

Photocatalytic Degradation of Imidacloprid by Phosphotungstic Acid Supported on a Mesoporous Sieve MCM-41

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Solid catalysts consisting of polyoxometalates (POM) namely phosphotungstic acid $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (HPW) supported on a mesoporous sieve MCM-41 have been prepared and characterized by FT-IR, X-ray diffraction, nitrogen adsorption and high resolution transmission electron microscope (HRTEM). The HPW/MCM-41 with different HPW loadings from 10 to 60 wt% possess large specific surface area and rather uniform mesopores. Keggin structure of HPW retains on the prepared composite catalysts. The photocatalytic performance of HPW/MCM-41 was examined by degradation of a durable pesticide imidacloprid. It is found that the prepared photocatalysts exhibit high activity under irradiation of 365 nm monochromatic light. For 50 mL of imidacloprid (10 mg/L), conversion of imidacloprid using 20 mg of HPW/MCM-41 with 50 wt% loading level and calcined at 300 °C reaches 58.0% after 5 h irradiation.

Keywords polyoxometalates, photocatalysis, degradation, immobilization, mesoporous material, imidacloprid, pesticide

Introduction

In the latest years, photocatalysis has been widely studied as an advanced oxidation process in degradation of contaminations in wastewater.^[1,2] Polyoxometalates (POM) such as $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (HPW), $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ (HSiW) and their salts arouse more and more attentions due to their favorable photocatalytic activity in degradation of persistent organic pollutants including organic halides, dyes, pesticides, *etc.*^[3-6] For the purpose of application, water-insoluble solid POMs are prepared by combining soluble POMs with supporting materials (*e.g.* semiconductor oxides SiO_2 , ZrO_2 and TiO_2 , layered double hydroxides, anionic exchange resin).^[7-13] The composite POMs show high photocatalytic activity because of the largely increased specific surface areas compared with the POM anions. POMs supported on microporous and mesoporous materials USY, MCM-41, MCM-48 or SBA-15 have also been reported in catalysis of hydroisomerization, alkylation, esterification and other organic reactions.^[14-18] Such porous materials with uniform and regular pores and large specific surface areas (BET specific surface areas of these mesoporous materials may reach 1000 m²/g), are prospective to be used as excellent supporting materials of photocatalysts. The photocatalytic degradation of dye Rhodamine B by $\text{K}_5[\text{Ni}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]$ supported on amine-functionalized MCM-41 has been studied by Li *et al.*^[19] To our best knowledge, the photocatalytic activity of heteropoly

acids $\text{H}_3\text{PW}_{12}\text{O}_{40}$ supported on MCM-41 in degradation of pesticide has never been reported before. In this work, POM-containing photocatalysts are prepared by impregnating heteropoly acids $\text{H}_3\text{PW}_{12}\text{O}_{40}$ on mesoporous material MCM-41. The photocatalytic activity of the prepared materials is evaluated afterwards by degradation of a world widely used pesticide imidacloprid.

Experimental

Materials

Chemical reagents cetyltrimethylammonium bromide (CTAB, 99%), $\text{NH}_3\cdot\text{H}_2\text{O}$ (25%—28%), tetraethyl orthosilicate (TEOS, 28%), phosphotungstic acid hydrate, methanol in the present work are AR grade and purchased from Beijing Chemical Reagent Co., China. Pesticide imidacloprid (powder, 97%) is provided by Institute of Plant Protection, Chinese Academy of Agricultural Sciences.

Preparation and characterization of catalysts

Mesoporous material, pure-silica MCM-41 is prepared by hydrothermal method following the procedures of Xiao *et al.*^[20] 3.2 g of cetyltrimethylammonium bromide (CTAB) is dissolved in 100 mL of deionized water at 25 °C with 48 mL $\text{NH}_3\cdot\text{H}_2\text{O}$, stirring for *ca.* 5 min, followed by addition of 18 mL tetraethyl orthosilicate (TEOS) dropwise. After stirring for 6 h, the mixture is

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loaded into an autoclave and statically heated at 100 °C for 24 h. The resulting solid product is recovered by filtration, washed with deionized water, dried at 50 °C and calcined in air at 550 °C with a programming rate of 1 °C/min.

POM catalysts with different loadings (10–60 wt%) of HPW over MCM-41 are prepared by impregnating method. In a typical run, 0.5 to 1 g of MCM-41 is dispersed under stirring in 20 mL of methanol containing a certain amount of HPW at room temperature for 24 h. The resulting mixtures are dried at 50 °C and calcined at different temperatures.

The samples are dispersed in KBr discs and their infrared spectra are obtained by an American Nicolet 6700 FT-IR spectrometer. The spectra are recorded in transmittance mode and scanned from 400 to 4000 cm^{-1} . Powder X-ray diffraction (XRD) data are analyzed in a Netherlands PaNalytical X'pert Pro MPD X-ray diffractometer with Cu $K\alpha$ radiation $\lambda=1.5418 \text{ \AA}$. The high resolution transmission electron microscope (HRTEM) is performed using a Japan Hitachi S-3500N microscope. Specific surface area and pore volume are measured by nitrogen adsorption at 77 K using a China Beishide 3H-2000PS2 surface analyzer. The samples are degassed at 423 K for 2 h under nitrogen atmosphere prior to the analysis.

Photocatalytic testing

The photocatalytic reactions are performed on a China Trusttech PLS-SXE300 photoreactor equipped with a 300 W Xe light source. Substrate suspension is put into a quartz beaker under Xe light. Distance from the suspension surface to light source is about 20 cm. Irradiation is filtered with a 365 nm optical filter to obtain the monochromatic light of $(365 \pm 10) \text{ nm}$.

The photocatalytic activity of the prepared catalysts is tested by degradation of model contaminant pesticide imidacloprid (its structure is shown in Figure 1). In a typical procedure, 0.02 g of solid catalysts is suspended in an aqueous solution of imidacloprid (10 mg/L, 50 mL), the suspension is stirred in dark for 30 min to ensure the establishment of adsorption-desorption equilibrium before irradiation. The concentration of imidacloprid is monitored by a Japan Shimadzu LC-ATVP 230V high-pressure liquid chromatography (HPLC) with a Sapphire C18 column. The mobile phase is a mixture of methanol-water ($V:V=1:1$) adjusted to pH 4.00 by phosphoric acid. Imidacloprid is detected at 270 nm with UV detector and the retention time is *ca.* 5.5 min. The transformation products (TPs) of the photocatalytic reactions are detected by ultra high performance liquid chromatography with an American Waters ACQUITY

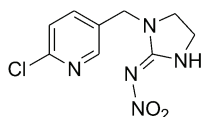


Figure 1 Structure of pesticide imidacloprid.

and tandem mass spectrometry with an American AB API 4000 (UPLC-MS/MS).

Results and Discussion

Characterization of catalyst

FT-IR spectra of as prepared support material MCM-41, HPW/MCM-41 as well as bulk HPW are shown in Figure 2. As seen from the figure, absorption peaks at 1088, 808 and 460 cm^{-1} of MCM-41 (Figure 2a) arise from asymmetrical stretching, symmetrical stretching and bending vibration of Si—O respectively. For the composite catalysts with 30 and 50 wt% loading level (Figures 2b, 2c) calcined at 300 °C, characteristic absorption bands at around 1082 cm^{-1} (P—O), 980 cm^{-1} (W=O), 814, 897 cm^{-1} (W—O—W) of HPW/MCM-41, are in good agreement with those of bulk HPW (Figure 2d). This indicates the Keggin structure is well retained in prepared composites. Slightly shifts 2–9 cm^{-1} for W=O and W—O—W compared to that of parent HPW are observed, indicating the chemical interactions exist between the Keggin anion of HPW and the MCM-41 inner surface. The Keggin unit of HPW decomposes for HPW/MCM-41 with low loading level namely 20 wt% (Figure 2e), due to a diluted HPW solution ($\text{pH} \geq 2$) having to be used when impregnating HPW on MCM-41, as is known Keggin structure of HPW is stable in solutions under pH 2. Figures 2f, 2g show 50 wt% HPW/MCM-41 calcined at 200 and 500 °C. It is seen that the Keggin structure of HPW anion is destroyed after thermal treatment at the temperature as high as 500 °C. However, all the prepared catalysts calcined at temperatures 300–500 °C show a small band adsorption at *ca.* 1245 cm^{-1} besides

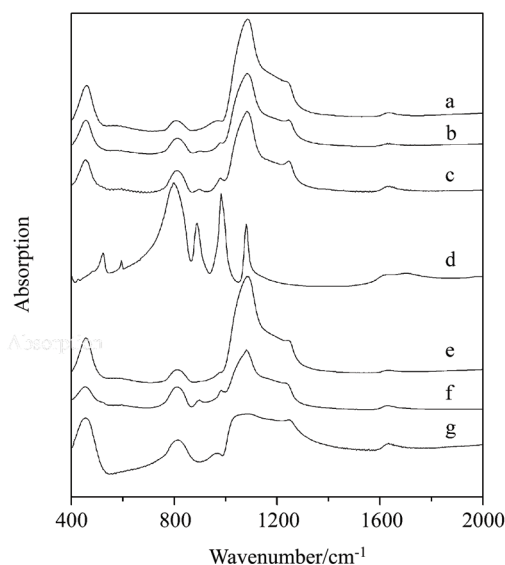


Figure 2 FT-IR spectra of the prepared HPW/MCM-41 catalysts. (a) MCM-41; (b), (c) are 30 wt% HPW/MCM-41, 50 wt% HPW/MCM-41, respectively, both calcined at 300 °C; (d) HPW; (e) 20 wt% HPW/MCM-41, calcined at 300 °C; (f), (g) are 50 wt% HPW/MCM-41, calcined at 200, 500 °C, respectively.

the typical bands of HPW. This result also suggests the chemical interaction between the Keggin unit and rich Si—OH of MCM-41 inner surface is achieved when calcined at temperatures higher than 300 °C.

Figure 3 shows the small angle XRD pattern of initial MCM-41 and calcined HPW/MCM-41. The MCM-41 support exhibits a typical XRD pattern at 2.23° (100), 3.87° (110) and 4.47° (200).^[21] Mesoporous structure of MCM-41 is undamaged after HPW loading from Figures 3a and 3b. Wide angle XRD patterns of the prepared HPW/MCM-41 with different loading levels from 10 to 50 wt% are shown in Figure 4. The diffraction peaks of HPW turn to be stronger when HPW loading level arises from 10 to 50 wt% in our experiments. However, 40 wt% HPW/MCM-41 contains only three weak peaks 20.5°, 25.3° and 34.4°, suggesting HPW tends to be highly dispersed in the mesopores of MCM-41. The crystal phase of HPW could be found clearly when the loading level increases to 50 wt%, indicating that the crystalline particles begins to aggregate on the outer surface of MCM-41 since the loading level is really high when arises to 50 wt%. This result implies most of the Keggin units (*ca.* 1.0 nm in diameter) of HPW disperse well in the inner surface of the mesopores of MCM-41 (2.7 nm in diameter). As far as 50 wt% HPW/MCM-41 is concerned, HPW occupies about 25% of MCM-41 specific surface area (842.9 m²/g) as calculated, assuming that HPW is arranged as a monomolecular layer on the surface of MCM-41.

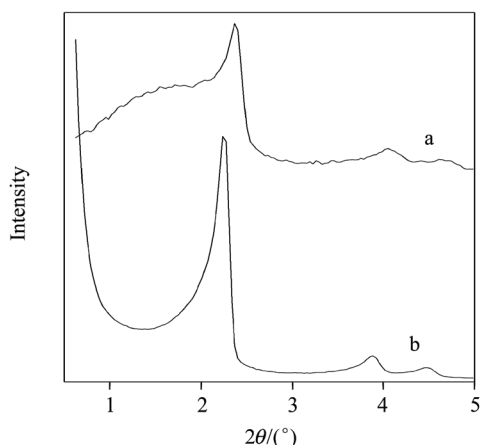


Figure 3 Small angle XRD pattern of the catalysts and MCM-41. (a) 50 wt% HPW/MCM-41, calcined at 300 °C; (b) MCM-41.

Table 1 shows the BET surface area, BJH pore volume and average pore diameter of the support MCM-41 and the catalysts loaded with 10–60 wt% HPW. As calculated from N₂ adsorption, the BET surface area, pore volume and pore diameter all decrease after loading HPW on MCM-41. Even so, at high loading level of 50 wt%, the prepared catalysts have rather large surface area and pore size. Most importantly, the composites retain the uniformity of their mesopores. Thus, the 50 wt% HPW/MCM-41 has a 268.5 m²/g BET surface area

and uniform pores of 2.5 nm in diameter (Figure 5).

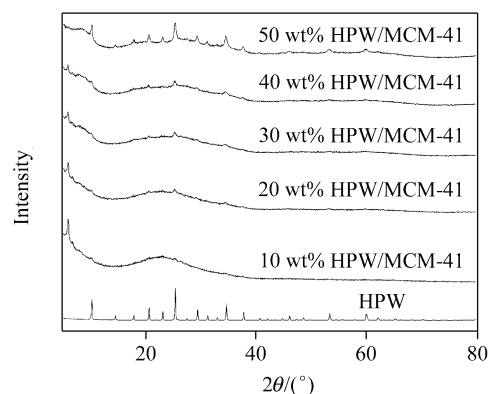


Figure 4 Wide angle XRD pattern of bulk HPW and HPW/MCM-41 with different loading levels, calcined at 300 °C.

Table 1 Surface and porosity of HPW/MCM-41 and MCM-41

Sample ^a	BET surface area/(m ² ·g ⁻¹)	Pore volume/(cm ³ ·g ⁻¹)	Average pore diameter/nm
MCM-41	842.9	0.75	2.7
20 wt% HPW/MCM-41	552.6	0.56	2.7
30 wt% HPW/MCM-41	463.1	0.42	2.6
40 wt% HPW/MCM-41	381.8	0.31	2.6
50 wt% HPW/MCM-41	268.5	0.22	2.5
60 wt% HPW/MCM-41	192.7	0.17	2.3

^a All of the HPW/MCM-41 catalysts are calcined at 300 °C.

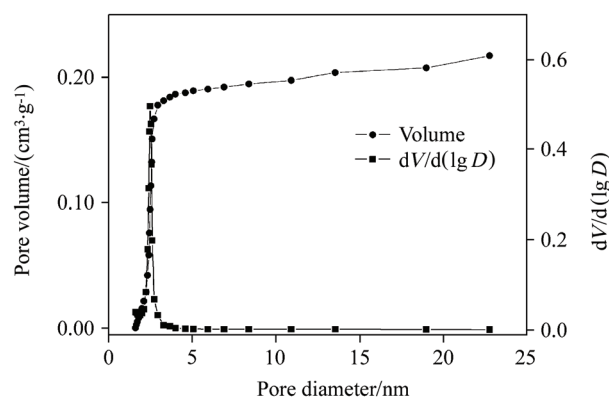


Figure 5 Pore size and volume distribution curve of 50 wt% HPW/MCM-41, calcined at 300 °C.

Figure 6 shows the high resolution transmission electron microscope of 50 wt% HPW/MCM-41. The prepared catalysts exhibit hexagonal crystal phase of MCM-41 at the macroscale level (Figure 6a). The hexagonal lattice cell is *ca.* 2 μm. The regular and uniform

hexagonal mesoporous structure is retained at the microcosmic level after HPW loading (Figure 6b).

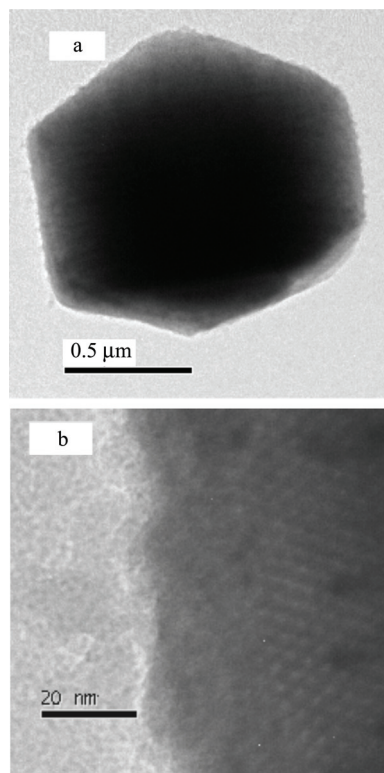


Figure 6 HRTEM of 50 wt% HPW/MCM-41, calcined at 300 °C.

Photocatalytic degradation of imidacloprid

Photocatalytic activities of the prepared HPW/MCM-41 catalysts are tested by photocatalytic degradation of pesticide imidacloprid under irradiation of 365 nm UV light. Photocatalytic activities of HPW/MCM-41 with different loading levels are shown in Figure 7. The results show that the best loading level is 50 wt% for the prepared HPW/MCM-41 catalysts. Conversion of imidacloprid using 50 wt% HPW/MCM-41 reaches 58.0% after 5 h irradiation, which is higher than that of 40, 60 wt% HPW/MCM-41 and other catalysts. When the loading level decreases to 20 wt%, the catalysis effect of HPW/MCM-41 on the degradation of imidacloprid may be neglected. The adsorption of imidacloprid on the HPW/MCM-41 catalysts with different loadings is observed in the condition of darkness. The maximum adsorption capacity is *ca.* 5% to 10% after the adsorption-desorption equilibrium of the reaction suspension is established.

The influence of calcined temperature of the prepared composites is observed using 50 wt% HPW/MCM-41 as the catalyst. The catalyst calcined at 300 °C exhibits the highest photocatalytic activity (Figure 8). Importantly, the catalyst calcined at 400 °C is rather close to 300 °C as far as the degradation conversion of imidacloprid is concerned, indicating that catalysts with high photocatalytic activity may be calcined in the range

of 300 to 400 °C. Catalysts show low activity when calcined at 200 or 500 °C, because the strong interaction between Keggin HPW anions and Si-OH of support MCM-41 can not be achieved when calcined at 200 °C, while on the other hand, active Keggin HPW structure would be damaged when calcined at temperature higher than 400 °C. These results are consistent with the FT-IR analysis as motioned above.

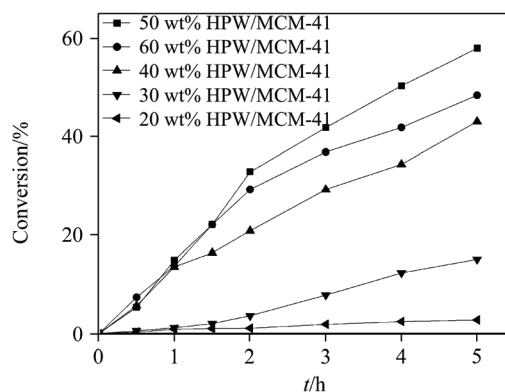


Figure 7 Photocatalytic degradation of imidacloprid by HPW/MCM-41 with different loading levels (all catalysts are calcined at 300 °C).

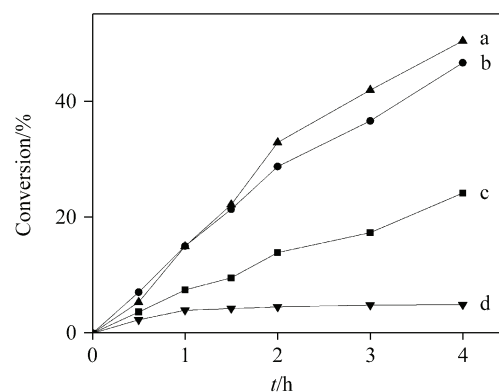


Figure 8 Influence of calcined temperature on photocatalytic activity of 50 wt% HPW/MCM-41. (a)–(d) are catalysts calcined at 300, 400, 500 and 200 °C, respectively.

Figure 9 shows the influence of the amount of 50 wt% HPW/MCM-41 (calcined at 300 °C) on degradation of imidacloprid. As seen in the figure, the highest conversion is achieved when using 20 mg of HPW/MCM-41 for the degradation of 50 mL of imidacloprid (10 mg/L). A further increase of the amount of the catalyst to 30 or 40 mg leads to a decrease of conversion of the substrate because too much milky solid catalyst would cause light scattering and reduce the quantum efficiency.

After the reaction finished, the reaction suspension is allowed to settle, the catalyst is filtered, washed with water and recovered by centrifugation, dried at 50 °C for the next run of degradation. HPW/MCM-41 mostly keeps its initial activity for 3 times' reuse and the leak-

age of the prepared HPW/MCM-41 is neglected, suggesting the strong interactions between HPW Keggin unit and the support MCM-41 ensure the little leaching of the Keggin anions from MCM-41 (Figure 10).

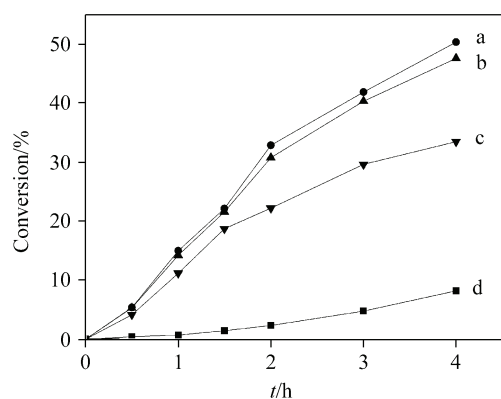


Figure 9 Influence of the amount of the catalysts on degradation of imidacloprid. (a)–(d) are 20, 30, 40 and 10 mg, respectively.

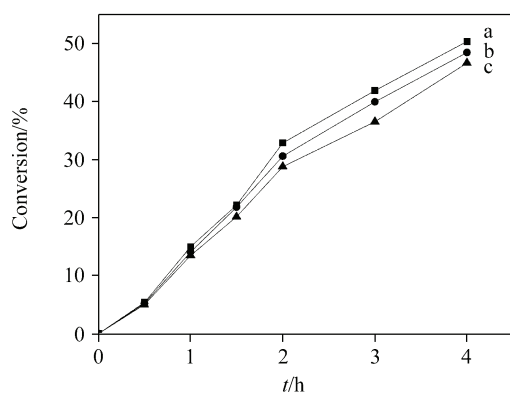


Figure 10 Reuse of 50 wt% HPW/MCM-41 (calcined at 300 °C). (a)–(c) are 1–3 time's run of degradation.

In order to analyze the transformation products produced by the photocatalytic degradation of imidacloprid, 14 h photocatalytic reaction is monitored by UPLC-MS/MS using 50 wt% HPW/MCM-41 as the catalyst. In the early stage of the photocatalytic degradation of imidacloprid, four alicyclic compounds 1-(6-chloro-3-pyridinyl)methyl-2-imidazolidinone, 6-chloro-nicotinic aldehyde, 6-chloronicotinic acid and 6-chloro-nicotinamide are detected as the main TPs. During 6 to 14 h irradiation, the concentrations of above compounds gradually decrease, however, three other intermediates including the heterocyclic compound 2-pyrrolidinone and two aliphatic compounds, namely, 2-methyl-1-nitropropane and amyl nitrite are detected, suggesting that the cleavage of aromatic ring occurs in this stage.

The photocatalytic reactions are carried out in near neutral conditions without adjusting pH, indicating the prepared catalysts are suitable for practical use in wastewater treatment. The large specific surface area and uniform mesoporous structure of MCM-41 provide

perfect microenvironment for the photocatalytic reaction of imidacloprid by HPW Keggin anions.

Conclusions

A series of solid mesoporous HPW/MCM-41 catalysts with different loading levels are prepared by impregnation method. The composites have regular and uniform mesopores with average pore diameter above 2 nm. Their BET specific surface areas are much higher than that of starting phosphotungstic acid. The prepared heterogeneous catalysts exhibit high photocatalytic activity in degradation of a durable pesticide imidacloprid under irradiation of near-visible 365 nm light. The influences of loading level, calcined temperature and the amount of catalysts are discussed and compared. For 50 mL of imidacloprid (10 mg/L), in the optimal reaction conditions, conversion of imidacloprid using 20 mg of HPW/MCM-41 with 50 wt% loading level and calcined at 300 °C reaches 58.0% after 5 h irradiation. The high photocatalytic activity of composites mainly comes from the uniform mesopores and large specific surface area of the catalysts.

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