in this study. On the contrary, the formation of Pt^0 should be favored in acidic conditions and in the presence of electron donors that prevent the Pt complexes from reacting with VB holes.

We prepared Pt$_{ox}$/TiO$_2$ and Pt^0/TiO$_2$ under different photodeposition conditions: the former in the ED-free condition (pH 10) and the latter in the ED-rich condition (pH 3). The XPS spectra in Figure 3a show that Pt$_{ox}$/TiO$_2$ and Pt^0/TiO$_2$ have Pt^{IV}/Pt^{II} and Pt^0 as main species, respectively. Although both Pt/TiO$_2$ samples had a similar Pt content, their photocatalytic activities were very different as shown in Figure 3b,c. Pt$_{ox}$/TiO$_2$ is particularly inactive for TCE degradation, and Pt^0/TiO$_2$ is generally more active than Pt$_{ox}$/TiO$_2$ except for 4-CP whose degradation appears to be little affected by the Pt oxidation state. Pt^0/TiO$_2$ was more active than Pt$_{ox}$/TiO$_2$ not only for the oxidative degradation of chlorinated organic compounds (TCE, DCA, CF) but also for the reductive degradation of TCA.[22] Incidentally, we also carried out the Pt photodeposition in the deaerated condition. The Pt/TiO$_2$ sample prepared in the deaerated suspension (ED-rich condition) exhibited a higher fraction of Pt^0 and hence a higher activity for TCE degradation than that prepared in the presence of oxygen (data not shown). Because O$_2$ should compete with chloroplatinic acids for CB
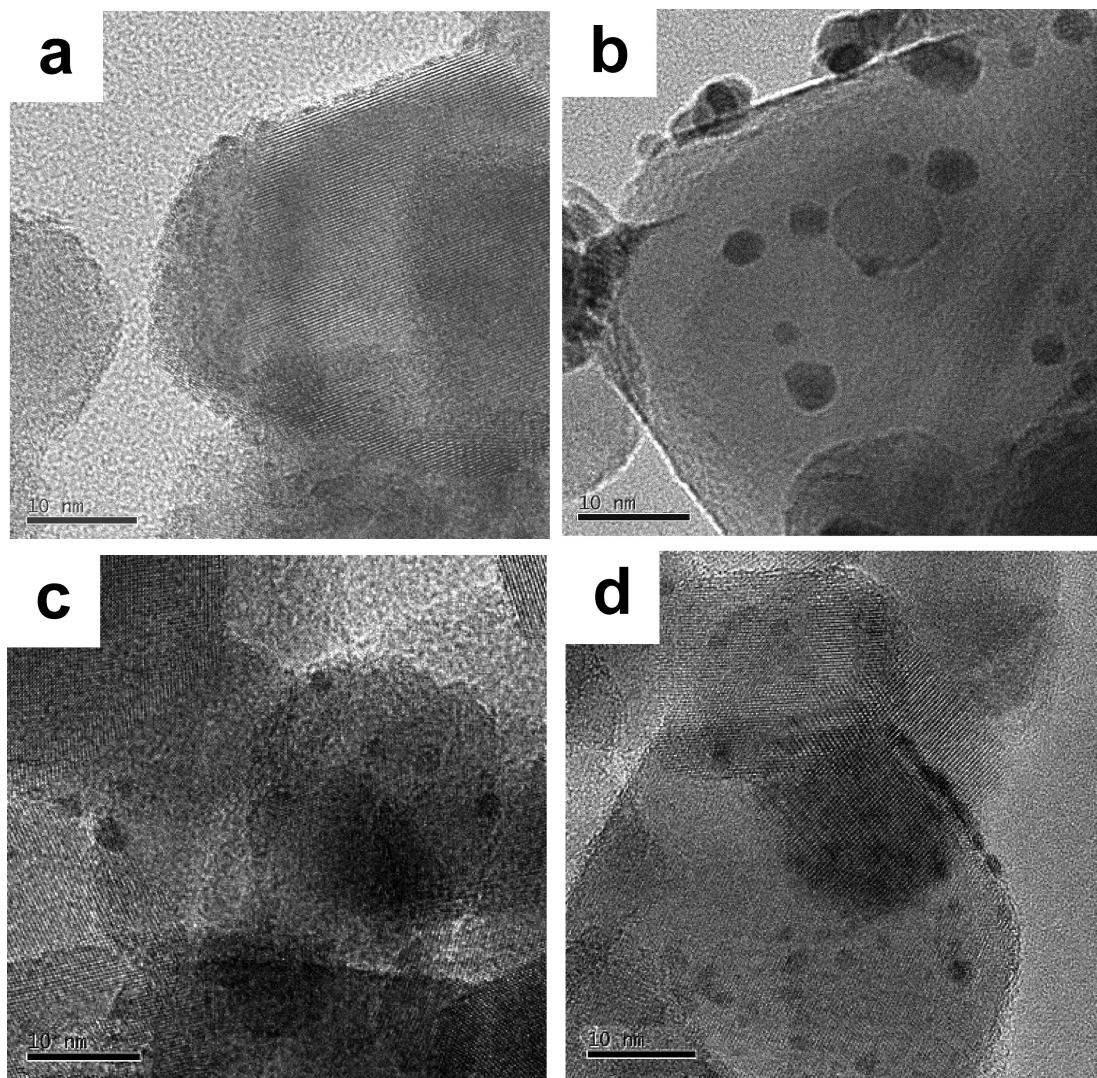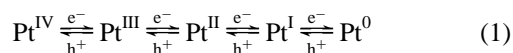
Figure 2. TEM images of Pt/TiO$_2$ catalysts prepared by (a) 1-min and (b) 30-min Pt photodeposition under the ED-rich condition and (c) 5-min and (d) 120-min Pt photodeposition under the ED-deficient condition.

electrons, the photoreductive conversion from Pt^{IV} to Pt^0 is more favored in the absence of O$_2$.

Pt^{II}/Pt^{IV} species on TiO$_2$ may act as a recombination center through the consecutive reduction/oxidation cycles consuming considerable amounts of photogenerated electrons and holes (reaction 1),[35] which explains why Pt$_{ox}$/TiO$_2$ is less active than Pt^0/TiO$_2$.

$$Pt^{IV} \underset{h^+}{\overset{e^-}{\rightleftharpoons}} Pt^{III} \underset{h^+}{\overset{e^-}{\rightleftharpoons}} Pt^{II} \underset{h^+}{\overset{e^-}{\rightleftharpoons}} Pt^{I} \underset{h^+}{\overset{e^-}{\rightleftharpoons}} Pt^0 \qquad (1)$$

In addition, Pt^0 metal serves as a thermal catalyst and changes the photocatalytic reaction pathways and products.[21−23,36,37] We recently demonstrated that aqueous ammonia can be converted directly into dinitrogen on illuminated Pt/TiO$_2$[21] and that anoxic PCD of TCA is highly enhanced on Pt/TiO$_2$ since the presence of Pt on TiO$_2$ provides an alternative reaction path.[22] In a similar context, dimethylamine can transform into trimethylamine on Pt/TiO$_2$ in deaerated solution whereas only demethylated products were generated with pure TiO$_2$.[23]

To investigate the effect of photodeposition time on the oxidation state of Pt, the XPS spectra of Pt/TiO$_2$ catalysts that were prepared with varying photodeposition time are compared in Figure 4. The oxidation states of Pt deposited in (a) the ED-rich condition (the same condition used in Figure 1) and (b)

the ED-deficient condition show very different dependence on the photodeposition time. As for the Pt/TiO$_2$ prepared in the ED-rich condition (Figure 4a), Pt^{II} was the major species in the early photodeposition period (1−2 min) but Pt^0 was dominant after longer photodeposition (30−60 min). This confirms that the photoactivity variation of Pt/TiO$_2$ in TCE degradation (Figure 1a) should be ascribed to the fact that the Pt oxidation state changes from Pt^{II} to Pt^0 with the photodeposition time. That is, the early photodeposition produces Pt$_{ox}$/TiO$_2$ that is particularly inactive for TCE degradation but further photodeposition recovers the photoactivity since Pt$_{ox}$/TiO$_2$ transforms into Pt^0/TiO$_2$. On the other hand, Pt photodeposition under the ED-deficient condition (Figure 4b) did not show such a change in the oxidation state as the photodeposition time increases. The formation of Pt^0 species was insignificant up to 120 min of photodeposition, and Pt^{II} was the dominant species throughout the photodeposition. Therefore, the TEM images of Figure 2a,c,d represent Pt$_{ox}$/TiO$_2$ while Figure 2b shows the image of Pt^0/TiO$_2$. It has been previously reported that platinized TiO$_2$ having PtO (or Pt(OH)$_2$) or PtO$_2$ as the main Pt species could be prepared through photodeposition in the absence of an electron donor.[38] The successive reduction from Pt^{IV} to Pt^0 should be driven by not only CB electrons but also methanol radicals ($\bullet$CH$_2$OH) that are much stronger reductants than the former
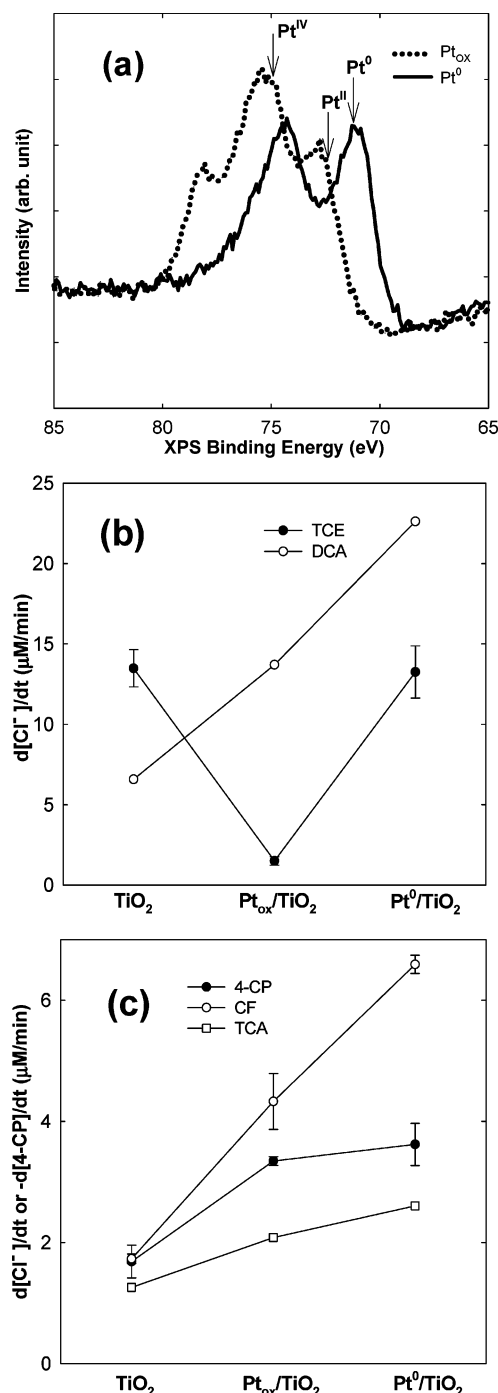
Figure 3. (a) XPS spectra of Pt (4f band) on Pt_{ox}/TiO_2 and Pt^0/TiO_2. Pt_{ox}/TiO_2 was prepared with 30-min photodeposition in the ED-free condition, and Pt^0/TiO_2 with 60-min photodeposition in the ED-rich condition. Comparison of the PCD of (b) TCE, DCA and (c) CF, TCA, 4-CP with naked TiO_2, Pt_{ox}/TiO_2, and Pt^0/TiO_2 ([TCE]$_0$ = 0.4 mM; [DCA]$_0$ = 0.5 mM; [CF]$_0$ = 1 mM; [TCA]$_0$ = 0.5 mM; [4-CP]$_0$ = 0.25 mM; pH$_i$ = 4.0). All suspensions were air-equilibrated except for the case of TCA that was carried out in the deaerated condition.

($E° = -0.74$ V$_{NHE}$ for the •CH$_2$OH/HCHO couple).[6f] It seems that the CB electrons alone in the ED-free condition or the methanol radicals in the ED-deficient condition are not sufficient to reduce Pt^{IV} fully to Pt^0.

Figure 5 shows the photoreactivities of Pt/TiO$_2$ that was prepared in the ED-deficient condition (i.e., Pt/TiO$_2$ of Figure 4b) for the PCD of DCA and TCE. Figure 5 can be directly compared with Figure 1a that shows the photoreactivities of Pt/TiO$_2$ prepared in the ED-rich condition. The two Pt/TiO$_2$
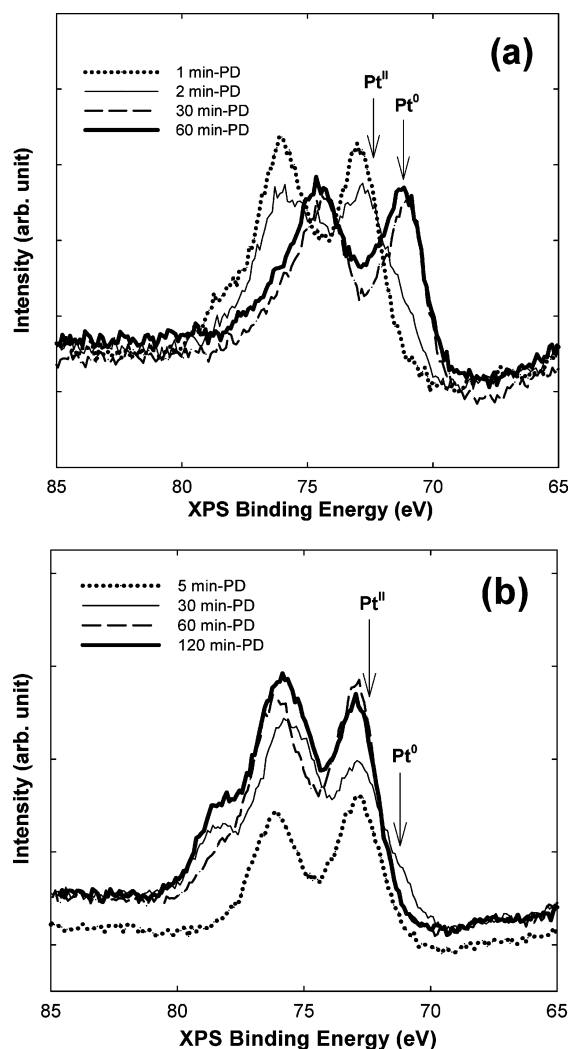

Figure 4. XPS spectra of Pt (4f band) on TiO$_2$ that was loaded with varying the time of photodeposition (PD), which was carried out under two different conditions: (a) 0.1 mM chloroplatinic acid and 1 M methanol (ED-rich) and (b) 1 mM chloroplatinic acid and 0.1 M methanol (ED-deficient).

catalysts are very different in their photoactivities: the PCD rate of TCE with Pt/TiO$_2$ in Figure 5 was not recovered at all at longer photodeposition time, whereas that in Figure 1a rebounded after 30-min photodeposition. The most plausible explanation for the different behaviors between the two Pt/TiO$_2$ samples is the different oxidation state of deposited Pt species. The photoreactivity recovery (in TCE degradation) shown in Figure 1a coincides with the appearance of Pt^0 species (Figure 4a); the failure in recovering the reactivity at longer photo-deposition time (Figure 5) is consistent with the absence of Pt^0 species on TiO$_2$ (Figure 4b). On the other hand, the PCD of DCA seems to be much less affected by the Pt oxidation state.

The oxidation states of Pt on TiO$_2$ might be further changed through post-photodeposition processes. For example, if Pt oxidation states can change gradually during photocatalytic reactions, the Pt speciation on fresh and used Pt/TiO$_2$ catalysts could be different. In such a case, the photocatalytic reactivity of a Pt/TiO$_2$ catalyst may change with repeated uses, which is exactly what Figure 6 shows. The photocatalytic reactivity of Pt/TiO$_2$ for TCE degradation gradually increased with repeated uses, whereas that for DCA degradation was little affected. The XPS spectra in Figure 6c show that a fraction of Pt species were reduced to Pt^0 after use. This reconfirms that the PCD of TCE strongly depends on the oxidation state of Pt on TiO$_2$.
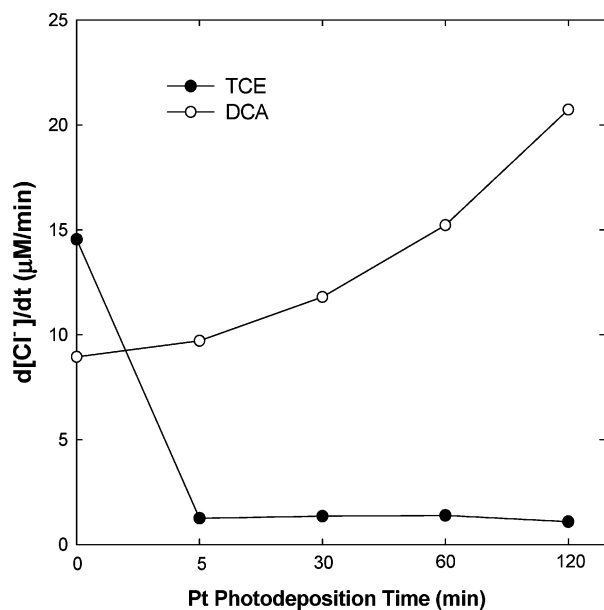
Figure 5. The initial rate of chloride production from the PCD of TCE and DCA with Pt/TiO_2 as a function of Pt photodeposition time ($[TCE]_0 = 0.4$ mM; $[DCA]_0 = 1$ mM; pH = 4.0). The photoplatinization was carried out in the ED-deficient condition.

As an alternative method to change the oxidation state of Pt photodeposited on TiO_2, Pt/TiO_2 was additionally reacted with a reducing agent in the dark after the completion of photodeposition. A polyoxometalate (POM), $PW_{12}O_{40}{}^{3-}$, was used as the reducing agent: reduced POMs (POM^-) are able to reduce metal ions (e.g., Ag^+, Pd^{2+}, $AuCl_4^-$, and $PtCl_6{}^{2-}$) into metal nanoparticles.[39,40] POM ($PW_{12}O_{40}{}^{3-}$, 10 mM) was rapidly reduced to POM^- ($PW_{12}O_{40}{}^{4-}$) in UV-illuminated TiO_2 suspension (0.5 g/L, deaerated) that contained methanol (6.25 M) as an electron donor (reaction 2).

$$PW_{12}O_{40}{}^{3-} + e_{cb}{}^- \rightarrow PW_{12}O_{40}{}^{4-} \qquad (2)$$
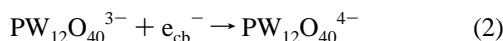
After 2 h of UV illumination, the formation of POM^- was confirmed by the deep blue coloration of the suspension. The colored suspension containing POM^- was filtered through a syringe filter (0.45-μm PTFE filter) to remove TiO_2 particles and then immediately added into a deaerated Pt/TiO_2 suspension (0.25 g/L). The mixed suspension was left for 1 h in the dark to allow POM^- to reduce Pt_{ox} species on TiO_2 (reaction 3).

$$nPOM^- + Pt^{n+}/TiO_2 \rightarrow nPOM + Pt^0/TiO_2 \qquad (3)$$
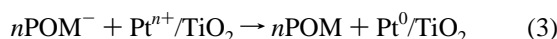
The XPS spectra in Figure 7a clearly show that the above POM treatment based on reaction 3 indeed reduced the surface Pt_{ox} species into Pt^0. As a result, the PCD rate of TCE was markedly enhanced with the POM-treated Pt/TiO_2 (Figure 7b).

We have shown that the oxidation state of Pt deposited on TiO_2 can be changed in several ways. The conditions of photodeposition, reusing Pt/TiO_2, and chemical treatment following the photodeposition all influenced the oxidation state of Pt. All the cases consistently showed that the presence of oxidized Pt species on TiO_2 strongly retarded the PCD of TCE but reducing Pt_{ox} to Pt^0 rapidly recovered the photoactivity of Pt/TiO_2 for TCE degradation. However, DCA degradation was much less influenced by the reduction of oxidized Pt species on TiO_2. Incidentally, the present Pt_{ox}/TiO_2 did not exhibit any visible light activity for 4-CP degradation whereas Zang et al.[41] reported that TiO_2 modified with chlorides of Pt^{IV} catalyzed the degradation of 4-CP under visible light.
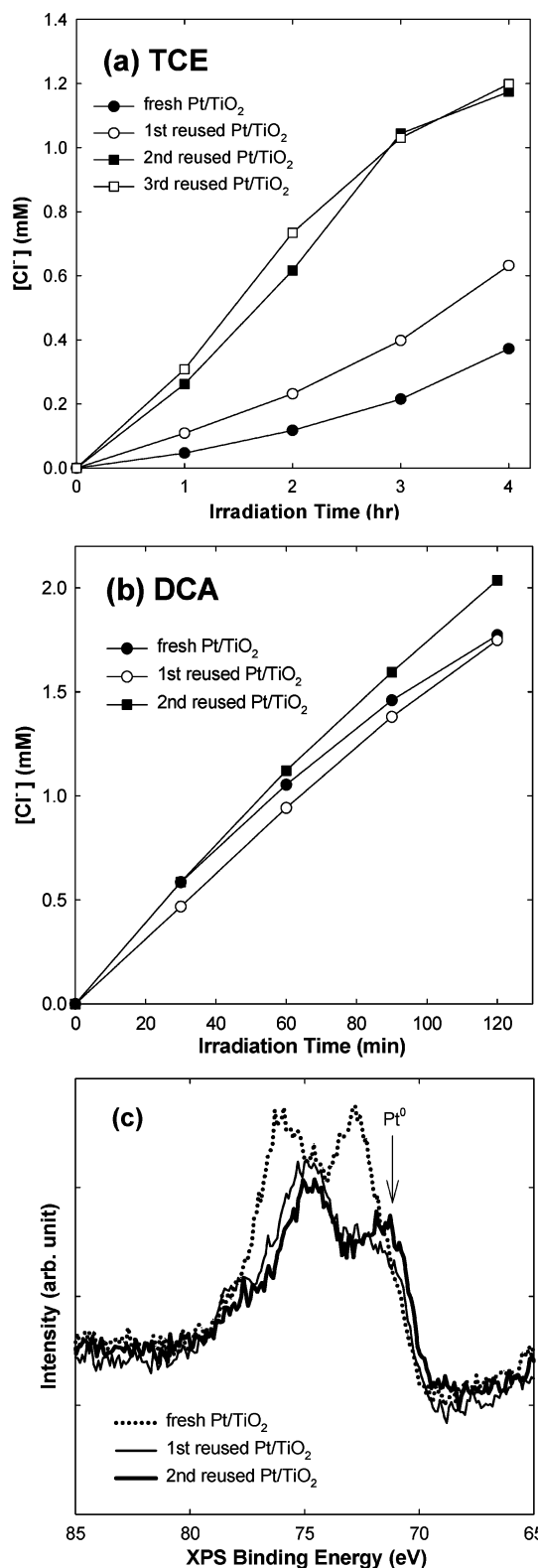

Figure 6. PCD of (a) TCE and (b) DCA with fresh and reused Pt/TiO_2 catalyst ($[TCE]_0 = 0.4$ mM; $[DCA]_0 = 1$ mM; pH = 4.0). (c) XPS spectra of Pt (4f band) on fresh and reused Pt/TiO_2. The fresh Pt/TiO_2 was prepared with 2-min photodeposition in the ED-rich condition.

Pt Effects on Photocurrent and PCD Mechanism. To investigate the effects of platinization on the electron transfer at the TiO_2/water interface, the photocurrents (I_{ph}) generated with TiO_2, Pt_{ox}/TiO_2, and Pt^0/TiO_2 electrodes in the presence of DCA or TCE are compared in Figure 8. Once CB electrons are photogenerated by the band gap excitation of the Pt/TiO_2
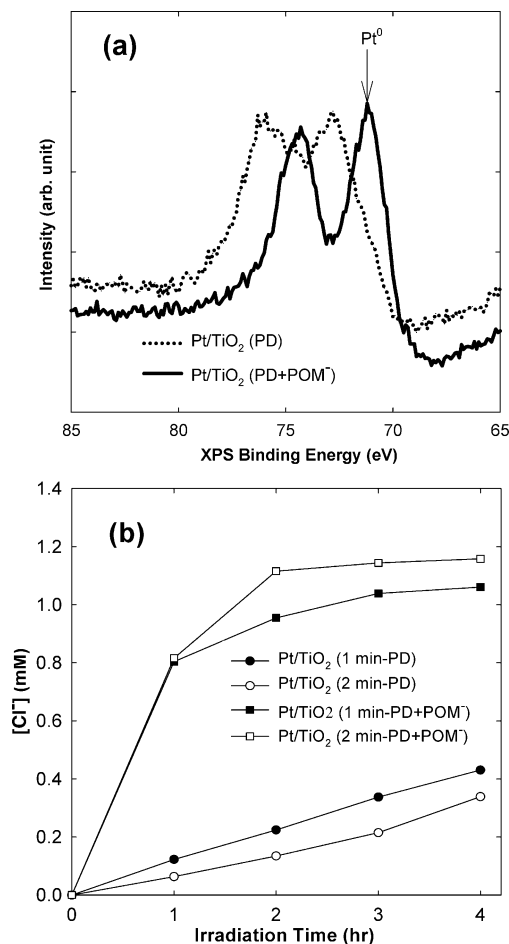
Figure 7. (a) XPS spectra of Pt (4f band) that was deposited on TiO$_2$ in two different ways: one following a normal photodeposition procedure (2-min deposition in the ED-rich condition), Pt/TiO$_2$ (PD), and the other combining the photodeposition and the subsequent chemical reduction by reduced POM, Pt/TiO$_2$ (PD + POM$^-$). (b) Comparison of the photocatalytic reactivity for TCE degradation between Pt/TiO$_2$ (PD) and Pt/TiO$_2$ (PD + POM$^-$) ([TCE]$_0$ = 0.4 mM; pH = 4.0).

electrode, they are recombined with VB holes directly or indirectly, trapped in defect sites or Pt deposits, transferred to electron acceptors (e.g., O$_2$) in the solution, or extracted into the external circuit to generate I_{ph}. The photocurrent profiles shown in Figure 8 indicate that the Pt deposits on TiO$_2$ indeed trap CB electrons to decrease I_{ph}. At the steady state, the photocurrent decreased in the order of TiO$_2$ > Pt^0/TiO$_2$ > Pt$_{ox}$/TiO$_2$ for both cases of DCA and TCE. Similar trends were also observed with PCE, 4-CP, or pure water. The fact that I_{ph} was lower with Pt$_{ox}$/TiO$_2$ than Pt^0/TiO$_2$ implies either that Pt$_{ox}$ species trap more CB electrons or that Pt$_{ox}$ species serve as a recombination center. Because Pt$_{ox}$/TiO$_2$ was less active than Pt^0/TiO$_2$ for all PCD reactions tested in this study, the lower photocurrents obtained with the Pt$_{ox}$/TiO$_2$ electrode should be ascribed to the faster recombination in Pt$_{ox}$/TiO$_2$. However, this does not explain why Pt$_{ox}$/TiO$_2$ is particularly inactive for TCE (or PCE) degradation.

The substrate-specific PCD activities of Pt/TiO$_2$ should be related to the intrinsic difference in the degradation mechanisms among various substrates. Here we propose a hypothesis that TCE (or PCE) has particularly strong chemical affinity with the Pt$_{ox}$ species on which the charge-pair recombination is chemically mediated through the redox cycling of TCE (or PCE). The specific chemical interaction between chlorinated ethenes and Pt$_{ox}$ needs to be verified in further studies. Scheme
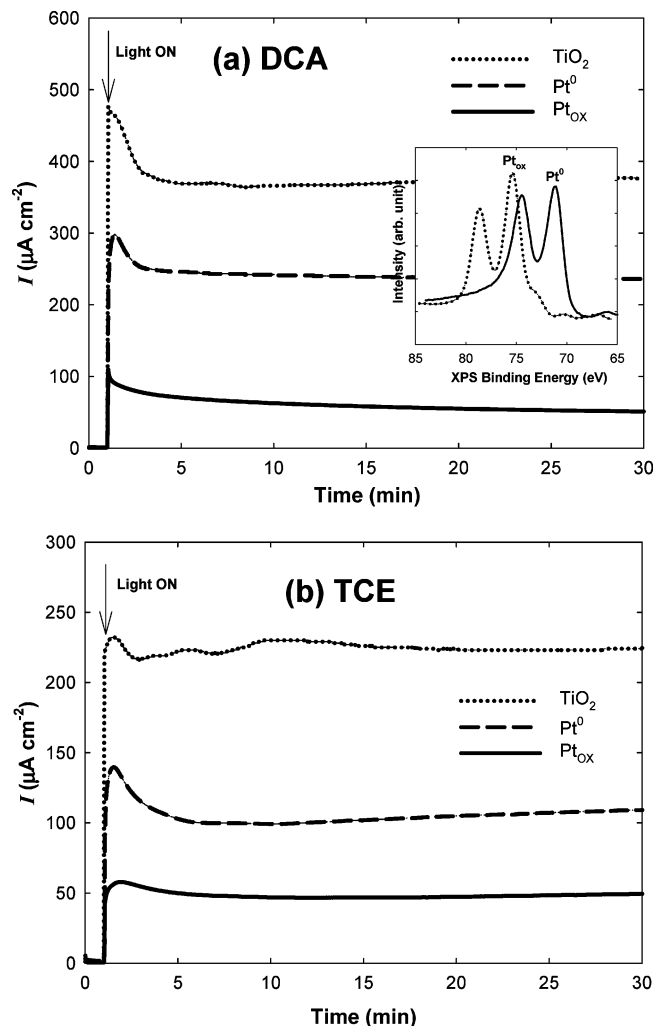

Figure 8. Time profiles of photocurrent, I_{ph}, obtained with pure TiO$_2$, Pt$_{ox}$/TiO$_2$, and Pt^0/TiO$_2$ electrodes in the presence of (a) DCA ([DCA]$_0$ = 1 mM) and (b) TCE ([TCE]$_0$ = 1 mM) under the air-equilibrated condition (pH 4). The inset shows the XPS spectra of the Pt 4f band of Pt^0/TiO$_2$ and Pt$_{ox}$/TiO$_2$ electrodes.

SCHEME 1: Proposed Photoinduced Electron Transfer Paths on Pt$_{ox}$/TiO$_2$ and Pt^0/TiO$_2$ in the Presence of TCE^a
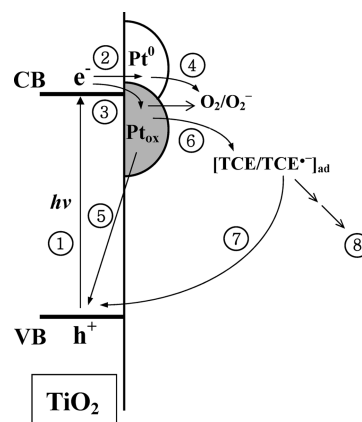
^{a} The numbers indicate major electronic pathways: (1) band gap excitation; (2) electron trapping in the Pt^0 phase; (3) electron trapping in the Pt$_{ox}$ phase; (4) trapped electron transfer to O$_2$; (5) Pt$_{ox}$-mediated recombination; (6) trapped electron transfer to TCE; (7) TCE-mediated recombination; (8) reductively initiated degradation of TCE.

1 illustrates the situation. Although both Pt^0 and Pt$_{ox}$ deposits can trap CB electrons that are subsequently transferred to electron acceptors such as O$_2$, Pt$_{ox}$ also serves as a recombination

center on the contrary. This seems to be why Pt_{ox}/TiO_2 is more active than pure TiO_2 but less active than Pt^0/TiO_2 in general. When TCE is adsorbed on the Pt_{ox} surface, it provides an additional recombination path in which TCE reacts successively with trapped electrons and holes (step $6 + 7$ in Scheme 1). This chemically mediated recombination path in the presence of TCE may explain the observation that I_{ph} generated in the presence of TCE was consistently lower than I_{ph} in the presence of DCA (Figure 8).

Once TCE•$^-$ radical anions are formed after accepting CB electrons, a small fraction of them may follow a reductive degradation path (step 8 in Scheme 1). TCE could be degraded in the absence of dissolved oxygen through this reductive path. Although most PCD reactions of organic compounds are almost completely inhibited in the absence of dissolved O_2, anoxic PCD pathways exist in special cases. For example, such anoxic mechanism can be highly enhanced by the surface platinization of TiO_2.[22,23] The reductive degradation of TCE in the anoxic condition seems to accelerate on Pt^0/TiO_2. In N_2-saturated suspensions, the PCD rates of TCE were markedly enhanced in the presence of Pt^0 deposits on TiO_2 (5.4 μM/min with Pt^0/TiO_2 versus 1.2 μM/min with TiO_2) whereas those in the air-equilibrated suspensions were little affected by the surface platinization (13.3 μM/min with Pt^0/TiO_2 versus 13.5 μM/min with TiO_2). This indicates that the anoxic degradation is initiated by the CB electron transfer to TCE (step 6 in Scheme 1), which occurs preferentially on the platinized surface.

Conclusions

The effects of platinization of TiO_2 on the photocatalytic reactivity should depend on many experimental factors that include not only the properties of Pt deposits (e.g., loaded amount, oxidation state, size, etc.) but also the interaction between substrates and Pt deposits. Although the interplay of all these parameters cannot be fully addressed in a single study, this work clearly demonstrated that the platinization effects are substrate-specific and hard to generalize. The case of TCE and PCE is a prominent example. Many studies on platinized TiO_2 have been reported in the literature, but they employed various methods of platinization to make "Pt/TiO_2" photocatalysts that should be quite different in many aspects. In addition, their photocatalytic reactivities were tested for a wide variety of substrates, which makes the reliable comparison of published results on the activity of Pt/TiO_2 very difficult. In particular, it should be noted that the oxidation state of Pt species is the most important parameter in determining the PCD activity of Pt/TiO_2 and needs to be carefully controlled to obtain the desired activity.

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