

Comparative Study of Homogeneous and Heterogeneous Photocatalytic Redox Reactions: $\text{PW}_{12}\text{O}_{40}^{3-}$ vs TiO_2

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Received: January 15, 2004; In Final Form: March 16, 2004

Polyoxometalates (POMs) as a homogeneous photocatalyst and semiconductor oxide as a heterogeneous photocatalyst share many aspects of similarity in their operating mechanisms. This study systematically compares various photocatalytic oxidation and reduction reactions of $\text{PW}_{12}\text{O}_{40}^{3-}$ (a POM) and TiO_2 in water to demonstrate that the two photocatalysts are very different in many ways. Both POM and TiO_2 can photooxidize various organic compounds with comparable rates, but the POM-mediated mineralization is markedly slower than the mineralization with TiO_2 under the experimental conditions employed in this study. Kinetic studies using *tert*-butyl alcohol as an OH radical scavenger suggest that OH radicals are the sole dominant photooxidant in POM-mediated degradations regardless of the kind of substrates tested, whereas both OH radicals and direct hole transfers take part in TiO_2 photocatalysis. POM immobilization on silica support and surface fluorination of TiO_2 significantly modified the kinetics and intermediate distribution. POM-mediated photoreductive dechlorination of CCl_4 and trichloroacetate was negligible, whereas the dechlorination with TiO_2 was markedly faster. The rate of electron transfer from POM^- to reducible substrates seems to be significantly slower than the rate of conduction band electron transfer on TiO_2 mainly due to the strong electron affinity of POM. The effects of H_2O_2 addition on photocatalytic reactivity are also very different between POM and TiO_2 . Detailed kinetic and mechanistic comparisons between $\text{PW}_{12}\text{O}_{40}^{3-}$ and TiO_2 photocatalysts are presented and discussed to understand the similarities and differences.

Introduction

Efficient physicochemical remediation methods that mineralize recalcitrant organic pollutants through in situ generation of reactive radicals (e.g., $\cdot\text{OH}$) have been intensively studied. Many of them are photochemical processes that are based on photo-induced electron transfer processes, among which photocatalysis is the most popular. In particular, TiO_2 has been widely investigated as a heterogeneous photocatalyst for the complete oxidation of toxic contaminants in water and air.^{1–3} The heterogeneous photocatalytic reactions are initiated by absorbing UV photons with concurrent generation of conduction band (CB) electrons and valence band (VB) holes in the TiO_2 lattice. Hydroxyl radicals that are subsequently generated through the reaction of VB holes with water or surface hydroxyl groups mainly account for the strong oxidizing power of the TiO_2 photocatalytic system.¹

On the other hand, a similar photochemical property of polyoxometalates (POMs) as a homogeneous photocatalyst has been recognized and their ability to oxidize organic compounds photocatalytically has been demonstrated.^{4–7} In addition, the ability of a POM as an effective electron transfer mediator or electron shuttle from the TiO_2 CB to electron acceptors such as O_2 has been recently reported.^{8–10} UV excitation of POMs induces a ligand (oxygen) to metal charge transfer (LMCT) with promoting an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), which can be considered as a parallel process to the band-gap excitation in semiconductor photocatalyst. The charge

transfer excited states of POM (POM^*) react with substrates to yield reduced POM (POM^-) and oxidized substrates as products. POM^- is subsequently reoxidized to POM by O_2 to close a photocatalytic cycle.⁴ This operating mechanism of POM-mediated photoreactions is similarly compared to interfacial charge transfers of electrons and holes on semiconductor surfaces. Similarities between the homogeneous and heterogeneous photocatalysts (POMs vs semiconductors) have been recognized, and a few comparative studies on their photocatalytic behaviors were carried out to reveal different views.^{11–16} Papaconstantinou and co-workers^{15,16} claimed that the two photocatalytic systems are similar in terms of the overall mechanism of photodecomposition of organic compounds and that both photocatalytic oxidation reactions are mainly mediated through the generation of OH radicals. On the other hand, Giannotti and co-workers^{12–14} pointed out the differences in reactivity and degradation mechanism between the two photocatalysts and proposed that the POM-mediated oxidation involves direct electron transfer or H-atom transfer between POM^* and substrates, not OH radicals.

In general, the activity and the mechanism of the photocatalytic process are influenced by the photoinduced electronic processes (e.g., recombination, electron transfer), the interaction between the catalyst and substrates, the concentration and kind of electron donors and acceptors available, the light intensity and wavelength, the pH, the redox potentials of substrates, the excited electronic states of the photocatalyst, etc. Although POM and TiO_2 share many aspects of similarities, specific photocatalytic behaviors should be different and explained in terms of basic physicochemical properties. First of all, the absence of

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well-defined surfaces in POMs should reduce the substrate–catalyst surface interaction and make the surface chemical mechanism that prevails on TiO₂ unfavorable. Second, the well-recognized electron holding ability⁴ of excited POMs might make the POM-induced photoreductive processes quite different from those on TiO₂, where the electron accumulation is negligible under normal reaction conditions. Understanding the similarities and differences between the two photocatalytic systems should provide useful information about their working mechanisms, and should tell us the advantages and disadvantages of each photocatalyst. In this study, we carried out photooxidative and photoreductive degradation of selected organic compounds using a POM or TiO₂ as a photocatalyst, and compared and discussed the photocatalytic reaction kinetics and mechanisms between the homogeneous and heterogeneous systems.

Experimental Section

Chemicals and Materials. Chemicals used in this study include 4-chlorophenol (4-CP; Sigma), 4-chlorocatechol (4-CC; TCI), resorcinol (Aldrich), 1,2,4-benzenetriol (Aldrich), 1,4-benzoquinone (BQ; Aldrich), hydroquinone (HQ; Aldrich), dichloroacetate (DCA, CHCl₂CO₂Na; Aldrich), trichloroacetate (TCA, CCl₃CO₂Na; Aldrich), formate (HCOONa; Acros), NaF (Samchun, Korea), H₂O₂ (Samchun, Korea), *tert*-butyl alcohol (TBA; Shinyo), CCl₄ (J. T. Baker), trichloroethylene (TCE; Junsei), perchloroethylene (PCE; Kanto), CHCl₃ (Matsunoen), CH₂Cl₂ (Sigma-Aldrich), Acid Orange 7 (AO7; Aldrich), and (C₂H₅O)₄Si (Aldrich). All reagents were used as received. Titanium dioxide powder (Degussa P25) that is a mixture of anatase and rutile (8:2) was used as a heterogeneous photocatalyst without any further treatment. HNa₂PW₁₂O₄₀ (Riedel-de Haën) (abbreviated as PW₁₂^{3−} or simply referred to as POM throughout the text) was used as a homogeneous POM photocatalyst. H₄SiW₁₂O₄₀ (Fluka) was used as an alternative POM when needed.

Silica-immobilized POM (SiO₂–POM) was prepared according to the literature method.¹⁷ A mixture of water (0.2 mol), ethanol (0.02 mol), and PW₁₂^{3−} (1.0 × 10^{−4} mol) was added into tetraethoxysilane (0.02 mol) and stirred at 80 °C for 3 h. The resulting hydrogel and additional 5 mL of water were placed in an autoclave and reacted hydrothermally at 150 °C for 24 h. After hydrothermal treatment, the gel was dried at 150 °C for 24 h in vacuo. The solid product was ground, washed with distilled water, and then dried again at 150 °C for 24 h in vacuo. The POM content in the SiO₂–POM sample was about 20 wt %. The SiO₂–POM powder was resuspended in water at 0.5 g/L, and the dissolution of POM from SiO₂–POM particles was negligibly small.

Photolyses and Analyses. TiO₂ (or POM) powder was dispersed (or dissolved) in distilled water by simultaneous sonication and shaking for 30 s in an ultrasonic cleaning bath. An aliquot of the substrate stock solution (1 mM) was subsequently added to the suspension to give a desired substrate concentration, and then the pH of the suspension was adjusted with HClO₄ or NaOH standard solution. When the absence of dissolved oxygen was needed, the reactor was purged with nitrogen gas for 30 min prior to the photolysis and sealed from the ambient air during irradiation. The typical background O₂ concentration in the N₂-purged suspension was less than 10 μM (measured by a dissolved oxygen meter) and maintained at this level throughout the photolysis. Photoirradiation employed a 300-W Xe arc lamp (Oriental) as a light source. Light passed through a 10-cm IR water filter and a UV cutoff filter (λ >

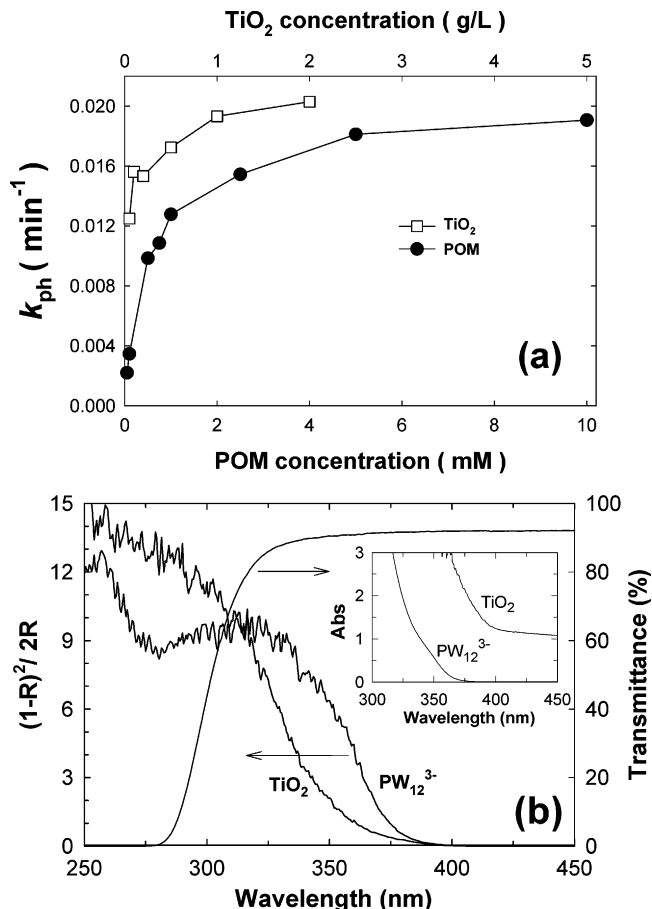


Figure 1. (a) Photocatalytic degradation rate constants of 4-CP as a function of catalyst concentration in water. The experimental conditions were pH 1 for PW₁₂^{3−} and pH 3 for TiO₂, [4-CP]₀ = 100 μM, and air-equilibrated. (b) UV absorption spectra of TiO₂ and HNa₂PW₁₂O₄₀ powders (the ordinate expressed in Kubelka–Munk unit; R , reflectance) and transmittance of UV cutoff filter used in this study. The inset shows the apparent UV absorption spectra of 0.5 g/L TiO₂ suspension and 1 mM PW₁₂^{3−} aqueous solution.

300 nm), and then the filtered light was focused onto a 100-mL Pyrex reactor with a quartz window. The reactor was filled with minimized headspace and stirred magnetically. Sample aliquots were withdrawn from the reactor intermittently during the illumination and filtered through a 0.45-μm PTFE syringe filter (Millipore). Multiple photolysis experiments were performed under identical reaction conditions to confirm the reproducibility.

To compare the photoreactivities between POM and TiO₂, we need to define the comparable catalyst concentration. However, comparing the concentrations of PW₁₂^{3−} (homogeneous photocatalyst) and TiO₂ (heterogeneous photocatalyst) on the basis of mass or molar units has little meaning. Therefore, by carrying out the photocatalytic degradation (PCD) of 4-CP as a function of the POM and TiO₂ concentration, the comparable concentrations of two photocatalysts were determined on the basis of measured photoreactivities. Figure 1a shows that the PCD rate constants (k_{ph}) rapidly increase and then reach a saturation region with increasing catalyst concentration for both POM and TiO₂. The photocatalyst concentrations employed in this study were [TiO₂] = 0.5 g/L and [PW₁₂^{3−}] = 1 mM, both of which lie in the inflection region. All POM reactions were carried out at pH 1 because of the excellent stability of PW₁₂^{3−} at this pH, whereas all TiO₂ suspensions were adjusted to pH 3. As a comparison, we carried out a POM-mediated photolysis of 4-CP at pH 3 and found that the

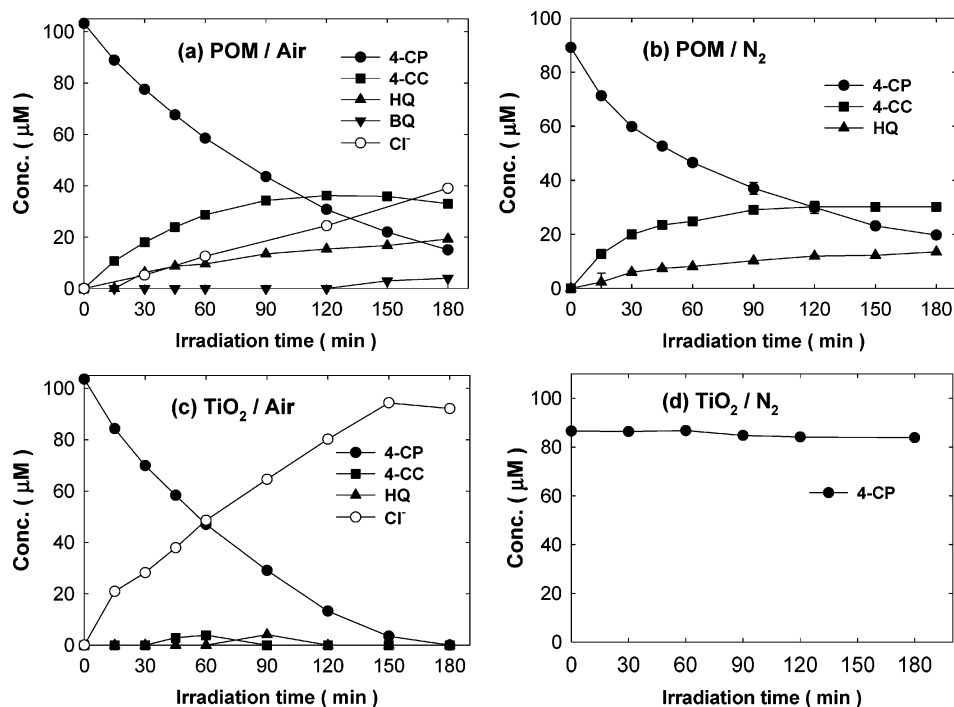


Figure 2. Photocatalytic degradation of 4-CP and formation of intermediates and products as a function of irradiation time in (a) air-saturated POM (pH 1) solution, (b) N_2 -saturated POM (pH 1) solution, (c) air-saturated TiO_2 (pH 3) suspension, and (d) N_2 -saturated TiO_2 (pH 3) suspension.

degradation rate and intermediates distribution at pH 3 were almost identical to those at pH 1.

The UV/visible absorption spectra of POM and TiO_2 photocatalysts were recorded with a UV-vis spectrophotometer (UV-2401PC, Shimadzu). UV reflectance spectra of TiO_2 and POM powder samples were obtained using the spectrophotometer equipped with a diffuse reflectance attachment (Shimadzu ISR-2200) and are shown in Figure 1b along with the transmission spectrum of the UV cutoff filter used in this study. TiO_2 and PW_{12}^{3-} are very similar in the absorption onset position, and their optical absorption significantly overlaps the filter transmittance profile. The inset in Figure 1b compares the UV absorption spectra of 0.5 g/L TiO_2 suspension and 1 mM PW_{12}^{3-} aqueous solution, which are used in the photolysis experiments. Although the strong scattering background in the TiO_2 spectrum makes a quantitative comparison with the POM spectrum difficult, UV absorption by the two photocatalysts in water seems to be very similar as well. The concentration of photoreduced POM was estimated by monitoring its absorbance at $\lambda = 751$ nm ($\epsilon_{751} = 2 \times 10^3$ M $^{-1}$ cm $^{-1}$).¹⁸

The degradation of 4-CP and the production of intermediates were monitored using a high performance liquid chromatograph (HPLC; Agilent 1100 series) equipped with a diode array detector and a Bondapak C18 column (3.9×150 mm). The eluent consisted of a binary mixture of water containing 0.1% phosphoric acid and acetonitrile (80:20 by volume). Identification and quantification of ionic intermediates and products were performed by using an ion chromatograph (IC; Dionex DX-120) which was equipped with a Dionex IonPac AS 14 (4 mm \times 250 mm) column and a conductivity detector. The eluent solution was 3.5 mM Na_2CO_3 /1 mM $NaHCO_3$. Dissolved organic carbon was measured using a total organic carbon analyzer (TOC-V_{CSH}, Shimadzu).

Results and Discussion

Photocatalytic oxidation of 4-CP. Figure 2 compares the PCD of 4-CP in water with POM or TiO_2 under air or N_2

TABLE 1: TOC Removal (%) as a Result of Photocatalytic Degradation^a

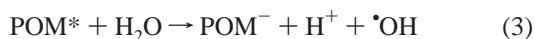
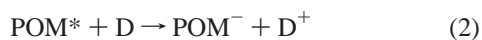
	PW_{12}^{3-} /pH 1	TiO_2 /pH 3
4-CP (3 h)	<1	97
DCA (2 h)	9	100
formate (2 h)	33	82

^a Experimental conditions: reaction volume 100 mL; initial substrate concentration = 100 μ M; [POM] = 1 mM; [TiO_2] = 0.5 g/L; air-equilibrated.

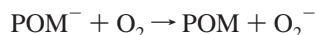
saturation. In the presence of dissolved oxygen, 4-CP degraded slightly faster with TiO_2 than with POM. However, the distribution of intermediates and products from the photocatalytic degradation of 4-CP was very different between the POM and TiO_2 systems (Figure 2a vs 2c). Most 4-CP transformed into hydroxylated aromatic intermediates such as 4-chlorocatechol (4-CC), hydroquinone (HQ), benzoquinone (BQ), and two other unidentified products (not shown in Figure 2) in the POM solution, whereas little aromatic intermediates were detected in the TiO_2 photocatalytic system. The total chlorine mass balance throughout the 4-CP photodegradation was met within $\pm 5\%$ in both POM and TiO_2 solutions. Under the air saturation condition, total organic carbon (TOC) reduction in the 3 h irradiated 4-CP solution was negligible with POM and 97% with TiO_2 , as shown in Table 1. The TOC reduction of 4-CP with POM was 15% after 16 h irradiation, indicating that the mineralization proceeds very slowly. The slow mineralization in the POM solution does not seem to be due to the lack of dissolved O_2 as a reagent because the aromatic intermediate concentrations remained unchanged even in the O_2 -saturated POM solution. Mylonas et al.¹⁹ also reported that PW_{12}^{3-} -mediated 4-CP mineralization was very slow: in 4 h irradiation of 2 mM 4-CP, they could generate only 3% CO_2 out of the total TOC, whereas 4-CP was completely removed in 2 h irradiation. In another comparative study of $W_{10}O_{32}^{4-}$ and TiO_2 (P25), Texier et al.¹² reported that the POM-mediated PCDs of chlorophenols including 4-CP and other aromatic pesticides achieved almost no mineralization, whereas TiO_2 -mediated

PCDs were followed by significant mineralization under a solar irradiation condition. Table 1 shows that the photocatalytic mineralization of DCA and formate was also markedly slower with POM than with TiO₂ under the present experimental conditions. A recent study reported that the addition of PW₁₂³⁻ to illuminated TiO₂ suspension accelerated the hydroxylation of 2,4-dichlorophenol but suppressed its mineralization on the contrary.²⁰ On the other hand, there are other reports that do not appear to agree with our results. Papaconstantinou and co-workers^{18,19,21} claimed that the POM-mediated mineralization of various organic compounds was efficient and comparable with TiO₂-mediated mineralization. For example, in comparison to PCD of 0.2 mM 4-nitrophenol, they reported mineralization efficiencies of 76% and 89% (in 3 h irradiation) with PW₁₂³⁻ and TiO₂, respectively.¹⁹ The POM-mediated mineralization of chloroacetic acid and acetic acid was also comparable to TiO₂ PCD. The apparent disagreement with ours seems to be due to different experimental conditions such as light intensity,²² the kind of TiO₂ samples,²³ the substrate/catalyst ratio, and other unidentified parameters. Therefore, the POM-mediated PCDs and mineralization seem to be highly dependent on the specific photolytic condition and the results and conclusions derived from different studies should not be compared directly unless the effects resulting from different experimental conditions are carefully deconvoluted.

4-CP photodegradation in the deaerated solution exhibits drastically different behaviors between the POM and TiO₂ systems as shown in Figure 2b,d. The PCD of 4-CP and the product formation in the POM/N₂ system were little different from those in the POM/air system, whereas no degradation of 4-CP was observed in the TiO₂/N₂ system. A similar observation was reported from a comparative study of POMs and semiconductor metal oxides on the photochemical oxidation of tetrahydrothiophene in acetonitrile (no water added): under deaerated conditions, all semiconductors were completely inactive whereas most POM-mediated photooxidation was effective.¹¹ It is well-known that heterogeneous PCD reactions of organic compounds do not occur in the absence of dissolved O₂ since O₂ is essential both as a CB electron scavenger and as a reagent.^{24,25} The fact that the photocatalytic conversion of 4-CP in the aqueous POM solution is not affected by O₂ implies that the role of O₂ as an electron acceptor from POM*, which is equivalent to the role of CB electron scavengers on TiO₂, is not essential in initiating POM-mediated PCD reactions. Along with the 4-CP conversion in deaerated POM solution, the blue coloration of the solution was observed, which indicates the reduction of POM. This confirms the well-known behavior that POM* can abstract an electron from reductants (e.g., H₂O, organic compound) and hold the electron (reactions 1–3).⁴ This enables the production of OH radicals even in deaerated POM solutions (reaction 3), whereas the OH radical formation is inhibited in deaerated TiO₂ suspensions due to the fast recombination between photogenerated electrons and holes.



The reduced POM (POM⁻) is quite stable but rapidly reoxidized in the presence of O₂ through reaction 4, and the main function of O₂ in POM reactions seems to be the reoxidation (regeneration) of the catalyst.^{4,10,21,26}



The reoxidation (reaction 4) should accompany the generation of superoxides. Superoxides are also produced on TiO₂ through the reaction of O₂ with CB electrons and have been proposed to play an important role in photocatalytic oxidation mechanisms.²⁷ It is also interesting to note that superoxides generated in UV-illuminated TiO₂ suspensions were suggested to be a main photooxidant of arsenites [As(III)] in recent studies.^{3d,28} A recent electron spin resonance study by Chen et al.²⁰ reported that the formation of free superoxide radical anions in UV-illuminated TiO₂ suspension was markedly suppressed on the addition of PW₁₂³⁻ and concluded that the electron transfer from POM⁻ to O₂ should occur through an inner-sphere complexation yielding an adduct (as noted in reaction 4). Therefore, the reactivity of free superoxides appears to be restricted in POM-mediated photocatalytic reactions and the mineralization in POM reactions could be reduced provided that the reaction of superoxides is responsible for the complete mineralization as Chen et al.²⁰ suggested. This argument also accounts for the fact that mineralization is slow and the presence of dissolved O₂ little changes the reactivity and product distribution in the POM-mediated PCD of 4-CP.

However, a very different effect of O₂ has been previously observed in the PW₁₂³⁻-mediated photodegradation of chloroacetic acid: the initial degradation rate in oxygenated solution increased by 18 times from that in deoxygenated solution.¹⁹ The PW₁₂³⁻-mediated PCD rate of 2,4-dichlorophenol was also significantly enhanced when dissolved O₂ was present in aqueous solution.²⁹ The discrepancy in the observed effects of O₂ on POM reactions appears to be attributed to the different ratios of [substrate]/[POM] that were employed in this work and previous studies. We used excess POM catalyst (1 mM) compared to 4-CP concentration (0.1 mM), whereas the POM concentration was lower than substrate concentrations (e.g., 0.7 mM POM vs 2 mM substrate) in the previous studies.^{19,29} With the high [substrate]/[POM] ratios, POM is rapidly depleted via reaction 2 and the regeneration of the catalyst (reaction 4) can be a rate-limiting step. Under the POM-deficient condition, the presence of O₂ that rapidly regenerates POM should increase the PCD rate markedly. On the other hand, with the POM-excessive condition the POM catalyst is never depleted and the role of O₂ that regenerates the catalyst is not critical in determining the overall PCD kinetics.

The very different behaviors observed in 4-CP PCD between POM and TiO₂ systems indicate different degradation mechanisms. One prominent issue in this respect is whether OH radicals are involved in POM-mediated PCD reactions. Although they are widely accepted to be a main photooxidant in TiO₂ photocatalysis,^{1–3} their role in POM photocatalysis is often questioned.^{12–14,30} The production of OH radicals in illuminated POM solutions is supported on the basis of ESR detection of the OH radical–POM adduct³¹ and the production of hydroxylated intermediates from aromatic compound degradation.^{6,19,21} However, a direct electron transfer reaction between POM* and an aromatic compound (reaction 2) and a subsequent hydration could lead to the formation of hydroxylated intermediates as well.³² To verify the role of OH radicals, the photocatalytic oxidation of 4-CP and 4-CC (a main degradation intermediate of 4-CP) on POM and TiO₂ was compared in the absence or presence of *tert*-butyl alcohol (TBA), a widely used OH radical scavenger (Figure 3). The PCD of 4-CP and 4-CC should be reduced in the presence of TBA when OH radicals are main

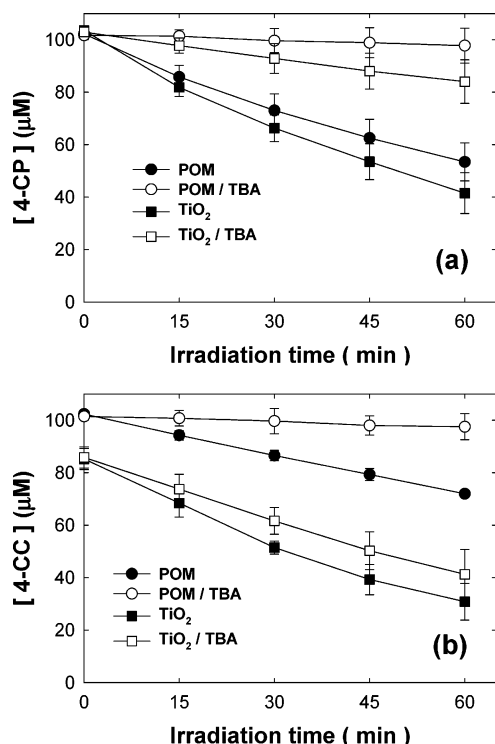


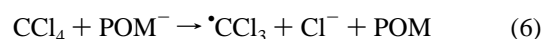
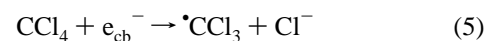
Figure 3. Effects of *tert*-butyl alcohol (TBA, 10 mM) addition on photocatalytic degradation of (a) 4-CP and (b) 4-CC in air-equilibrated solutions of POM (pH 1) and TiO₂ (pH 3).

oxidants.³³ Its inhibitory effects were different between POM and TiO₂. The complete inhibition of 4-CP and 4-CC degradations was observed in the POM/TBA system, whereas the inhibition in the TiO₂/TBA system was only partial. In particular, the TBA inhibition effect on 4-CC degradation was insignificant in the TiO₂ suspension. This could be ascribed to the fact that 4-CC forms a strong surface complex on TiO₂.³⁴ In this situation, the degradation of 4-CC on TiO₂ is initiated mainly via the direct hole transfer without the involvement of OH radicals. Therefore, the PCD of 4-CC on TiO₂ is little affected by the presence of the OH radical scavenger (TBA). This also indicates that the direct reaction of TBA with VB holes is insignificant under this experimental condition. Similarly, the direct reaction between POM* (PW₁₂³⁻) and TBA is known to be inefficient.³⁵ In this context, the results of Figure 3 support that the degradation of 4-CP and 4-CC in the POM solution is largely mediated by OH radicals, not by the direct electron transfer between POM* and substrates. This is contradictory to a previous report by Ozer and Ferry,³⁰ who concluded that POM-mediated photocatalytic oxidation of aqueous 1,2-dichlorobenzene takes place via an electron transfer mechanism rather than an OH radical mechanism on the basis of kinetic effects of added OH radical scavengers. On the other hand, in POM-mediated oxidation of tetrahydrothiophene in acetonitrile solution, where OH radical generation is not possible, the photoreactivity of PW₁₂³⁻ was completely absent regardless of the presence of O₂ whereas other POMs exhibited significant reactivities.¹¹ This seems to suggest that PW₁₂³⁻ particularly favors the OH radical mediated path in aqueous solutions. However, it should not be generalized that POM PCD reactions are mediated by OH radicals. Whether a specific PCD reaction follows an OH radical mediated path or a direct charge transfer path should depend on various experimental parameters (e.g., the kind of substrates and POMs, substrate concentration, and substrate–POM interaction) and should be understood on a case-by-case basis.

Photocatalytic Oxidation of Other Organic Compounds.

The homogeneous and heterogeneous PCD reactions were compared for eight organic compounds whose structures are quite different from one another and shown in Figures 4 and 5. The effects of TBA addition are shown as well. POM PCD reactions are generally slower than TiO₂ PCD reactions. In particular, DCA and formate degradation (Figure 4a,b) and their mineralization (see Table 1) are markedly slower with POM than with TiO₂. It should be also noted that the addition of TBA completely quenched the POM-mediated PCD reactions for all substrates tested, whereas the TBA effects on TiO₂ PCD reactions are different depending on the kind of substrates. This also strongly supports the fact that PW₁₂³⁻-mediated PCD reactions are initiated almost entirely by OH radicals. In addition, the POM-mediated degradation of methylammonium (a cationic substrate) whose interaction with PW₁₂³⁻ is electrostatically favored (hence the direct charge transfer path) was negligible, whereas its degradation on TiO₂ took place (data not shown). On the other hand, TiO₂ photocatalytic reactions can be initiated by either OH radicals or VB holes and the two paths are usually competing. In particular, when a substrate is strongly adsorbed on TiO₂ surface, the direct hole transfer path is favored. This is the case for formate and AO7 degradation on TiO₂ (Figure 4b,c), in which there is little (or no) TBA inhibition effect. The degradation of DCA and phenol on TiO₂ was partially inhibited in the presence of TBA, which implies that both OH radicals and VB holes are responsible for their PCD reactions. As for chlorinated methanes and ethenes (Figure 5), the TBA addition completely inhibited PCD reactions in both POM and TiO₂ solutions. Since these compounds have little affinity for TiO₂ surface and POM, their PCD reactions should be mainly mediated by OH radicals (not by direct charge transfer); hence the TBA inhibition is very efficient. In addition, the order of initial dechlorination rates among these compounds (PCE ~ TCE > CH₂Cl₂ > CHCl₃ in both POM and TiO₂ photocatalytic systems) is in agreement with the order of bimolecular rate constants with OH radicals (i.e., k_{OH} [M⁻¹ s⁻¹]: ³⁶ 2.6 × 10⁹ (PCE), 4.2 × 10⁹ (TCE), 5.8 × 10⁷ (CH₂Cl₂), 5 × 10⁶ (CHCl₃)), which also supports the OH radical mediated mechanism.

Photocatalytic Reduction on POM and TiO₂. Now we discuss the photoreduction activity of POM and TiO₂ photocatalysts. The photoreductive dechlorination (reactions 5–8) of CCl₄^{37,38} and TCA²⁵ in the presence of POM or TiO₂ was tested as probe reactions and the results are compared in Figure 6.



The reactions were carried out in the presence of excess 2-propanol as an electron donor (reaction 2) to ensure photoreductive conditions.²⁵ Therefore, a possible photooxidative path of TCA degradation (reactions 9 and 10)^{19,39} can be excluded.



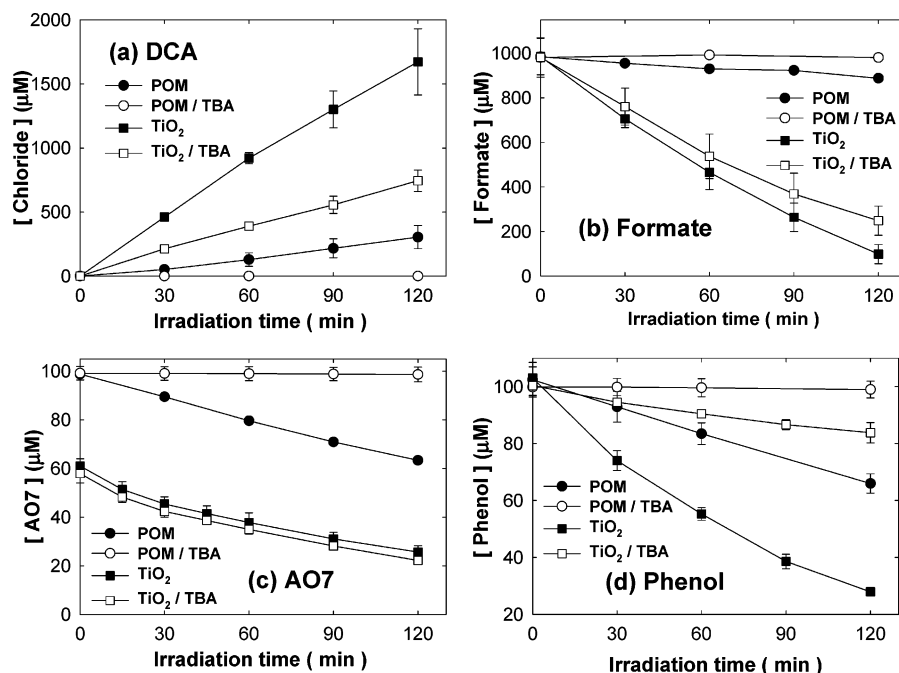


Figure 4. Comparison of POM- and TiO₂-induced PCD of (a) DCA (1 mM), (b) formate (1 mM), (c) AO7 (0.1 mM), and (d) phenol (0.1 mM) in air-equilibrated solutions of POM (pH 1) or TiO₂ (pH 3) and effects of TBA (10 mM) addition.

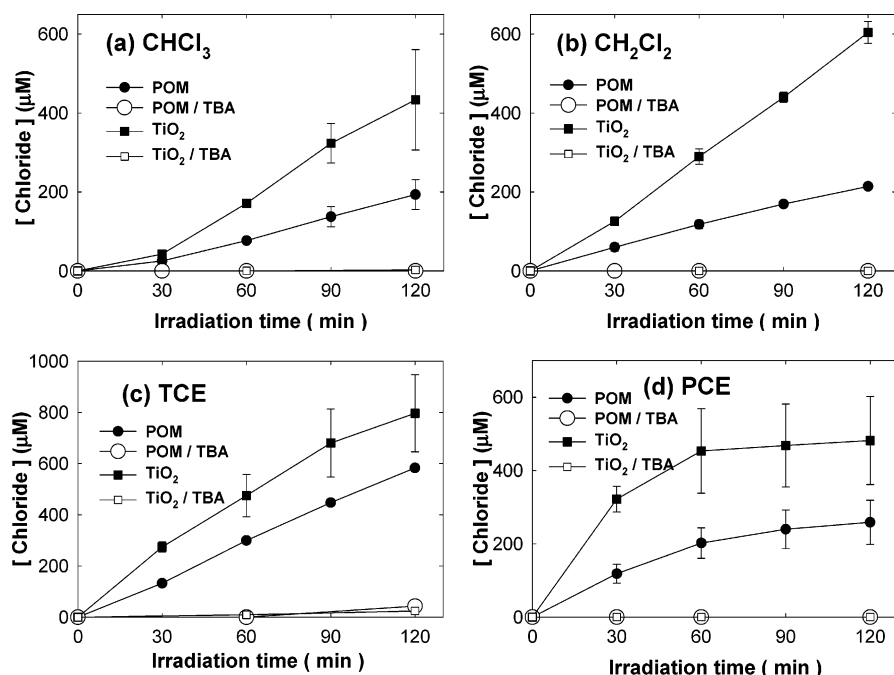


Figure 5. Comparison of the POM- and TiO₂-induced PCD (chloride production) of (a) CHCl₃ (1 mM), (b) CH₂Cl₂ (1 mM), (c) trichloroethylene (TCE, 0.83 mM), and (d) perchloroethylene (PCE, 0.24 mM) in air-equilibrated solutions of POM (pH 1) or TiO₂ (pH 3) and effects of TBA (10 mM) addition.

An alternative dechlorination path through the reaction of 2-propanol radical might be also involved (reactions 11 and 12).^{37,38}

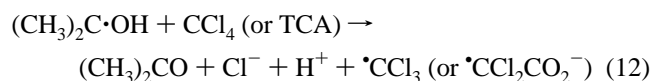


Figure 6 shows that the POM-mediated photoreductive dechlorination is negligibly slow in both air-equilibrated and

N₂-saturated solutions, whereas the TiO₂-mediated dechlorination is markedly faster.

The electron transfer from POM⁻ to electron acceptors can be easily monitored spectrophotometrically. POM was gradually reduced in the presence of 2-propanol (as an electron donor in reaction 2) under UV irradiation with accompanying blue coloring whose absorbance is maximal at 751 nm (*A*₇₅₁) (Figure 7a). A much slower increase in *A*₇₅₁ in pure water indicates that water oxidation by POM* (reaction 3) is inefficient but not completely negligible, which implies that reaction 3 is allowed to generate OH radicals in illuminated aqueous POM solutions. Subsequent reoxidation of reduced POM upon adding

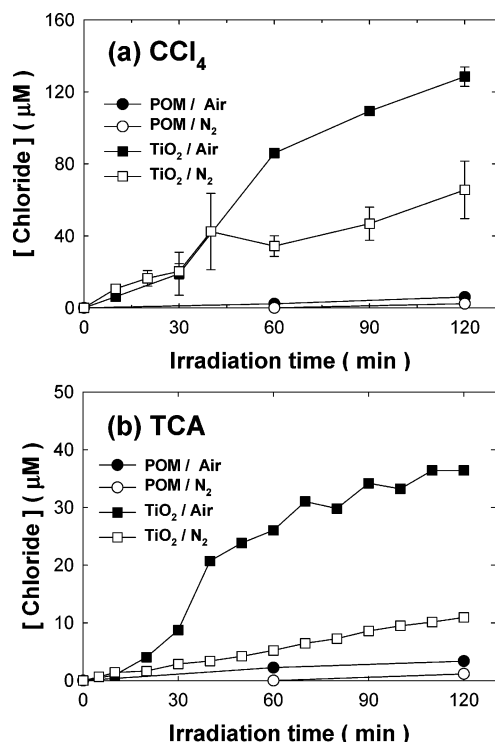


Figure 6. Chloride production from photoreductive degradation of (a) CCl₄ and (b) TCA in the presence of POM or TiO₂ photocatalyst. The experimental conditions were [CCl₄]₀ = [TCA]₀ = 0.1 mM, [2-propanol]₀ = 0.1 M (electron donor), pH_i = 1 (POM solution) or 3 (TiO₂ suspension), and air- or N₂-saturated.

various electron acceptors was followed by monitoring the decrease of A_{751} (Figure 7b). Tested electron acceptors include O₂, H₂O₂, TCA, CCl₄, Ag⁺, and Fe³⁺, all of which are known electron acceptors of CB electrons in TiO₂ photocatalysis. It has been also reported that aqueous metal ions can be rapidly reduced by POM⁻ to lower or zero oxidation states.⁴⁰ In agreement with the dechlorination data (Figure 6), the addition of TCA or CCl₄ (1 mM) did not reoxidize POM⁻ at all within 2 h, whereas adding 1 mM O₂, H₂O₂, Ag⁺, or Fe³⁺ rapidly reoxidized POM⁻ within 10 min. The POM-mediated dechlorination of CCl₄ under UV illumination and the subsequent reoxidation of POM⁻ by CCl₄ in the dark took place very slowly even with a much higher concentration of CCl₄ (5 mM) as shown in Figure 7c. The photodechlorination of CCl₄ and TCA was also tested with SiW₁₂⁴⁻, whose reduced form (SiW₁₂⁵⁻) has a higher reduction power than PW₁₂⁴⁻. The first two one-electron-reduction potentials are 0.22 and -0.025 V (vs NHE) for PW₁₂³⁻ and 0.054 and -0.204 V for SiW₁₂⁴⁻.⁴ Therefore, POM-mediated photoreductive reactions are more efficient and faster with SiW₁₂⁴⁻ than with PW₁₂³⁻. For example, the SiW₁₂⁵⁻-induced reduction of water (i.e., H₂ production) and the reoxidation of SiW₁₂⁵⁻ by O₂ were 25 and 87 times faster than that of PW₁₂⁴⁻, respectively.⁴¹ However, the reactivity of SiW₁₂⁵⁻ with CCl₄ and TCA was negligible as well (data not shown). The fact that the photoreductive dechlorination reactions of perchloro compounds in POM solutions are much slower than those on TiO₂ implies that the electron transfer from POM⁻ to reducible substrates is significantly slower than the rate of CB electron transfer on TiO₂, probably due to the strong electron affinity of the reduced POM. There could be a surface effect as well: the stabilization of radical species (e.g., •CCl₃) on TiO₂ surface may play a critical role in the overall reaction. For any reason, the differences between POM and TiO₂ photocatalysts are particularly prominent in photoreductive reactions.

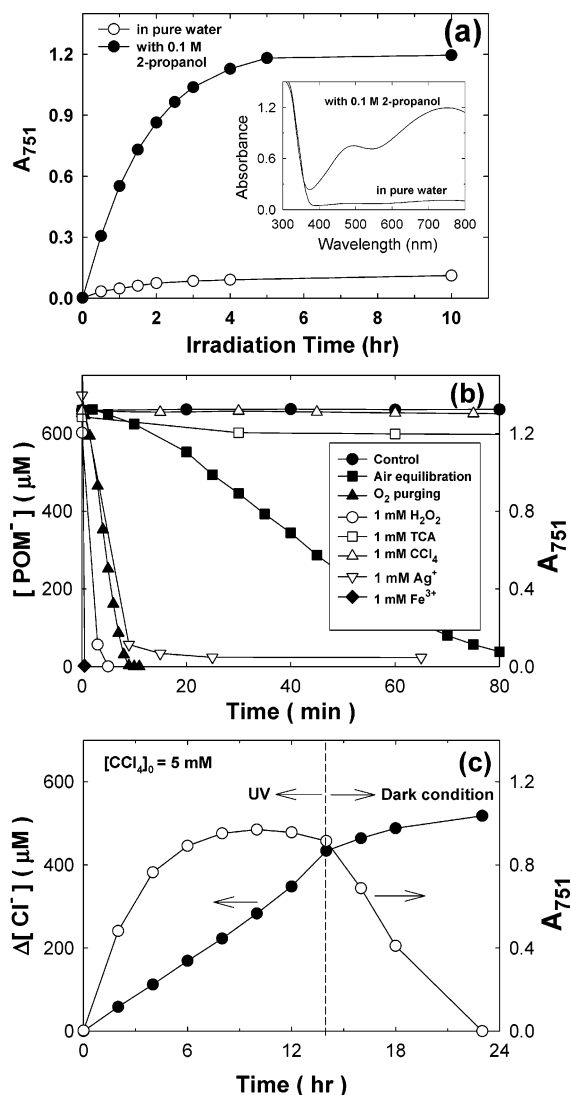
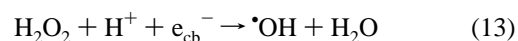


Figure 7. (a) Time profiles of photoproduction of POM⁻ (PW₁₂⁴⁻; monitored at absorbance of 751 nm, A_{751}) with and without 0.1 M 2-propanol (electron donor) in N₂-saturated aqueous solution. The inset shows the absorption spectra of the reduced POM after 10 h irradiation. (b) Time-dependent profiles of the dark reoxidation of POM⁻ in the presence of various electron acceptors (O₂, H₂O₂, CCl₄, TCA, Ag⁺, and Fe³⁺). (c) Chloride production from photoreductive degradation of CCl₄ (saturated, ~5 mM) and concurrent production and decay of POM⁻, which was followed by measuring A_{751} , in the presence of 2-propanol (0.1 M) at pH_i = 1.

Effect of H₂O₂. Since H₂O₂ seems to be an efficient electron acceptor in both PW₁₂³⁻ and TiO₂ photocatalytic systems, its effect on PCD reactions was tested. Figure 8 shows how the PCD rate of 4-CP is affected by the addition of H₂O₂ in the POM or TiO₂ system. The H₂O₂ addition to TiO₂ suspension increases the PCD rate to a maximum at [H₂O₂] = 10⁻² M, but further addition of H₂O₂ above this level decreases the efficiency. The fact that the addition of H₂O₂ to TiO₂ suspension enhances the PCD rates has been often reported⁴² and ascribed to its reaction with CB electrons (reaction 13) that not only generates additional OH radicals but also reduces the charge-pair recombination.



H₂O₂ is known to form a surface complex on TiO₂.⁴³ The reduced PCD rate in the presence of excess H₂O₂ can be ascribed

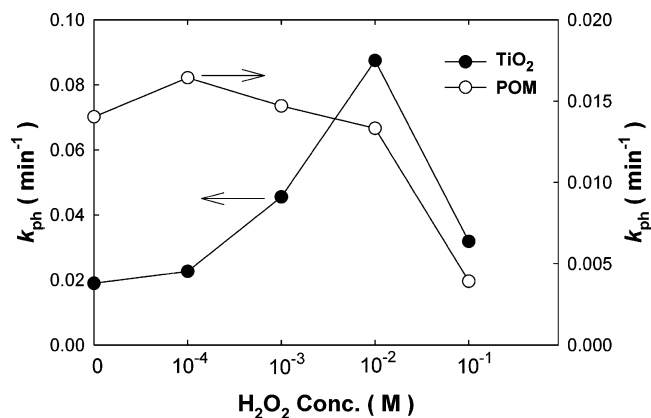
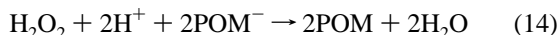


Figure 8. Effects of H_2O_2 addition on photocatalytic degradation rate constant (k_{ph}) of 4-CP in air-equilibrated solutions of POM (pH 1) or TiO_2 (pH 3).

to both the blocking of surface sites by H_2O_2 and the OH radical scavenging by H_2O_2 ($H_2O_2 + \cdot OH \rightarrow HO_2\cdot + H_2O$). A contribution from direct photolysis of H_2O_2 ($H_2O_2 + h\nu \rightarrow 2\cdot OH$) could be neglected under the present irradiation condition ($\lambda > 300$ nm) since the molar absorption coefficient of H_2O_2 is negligibly small (less than $1\text{ M}^{-1}\text{ cm}^{-1}$)⁴⁴ in this wavelength region. On the other hand, H_2O_2 addition to the POM solution shows little enhancement in the PCD rate. Although POM^- is rapidly reoxidized by H_2O_2 as shown in Figure 7b, its reaction with H_2O_2 does not seem to generate OH radicals (reaction 13) but to follow the two-electron-reduction path (reaction 14).



The data of Figure 2 and Figure 8 indicate that the presence of suitable electron acceptors such as O_2 and H_2O_2 is critical for TiO_2 PCD reactions, but not essential for POM PCD reactions mainly due to the electron accumulating property of POM. The interfacial electron transfer is a rate-determining step in TiO_2 photocatalysis, but it little affects the overall kinetics in POM photocatalysis as long as the catalyst regeneration by electron acceptors (e.g., O_2) is not rate-limiting. This should be taken as one of the most prominent differences between the two photocatalytic systems.

Surface Effects. Although the working mechanisms of POM and TiO_2 photocatalysts are similar in terms of photoinduced electron transfers, they significantly differ from each other in the availability of surface. The photocatalytic reaction pathways should critically depend on the surface interactions with substrates and intermediates. Modifying TiO_2 surface properties significantly changes the photocatalytic reaction kinetics and product distribution.^{3f,25,45–47} However, the interaction between POM and substrates is largely of a homogeneous nature and lacks heterogeneous surface effect. In general, the complete mineralization of organic compounds cannot be effectively achieved with the reaction of OH radicals alone. Stafford et al.⁴⁸ compared radiolytic (homogeneous) and TiO_2 photocatalytic (heterogeneous) degradation of 4-CP in aqueous solution and found that more hydroxylated aromatic intermediates such as 4-CC and HQ were produced in γ -radiolysis (under conditions favoring OH radical oxidation) than in TiO_2 suspension where the PCD reaction proceeds via a combination of OH radical oxidation and direct surface oxidation by VB holes. When 4-CP was oxidized through direct electron transfer by azide radicals in γ -radiolysis (under conditions that OH radicals were not available), no aromatic intermediates were detected. On the basis of this observation, they concluded that direct electron transfer

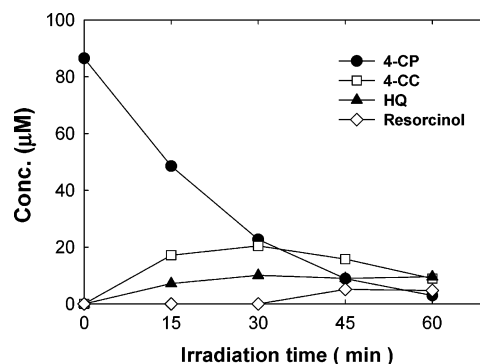


Figure 9. Photocatalytic degradation of 4-CP on surface-fluorinated TiO_2 (F- TiO_2) in the presence of 10 mM NaF. The suspension was air-equilibrated at pH 3.

and surface chemical reactions contribute significantly to the ring cleavage reaction of 4-CP in TiO_2 suspensions. This study that compares the 4-CP degradation between POM and TiO_2 photocatalytic systems might be similarly compared with the work of Stafford et al.⁴⁸ The POM-mediated degradation of 4-CP generates hydroxylated aromatic intermediates as main products like radiolysis, and is inefficient in achieving mineralization. If we adopt the conclusion by Stafford et al.,⁴⁸ our proposal that PW_{12}^{3-} -mediated degradation of 4-CP and other substrates is mainly mediated by OH radicals sounds more plausible. The unfavorable direct electron transfer between POM^* and substrates (reaction 2) might be ascribed to the lack of surface chemical interaction. In this situation, POM-mediated photocatalytic reaction converts 4-CP to hydroxylated intermediates whose further degradation is limited. On the other hand, TiO_2 photocatalysts on which degradation of intermediates is facilitated through direct hole transfers and surface chemical reactions produce fewer intermediates and achieve complete mineralization.

To investigate the effect of surface on PCD reactions in POM and TiO_2 systems, surface-fluorinated TiO_2 (F- TiO_2) and silica-immobilized POM (SiO₂-POM) were prepared and used as a photocatalyst in 4-CP degradation (Figures 9 and 10). F- TiO_2 is prepared through a simple ligand exchange between fluoride anions (F^-) and surface hydroxyl groups on TiO_2 in water (reaction 15).⁴⁶

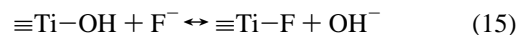


Figure 9 shows that the degradation of 4-CP and the concomitant formation of intermediates on F- TiO_2 are markedly different from those on naked TiO_2 (see Figure 2c). The 4-CP degradation rate with F- TiO_2 was faster, but more aromatic intermediates were produced. Previous studies have shown that the surface fluorination of TiO_2 enhances the OH radical mediated degradation (e.g., phenol⁴⁶ and tetramethylammonium⁴⁷ degradation) but inhibits the hole transfer mediated path on the contrary since the substrate adsorption or complexation is prohibited on F- TiO_2 .⁴⁹ The faster 4-CP degradation and more hydroxylated intermediates generation on F- TiO_2 implies that OH radical generation is enhanced but the direct hole transfer and surface chemical reactions are retarded on F- TiO_2 . In general, F- TiO_2 facilitates the OH radical mediated path but suppresses the direct hole transfer path. Therefore, it might be said that F- TiO_2 is closer to PW_{12}^{3-} in terms of PCD reaction mechanisms. The fact that the aromatic intermediates distribution was significantly altered by the presence of surface fluorides reaffirms the role of surface chemistry in TiO_2 PCD reactions.

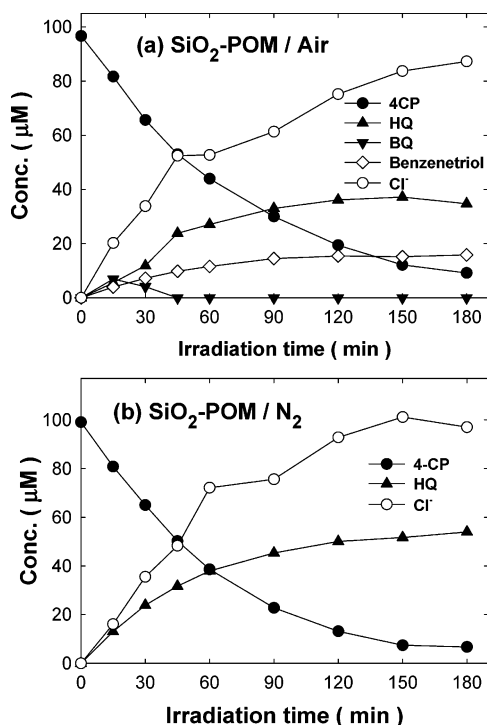


Figure 10. Photocatalytic degradation of 4-CP with PW_{12}^{3-} immobilized on silica particles ($\text{SiO}_2\text{-POM}$) in (a) air-equilibrated and (b) N_2 -saturated suspensions at pH 3. $[\text{SiO}_2\text{-POM}] = 0.5 \text{ g/L}$. The net concentration of POM in the $\text{SiO}_2\text{-POM}$ suspension corresponds to about $33 \mu\text{M}$.

Figure 10 shows the 4-CP degradation and intermediates production profiles in the $\text{SiO}_2\text{-POM}$ system. The POM concentration in 0.5 g/L $\text{SiO}_2\text{-POM}$ suspension corresponds to $34 \mu\text{M}$, whereas 1 mM POM concentration was used in homogeneous solutions. Compared with Figure 2a,b, it is noted that the 4-CP degradation rate in the heterogenized POM suspension is similar to that in the homogeneous POM solution despite a much lower POM content in $\text{SiO}_2\text{-POM}$. This implies that the surface interaction between silica support and 4-CP enhances the PCD rate and that the surface effect is important in POM-mediated reactions. As for the mineralization of 4-CP, however, $\text{SiO}_2\text{-POM}$ was as inefficient as homogeneous POM: the TOC reduction was less than 2% after 3 h irradiation in both air- and N_2 -saturated suspensions. The presence of a solid surface does not help achieve mineralization in POM-mediated PCD. On the other hand, the intermediates distribution is quite different between the homogeneous and heterogenized POM photocatalytic systems. Although it has been previously reported that POM immobilized on solid supports such as silica and zeolite induced faster PCD reactions than POM alone,^{17,50} the effect of solid supports on product distribution has not been recognized before. Whereas 4-CC was a main intermediate generated in POM solution, its production was completely absent with $\text{SiO}_2\text{-POM}$. It was not due to 4-CC adsorption on the silica support since it has little affinity to SiO_2 surface. The production of 1,2,4-benzenetriol was detected with $\text{SiO}_2\text{-POM}$ photocatalyst in air-equilibrated solution, but not in N_2 -saturated solution. Although the detailed molecular mechanism that controls the product distribution is unknown, this clearly shows that the introduction of solid support surface changes the surface chemistry and alters the reaction path of POM-mediated PCD.

Conclusions

By performing a comprehensive comparative study of homogeneous PW_{12}^{3-} and heterogeneous TiO_2 photocatalysts, we

are able to understand the similarities and differences between them. PW_{12}^{3-} and TiO_2 are similar in UV absorption onset, their initiation mechanisms that are based on photoinduced charge transfers, and the involvement of OH radicals as a main photooxidant, all of which are known from previous studies. However, this study reveals that they are very different in many aspects. First of all, POM-mediated PCD of 4-CP is much slower than TiO_2 photocatalysis in achieving mineralization whereas the removal rates of the parent substrate are comparable. The presence of dissolved O_2 is essentially required in TiO_2 -mediated PCD, but not in POM-mediated PCD as long as the POM regeneration by O_2 is not a rate-limiting step. Second, TiO_2 PCDs are mediated by either OH radicals or direct hole transfers or the combination of both, depending on the kind of substrates and the substrate-surface interactions. On the other hand, OH radicals seem to be the sole dominant photooxidant in PW_{12}^{3-} -mediated PCDs regardless of the kind of substrates under the present experimental conditions. However, the direct charge transfer path should be important when the substrate-POM interaction is significant. Third, for photoreductive reactions, the differences between POM and TiO_2 are outstanding. The electron transfer from POM^- to reducible substrates (e.g., CCl_4 and TCA) is significantly slower than the rate of CB electron transfer on TiO_2 , probably due to the strong electron affinity of POM. The effects of H_2O_2 addition on 4-CP photodegradation are also markedly different between POM and TiO_2 photocatalytic systems. Finally, this study suggests that surface chemical reactions of substrates and intermediates, which are absent in POM reactions, play an important role in PCD reactions. The importance of surface effects in POM- and TiO_2 -mediated PCDs was demonstrated by carrying out PCD reactions of 4-CP using $\text{SiO}_2\text{-POM}$ and F-TiO_2 . Introduction of solid support surface in POM and surface fluorination of TiO_2 significantly changed the kinetics and intermediate distribution.

POMs as an alternative photocatalyst have received much interest mainly due to their apparent similarity to semiconductor photocatalysts. Development of POM-based photocatalytic technologies and the possible substitution of POMs for semiconductor photocatalysts require proper understanding of their characteristics. Detailed kinetic and mechanistic comparisons between PW_{12}^{3-} and TiO_2 in this work should provide valuable knowledge in this respect. However, it should be kept in mind that a specific conclusion obtained from this study may not be generalized since POM-mediated PCD kinetics and mechanisms could be dependent on the kind of POMs and reactants and reaction conditions.

Acknowledgment. This work was supported by KOSEF (Grant R01-2003-000-10053-0) and partly by the Center for Integrated Molecular Systems (CIMS).

References and Notes

- (1) Hoffmann, M. R.; Martin, S. T.; Choi, W.; Bahnemann, D. W. *Chem. Rev.* **1995**, *95*, 69.
- (2) *Photocatalytic Purification and Treatment of Water and Air*; Ollis, D. F., Al-Ekabi, H., Eds.; Elsevier: Amsterdam, 1993.
- (3) (a) Choi, W.; Hong, S. J.; Chang, Y.-S.; Cho, Y. *Environ. Sci. Technol.* **2001**, *34*, 4810. (b) Choi, W.; Ko, J. Y.; Park, H.; Chung, J. S. *Appl. Catal. B* **2001**, *31*, 209. (c) Kim, S.; Choi, W. *Environ. Sci. Technol.* **2002**, *36*, 2019. (d) Lee, H.; Choi, W. *Environ. Sci. Technol.* **2002**, *36*, 3872. (e) Lee, M. C.; Choi, W. *J. Phys. Chem. B* **2002**, *106*, 11818. (f) Hwang, S.; Lee, M. C.; Choi, W. *Appl. Catal. B* **2003**, *46*, 49. (g) Choi, W.; Lee, J.; Kim, S.; Hwang, S.; Lee, M. C.; Lee, T. K. *J. Ind. Eng. Chem.* **2003**, *9*, 96.
- (4) Papaconstantinou, E. *Chem. Soc. Rev.* **1989**, *18*, 1.
- (5) Maldotti, A.; Amadelli, R.; Varani, G.; Tollari, S. P. F. *Inorg. Chem.* **1994**, *33*, 2968.
- (6) Mylonas, A.; Papaconstantinou, E. *Polyhedron* **1996**, *15*, 3211.

- (7) Hiskia, A.; Ecke, M.; Troupis, A.; Kokorakis, A.; Hennic, H.; Papaconstantinou, E. *Environ. Sci. Technol.* **2001**, *35*, 2358.
- (8) Ozer, R. R.; Ferry, J. L. *Environ. Sci. Technol.* **2001**, *35*, 3242.
- (9) Yoon, M.; Chang, J. A.; Kim, Y.; Choi, J. R.; Kim, K.; Lee, S. J. *J. Phys. Chem. B* **2001**, *105*, 2539.
- (10) Park, H.; Choi, W. *J. Phys. Chem. B* **2003**, *107*, 3885.
- (11) Chambers, R. C.; Hill, C. L. *Inorg. Chem.* **1991**, *30*, 2776.
- (12) Texier, I.; Giannotti, C.; Malato, S.; Richter, C.; Delaire, J. *Catal. Today* **1999**, *54*, 297.
- (13) Texier, I.; Ouazzani, J.; Delaire, J.; Giannotti, C. *Tetrahedron* **1999**, *55*, 3401.
- (14) Texier, I.; Delaire, J. A.; Giannotti, C. *Phys. Chem. Chem. Phys.* **2000**, *2*, 1205.
- (15) Hiskia, A.; Mylonas, A.; Papaconstantinou, E. *Chem. Soc. Rev.* **2001**, *30*, 62.
- (16) Antonaraki, S.; Androulaki, E.; Dimotikali, D.; Hiskia, A.; Papaconstantinou, E. *J. Photochem. Photobiol. A: Chem.* **2002**, *148*, 191.
- (17) Yue, B.; Xhou, Y.; Xu, J.; Wu, Z.; Zhang, X.; Zou, Y.; Jin, S. *Environ. Sci. Technol.* **2002**, *36*, 1325.
- (18) Androulaki, E.; Hiskia, A.; Dimotikali, D.; Minero, C.; Calza, P.; Pelizzetti, E.; Papaconstantinou, E. *Environ. Sci. Technol.* **2000**, *34*, 2024.
- (19) Mylonas, A.; Hiskia, A.; Papaconstantinou, E. *J. Mol. Catal. A: Chem.* **1996**, *114*, 191.
- (20) Chen, C.; Lei, P.; Ji, H.; Ma, W.; Zhao, J.; Hidaka, H.; Serpone, N. *Environ. Sci. Technol.* **2004**, *38*, 329.
- (21) Mylonas, A.; Papaconstantinou, E. *J. Photochem. Photobiol. A* **1996**, *94*, 77.
- (22) In refs 18, 19, and 21, the light intensity (normalized per unit reaction volume) employed in photolysis experiments was very different from ours: the authors used much higher light intensity (4 mL solution irradiated with 1000-W Xe arc lamp) than that in our experiments (100 mL solution irradiated with 300-W Xe arc lamp). The light intensity dependence of photoreactivities seems to be quite different between POM and TiO₂ photocatalysts.
- (23) It is well recognized that TiO₂ samples exhibit widely varying photocatalytic reactivities depending on commercial providers or preparation methods. No specific information about the TiO₂ sample they used is available from ref 19.
- (24) Gerischer, H.; Heller, A. *J. Phys. Chem.* **1991**, *95*, 5261.
- (25) Kim, S.; Choi, W. *J. Phys. Chem. B* **2002**, *106*, 13311.
- (26) Hiskia, A.; Papaconstantinou, E. *Inorg. Chem.* **1992**, *31*, 163.
- (27) Cermenati, L.; Pichat, P.; Guillard, C.; Albini, A. *J. Phys. Chem. B* **1997**, *101*, 2650.
- (28) Ryu, J.; Choi, W. *Environ. Sci. Technol.* **2004**, *38*, 2928.
- (29) Troupis, A.; Hiskia, A.; Papaconstantinou, E. *New J. Chem.* **2001**, *25*, 361.
- (30) Ozer, R. R.; Ferry, J. L. *J. Phys. Chem. B* **2000**, *104*, 9444.
- (31) Yamase, T.; Kurozumi, T. *J. Chem. Soc., Dalton Trans.* **1983**, 2205.
- (32) Fox, M. A.; Dulay, M. T. *Chem. Rev.* **1993**, *93*, 341.
- (33) For example, with the present experimental conditions and the literature rate constants ($k(\text{TBA}+\cdot\text{OH}) = 6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, $k(4\text{-CP}+\cdot\text{OH}) = 7.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$; $[\text{TBA}] = 10^{-2} \text{ M}$, $[4\text{-CP}] = 10^{-4} \text{ M}$), we calculate that 89% of free OH radicals should be scavenged by TBA.
- (34) Martin, S. T.; Kesselman, J. M.; Park, D. S.; Lewis, N. S.; Hoffmann, M. R. *Environ. Sci. Technol.* **1996**, *30*, 2535.
- (35) Dimotikali, D.; Papaconstantinou, E. *Inorg. Chim. Acta* **1984**, *87*, 177.
- (36) Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1988**, *17*, 513.
- (37) Choi, W.; Hoffmann, M. R. *Environ. Sci. Technol.* **1995**, *29*, 1646.
- (38) Sattari, D.; Hill, C. L. *J. Chem. Soc., Chem. Commun.* **1990**, 634.
- (39) Hori, H.; Takano, Y.; Koike, K.; Takeuchi, K.; Einaga, H. *Environ. Sci. Technol.* **2003**, *37*, 418.
- (40) Troupis, A.; Hiskia, A.; Papaconstantinou, E. *Angew. Chem., Int. Ed.* **2002**, *41*, 1911.
- (41) Akid, R.; Darwent, J. R. *J. Chem. Soc., Dalton Trans.* **1985**, 395.
- (42) Auguliaro, V.; Davi, E.; Palmisano, L.; Schiavello, M.; Sclafani, A. *Appl. Catal.* **1990**, *65*, 101.
- (43) Boonstra, H.; Mutsaers, C. H. A. *J. Phys. Chem.* **1975**, *79*, 1940.
- (44) Pignatello, J. J. *Environ. Sci. Technol.* **1992**, *26*, 944.
- (45) Lee, J.; Park, H.; Choi, W. *Environ. Sci. Technol.* **2002**, *36*, 5462.
- (46) Minero, C.; Mariella, G.; Maurino, V.; Pellizzetti, E. *Langmuir* **2000**, *16*, 2632.
- (47) Vohra, M. S.; Kim, S.; Choi, W. *J. Photochem. Photobiol. A: Chem.* **2003**, *160*, 55.
- (48) Stafford, U.; Gray, K. A.; Kamat, P. V. *J. Phys. Chem.* **1994**, *98*, 6343.
- (49) Park, H.; Choi, W. *J. Phys. Chem. B* **2004**, *108*, 4086.
- (50) Ozer, R. R.; Ferry, J. L. *J. Phys. Chem. B* **2002**, *106*, 4336.