Chem. Mater. **2000,** *12,* 3501−3508 3501

Microporous Polyoxometalates POMs/SiO_2: Synthesis and Photocatalytic Degradation of Aqueous Organocholorine Pesticides

Yihang Guo, Yuanhong Wang, Changwen Hu,* Yonghui Wang, and Enbo Wang

Institute of Polyoxometalate Chemistry, Faculty of Chemistry, Northeast Normal University, Changchun 130024, P. R. China

Yongchun Zhou and Shouhua Feng*

Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Jilin University, Changchun 130023, P. R. China

Received January 27, 2000. Revised Manuscript Received September 5, 2000

Microporous Keggin-type polyoxometalate materials were synthesized by incorporating $H_3PW_{12}O_{40}$ and/or $H_4SiW_{12}O_{40}$ into a silica matrix via a sol−gel technique. The silica-impregnated polyoxometalates (POMs/SiO_2) thus obtained are insoluble and readily separable porous materials with uniform micropores and high specific surface areas. Trace aqueous organocholorine pesticides, hexachlorocyclohexane (HCH) and pentachloroenitrobenzene (PCNB), were totally degraded and mineralized into CO_2 and HCl by irradiating a POMs/SiO_2 slurry in the near-UV area. The disappearance of the *organocholorine* compounds follows Langmuir−Hinshelwood first-order kinetics. Studies on the reaction mechanism indicate that photogeneration of $OH^{\bullet}$ radicals originating from neutralization of OH^- groups on the catalyst surface with positive photoholes is responsible for the oxidation of the organic substrates in aqueous solution.

Introduction

Halogenated compounds such as halogenated hydrocarbons, pesticides, polychlorinated biphenyls (PCBs), and halogenated waste solvents constitute a problem for the environment to some degree because of their carcinogenicity and/or toxicity.[1−5] Recently, a number of new approaches to the dehalogenation of the halogenated compounds have been studied, including superoxide dehalogenation,[6] dehalogenation by the excited state of Rh^I complexes[7] and radicals derived from the photolysis of alcohol-ligated Fe porphyrins, and photocatalytic degradation by semiconductors or polyoxometalates.[3−5,8,9] Photocatalytic detoxification of organic pollutants in water is technologically and environmentally attractive, as it can be applied on a very large scale to industrial or domestic wastewater treatment or purification of contaminated groundwater. Dispersed solid particles of TiO_2 have been extensively used as an efficient photocatalyst in the chemical decomposition of many organic substrates. This method generally leads to the total mineralization of organic compounds into CO_2 under mild conditions,[6,10−14] but the TiO_2 ultrafine particles used are easy to lose and it is difficult to separate them from the reaction systems due to the formation of a milky dispersion of the TiO_2 particles.

Polyoxometalates (POMs) exhibit a unique combination of physical and chemical properties. They have been widely used as acid and oxidation catalysts in homogeneous and heterogeneous systems. However, the catalytic activities of the POMs are greatly limited due to their very low specific surface areas (e.g., $H_3PW_{12}O_{40} \leq 9$ m^2/g and $H_4SiW_{12}O_{40} \leq 10$ m^2/g[15,16]), so polar molecules can only react on the surface of the POMs. Therefore, many attempts have been made to enhance the catalytic activity of the POMs: preparation of POMs containing layered double hydroxide (LDH) by intercalating the POMs into LDH,[17−19] synthesis of the POMs

---

* To whom correspondence should be addressed.

(1) Sattari, D.; Hill, C. L. *J. Am. Chem. Soc.* **1993**, *115*, 4649.

(2) Sattair, D.; Hill, C. L. *J. Chem. Soc., Chem. Commun.* **1990**, 634.

(3) Maillaro-Dupuy, C.; Guillard, C.; Pichat, P. *New J. Chem.* **1994**, *18*, 941.

(4) Mylonas, A.; Papacontantinous, E.*J. Photochem. Photobiol. A* **1996**, *94*, 77.

(5) O'shea, K. E.; Beightal, S.; Garcia, I.; Aguilar, M.; Kalen, D. V.; Cooper, W. J. *J. Photochem. Photobiol. A* **1996**, *107*, 221.

(6) Herrmann, J.-M. *Catal. Today* 1Z999, *53*, 115.

(7) Che, C.-M.; Lee; W−M. *J. Chem. Soc., Chem. Commun.* **1986**, 616.

(8) Bartocci, C.; Maldotti, A.; Varani, G.; Carassiti, V.; Battioni, P.; Mansuy, D. *J. Chem. Soc., Chem. Commun.* **1989**, 964.

(9) D'ollveira, J.-C,; Al-Sayyed, G.; Pichat, P. *Environ. Sci. Technol.* **1990**, *24*, 990.

(10) Wang, K.-H,; Hsieh, Y.-H.; Chou, M.-Y.; Chang, C.-Y. *Appl. Catal. B* **1999**, *21*, 1.

(11) Ilisze, I.; Laszlo, Z.; Dombi, A. *Appl. Catal. A* **1999**, *180*, 25.

(12) Doong, R.; Chang, W. *J. Photochem. Photobiol. A* **1997**, *107*, 239.

(13) Bems, B.; Jentoft, F. C.; Schlogl, R. *Appl. Catal. B* **1999**, *20*, 155.

(14) Ralph, W.; Matthews, A. *Water Res.* **1986**, *20*, 569.

(15) Hu, C.; Hashimoto, M.; Okuhara, T.; Misono, M. *J. Catal.* **1993**, *143*, 437.

(16) Hu, C.; Nishimura, T.; Misono, M. *Sekiyu Gakkaishi* **1993**, *36* (5), 386.

(17) Hu, C.; He, Q.; Zhang, Y.; Liu, Y.; Tang, T.; Zhang, J.; Wang, E. *J. Chem. Soc., Chem. Commun.* **1996**, 121.

10.1021/cm000074+ CCC: $19.00

in carbon fiber, and impregnation of the POMs on TiO_2 or silica gels.

POMs are also effective photocatalysts, and their photochemical activities originate from their unique structure.[20,22−25] They have a number of features in common with semiconductor metal oxide clusters and can be considered as the analogues of the latter. Both classes of materials are constituted by d^0 transition-metals and oxide ions and exhibit similar electronic attributes including well-defined HOMO−LUMO gaps (semiconductor "band gaps"). The "gaps" inhibit the recombination of electrons and holes that are generated by the irradiation of the surface of the photocatalysts with light of higher energy than the band gaps. The electrons and holes thus formed are capable of initiating chemical reactions because of the formation of $OH^•$ radicals resulting from the subsequent reaction of holes and OH^- groups coming from water.[20] In addition to their possible ability to degrade pollutants under UV irradiation, POMs present two advantages for their potential application to detoxification processes, namely, a low toxicity, as in the case of TiO_2, and its behavior as a kind of environmentally benign catalyst. Industrial processes involving the supported photocatalysts could be considered. Indeed, because of the strong Brönsted acid property of POMs, they are soluble in aqueous solution and not easily separated from the reaction system for recycling. Therefore, the synthesis of POMs embedded in some kind of support is of fundamental and practical significance. In the present study, we synthesized some silica-impregnated Keggin-type POMs [$H_3PW_{12}O_{40}/SiO_2$, (**1**) and $H_4SiW_{12}O_{40}/SiO_2$ (**2**)] by a sol−gel technique involving the hydrolysis of tetraethyl orthosilicate (TEOS). The silica-impregnated $H_3PW_{12}O_{40}$ or $H_4SiW_{12}O_{40}$ thus obtained represents a new type of supported nanometer particle system with high specific surface areas and well-distributed micropores. For the first time, these POMs/SiO_2 have been used as heterogeneous photocatalysts to degrade trace organochlorine pesticides in aqueous solution. They exhibit significant photocatalytic activity in the oxidation of organochlorine pesticides, and the final products of degradation, mainly CO_2 and HCl, are environmentally acceptable. The kinetics, pathway, and mechanism for the degradation were also studied.

Experimental Section

Materials. 1-Butanol, TEOS, acetonitrile, and petroleum ether were of analytical grade. $H_3PW_{12}O_{40}•6.7H_2O$ and $H_4SiW_{12}O_{40}•26H_2O$ were prepared according to the literature methods.[26,27] Doubly distilled water was used in all experiments. Hexachlorocyclohexane and pentachloroenitrobenzene were certified reference materials purchased from the State Bureau of Technical Supervision, P. R. China. The stock solution of HCH or PCNB was prepared by dissolving it in a small amount of acetonitrile and then diluting with water to suitable concentrations.

Synthesis of the POMs/SiO_2. The POMs/SiO_2 were synthesized by the improved literature methods:[28,29] a mixture of water (2 mol), 1-butanol (0.2 mol), and $H_3PW_{12}O_{40}•6.7H_2O$ or $H_4SiW_{12}O_{40}•26H_2O$ (0.5 mmol) was added to TEOS solutions with different amounts (0.2−0.8 mol), and the mixture was stirred at 80 °C for 3 h. The hydrogel thus obtained was dehydrated slowly at 80 °C for 3 h and dried in a vacuum at 60 °C for 12 h. The dried gel was calcined in a vacuum at 150 °C for 2 h to fasten the silica network and then extracted with water at 90 °C until the filtrate was neutral. The silica-impregnated $H_3PW_{12}O_{40}$ (**1**) or $H_4SiW_{12}O_{40}$ (**2**) was dried in a vacuum at 150 °C for 3 h prior to use for photocatalytic reactions.

Photoreactor. The photoreactor was designed with an internal light source surrounded by a quartz jacket. The temperature of the liquid/solid slurry was maintained at 28 ± 1 °C by circulation of water through an external cooling coil. The optical path length was about 2 cm. The light source was a 125 W high-pressure mercury lamp (HPML, 313.2 nm) or a 20 W low-pressure mercury lamp (LPML, 253.7 nm). Trace aqueous solution of PCNB or HCH was prepared by dilution of the stock solution of PCNB or HCH with water.

Procedure. A typical run for photodegradation of HCH or PCNB was carried out as follows: each POM/SiO_2 (**1** or **2**) was suspended in a fresh aqueous solution of the substrates. The slurry (70 mL) obtained was ultrasonicated for 5 min and stirred in the dark for 30 min to obtain a good dispersion. The lamp was inserted into the slurry when its intensity became stable. The suspension was vigorously stirred during the whole process. The system was open to air.

Analyses. The concentration of the product chloride ion was determined continuously with an Orion Model 720 special chloride ion selective electrode in the photoreactor (0.1 M KNO_3 was added to adjust the ionic strength). Formation of the product CO_2 was confirmed by following method: air was passed from the reaction vessel through a saturated solution of $Ba(OH)_2$ in 1.0 M NaOH (closed system) and the CO_2 produced during photocatalysis was trapped as solid $BaCO_3$ and measured gravimetrically. The concentration of HCH or PCNB was analyzed by a Varian 3400 GC-ECD equipped with a capillary column (SE-54) whose column temperature was 200 °C, and heptachloro epoxide was used as an internal standard. The liquid reaction solution withdrawn at regular intervals was extracted three times with petroleum ether before GC analysis. The intermediate products were identified by a HP 6890 GC/5973 MS equipped with a HP-5 column and a DX-300 ion chromatograph (IC) equipped with a conductivity detector and an ICE-ASI anion column. The loads of $H_3PW_{12}O_{40}$ or $H_4SiW_{12}O_{40}$ on **1** or **2** were estimated by a Leeman Plasma Spec (I) ICP-AES. UV and IR spectra were recorded on a Shimadzu UV-2201 UV−vis spectrophotometer and a Nicolet Magna 560 IR spectrophotometer, respectively. Thermogravimetric analysis (TGA) was performed on a P-E TG 7 thermal analysis system. Scanning electron microgaghs (SEM) and transmission electron micrograghs (TEM) were obtained on a Hitachi S-570 scanning electron microscope and a Hitachi H-600 transmission electron microcsope, respectively. The BET areas and pore size distributions of **1**, **2**, and SiO_2 were calculated from nitrogen adsorption data determined at 77.5 K using an ASAP 2010M surface analyzer, and the pretreatment temperature was 300 °C.

Results and Discussion

Characterization of the Silica-Impregnated Polyoxometalates, POMs/SiO_2.

The results of elemental

---

[18] Hu, C.; He, Q.; Zhang, Y.; Wang, E.; Okuhara, T.; Misono, M. *Catal. Today* **1996**, *30*, 141.

[19] Hu, C.; He, Q.; Wang, E. *Prog. Nat. Sci.* **1996**, *6* (5), 524.

[20] Yamase, T. *Inorg. Chim. Acta.* **1983**, *76*, 25.

[21] Tahiri, H.; Ichou, Y. A.; Herrmann, J.-M. *J. Photochem. Photobiol. A* **1998**, *114*, 219.

[22] Chambers, R. C.; Hill, C. L. *J. Am. Chem. Soc.* **1990**, *112*, 8427.

[23] Einaga, H.; Misono, M. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 3435.

[24] Einaga, H.; Misono, M. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 1551.

[25] Hu, C.; Yue, B.; Yamase, T. *Appl. Catal. A* **2000**, 194−195, 99.

[26] Roccicciolі-Deltcheff, C.; Frank, M.; Thouvenot, R. *Inorg. Chem.* **1983**, *22*, 207.

[27] Ginsberg, A. P. *Inorg. Synth.* **1990**, *27*, 85.

[28] Izumi, Y.; Ono, M.; Kitagawa, M.; Yoshida, M., Urabe, K. *Micropor. Mater.* **1995**, *5*, 255.

[29] Izumi, Y.; Hisano, K.; Hida, T. *Appl. Catal. A* **1999**, *181*, 277.

Table 1. Data of ICP-AES, UV, and IR Spectra for the POMs/SiO$_2$

catalyst[a]	HPW or HSiW[b] content (wt %)[c]	OMCT bands (nm)	σ (cm^{-1})			
			P(Si)$-$O$_a$	W=O$_d$	W$-$O$_b$$-$W	W$-$O$_c$$-$W
1(a)	13.5 (6.5)	266	1084.5	954.2	798.7	789.3
1(b)	8.1 (11.3)	266	1086.0	952.9	799.3	788.9
1(c)	5.2 (18.2)	266	1082.4	951.1	880.9	795
2	3.0 (32.2)	263	1086.1	951.2	805.6	672.8
SiO$_2$[d]	*e*	*e*	1086.6	*e*	*e*	*e*
HPW[f]	100	260	1079.2	983.2	890$-$850	800$-$760
HSiW[f]	100	260	1080.1	988.6	890$-$850	800$-$760

[a] **1(a)**, **1(b)**, and **1(c)** were prepared with various loads of $H_3PW_{12}O_{40}$ on silica. [b] HPW = $H_3PW_{12}O_{40}$; HSiW = $H_4SiW_{12}O_{40}$. [c] Data in the brackets represented the weight ratios of SiO$_2$ to $H_3PW_{12}O_{40}$ or $H_4SiW_{12}O_{40}$. [d] SiO$_2$ was prepared by hydrolysis of TEOS at pH 1 (pH was adjusted with 4 mol/L HNO$_3$). [e] Not found. [f] See refs 26 and 27.

analysis, UV diffusion spectra, and IR spectra for **1** and **2** are summarized in Table 1. According to the different ratios of TEOS to $H_3PW_{12}O_{40}$, samples of **1** with various loads of $H_3PW_{12}O_{40}$ (0$-$13.5%) were prepared and their contents were estimated by ICP-AES. The POMs/SiO$_2$ have a maximum UV absorption peak at 263$-$266 nm, similar to that of the parent $H_3PW_{12}O_{40}$ or $H_4SiW_{12}O_{40}$, attributed to the oxygen-to-tungsten charge-transfer absorption band for the Keggin anions. This indicates that the primary Keggin structure is retained after immobilizing the $H_3PW_{12}O_{40}$ or $H_4SiW_{12}O_{40}$ into a silica matrix. The FT-IR characteristic bands of the POMs/SiO$_2$ have some shifts of ca. 30 cm^{-1} compared with those for the parent $H_3PW_{12}O_{40}$ or $H_4SiW_{12}O_4$ (e.g., W=O$_d$ and W$-$O$_b$$-$W vibration peaks). Therefore, it is confirmed that a strong chemical interaction, not simple physical adsorption, exists between the POM and the silica surface. As the OH groups of silanol are protonated in the acidic medium of $H_3PW_{12}O_{40}$ or $H_4SiW_{12}O_{40}$, it is supposed that one proton of $H_3PW_{12}O_{40}$ or $H_4SiW_{12}O_{40}$ will react with the OH of silanol and form a $SiOH_2^+$ group which should act as a counterion for the polyanion. The formula of the polyanion in such an environment can be written as $(\equiv SiOH_2^+)(H_2PW_{12}O_{40}^-)$ or $(\equiv SiOH_2^+)(H_3SiW_{12}O_{40}^-)$. Thus, the reaction of the polyanion with SiO$_2$ is not described as an ion exchange but as an acid$-$base reaction between the silanol group (acting as the base) and the polyanion (acting as a Brönsted acid). This interaction results in a shift in the IR bands of the POMs/SiO$_2$ compared with those of the parent $H_3PW_{12}O_{40}$ or $H_4SiW_{12}O_{40}$. Thouvenot[30] and Lefebvre[31] et al. also evidenced an interaction between POM and silica through ^{31}P MAS NMR**,** where two peaks were detected in $H_3PW_{12}O_{40}$/SiO$_2$ at δ $-$14.5 and $-$15.1 ppm, respectively, different from that of the pure $H_3PW_{12}O_{40}$ having one peak at δ $-$15.1 ppm with a small line width. Because of this strong chemical interaction, when particular weight ratios of SiO$_2$/$H_3PW_{12}O_{40}$ or SiO$_2$/$H_4SiW_{12}O_{40}$ were chosen, leakage of $H_3PW_{12}O_{40}$ or $H_4SiW_{12}O_{40}$ from the silica matrix was hardly observed in the process of photocatalysis, even if the POMs/SiO$_2$ were reused eight times (see below).

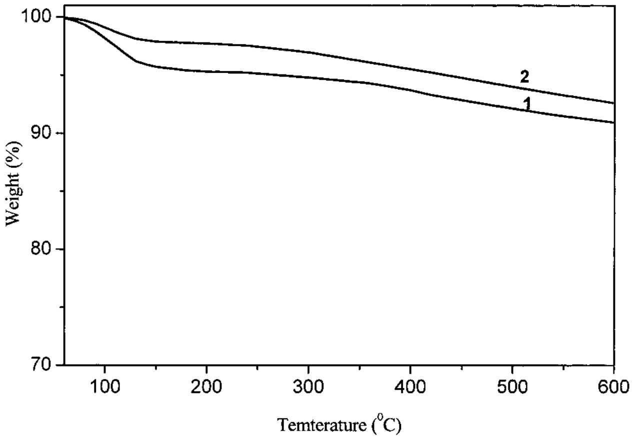


Figure 1. TG plots of the POMs/SiO$_2$.

The TGA (Figure 1) of the samples shows an initial weight loss (5.0% for **1** and 2.2% for **2**) from 50 to 160 °C. This is attributed to the loss of excess or included 1-butanol (its boiling point is 117 °C), which cannot be removed completely by water washing. The second weight loss (1.9% for **1** and 4.0% for **2**) from 350 to 550 °C is attributed to the loss of constitutional water from the POMs/SiO$_2$, indicating that the $H_3PW_{12}O_{40}$ or $H_4SiW_{12}O_{40}$ impregnated in a silica matrix began to decompose at a temperature higher than 350 °C. Thus, the TGA shows that microporous Keggin-type polyoxometalate materials are thermally stable at temperatures below 350 °C. The nitrogen adsorption at 77.5 K on **1**, **2**, and SiO$_2$ was measured, and the adsorption isotherms and pore size distributions are shown in Figures 2a,b, and 3, respectively. The BET surface areas and median pore diameters are summarized in Table 2. The presence of micropores for **1** and **2** was indicated by the sharp increase in the amount of nitrogen adsorbed at a very low relative pressure, i.e., $P/P_0 \leq 0.01$.The sharp peak in the pore size distribution curve indicates that the pores in the POMs/SiO$_2$ mainly occur at a pore diameter of ca. 0.60 nm, suggesting that the micropores in **1** or **2** are uniform. SEM and TEM (Figure 4) show that the silica-impregnated $H_3PW_{12}O_{40}$ or $H_4SiW_{12}O_{40}$ forms relatively uniform nanometer particles of diameter less than 20 nm.

The formation of the micropores in the POMs/SiO$_2$ originates from the porous structure of silica particle gels obtained from hydrolysis of TEOS under the acidic conditions. The mesoporosities of the silica gels are confirmed by the pore size distribution curve for the pure SiO$_2$ (Figure 3). The median pore diameter of the silica is ca. 3.8 nm. During the course of hydrolysis of TEOS in the presence of $H_3PW_{12}O_{40}$ or $H_4SiW_{12}O_{40}$, the Keggin anions were entrapped by the silica network, resulting in the decrease of the pore size and formation of the POMs/SiO$_2$ composite with micropores. The entrapped Keggin anions appeared to be a highly concentrated aqueous solution in the silica network and the silica network seemed to be narrow enough to

---

(30) Thouvenot, R.; Fournier, M.; Rocchiccioli-Deltcheff, C. *J. Chem. Soc., Faraday Trans* **1991**, *87*, 2829.

(31) Lefebvre, F. *J. Chem. Soc., Chem. Commun.* **1992**, 756.

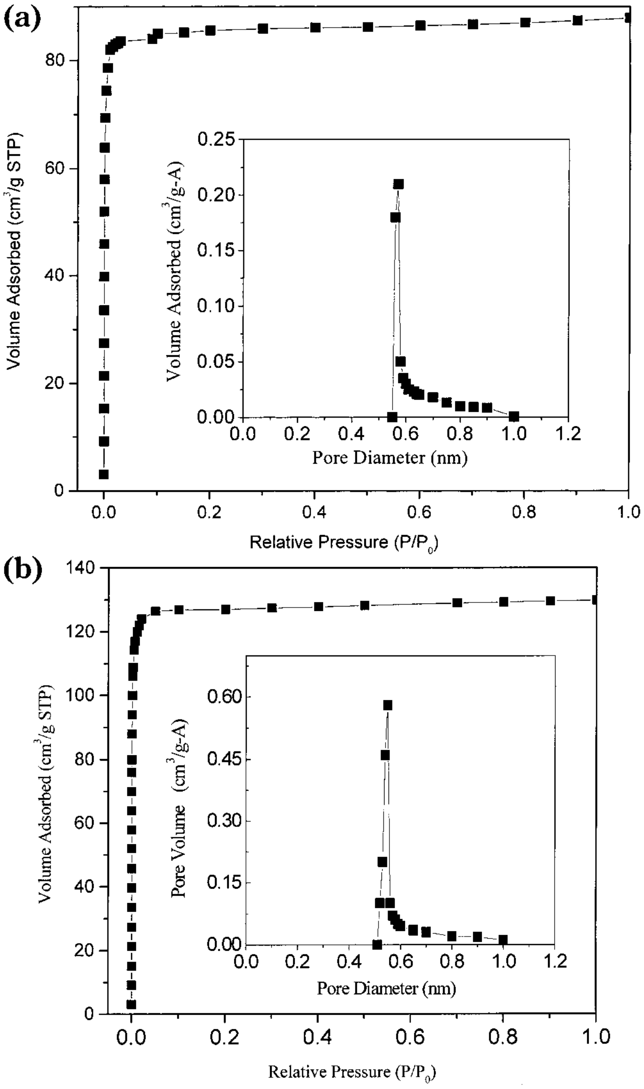


Figure 2. Plots of the nitrogen adsorption isotherms and pore size distributions for the POMs/SiO_2 (a) **1** and (b) **2**.

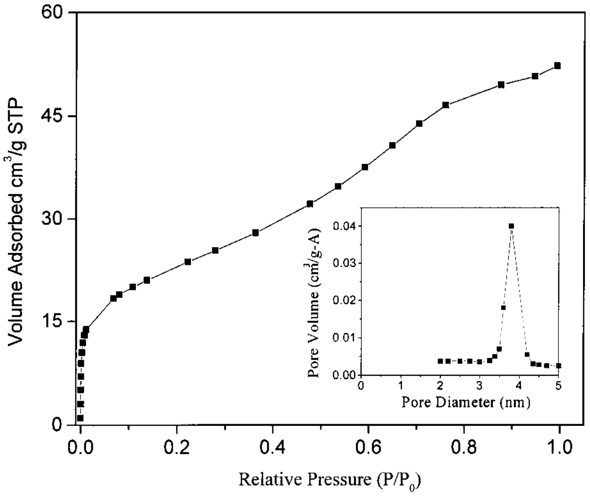


Figure 3. Plot of the nitrogen adsorption isotherm and pore size distribution for the pure SiO_2 matrix.

prevent the removal of the $H_3PW_{12}O_{40}$ or $H_4SiW_{12}O_{40}$ molecules from the silica networks. On the other hand, small organic molecules such as HCH and PCNB are permitted to enter the pores of the silica and perform the photocatalytic reactions.

Table 2. Surface Characterization of the POMs/SiO_2 and Langmuir Rate Parameters for HCH Degradation

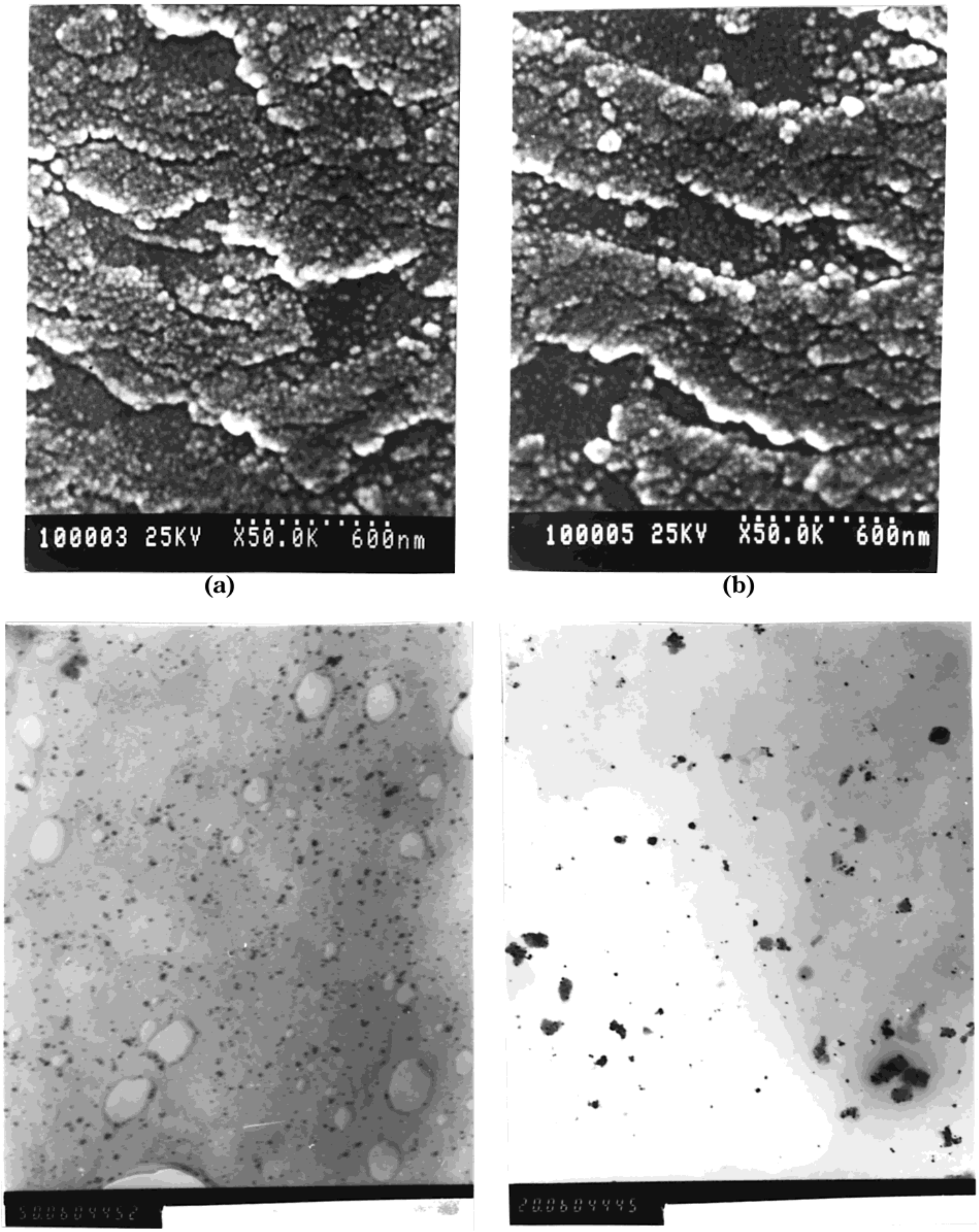
catalyst	BET surface area (m^2/g)	median diameter (nm)	*K* (L mg^{-1})	*k* (mg L^{-1}•min^{-1})
1(b)	350.5	0.57	0.019	0.26
2	541.7	0.59	0.070	0.12
SiO_2	70.5	3.8		

Photocatalytic Activity of the POMs/SiO_2. Photodegradation of 7 mg/L of HCH was examined at different contents of POMs in the POMs/SiO_2. After the slurry was mixed for 24 h in the dark, Cl^- was not detected. In the absence of the POMs/SiO_2, there was no apparent change in the concentration of HCH after the slurry was irradiated for 4 h with HPML. However, a significant conversion of HCH into CO_2 and HCl was observed as the contents of the POMs/SiO_2 increased to 2.5 g/L for **1** and 3.5 g/L for **2**, respectively (Figure 5). This indicates that degradation of HCH results from photoexcitation of the POMs/SiO_2, rather than direct photolysis or a catalyzed reaction on the POMs/SiO_2 without irradiation. Apparently, the unique structure of the Keggin anions and the high specific surface area and microporous structure of the POMs/SiO_2 play an important role in the degradation of HCH.

Photocatalytic Degradation of Trace HCH and PCNB in Aqueous Solution. 5 mg/L of PCNB could be directly photolyzed in solution by HPML without the POMs/SiO_2, but a reaction time of 5 h was needed for the complete photolysis of PCNB. However, in our experiment, 5 mg/L of PCNB was totally photodegraded by HPML for only 50 min in the presence of **2**, suggesting that the photocatalytic reaction for PCNB is so rapid that it was difficult to study its kinetics. Therefore, HCH was selected as a target substrate in the study on the kinetics and mechanism of the photocatalytic reaction. Figure 6 shows conversions of the photocatalysis of HCH with **1** or **2** under various conditions. The results obtained in the process of photocatalytic degradation of aqueous HCH are summarized as follows:

(i) Within the same reaction time, the conversion of HCH was higher when the slurry was irradiated by HPML than by LPML. However, when the pure SiO_2 support was used, conversion was hardly observed, suggesting that the photocatalytic activity of the POMs/SiO_2 derives from the impregnated POMs rather than the SiO_2 support.

(ii) Conversion of HCH was higher at a lower weight ratio of $SiO_2/H_3PW_{12}O_{40}$ (i.e., 6.5) in **1(a)** than that at a higher weight ratio (i.e., 19). However, it was observed in the experiment that ca. 2.8% of $H_3PW_{12}O_{40}$ in **1(a)** was released into the solution after the slurry was irradiated by HPML for 4 h. The leakage of $H_3PW_{12}O_{40}$ from the silica matrix was estimated by ICP-AES and UV−vis absorption spectroscopy (the solution and the surface of the catalyst were blue). In the present experiment, the weight ratios of $SiO_2/H_3PW_{12}O_{40}$ or $SiO_2/H_4SiW_{12}O_{40}$ are the most important criterion for preparing such an impregnation compound. A higher SiO_2 content resulted in less leakage of $H_3PW_{12}O_{40}$ or $H_4SiW_{12}O_{40}$ because the silica network has entrapped all of the Keggin anions. For **1(c)** or **2**, the leakage of the Keggin anions was not found under the same



(a) (b) (c) (d)

Figure 4. SEM and TEM of the POMs/SiO$_2$: (a) SEM for **1**, (b) SEM for **2**, (c) TEM for **1**, (d) TEM for **2**.

conditions. Since $H_3PW_{12}O_{40}$ or $H_4SiW_{12}O_{40}$ is soluble in water, a high weight ratio is necessary to ensure a better inclusion and to suppress the leakage of the Keggin anions. The blue color of the suspension results from the reduced form of $PW_{12}O_{40}^{3-}$, which is commonly referred to as heteropolyblue (HPB). In the process of oxidation of HCH, the excited state of $PW_{12}O_{40}^{3-}$ was reduced to $PW_{12}O_{40}^{4-}$. The $PW_{12}O_{40}^{4-}$ has strong intervalence charge-transfer (IVCT) absorption bands at 498 and 750 nm. To prevent the leakage of the Keggin anions, suitable weight ratios of SiO$_2$/$H_3PW_{12}O_{40}$ (i.e., 18.2) and SiO$_2$/$H_4SiW_{12}O_{40}$ (i.e., 32.2) were chosen for further experiments.

(iii) Acetonitrile was used as solvent, for it has no absorption in the near UV area, whereas acetone affected the photocatalytic activity of the POMs/SiO$_2$ and retarded the reaction by its absorption of the light energy (at 330 nm).

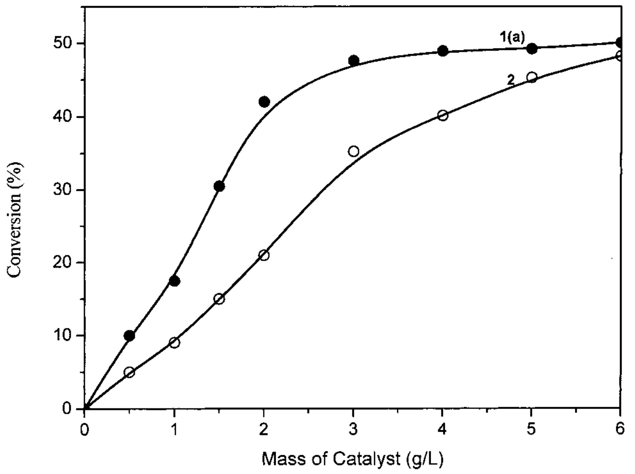


Figure 5. Photocatalytic activity of the POMs/SiO_2. **1**(**a**), **2**, and LPML were used, with an irradiation time of 4 h. Conversion (%) = $(1 - [HCH]_t/[HCH]_0) \times 100$.

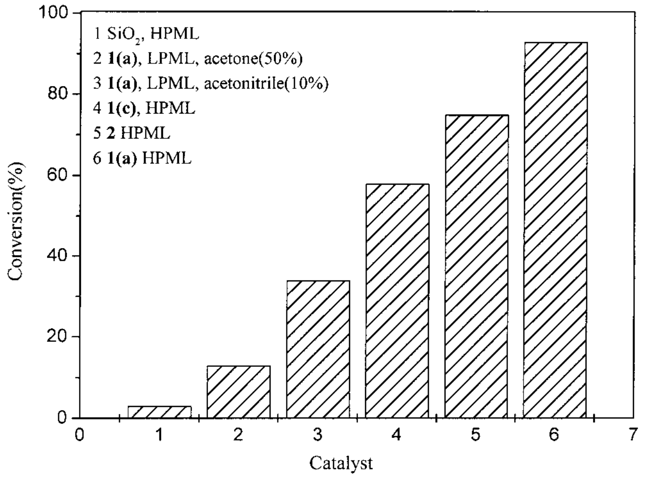


Figure 6. Conversion of the photocatalytic degradation of aqueous HCH under various conditions; $C_0^{HCH} = 6.5$ mg/L, irradiating time of 4 h.

(iv) The photocatalytic system for $HCH-H_2O(CH_3CN)-H_3PW_{12}O_{40}/SiO_2$ or $HCH-H_2O(CH_3CN)-H_4SiW_{12}O_{40}/SiO_2$ was operated at room temperature because the catalyst (**1** or **2**) was photonically activated at the beginning of the reaction. The optimum temperature was generally between 20 and 80 °C. This absence of heating is attractive for a photocatalytic reactions carried out in aqueous media, in particular for environmental purposes.

(v) As the reaction was going on, the color of the suspension changed from colorless to bright yellow, suggesting the formation of a POM−HCH or POM−PCNB charge-transfer complex,[32] a necessary prerequisite for the oxidation of HCH or PCNB.

(vi) For the potential applications of this method to deal with environmental problems, 50 μg/L of HCH and PCNB were chosen, because this is a representative level of the pesticides existing in plant bodies and drinking water. An irradiation time of 8 h was employed under the same conditions as described above. The conversions were 60% for HCH and 99% for PCNB, respectively. The decomposition rate at the microgram/liter level of HCH or PCNB is low but acceptable. Therefore, it is possible to apply this technique to degrade trace aqueous pollutants.

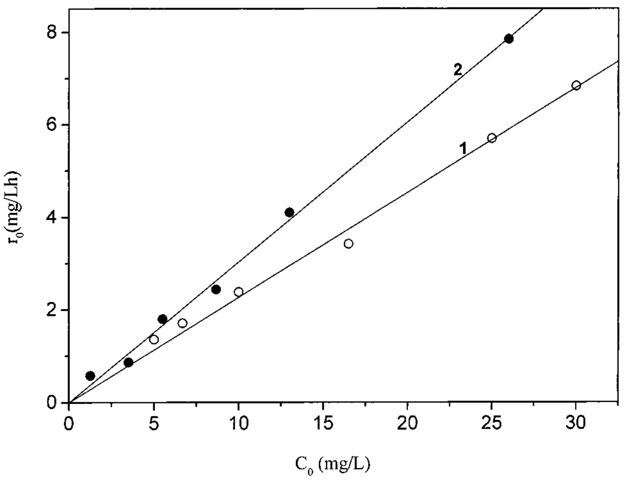


Figure 7. Initial dehalogenation rate (r_0) vs initial concentration (C_0) of aqueous HCH. **1**(**c**), **2**, and HPML were used.

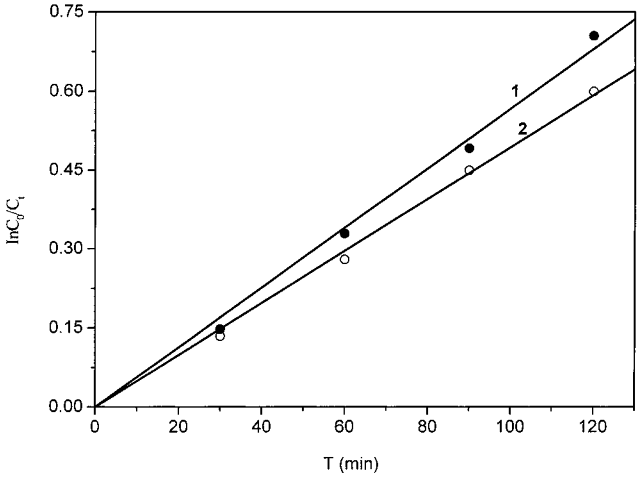


Figure 8. First-order linear transform ln $C_0/C = f(t)$ for the kinetics of HCH disappearance. **1**(**c**), **2**, and HPML were used.

Kinetic Study. The influence of the initial HCH concentration (C_0) on the initial HCH rates (r_0) for photocatalytic degradation of HCH was studied, and the results are shown in Figures 7 and 8. By changing C_0 in the range of 0−30 mg/L, a plot of r_0 vs C_0 exhibits a straight line, and the linear correlation coefficients (R) are 0.995 for **1** and 0.998 for **2**. This indicates that the disappearance of HCH follows a Langmuir−Hinshelwood first-order kinetic law for the initial HCH concentration chosen. The linear relationship between ln C_0/C and t (Figure. 8) is also in agreement with a Langmuir−Hinshelwood first-order linear transformation for HCH. The values of k (the reaction rate constant) and K (the adsorption equilibrium constant) from the intercept and slope of the line of r_0^{-1} vs C_0^{-1}, respectively, were determined and are summarized in Table 2.

The first-order linear relationship for the photocatalytic degradation of trace HCH by the POMs/SiO_2 can be explained by a Langmuir−Hinshelwood model (eq 1)

$$r = -dC/dt = -kKC/(1 + KC)$$

---

[32] Hill, C. L.; Renneke, R. F.; Combs, L. *Tetrahedron* **1988**, *44*, 7499.

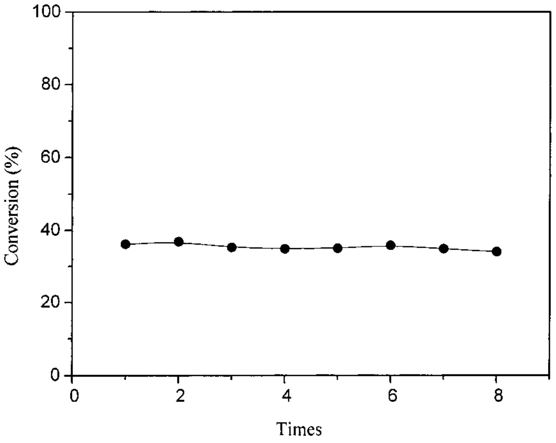


Figure 9. Lifetime of the POMs/SiO$_2$ in the process of photocatalytic degradation of aqueous HCH; $C_0^{HCH} = 3.5$ mg/L, irradiating time of 3 h. **2** and HPML were used.

or

$$r^{-1} = (1/kK)C^{-1} + 1/k \quad (1)$$

As for the dilute solution, where $KC \ll 1$ because of the weak adsorption of HCH, the above model can be expressed by eq 2 or 3:

$$r_0 = kKC_0 \quad (2)$$

$$\ln C_0/C = kKt \quad (3)$$

Therefore, the reaction for the photocatalytic degradation of trace HCH by the POMs/SiO$_2$ exhibits the first-order kinetics of the Langmuir–Hinshelwood model. This relationship was applied in the low range of HCH concentration.

Separation, Recovery, and Reuse of the POMs/SiO$_2$. After the reaction finished, the suspension was allowed to settle and then the reaction solution was withdrawn. The catalyst **1** or **2** was washed with water and recovered by centrifugation for the next degradation reaction. Silica-impregnated $H_3PW_{12}O_{40}$ or $H_4SiW_{12}O_{40}$ kept its initial activity during eight times of reuse (Figure 9) and the leakage of the Keggin anions was hardly observed, as determined by ICP-AES. In addition, the Keggin structure in the reused POMs/SiO$_2$ was retained, as determined by FT-IR.

Reaction Mechanism. From the results of IC (Figure 10) and GC/MS (Figure 11) analyses, the intermediate products were identified and detected. According to the kinetic study and the distribution of the intermediate products, the reaction mechanism for the photocatalytic degradation of aqueous HCH by the POMs/SiO$_2$ is proposed as follows:

(i) As a heterogeneous photocatalyst, the POM/SiO$_2$ has the dual features of simultaneous adsorption of both reactants (the organic substrates and dioxygen dissolved in the reaction slurry) on the catalyst surface and absorption of the suitable light energy. The photocatalytic reaction occurs in the adsorbed phase (on the surface and in the micropores of the catalyst), and the model of activation of the catalysts is photonic activation by exciting the POM/SiO$_2$ with light energy higher than the band gap of POM, which leads to an intramolecular O(2p)→W(5d) charge transfer and the formation of the excited-state species (POM/SiO$_2$)*. By using semiconductor notation, the excitation of the POM/SiO$_2$ at its OMCT band can be presented by eq 4.

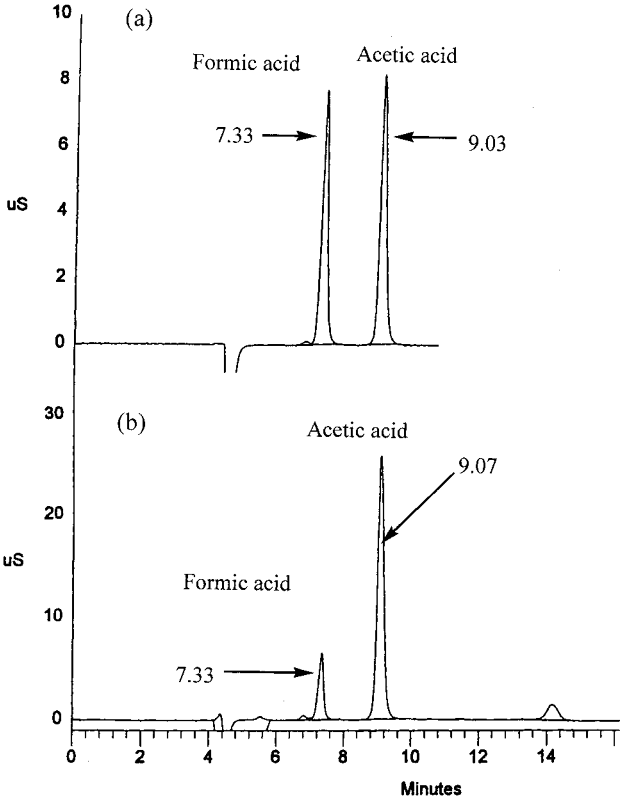


Figure 10. Ion chromatographic effluent curves for HCH photocatalytic degradation products: (a) standard sample for formic acid and acetic acid, (b) the slurry (HCH + **2**) irradiated by HPML for 2 h.

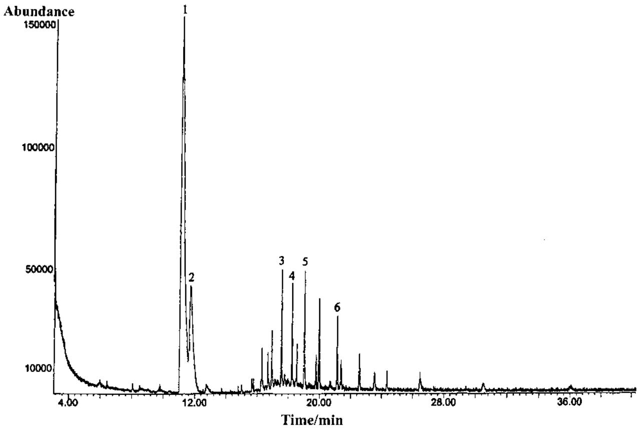


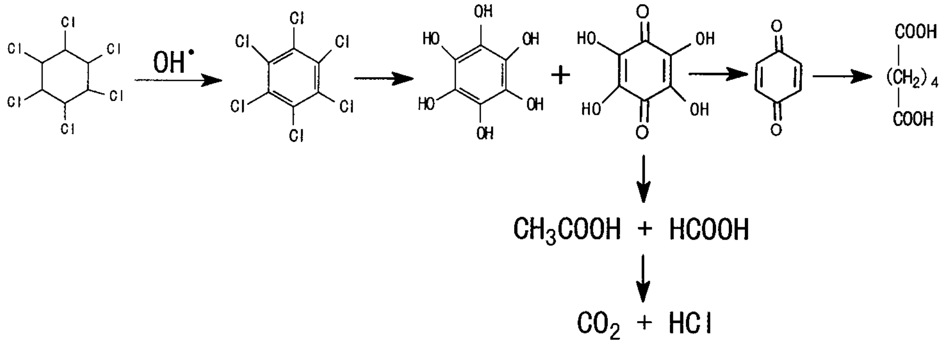
Figure 11. GC/MS effluent curves for HCH photocatalytic degradation products, i.e., the slurry (HCH + **2**) irradiated by HPML for 2 h: (1) HCH, (2) phenyl-hexachloride, (3) benzoquinone, (4) polyphenol, (5) tetrahydroxybenzoquinone, and (6) 1,6-hexanedicarboxylic acid.

$$\mathrm{POM/SiO_2} + h\nu \leftrightarrow \mathrm{POM/SiO_2(e^- + h^+)} \quad (4)$$

In principle, h^+ causes oxidations and e^- reductions.

The excited-state species POM/SiO$_2$(e^- + h^+) have more powerful redox abilities by forming electron–hole pairs. In the presence of water molecules, the reaction of photoholes with the surface hydroxyl groups occurs,

Scheme 1. Pathway of Photocatalytic Degradation of Aqueous HCH



and OH$^•$ radicals are generated (eq 5).

$$POM/SiO_2(e^- + h^+) + H_2O \leftrightarrow POM/SiO_2(e^-) + OH^• + H^+ \quad (5)$$

OH$^•$ radicals are strong and unselective oxidant species in favor of totally oxidative degradation and mineralization for organic substrates.

(ii) The reoxidation of the catalyst is the primary function of dioxygen in the mineralization process (eqs 6−8):

$$POM/SiO_2(e^-) + O_2 \rightarrow [POMO_2/SiO_2]^- \quad (6)$$

The O_2^-/HO_2 species thus formed inhibit the recombination of h$^+$ and e$^-$, which is important in the degradation and final mineralization of the intermedites.[4]

$$[POMO_2/SiO_2]^- \rightarrow POM/SiO_2 + O_2^- \quad (7)$$

$$O_2^- + H^+ \rightarrow HO_2 \quad (8)$$

(iii) For the degradation of HCH ($C_6H_6Cl_6$) by the POM/SiO$_2$, Scheme 1 has been proposed according to the intermediates detected during the course of the mineralization of $C_6H_6Cl_6$.

Therefore, we can infer that electrophilic OH$^•$ radicals are responsible for the pathway of the photocatalytic degradation of aqueous HCH. Several groups' studies of OH$^•$ radicals generated by TiO$_2$ photolysis of aqueous solution were also adopted.[3,6,9]

At first, OH$^•$ radicals oxidize $C_6H_6Cl_6$ to form phenyl hexachloride, as detected by GC/MS, and H$^+$ is abstracted. Second, the aromatic ring is successively hydroxylated at a C−Cl bond by OH$^•$ radicals to form polyphenol, tetrahydroxybenzoquinone, and then benzoquinone, as also detected by GC/MS, while Cl$^-$ is released into the slurry. Third, aromatic ring was opened and formed 1,6-hexanedicarboxylic acid, which degraded continuously and generated acetic acid and formic acid, as detected by IC, and then the final products, CO$_2$ and HCl.

The overall reaction is shown as follows:

$$C_6H_6Cl_6 + 6O_2 \xrightarrow[\text{cat. } \mathbf{1} \text{ or } \mathbf{2}]{h\nu} 6CO_2 + 6HCl$$

Conclusions

Microporous polyoxometalates $H_3PW_{12}O_{40}/SiO_2$ and $H_4SiW_{12}O_{40}/SiO_2$, containing various amounts of $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$, were synthesized by encapsulating $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ into a silica matrix via hydrolysis of TEOS in the presence of $H_3PW_{12}O_{40}$ or $H_4SiW_{12}O_{40}$. By irradiating the system of HCH-(PCNB)−$H_2O(CH_3CN)$−$H_3PW_{12}O_{40}/SiO_2$ or HCH(PCNB)−$H_2O(CH_3CN)$−$H_4SiW_{12}O_{40}/SiO_2$ with energy in the near-UV region, trace aqueous organocholorine pesticides were totally degraded and mineralized into CO$_2$ and HCl under mild conditions. The photocatalytic activities of POMs are greatly improved when the POMs were entrapped by the silica matrix. The reaction for photocatalytic degradation of trace aqueous HCH by the POMs/SiO$_2$ exhibits the apparent first-order kinetics of the Langmuir−Hinshelwood model, and the electrophilic OH$^•$ radicals are responsible for the pathway of the photocatalytic degradation of aqueous HCH. Both of the silica-impregnated Keggin anions present the important advantages of being more easily handled than pure Keggin anions. Leakage of $H_3PW_{12}O_{40}$ or $H_4SiW_{12}O_{40}$ from the silica matrix was hardly observed during eight times of reuse when POMs/SiO$_2$ with suitable weight ratios of silica/acid were used. The present study confirms the potentialities of heterogeneous photocatalytic decontamination of wastewater containing organochlorine compounds by the POMs/SiO$_2$.

Acknowledgment. The Natural Science Fund Council of China is acknowledged for financial support (No. 20071007). The present work is also supported by the Foundation for University Key Teacher by the Ministry of Education of China.

CM000074+