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Preparation and characterization of molecularly imprinted SiO_2-TiO_2 and photo-catalysis for 2, 4-dichlorophenol

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ABSTRACT

A novel 2, 4-dichlorophenol imprinted TiO_2-SiO_2 catalyst was prepared by molecular imprinting technique in combination with sol-gel method. The prepared material was characterized by X-ray diffraction (XRD), infrared spectroscopy (IR), scanning electron-microscopy (SEM), transmission electron microscopy (TEM) and N_2 adsorption measurement. The effect of the preparation condition on the degradation behavior, the photo-catalytic ability and selectivity of the prepared material were evaluated. The results show that the imprinted material has good photo-degradation capacity and selectivity toward the target pollutant, which was shown to be promising for selective removal of 2, 4-dichlorophenol from environmental samples. Copyright © 2010 VBRI press.

Keywords: 2, 4-dichlorophenol; molecular imprinting; sol-gel method; TiO_2-SiO_2.

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Introduction

The application of semiconductors in heterogeneous photo-catalysis to eliminate various pollutants has gained significant attention in the last decade [**1, 2**]. Among various oxide semiconductor photo-catalysts, TiO_2, as it is non-toxic, highly chemically resistant and available at low cost, is investigated and widely used as photo-catalyst in various applications [**3-5**].

But several important scientific and technologic problems are still to be solved in the application of TiO_2 semiconductor photo-catalysis for the treatment of industrial wastewater [**6, 7**]. One problem is the aggregation and difficulty in recovering. Several attempts have been adopted to enhance separation performance of TiO_2. Titania nano-particles supported on silica can take the advantage of high surface areas and improved recovery properties as compared to pure titania, which may facilitate the separation [**8-13**].

Another drawback being faced by the TiO_2 semiconductor photo-catalysis is its poor selectivity. It is still difficult to realize selective removal of harmful low-level pollutants from complicated wastewaters in the presence of other high-level less-harmful pollutants via photo-catalytic treatment, because TiO_2 has a very poor selectivity and cannot differentiate the pollutants [**14, 15**]. Thus, it is urgently necessary to promote the selectivity of TiO_2 photo-catalysts. Several approaches have been proposed to enhance the selectivity of TiO_2 such as controlling the surface's electric charge by adjusting pH [**16**], modifying the surface of TiO_2 with specific molecules [**17, 18**], and developing double-region-structured photo-catalysts [**19**].

Recently, Zhu et al. are trying to develop another way to obtain high selectivity by imprinting cavities of target molecules on the photo-catalyst's surface. They reported a possibility of increasing the selectivity of TiO_2 by increasing selective adsorption of target molecules on surface-modified TiO_2 [**15**]. The modified TiO_2 photo-catalyst was prepared by coating a thin layer of molecular-imprinted polymer (MIP) via polymerization of *o*-phenylenediamine in the presence of target molecules and TiO_2 nanoparticles. The novel photo-catalysts were able to remove selectively low level target 2-chlorophenol or 4-chlorophenol via a photo-catalytic treatment. To get more efficient photo-catalysts with high selectivity and confirm the MIP coating as a general way of increasing the selectivity of TiO_2 photo-catalysts, they further investigated the selective photo-catalytic degradation of nitrophenols on TiO_2 nanoparticles coated with a thin layer of MIP and obtained satisfactory results [**14**].

In this work, a simple way was developed to prepare the 2, 4-dichlorophenol (2, 4-DCP) imprinted TiO_2-SiO_2 composite catalyst by using molecular imprinting technique and sol-gel method. The process involves a conventional sol-gel process and incorporation of the template molecules into rigid inorganic-organic networks. After removal of the template by calcination, special cavities with distinct pore size, shape remain in the cross-linked host. These special cavities show higher affinities for the template molecule over other structurally related compounds. Meanwhile pulling SiO_2 into the catalyst can increase absorption capacity and recovery property.

Experimental

Materials

Tetraethoxysilicane (TEOS), 3-aminopropyltriethoxysilane (APTES) (Wuhan University Chemical Factory, Wuhan, China), tetrabutyl titanate (TBOT), 2, 4-dichlorophenol (2,4-DCP), phenol (Linfeng Chemical Co., Shanghai, China), acetic acid (HAc) (Shanghai Chemical Reagent Co., Shanghai, China) were used in this study. Doubly deionized water (DDW, 18 MΩ/cm) obtained from a WaterPro water system (Labconco Corporation, Kansas City, USA) was used throughout the experiments. The mobile phase used for HPLC experiments was a mixture of methanol (Concord Technology Co. Ltd. Tianjin, China) and water (*v*/*v* = 7:3), and was filtered through 0.45-μm filter prior to use. All reagents used were of at least analytical grade.

Catalyst preparation

To prepare the 2, 4-DCP imprinted TiO_2-SiO_2 composite catalyst, 1g of 2, 4-DCP was dissolved in 5 mL of ethanol, and mixed with 2 mL of APTES. The mixture was stirred for 20 min then 4 mL of TEOS was added. After stirring for 5 min, appropriate volume of TiO_2 sol solution (prepared beforehand by a hydrolysis-condensation reaction of TBOT with ethanol as solvent) and 1 mL of 1 mol L^{-1} HAc (as catalyst) were added. The mixture began to co-hydrolyze and co-condense after stirring for a few minutes, then incubated for 10 h at room temperature. The product was filtrated and dried in a vacuum oven at 100^oC for 8 h. Finally, the catalyst was put into high temperature furnace and heated in the rate of 1^oC/min and calcined at the treatment temperature for 3 h. For comparison, the non-imprinted TiO_2-SiO_2 composite catalyst was also prepared using an identical procedure, without the addition of 2, 4-DCP.

Photo-catalytic activity

2, 4-DCP imprinted and non-imprinted TiO_2-SiO_2 composite catalyst were applied to the 2, 4-DCP degradation. A 30-W Hg-lamp was used as the light source at λ_{max} = 254 nm. During the experiment, the catalyst suspension was well-stirred by using a magnetic stirrer. The aqueous solution of 2, 4-DCP (50 mL) and 10 mg of the photo-catalyst were placed in the photo-reactor at room temperature, then stirred for 10 min to favor the organic adsorption onto the catalyst surface in the dark (the adsorption experiment shows that the adsorption equilibrium can be reached within 10 min), the concentration of the pollutant was determined as the initial concentration C_0, and then the photo-irradiation started. Aliquots of the reaction solution were sampled at given time intervals. After the samples were filtered through 0.45 μm filters to remove the photo-catalyst particles, the remaining concentrations of the pollutants was measured by high-performance liquid chromatography (LC-1200, Agilent). The photo-degradation efficiency of 2, 4-DCP was calculated by the following equation:

$$\eta = (C_0 - C_e)/ C_0 \times 100\% \qquad \text{---------------} \ (1)$$

where η is the photo-degradation efficiency; C_0 is the initial concentration, C_e is the remaining concentration.

Characterization

The structure of the composite catalyst was characterized by Fourier transform infrared spectroscopy (Nicolet 6700, USA) and X-ray diffraction patterns (D8 Advance X-ray polycrystaline diffractometer, Germany). The images of the samples were obtained by transmission electron microscopy (Tecnai G2F30, Holland) and scanning electron microscopy (S-4700-II, Japan) equipped with energy dispersive spectrum to measure the element content of the samples. The specific surface area and pore size were measured by nitrogen adsorption/desorption measurement at 77 K using BET method (Gemini V 2380, USA).

Results and discussion

FT-IR spectroscopy

The FT-IR spectra of the 2, 4-DCP imprinted TiO_2-SiO_2 composite catalyst ($m_{(Ti)}/m_{(Si)}$ = 1.5, calcined at 600 ^oC) is shown in **Fig. 1**. The band at 1077 cm^{-1} is assigned to the characteristic vibration of the Si-O bond. Meanwhile, the absorption peaks at 466 cm^{-1} can be assigned to the Si-O-Si vibration, 937 cm^{-1}, which is associated with the formation of Si-O-Ti bridges. The peaks are assigned to the OH binding and stretching of water at 1618 and 3398 cm^{-1}, respectively. These findings are in agreement with previous studies [**9, 11**]. Complementary FT-IR spectra of non-imprinted composite catalyst showed similar location and appearance of the major bands.

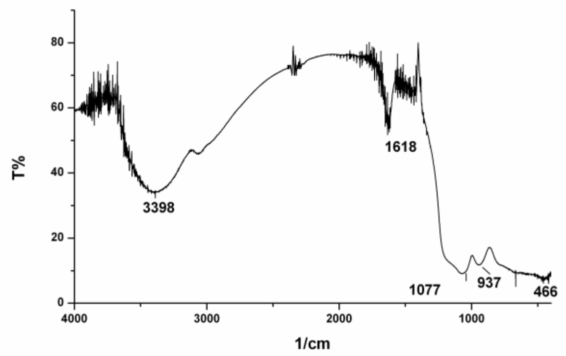

Fig.1. IR spectra of 2,4-DCP imprinted TiO_2–SiO_2 composite catalyst.

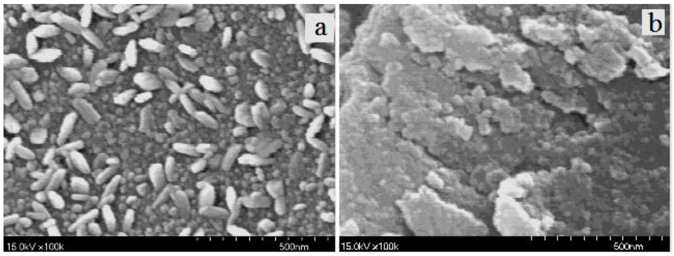

Fig. 2. SEM of composite catalysts: (a) imprinted TiO_2–SiO_2 composite catalyst (b) non-imprinted TiO_2–SiO_2 composite catalyst.

The morphologies of catalysts

Fig. 2 shows the scanning electron microscopy pictures of the 2, 4-DCP imprinted and non-imprinted TiO_2-SiO_2 composite catalyst ($m_{(Ti)}/m_{(Si)} = 1.5$, calcined at 600 °C). It is found that particles in 2, 4-DCP imprinted catalyst distribute much better than that in non-imprinted TiO_2-SiO_2 composite catalyst. The TEM image of imprinted TiO_2-SiO_2 in **Fig. 3** shows that the catalyst was aggregated by nano-particles. The specific surface areas and pore sizes were listed in **Table 1**. The specific surface area of the 2, 4-DCP imprinted composite catalyst decreases gradually with the increase of the heat treatment temperature. Under the same preparation conditions, TiO_2-SiO_2 has significantly higher surface area than that of TiO_2.

Table 1. Surface area and average pore size of the different catalysts

Photocatalyst	Calcination temperature (°C)	Surface area (m^2/g)	Average pore size (nm)
	500	125.2	3.3
Imprinted	600	94.3	6.5
	700	90.2	7.0
Non-imprinted	600	38.7	2.2
Pure TiO_2	600	8.9	13.1

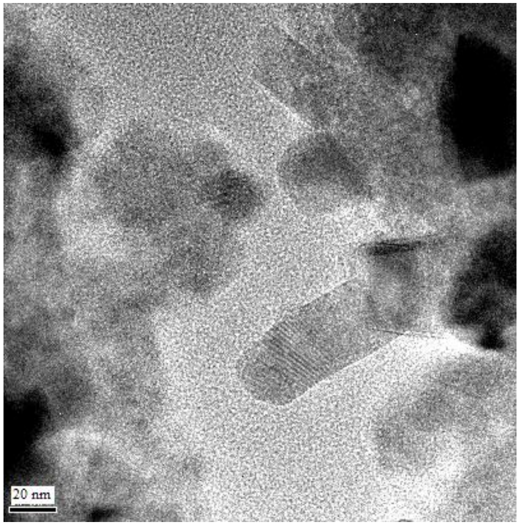

Fig. 3. TEM image of TiO_2-SiO_2 calcinated at 600 °C.

X-ray diffraction patterns

The XRD patterns of the 2, 4-DCP imprinted TiO_2-SiO_2 composite catalysts with different calcination temperatures ($m_{(Ti)}/m_{(Si)} = 1.5$) are shown in **Fig. 4**. The results show that the most intense reflection at 2θ = 25.3° is assigned to anatase (d101). Miller indices of imprinted composite are all in accord with that of standard anatase. No significant rutile phase was observed even at 700 °C according to the absence of the (d110) rutile reflection at 2θ=27.4°, which suggested that the presence of silica gel inhibited the phase transformation of TiO_2 from anatase to rutile. Similar results were also found by Chen et al. [**11**].

Photo-catalytic activity

The degradation efficiency of the imprinted TiO_2-SiO_2 composite catalyst (calcined at 600 °C) with different ratio of $m_{(Ti)}/m_{(Si)}$ was tested (**Fig. 5**). The experiment shows that the photo-catalytic activity of imprinted TiO_2-SiO_2 increases with increasing of the ratio of $m_{(Ti)}/m_{(Si)}$ from 0.5 to 1.5 (mass ratio), whether it is irradiated for 60 min or 120 min. However, when the ratio of $m_{(Ti)}/m_{(Si)}$ is greater than 1.5, the photo-catalytic activity of the composite decreases gradually. The above results may be interpreted as follows: When the ratio of $m_{(Ti)}/m_{(Si)}$ increases, the surface area of the catalyst decreases (**Table 2**) which may reduce its adsorption capacity, but the amount of TiO_2 increases accordingly which may enhance its photo-degradation capacity. Furthermore, the phase of the TiO_2-SiO_2 system will change with the increase of TiO_2 content. Stakheev et al. [**20**] reveals that the TiO_2-SiO_2 system exists as a homogeneous solid solution of TiO_2 in SiO_2 at low TiO_2 concentration. On increase of the TiO_2 concentration, formation of a new TiO_2-rich phase occurs. At low SiO_2 concentrations, silicon forms a monolayer titanium silicate coating on the TiO_2 particles. Due to the influence of above multi-factors, When the ratio of $m_{(Ti)}/m_{(Si)}$ is 1.5, the photo-catalytic activity of imprinted TiO_2-SiO_2 composite is at its best.

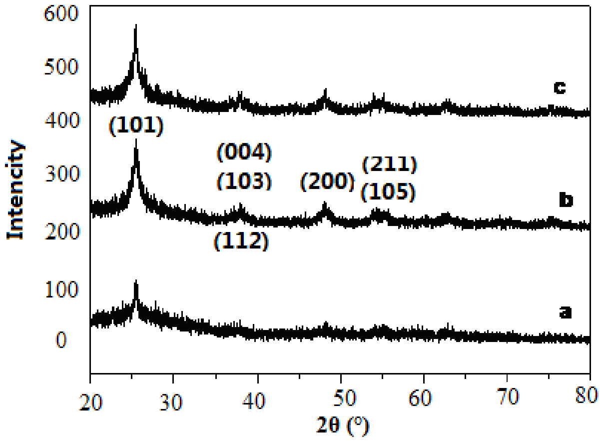

Fig. 4. XRD patterns of 2, 4-DCP imprinted TiO_2–SiO_2 composite catalyst with different calcination temperatures: (a) 500 ^oC (b) 600 ^oC (c) 700 ^oC.

Table 2. Surface area of the imprinted TiO_2–SiO_2 (calcined at 600 ^oC) with different ratio of m(Ti)/m(Si).

Ratio of m(Ti)/m(Si)	0.5	1.0	1.5	2.0
Surface area(m^2/g)	101.2	96.5	94.3	91.2

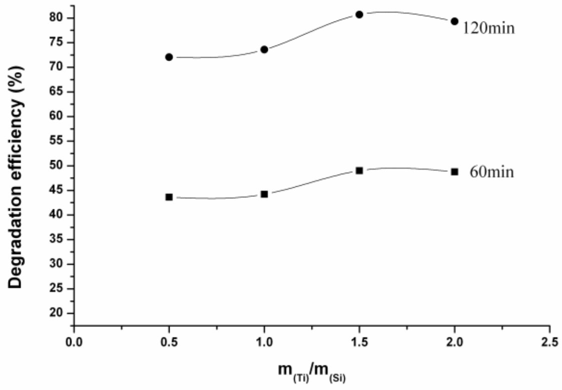

Fig. 5. Degradation efficiency of 2, 4-DCP using imprinted TiO_2–SiO_2 composite catalyst with different ratio of $m_{(Ti)}/m_{(Si)}$.

The effect of different calcination temperatures on the photo-catalytic activity of imprinted TiO_2-SiO_2 composite catalyst is shown in **Table 3**. The photo-catalytic activity of imprinted TiO_2-SiO_2 varies with different heat treatment temperatures and the best calcination condition is 600 ^oC, the efficiency of photo-catalytic degradation of 2, 4-DCP can reach 80.05% with 120 min irradiation. This phenomenon may be attributed to the fact that the difference of heat treatment conditions lead to the differences in specific surface area, hydroxyl group, the defects of surface and active sites [**21**].

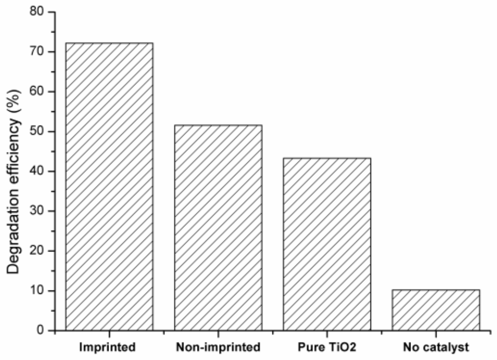

Fig. 6. Degradation efficiency of 2, 4-DCP in single system by using different catalysts and no catalyst after 2 h irradiation.

The photo-catalytic ability and selectivity of the imprinted TiO_2-SiO_2 composite catalyst were evaluated in single system (only one organic substrate in the suspension) and in binary system (with a coexisting pollutant in the suspension). **Fig. 6** shows the degradation efficiency of 2, 4-DCP by using imprinted TiO_2-SiO_2, non-imprinted composite catalyst, pure TiO_2 (prepared with TiO_2 sol solution in the same procedure) and no catalyst in single system respectively. Obviously, the degradation efficiency of 2, 4-DCP with imprinted TiO_2-SiO_2 is higher than that with non-imprinted composite catalyst and the degradation efficiency will be increased by pulling SiO_2 into TiO_2 catalyst. Meanwhile, from **Fig. 6** one can see that the degradation efficiency of 2, 4-DCP caused by direct UVC lamp is only about 10%, so the major contribution of the degradation efficiency of 2, 4-DCP comes from the catalyst. The degradation efficiency of imprinted and non-imprinted TiO_2-SiO_2 composite catalyst in binary system composed of target pollutant (2, 4-DCP) and the non-target (phenol) under the same concentration is shown in **Fig.7**. It shows that the imprinted photo-catalyst can provide much better selectivity toward the photo-degradation of the target pollutant in the presence of the non-target one at the same

Table 3. Degradation efficiency of 2, 4-DCP by using imprinted TiO_2–SiO_2 composite catalyst ($m_{(Ti)}/m_{(Si)}$ = 1.5) with different calcination temperatures level.

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Calcination temperature (°C)	Irradiation time (min)	Degradation efficiency (%)
500	30	23.53
	60	37.76
	90	60.97
	120	76.82
600	30	28.31
	60	42.31
	90	67.12
	120	80.05
700	30	27.47
	60	40.56
	90	66.05
	120	77.96

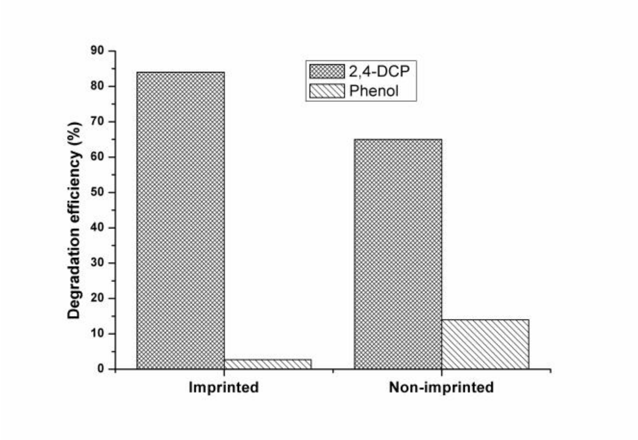

Fig.7. Degradation efficiency of imprinted and nonimprinted TiO_2–SiO_2 composite catalyst in binary system composed of target pollutant (2, 4-DCP) and the nontarget (phenol) after 2h irradiation.

Conclusion

2, 4-dichlorophenol imprinted TiO_2-SiO_2 composite catalyst was prepared by molecular imprinting technique in combination with sol-gel method. The preparation conditions such as calcinations temperatures, ratio of $m_{(Ti)}/m_{(Si)}$ can affect the photo-degradation efficiency. The photo-degradation experiments in both single and binary systems have confirmed that the imprinted TiO_2-SiO_2 had good photo-catalytic degradation capacity and selectivity toward the target. This study provides a viable approach for the photo-catalytic removal of highly toxic low-level organic pollutants in polluted waters in the presence of other less toxic high-level pollutants.

Acknowledgement

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