

Photocatalytic Degradation of Aqueous 4-Chlorophenol by Silica-Immobilized Polyoxometalates

BIN YUE,* YAN ZHOU, JINGYU XU, ZHUZHI WU, XUAN ZHANG, YEFEN ZOU, AND SONGLIN JIN

Department of Chemistry, Fudan University, Shanghai 200433, China

The degradation of 4-chlorophenol with near-UV light by silica-immobilized polyoxometalate (POM-in-SiO₂) catalysts has been studied. The silica-immobilized Na₆W₇O₂₄ (SW7), H₄W₁₀O₃₂ (SW10), H₃PW₁₂O₄₀ (SPW12), and H₆P₂W₁₈O₆₂ (SP2W18) were prepared by means of the sol-gel hydrothermal technique through the hydrolysis of tetraethoxysilane in aqueous solution of the corresponding polyoxometalate, respectively. The degradation of 4-chlorophenol was monitored by measuring Cl⁻ and CO₂ concentrations and analyzing reaction intermediates by GC/MS analysis. During irradiation, 4-chlorophenol first dechlorinated to form hydroquinone and *p*-benzoquinone, and then these intermediates further mineralized to form CO₂ and H₂O. The degree to which 4-chlorophenol was mineralized by photocatalytic oxidation was investigated. Results indicate less than 15% for SW7 but nearly complete mineralization for SW10 after 60 min of photoradiation. The present studies suggest that POM-in-SiO₂ catalysts may be a novel type of photocatalysts for the purification of the environmentally chlorophenol-contaminated water.

Introduction

The increasing contamination of land, water, and air has raised serious environmental problems (1, 2). To reduce the impact of environmental pollution, many efforts have been made in two directions: green industry and purification technology.

Among the top priority pollutants, chlorophenols represent an important class of environmental water pollutants (3, 4). Most chlorophenolic compounds present in wastewaters mainly arise from chemical intermediates or byproducts in petrochemical, paper making, plastic, pesticidal, and insecticidal industries and also the conventional drinking water disinfection (5, 6). Various methods have been used to degrade these organic compounds by chemical, photochemical, and microbiological processes (7–9), of which photocatalytic degradation of chlorophenols over semiconductor oxides (e.g., TiO₂, ZnO, and WO₃) in aqueous dispersions seems to be quite effective (10–13). However, the post-treatment removal requires the costly liquid–solid separation, which is due to the formation of fine milky dispersions of the catalysts during irradiation (2, 14). To improve the mechanical resistance of the catalysts to the erosion and disaggregation, many studies have been carried

out on the modification of the semiconductor oxides surface structure by being supported on another metal oxides or using in the fixed-bed systems (15–17). However, the negative effect on the photocatalytic activity is often observed in some of these cases. Another approach to solve this problem is to find novel active photocatalysts (18–20).

Polyoxometalates (POMs) are widely used as oxidation catalysts as well as acid catalysts (21). They are also employed as effective homogeneous photocatalysts in the oxidation of organics, which is due to the ability of POMs acting as electron and oxygen relays (22). On the other hand, it is often stated that there are a number of similarities between POMs and semiconductor metal oxides. The photochemistry of POMs can be regarded as a model for the photochemical processes on semiconductor metal oxide surfaces (23). Recently, several groups reported that the homogeneous photocatalytic degradation of organic pollutants in water by W₇O₂₄⁶⁻, W₁₀O₃₂⁴⁻, PW₁₂O₄₀³⁻, and P₂W₁₈O₆₂⁶⁻ is a very efficient process (24, 25). However, in the view of application, to develop such photocatalytic process in a heterogeneous system will certainly be potentially useful for water purification (26, 27).

In the present study, the representative POMs (namely, W₇O₂₄⁶⁻, W₁₀O₃₂⁴⁻, PW₁₂O₄₀³⁻, and P₂W₁₈O₆₂⁶⁻) were immobilized into a silica matrix through the sol-gel hydrothermal technique. POM-in-SiO₂ solids were insoluble and readily separable microporous materials with a large surface area and a shape pore-size distribution. These solids present absorption bands in the region of 190–410 nm in UV-Vis diffuse reflectance spectra. The photocatalytic activity of these four solids was tested using 4-chlorophenol degradation in aqueous dispersions as a probe reaction by the irradiation of near-UV light under aerobic conditions. 4-POBN spin trap ESR spectra indicate that the generation of •OH radicals during irradiation is responsible for the oxidation of the organic substrates. The degree of mineralization is relevant to the POM structures. SW10 shows the highest activity, and complete mineralization can be observed after 60 min in the SW10 dispersion.

Experimental Section

Chemicals. Tetraethoxysilane ([OC₂H₅]₄Si) 12-tungstophosphoric acid (H₃PW₁₂O₄₀), and 4-chlorophenol purchased from Kanto Chemical Co. were used without further purification. (α-(4-Pyridyl 1-oxide)-*N*-tert-butyl)nitron, 4-POBN, was purchased from Aldrich Chemical Co. Na₂WO₄·2H₂O and H₃-PO₄ were purchased from Shanghai Feida Co. Deionized and doubly distilled water was used throughout. Na₆W₇O₂₄·21H₂O (28), H₄W₁₀O₃₂ (29), and H₆P₂W₁₈O₆₂ (30) were prepared according to the literature methods.

Preparation and Characterization of the Catalysts. Silica-immobilized polyoxometalates were prepared by the sol-gel hydrothermal method. The details of a typical preparation is as follows: a mixture of water (0.2 mol), 1-butanol (0.02 mol), and POM (1.0 × 10⁻⁴ mol, POM = Na₆W₇O₂₄, H₄W₁₀O₃₂, H₃PW₁₂O₄₀, and H₆P₂W₁₈O₆₂) was added into tetraethoxysilane (0.02 mol) and stirred at 80 °C for 3 h. The resulting hydrogel and an additional 5 cm³ of water were placed in a 15-cm³ sealed 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 (20 Torr). To remove the surplus POM and organics, the solid product was ground, extracted with water at 80 °C for 3 h, and then dried at 150 °C for 24 h in vacuo (20 Torr). The XRD patterns of the catalysts were collected at room temperature on a Rigaku RINT 2000/PC X-ray diffractometer using monochromatized Cu Kα radia-

* Corresponding author phone: +86-21-6564-2779; fax: +86-21-6511-7829; e-mail: ymtianc@online.sh.cn.

tion. The molar ratio of W/Si was measured on a JEDL JSX-3200 EDX spectrometer. Surface area and pore sizes distribution were measured by the BET method using nitrogen adsorption at 77.5 K on a BELSORP 28SA automatic gas adsorption apparatus. The FT-IR spectra were taken on a JASCO FT/IR-5000 spectrophotometer, using KBr pellets. UV-Vis diffuse reflectance spectra (DRS) in the wavelength range of 190–500 nm were recorded on a JASCO V-570 UV/VIS/NIR spectrophotometer.

Photocatalysis and Analyses. A GGY 125-W medium pressure mercury lamp in conjunction with a Pyrex water jacket was used as the light source, and a cutoff filter was placed around the lamp to remove radiation below 350 nm. The jacket was surrounded by the magnetically stirred sample solution of optical path length of about 2 cm. Cooling water was circulated through the jacket to keep the temperature of the sample solution at 305 ± 2 K during the photoirradiation. In a typical run for photocatalytic degradation of 4-chlorophenol, the aqueous suspension was prepared by adding a certain amount of the silica-immobilized POM powder (containing [POM] = 3.0×10^{-4} M) to 100 mL of an aqueous 4-chlorophenol solution ([4-chlorophenol] = 2.0×10^{-3} M) without adjusting pH values. (The pH value of the dispersions is determined by the dissociation of 4-chlorophenol and hydroxylation of the catalyst surface before reaction and decreases with increasing concentration of HCl formed during irradiation.) Prior to irradiation, the suspensions were magnetically stirred in the dark for 1 h to ensure establishment of an adsorption/desorption equilibrium of 4-chlorophenol on the surface of the catalyst. During irradiation, the dispersion was vigorously stirred and aerated by bubbling with air. At various intervals, 3-mL aliquots were taken from the photolyte, centrifuged, and then filtered with a Millipore membrane (0.22 μ m pore diameter) to remove the solid particulates. Cr was analyzed by the selective Cl⁻ electrode (Cl-125B, TOA Electronic Ltd.) with reference to platinum electrode on TOA ion meter (IM-5S). The filtrates were extracted three times with 20 cm³ of anhydrous ethyl ether and concentrated to 5 cm³ by evaporation of solvent in rotary evaporator. The organic intermediates were identified by HP 6890/5973 GC/MS (HP Inc.) equipped with ECD and FID. The concentrations of reactant and intermediates were determined with a GC 353B (GL Science, Inc.) equipped with 19% OV 10180/100 Supelcoport column and FID by comparison with the standard samples. The formation of the end product CO₂ during photocatalysis was monitored using a conductivity method previously reported (31, 32).

A Bruker ER200D-SRC spectrometer was used to measure the paramagnetic species formed during irradiation of the 4-chlorophenol dispersion (2.0×10^{-3} M) containing 0.5 g of SW10 particles with 4-POBN (0.1 M). In this case, a W-Germany Hereavs mercury lamp with a cutoff filter ($\lambda > 350$ nm) was used as the irradiation source. The photolysis cell containing the sample dispersion was inserted into the resonant cavity fitted for the ESR spectrometer. The settings for ESR measurement were microwave, 20 mW; microwave frequency, 9.81 GHz; modulation frequency, 12.5 kHz; modulation unit, 0.08 mT.

Under anaerobic conditions, prior to photoirradiation, the deaeration of the photolytes was carried out by bubbling with Ar for 2 h. ESR spectra of the frozen dispersions of the colored particles were recorded using the spectrometer above.

Results and Discussion

Characterization of Silica-Included POMs. The results for chemical and physical analyses of silica-immobilized POM (POM-in-SiO₂) samples are summarized in Table 1. As it was already pointed out, a POM-in-SiO₂ sample prepared by the sol-gel method showed a considerable extraction of POM

TABLE 1. Physical Characterization of Silica-Included POM Samples

sample	POM content (wt %)		BET surface area (m ² g ⁻¹)	median pore size (nm)
	calcd ^a	found ^b		
SiO ₂			645	0.57
SW7	11.1	10.1	407	0.54
SW10	15.8	13.7	381	0.68
SPW12	19.3	14.3	326	0.60
SP2W18	26.6	18.5	275	0.63

^a Wt % calculated from the amounts of reagents charged at the preparation. ^b Wt % determined through EDX analysis.

by hot water (33–35). In contrast, the one prepared by a sol-gel method containing hydrothermal post-treatment in the present work shows a small extraction of POM by hot water. The BET results indicate that POMs-in-SiO₂ is a novel kind of microporous materials with well-distributed micropores, which is important to catalytic reaction. The surface area of POM-in-SiO₂ decreases in comparison with SiO₂, implying that the inclusion of POM into SiO₂ matrix results in diminution of the porosity of SiO₂ or increases in the particle dimension.

FT-IR bands of POM-in-SiO₂ in the POM fingerprint region of 400–1200 cm⁻¹ are listed in Table 2. The spectrum of SiO₂ shows two bands at 1100 and 817 cm⁻¹, which were assigned to Si–O–Si and Si–O stretching modes, while the band at 466 cm⁻¹ was assigned to a Si–O bonding vibration (39). In the spectra of POM-in-SiO₂ samples, most of the characteristic bands of POM appear with slight shifts as compared to those of parent POM, although the bands are superimposed to SiO₂ bands. Thus, it is concluded that the POM structures remain stable after immobilizing in SiO₂ matrix and that the shifts of bands account for the interaction between POM and SiO₂ matrix (40).

The XRD patterns of POM-in-SiO₂ show no characteristic reflections of POM, but two humps centered around $2\theta = \sim 10^\circ$ and $\sim 25^\circ$ appear, which indicate that the POM-in-SiO₂ samples are amorphous and suggest the fine dispersion of POM within the silica matrix.

In Figure 1, UV-Vis DRS of the POM-in-SiO₂ samples are shown. The band gaps of the samples are estimated from the spectra. The data with that of the parent POM solid samples are also shown in Table 2. A red shift in the band gap of 0.06–0.16 eV is observed when compared to the parent POM. The difference of the band gap between SiO₂-in-POM and the parent POM may be due to a considerable increase in the particle dimension (41). The absorption bands can be attributed to the oxygen to metal (O→W) charge transfer (42), and the position of the absorption peaks has a slight change before and after POM immobilized within SiO₂ matrix.

Photocatalytic Degradation of 4-Chlorophenol in Aqueous Dispersions. After POM-in-SiO₂ catalyst with organic substrate was mixed in the dark under aerobic conditions for 24 h, Cl⁻ cannot be detected whereas the concentration of 4-chlorophenol reduces ca. 10–21% in different POM-in-SiO₂ catalysts, which is due to adsorption of the reactant molecules on/into the surface and pores of the catalyst. In the absence of POM-in-SiO₂, less than 5% of dechlorination conversion and no apparent mineralization can be observed after 4 h of irradiation of the 4-chlorophenol solutions.

The typical time course of photocatalytic degradation over SW10 is shown in Figure 2a. The photocatalytic dechlorination is a relatively rapid reaction. The concentration of Cl⁻ in solution shows that the dechlorination conversion of 4-chlorophenol is 95% after 30 min of irradiation, whereas the amount of CO₂ is only equivalent to 67% conversion. These results suggest the involvement of several intermediates. As indicated in Figure 2b, irradiation of the dispersion

TABLE 2. FTIR Bands (400–1200 cm⁻¹), Band Gaps, and Absorption Peaks of SiO₂-in-POMs

sample	IR (cm ⁻¹)					band gap (eV)	
Na ₆ W ₇ O ₂₄ (36)	960	945	925	910	890	3.55	250 (sh)
SW7	850	665	580	490	415	3.45	252 (sh)
	962	— ^b	920	— ^b	890		
H ₄ W ₁₀ O ₃₂	850	670	— ^b	485	— ^b	3.23	320
	975	810	580	445	— ^b	3.07	263 (sh)
SW10	978	805	572	— ^b	— ^b	3.42	324
H ₃ PW ₁₂ O ₄₀ (37)	1080	982	890	810	— ^b	3.36	265
SPW12	1084	965	880	— ^b	— ^b	3.38	268
H ₆ P ₂ W ₁₈ O ₆₂ (38)	1091	963	911	778	— ^b	3.23	301
	SP2W18	1090	954	900	— ^b	3.23	250 (sh)

^a Only the characteristic vibration bands of POM are shown. ^b The band is masked by the bands of SiO₂.

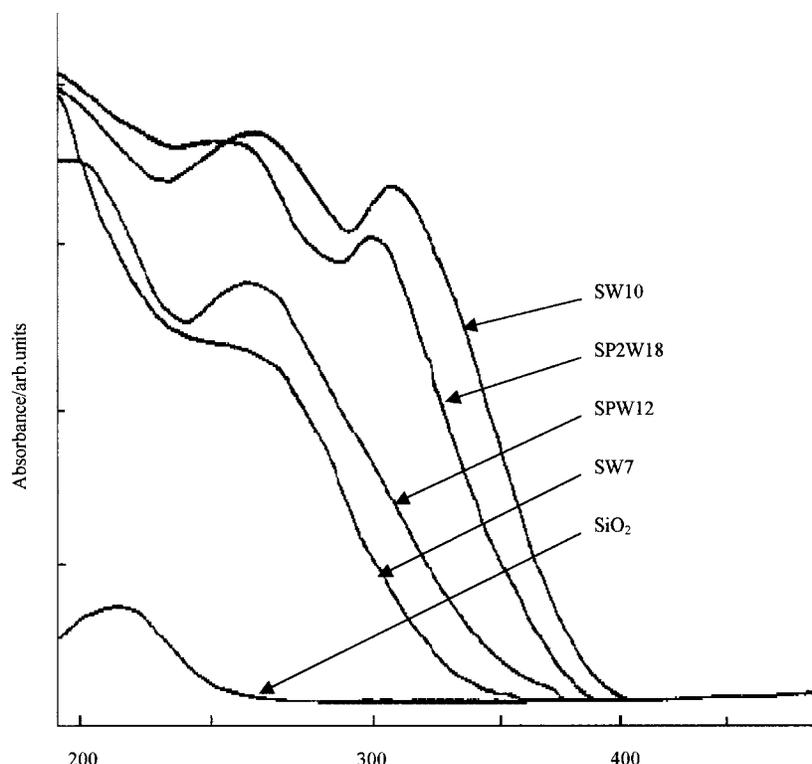


FIGURE 1. UV-Vis DRS of SiO₂-in-POM samples with bulk SiO₂.

first shows the fast dechlorination of 4-chlorophenol to yield hydroquinone and *p*-benzoquinone with other minor intermediates and then further mineralization of these intermediates to the end product CO₂. During the degradation processes, the total content of the minor intermediates, except quinol and quinone, is estimated less than ca. 2% after balance of the amount of chloride, carbon dioxide, quinol, and quinone formed with that of 4-chlorophenol disappeared.

Figure 3 shows the results of dechlorination and mineralization during 30 min of irradiation over the heterogeneous POM-in-SiO₂ dispersions as compared with the homogeneous systems of the parent POM and in the presence of bulk SiO₂ and in the absence of catalyst. In the homogeneous systems, W₁₀O₃₂⁴⁻ has the highest activity and W₇O₂₄⁶⁻ has the lowest. The activity of various POM in the reaction follows the order of H₄W₁₀O₃₂ > H₆P₂W₁₈O₆₂ > H₃PW₁₂O₄₀ > Na₆W₇O₂₄. The bulk SiO₂ shows little activity for dechlorination or mineralization of 4-chlorophenol as very little Cl⁻ and CO₂ was formed, which is similar to the case of direct photolysis in the absence of catalyst above. Therefore, SiO₂ is photoinsensitive (26), and the active species is POM in the SiO₂-in-POM catalyst although the microporous silica framework plays a profound and important role for the

reaction. The order of absorption intensity of POM-in-SiO₂ samples in the irradiation region (λ > 350 nm) is SW10 > SP2W18 > SPW12 > SW7, which is the same as the activity observed for the POM-in-SiO₂ catalysts. In the case of SW10, the nearly complete mineralization is observed after 60 min of irradiation. As a heterogeneous catalyst with high specific surface area and well-distributed micropores, POM-in-SiO₂ has the ability for adsorption of both reactants (organic molecules and solvated oxygen) on the surface of the catalyst. The silica matrix of POM-in-SiO₂ provides the active sites (POM) bound to the adsorbed phase, which may be mainly responsible for the highly photocatalytic activity in comparison with the corresponding homogeneous system.

Separation, Recovery, and Reuse of POM-in-SiO₂. After the reaction finished, the POM-in-SiO₂ catalysts can be recovered by decanting from the dispersions in ca. 30 min of sedimentation. The recovered POM-in-SiO₂ catalysts were washed with water and recovered by filtering for the next degradation run. Deactivation of POM-in-SiO₂ was hardly observed, and the leakage of POM was less than 2% after five cycles, indicating the mechanical resistance of the silica-immobilized POM catalysts to the erosion and disaggregation during photoirradiation. Also, the measurements of FT-IR

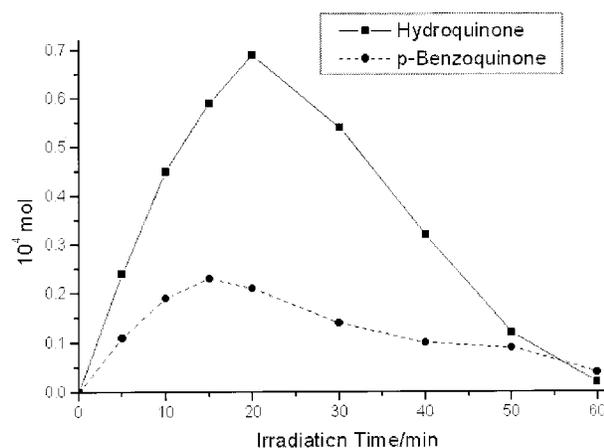
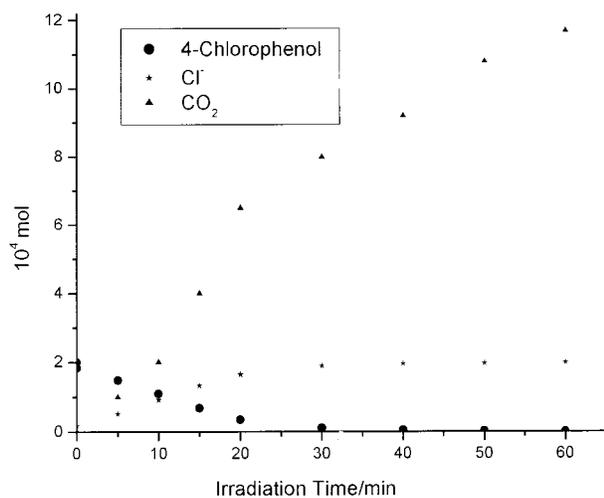


FIGURE 2. Photocatalytic degradation of an air-saturated aqueous dispersion of 4-chlorophenol in the presence of SW10. [4-Chlorophenol] = 2 mM, [POM] = 3.0×10^{-4} M, volume of the photolyzed dispersion = 100 cm³, 4-chlorophenol remaining in dispersion, Cl⁻ and CO₂ produced (a); formation and decay of some intermediates detected during irradiation (b).

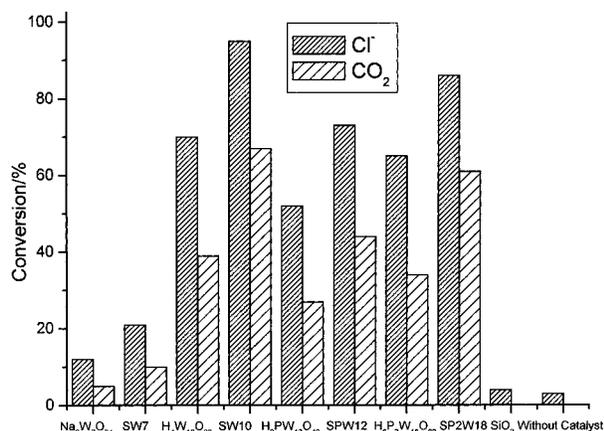


FIGURE 3. Dechlorination and CO₂ formation during 30 min of irradiation over the SiO₂-in-POM catalysts as compared with the parent POMs and in the presence of bulk SiO₂ (0.5 g dm⁻³) and in the absence of catalyst. [4-Chlorophenol] = 2 mM, [POM] = 3.0×10^{-4} M, volume of the photolyzed dispersion = 100 cm³.

and DRS show that the structure of POM was retained in the reused POM-in-SiO₂, indicating the high stability of POM within silica matrix in the photocatalytic cycles.

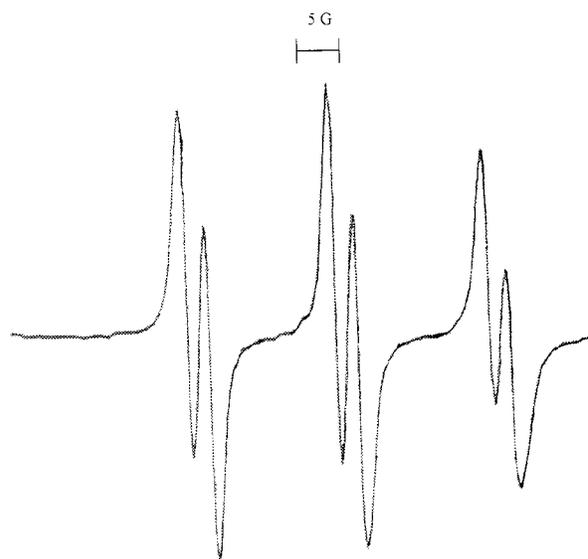


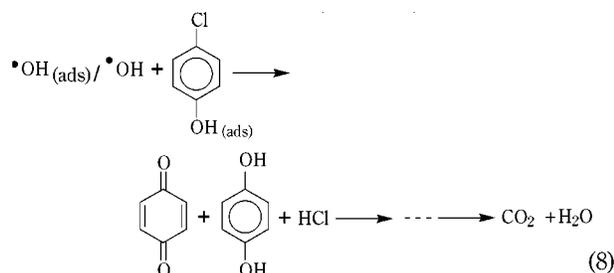
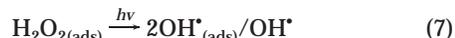
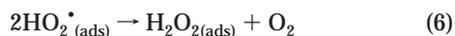
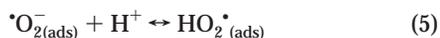
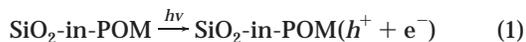
FIGURE 4. Experimental spectrum of an irradiated 4-chlorophenol dispersion containing 0.1 M POBN and 0.5 g of SW10 dm⁻³: $\alpha_N = 14.5$ G, $\alpha_{H\beta} = 2.5$ G.

ESR Spectra. Additional experiments have been carried out using POM-in-SiO₂ catalysts in the anaerobic condition under irradiation. This was selected to show the role of dioxygen. In such experiments, only a little Cl⁻ was liberated, but no CO₂ was formed. Concomitantly, the coloration from white or light yellow to blue on the surface of the various POM-in-SiO₂ catalysts was found during 100 min of irradiation. The frozen dispersions gave out ESR signals at $g = 1.734$ (SW7, $\Delta H = 165$ G), 1.852 (SW10, $\Delta H = 38$ G), 1.831 (SPW12, $\Delta H = 140$ G), and 1.863 (SP2W18, $\Delta H = 135$ -G) at 77 K, which correspond with the signals of 1-e reduced POM species in homogeneous frozen solution (43), suggesting that POM within silica matrix underwent 1-e reduction during irradiation. (The original color of the catalysts was regained by bubbling with air.) On the other hand, no apparent coloration can be observed from the surface of POM-in-SiO₂ catalysts in absence of 4-chlorophenol. Previous researches have stated that the photochemical pathway of polyoxometalate along with organic substrate involves absorption of light by O→M charge-transfer bands of the ground state, then producing a charge-transfer excited state, which leads to a 1-e reduction of the polyoxometalate with the formation of the well-characterized blue species through the transfer of hydrogen atom or electron from the organic substrate to the polyoxometalate (44, 45). In absence of 4-chlorophenol, the blue species cannot be formed, or the blue species can be rapidly reoxidized by the active species produced during irradiation (see below).

It has been noticed that there exists a number of similarities between TiO₂ and POM (46). The formation of •OH radicals during photoirradiation in either TiO₂ dispersions or POM aqueous solution has been identified by ESR using spin trap reagents (47, 48). To confirm the formation of hydroxyl radicals (•OH) in the SiO₂-in-POM dispersions, 4-POBN was used as a spin trap reagent. The photoirradiation of 4-chlorophenol dispersion containing SW10 in the presence of 4-POBN resulted in the ESR signal, exhibiting $\alpha_N = 14.5$ G and $\alpha_{H\beta} = 2.5$ G as shown in Figure 4. The spectrum is comparable to that attributed to the •OH spin adduct of 4-POBN (47, 49), indicating that photoinduced formation of •OH for the SW10 dispersion is the same as in the case of TiO₂ dispersion.

Proposed Pathway. On the basis of the above observations, the process for photocatalytic degradation of 4-chlo-

rophenol by POM-in-SiO₂ catalysts can be summarized as follows:



The initial step is the formation of electron hole pairs on the surface of SiO₂-in-POM particles when irradiated by the light in the region of absorption tail of the O→M charge-transfer bands (eq 1). The electron migrates to the WO₆ site leading to the 1-e reduced POM (eq 2). The generated holes can react with hydrated surface of SiO₂-in-POM, resulting in the formation of surface-bound ·OH radicals (eq 3). Under anaerobic condition, in absence of 4-chlorophenol the active ·OH radicals may react with the 1-e reduced species to regain the parent one so that the net coloration cannot be observed in such cases; however, in the presence of 4-chlorophenol, the steady state is achieved when the 1-e reduced species, SiO₂-in-POM⁻, is formed, which accounts for ESR signals of characteristic W(V) as a result of the coloration on the catalyst surface. In the presence of dioxygen, the reduced catalyst undergoes an easy reoxidation to parent one through the transfer of electron from reduced species to dioxygen (eq 4), keeping the photocatalytic cycle persisting (50). Thus the activated oxygen species, ·OH, ·O₂⁻, and HO₂[·] radicals formed (eqs 3–5 and 7). However, it is believable that surface-bound and solvated ·OH radicals are a main oxidant to attack 4-chlorophenol, causing hydroxylation and oxidation intermediates, then the opening of the ring, and finally the complete mineralization to CO₂, H₂O, and HCl (eq 8).

The results of this study show that the freely water-soluble POM can be immobilized into a silica matrix by means of the sol-gel hydrothermal technique, which shows a new way to prepare an insoluble and readily separable solid for photocatalytic degradation of organic pollutants in the aqueous phase.

Acknowledgments

This research was supported by China National Science Foundation (20171013). Y.B. thanks the Toshihiro Yamase Laboratory (Tokyo Institute Technology, Japan) for supplying part of the measurements. We also thank Professor Heyong He (Fudan University) for improving the manuscript.

Literature Cited

- (1) Fox, M. A.; Dulay, M. T. *Chem. Rev.* **1993**, *93*, 341.

- (2) *Photocatalytic Purification and Treatment of Water and Air*; Ollis, D. F., Al-Ekabi, H., Eds.; Elsevier Science Publishers: Amsterdam, 1993.
- (3) Keith, L. H.; Telliard, W. A. *Environ. Sci. Technol.* **1979**, *13*, 416.
- (4) Patterson, J. W. *Industrial Wastewater Treatment Technology*, 2nd ed.; Butterworth Publishers: Boston, 1985.
- (5) Sax, N. I. *Dangerous Properties of Industrial Materials*, 3rd ed.; VanNostrand-Reinhold: New York, 1968; p 550.
- (6) D'Olivera, J. C.; Al-Sayed, G.; Pichat, P. *Environ. Sci. Technol.* **1990**, *24*, 990.
- (7) Legrim, O.; Oliveros, E.; Brown, A. M. *Chem. Rev.* **1993**, *93*, 671.
- (8) Besner, A.; Gilbert, R.; Tetreault, P.; Lepine, L.; Archambault, J. F. *Anal. Chem.* **1995**, *67*, 442.
- (9) Haggblom, M. *Water Res.* **1988**, *22*, 171.
- (10) Hermann, J. M.; Pichat, P. *J. Chem. Soc., Faraday Trans.* **1980**, *76*, 1138.
- (11) Okamoto, K.; Yamamoto, Y.; Tanaka, H.; Haya, A. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 2023.
- (12) Bolton, J. R.; Sun L. *J. Phys. Chem.* **1996**, *100*, 4127.
- (13) Vinodgopal, K.; Kamat, P. K. *Environ. Sci. Technol.* **1994**, *29*, 841.
- (14) Hoffmann, M. R.; Martin, S. T.; Choi, W.; Bahneman, D. W. *Chem. Rev.* **1995**, *95*, 69.
- (15) Matthews, R. W. *Sol. Energy* **1987**, *38*, 405.
- (16) Tennakone, K.; Kottegoda, I. R. M. *J. Photochem. Photobiol. A* **1996**, *93*, 79.
- (17) Navio, J. A.; Colon, G.; Macias, M.; Real, C.; Litter, M. I. *Appl. Catal. A* **1999**, *178*, 191.
- (18) Ahuja, S.; Kutty, T. R. *J. Photochem. Photobiol. A* **1996**, *97*, 99.
- (19) Inoue, Y.; Asai, Y.; Sato, K. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 797.
- (20) Leyva, E.; Moctezuma, E.; Ruiz, M. G.; Torres-Martinez, L. *Catal. Today* **1998**, *40*, 367.
- (21) Kozhevnikov, I. V. *Chem. Rev.* **1998**, *98*, 171.
- (22) Papaconstantinou, E. *Chem. Soc. Rev.* **1989**, *18*, 1.
- (23) Yamase, T. *Chem. Rev.* **1998**, *98*, 307.
- (24) Mylonas, A.; Papaconstantinou, E. *J. Mol. Catal. A* **1994**, *92*, 261.
- (25) Hu, C.; Yue, B.; Yamase, T. *Appl. Catal. A* **2000**, *194–195*, 99.
- (26) Gratzel, M.; Thampi, K. R.; Kiwi, J. *J. Phys. Chem.* **1989**, *93*, 4128.
- (27) Guo, Y.; Wang, Y.; Hu, C.; Wang, E. *Chem. Mater.* **2000**, *11*, 3501.
- (28) Petrun'kov, K. B.; Burtseva, K. G.; Semchenko, I. D. *Zh. Neorg. Khim.* **1976**, *21*, 2380.
- (29) Zhu, S.; Yue, B.; Wu X.; Wang, Q.; Gu, Y. *Chin. Appl. Chem.* **1991**, *8*, 23.
- (30) Jander, G.; Banthien, H. Z. *Z. Anorg. Allg. Chem.* **1936**, *229*, 142.
- (31) Lawton, L. A.; Robertson, P. K. J.; Cornish, B. J. P. A.; Jaspars, M. *Environ. Sci. Technol.* **1999**, *33*, 771.
- (32) Matthews, R. W.; Abdullah, M.; Low, G. K.-C. *Anal. Chim. Acta* **1990**, *233*, 171.
- (33) Molnár, Á.; Keveszegi, C.; Török, B. *Appl. Catal. A* **1999**, *189*, 217.
- (34) Izumi, Y.; Urabe, K.; Omaka, M. *Microporous Mesoporous Mater.* **1998**, *21*, 227.
- (35) Izumi, Y.; Ono, M.; Kitayauwa, M.; Yoshida, M.; Urabe, K. *Microporous Mater.* **1995**, *5*, 255.
- (36) Tytko, K. H.; Glemser, O. *Adv. Inorg. Chem. Radiochem.* **1976**, *19*, 239.
- (37) Rocciccioli-Deltcheff, C.; Frank, M.; Thouvenot, R. *Inorg. Chem.* **1983**, *22*, 207.
- (38) Baronetti, G.; Briand, L.; Sedran, R.; Thomas, H. *Appl. Catal. A* **1998**, *172*, 265.
- (39) Farmer, V. C.; Russell, J. D. *Spectrochim. Acta* **1964**, *20*, 1149.
- (40) Lefebvre, F. J. *J. Chem. Soc., Chem. Commun.* **1992**, 756.
- (41) Kayanuma, Y. *Phys. Rev. B* **1988**, *38*, 9797.
- (42) Nomiya, K.; Sugie, Y.; Amimoto, K.; Miwa, M. *Polyhedron* **1987**, *6*, 519.
- (43) Yue, B. Ph.D., Fudan University, Shanghai, 1994, p 45.
- (44) Yamase, T.; Takabashi, N.; Kaji, M. *J. Chem. Soc., Dalton Trans.* **1984**, 893.
- (45) Yue, B.; Lin, X.; Zhu, S. *Chem. Res. Chin. Univ.* **1995**, *11*, 269.
- (46) Hiskia, A.; Mylonas, A.; Papaconstantinou, E. *Chem. Soc. Rev.* **2001**, *30*, 62.
- (47) Jaeger, C. D.; Bard, A. J. *J. Phys. Chem.* **1979**, *83*, 3146.
- (48) Yamase, T. *Inorg. Chim. Acta* **1983**, *76*, L25.
- (49) Watanabe, T. *Anal. Chem.* **1982**, *54*, 2470.
- (50) Yue, B.; Zhu, S.; Xie, G.; Gu, Y. *Chin. Chem. Lett.* **1995**, *6*, 215.

Received for review June 6, 2001. Revised manuscript received November 28, 2001. Accepted November 28, 2001.

ES011038U



本文献由“学霸图书馆-文献云下载”收集自网络，仅供学习交流使用。

学霸图书馆（www.xuebalib.com）是一个“整合众多图书馆数据库资源，提供一站式文献检索和下载服务”的24小时在线不限IP图书馆。

图书馆致力于便利、促进学习与科研，提供最强文献下载服务。

图书馆导航：

[图书馆首页](#) [文献云下载](#) [图书馆入口](#) [外文数据库大全](#) [疑难文献辅助工具](#)