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Article

Ordered mesoporous carbon-based titania as a reusable adsorbent-catalyst for removing phenol from water

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ARTICLE INFO

Article history:

Received 6 February 2013

Accepted 25 February 2013

Published 20 June 2013

Keywords:

Phenol

Visible light

Titania

Carbon-doping

Mesoporous photocatalyst

ABSTRACT

The high efficiency of ordered mesoporous carbon-based anatase for the visible light-driven photo-degradation of phenol in water is reported. Adsorption-photocatalysis cycles were used to treat polluted water. Contaminated water containing 200 mg/L phenol can be completely mineralized within 10 cycles, in which each cycle consisted of adsorption for 8 h and visible light-driven illumination for 8 h. The roles of non-metal doping in the anatase lattice, aggregation-free confinement of anatase nanoparticles by the carbon pore wall, and adsorption of phenol in the mesopores on the catalytic performance are discussed. The present work provides an effective combination of physical and chemical treatments to remove relatively high concentrations of non-biodegradable organic substances using a mesoporous photocatalyst.

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1. Introduction

The widespread contamination of water by phenol is an issue of growing importance. Phenol is resistant to biodegradation and persists in the environment for long periods, and it is a carcinogen even at low concentration. The phenolic compounds originate from many industries such as refining, chemical and petrochemicals, pharmaceuticals, pulp and paper industries. The remediation of waste streams and groundwater contaminated with phenols is a difficult task, and there is growing demand for an effective, economic, and environmentally friendly way to deal with it [1]. A biological treatment, which is primarily used to remove biodegradable organic substances (colloidal or dissolved) in wastewater, is not applicable because phenolic compounds cannot be easily degraded and

they can even kill or at least damage the microorganisms used for biological activity [2]. Physical treatments, like mixing, flocculation, sedimentation, flotation, filtration, extraction, and adsorption, can treat a high concentration of pollutants, but they have the drawback that the hazardous compounds are not actually destroyed and there is need of a subsequent treatment, like the regeneration of the adsorbent [3]. Chemical operations are particularly useful for cleaning biologically toxic and non-degradable materials. The goals of waste water purification by a chemical process include the reduction of the chemical contaminants and the toxicity to a low level so that the cleaned waste water can be reintroduced into receiving streams. Photocatalysis by a semiconductor such as TiO_2 is an efficient and green chemical degradation process for persistent organic chemicals [4]. TiO_2 nanoparticles have attracted much

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This work was supported by the National Basic Research Program of China (973 Program, 2013CB934102), Program for Changjiang Scholars and Innovative Research Team in University (IRT1269), the National Natural Science Foundation of China (21073122 and 21173149), the Specialized Research Fund for the Doctoral Program of Higher Education (20123127110004), Shanghai Science and Technology Committee (11JC1409200, S30406 and DZL123), and Fok Ying Tung Education Fund (121013).

DOI: 10.1016/S1872-2067(12)60567-1 | <http://www.sciencedirect.com/science/journal/18722067> | Chin. J. Catal., Vol. 34, No. 6, June 2013

attention because of their promising performance for water purification by photocatalysis. Organic pollutants such as alcohols, phenols, dyes, and carboxylic acids can be photodegraded by TiO_2 under UV light irradiation [5]. Many attempts have been made to shift the light sensitivity of titania into the visible region [6,7]. Non-metal doping of titanium dioxide by nitrogen, hydrogen, carbonaceous species, etc. to modify the titania band gap has produced visible light activity in photodetoxification. In particular, carbon doping has been very effective [8–13]. However, carbon-doped TiO_2 is generally more difficult to fabricate than N-doped TiO_2 , and it has been less widely applied to date [14]. The synthesis methods include flame oxidation, chemical vapor deposition, high temperature sintering, etc., many of which involve multiple stages, unstable reagents, and high cost [13,14]. Second, when titania is used as a catalyst in the form of fine particles, a big problem encountered is their aggregation into bigger particles during the reaction, resulting in a serious loss of catalytic activity. This problem is normally overcome by dispersing the active phase of the catalyst on a porous support such as carbon, alumina, silica, and zeolites [15]. Lastly, the photodegradation can only treat an extremely low content of phenol, which in general is below 10 mg/L [4,5]. The treatment of pollutants with a relatively high concentration is still a problem.

Very recently, our group reported a facile self-assembling synthesis of carbon-based titania catalysts [16,17]. Ordered mesoporous carbon was used as the support to disperse and isolate anatase nanoparticles. On the basis of the high surface area and large pore size of the ordered carbon-based anatase catalyst, we designed an adsorption-photocatalysis cycle, in which the photodegradation of dye over the anatase was made efficient by using as a first step physical adsorption inside the carbon pores [16]. This catalyst displayed remarkable ability in mineralizing dyes [18]. Here, this work is extended to the degradation of phenol, especially in visible light.

This work further evaluated the ordered mesoporous carbon-based anatase catalysts obtained by the self-assembly approach for the visible light-driven photodegradation of phenol in water. Adsorption-photocatalysis cycles were used to treat polluted water. Contaminated water with 200 mg/L phenol can be completely mineralized within 10 cycles comprising adsorption for 8 h in dark and visible light-driven illumination for 8 h in each cycle. By taking into consideration the adsorption of phenol on the mesoporous carbon-titania pore surface, anatase lattice doping by carbon, and inhibition of aggregation of anatase particles by the carbon pore wall, the improvement obtained in the catalytic performance with the mesoporous carbon-based anatase catalysts is discussed. The combination of physical and chemical treatments paves the way for decontaminating relatively high concentrations of non-biodegradable organic substances.

2. Experimental

2.1. Synthesis of ordered mesoporous C- TiO_2 (OMC- TiO_2)

A typical synthesis of OMC- TiO_2 is as follows [16]. Solution A

containing 1.5 g of triblock poly (ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide) copolymer F127 (molecular weight = 12600, Aldrich), 1.0 g of deionized water, and 8.0 g of ethanol (99.7 wt%) was stirred at 40 °C for 2 h. Stöber solution B containing 1.92 g (10.1 mmol) of TiCl_4 (98 wt%), 0.5 g of deionized water, and 7.5 g of ethanol was stirred at 0 °C for 30 min. Solutions A and B were mixed together and the color turned to orange rapidly. After 30 min, the solution was mixed with 5.0 g of ethanolic phenolic resin solution (20 wt%). The phenolic resin precursor was synthesized by a base-catalyzed polymerization of phenol (99.9 wt%) and formaldehyde (37.0–40.0 wt%), as reported in the literature [19]. Before use, MgSO_4 (98 wt%) was used to remove residual water in the phenolic resin. The mixture was then poured onto a Petri dish. The dish was placed in an oven to evaporate ethanol at 30–40 °C and to thermopolymerize at 100 °C. Both treatments took about 24 h. The orange sample was collected and heated at 350 °C for 10 h to remove the triblock copolymer template. Further crystallization to titania was carried out at 550 °C for 30 min in a nitrogen atmosphere. The heating rate was 1 °C/min below 350 °C and 5 °C/min above 350 °C.

The reference samples were a titania product (TiO_2 -cal) from the mother OMC- TiO_2 composite obtained by removing the free carbon component (the mother sample was placed in a muffle oven and then heated at 350 °C for 9 h in air), pristine mesoporous carbons calcined at 550 °C for 30 min (OMC) and at 900 °C for 2 h (OMC-900) [20], and mesoporous titania (MTiO_2) [21]. The synthesis solution of OMC contained 2.54 g of triblock copolymer F127, 3.0 g of phenolic resins, and 42.0 g of ethanol. The subsequent treatments were exactly the same as OMC- TiO_2 except for the final calcination temperature and time. The synthesis solution of OMTiO_2 contained 1.14 g of TiCl_4 , 4.00 g of $\text{Ti}(\text{OC}_4\text{H}_9)_4$, 1.0 g of P123, and 10 g of ethanol. After stirring for 3 h, the mixture was poured onto a dish. Then the dish was placed under a hood to evaporate ethanol at 40 °C for 48 h. The as-made film was scraped from the dish and put in an air muffle oven. The heating temperature was 380 °C, and the time was 5 h.

2.2. Characterization

Small angle X-ray diffraction (XRD) measurements were taken on a Rigaku D/max B diffractometer using $\text{Cu K}\alpha$ radiation (40 kV, 20 mA). The d spacing values were calculated by the formula $d = 0.15408 / (2 \sin \theta)$. The unit cell parameters were calculated from the formula $a_0 = 2d_{100} / \sqrt{3}$. N_2 adsorption-desorption isotherms were measured at -196 °C with a Micromeritics Tristar II 3020 analyzer. Before measurement, the sample was degassed in a vacuum at 100 °C for at least 6 h. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas (A_{BET}). By using the Barrett-Joyner-Halenda (BJH) model, the pore volumes and pore size distributions were derived from the adsorption branches of the isotherms. The micropore volumes (V_m) and micropore surface areas were calculated from the $V-t$ plot method. Transmission electron microscopy (TEM) experiments were conducted on a JEOL 2011 microscope operated at 200 kV. The

samples for TEM measurements were suspended in ethanol and supported on a holey carbon film on a Cu grid. Thermal gravimetric analysis (TG) curves were monitored on a Mettler Toledo 851e apparatus. The C, H, and O contents were measured on a Vario EL III elemental analyzer (Germany). X-Ray photoelectron spectroscopy (XPS) measurements were performed on a Perkin-Elmer PHI 5000CESCA system with a base pressure of 1×10^{-9} Torr. The energy positions of the peaks were calibrated by fixing the position of the C 1s peak at 284.6 eV. Diffuse reflectance spectra of the samples over a range of 200–800 nm were recorded by a Varian Cary 300 Scan UV-vis system equipped with a Labsphere diffuse reflectance accessory. Fourier transform infrared (FT-IR) spectra were acquired on a Nicolet Fourier spectrophotometer using solid samples in KBr pellets. Raman spectra were collected on a Super LabRam microscopic Raman spectrometer using a He-Ne laser with an excitation wave length of 633 nm.

2.3. Catalytic tests

The photocatalytic activity of the ordered mesoporous C-TiO₂ (OMC-TiO₂) was tested by the titania catalyzed photodegradation of phenol. Adsorption-photocatalysis cycles were adopted for the removal of phenol from water. OMC-TiO₂ (0.20 g) was suspended in 100 ml of aqueous solution containing 50–200 mg/L of phenol. The mixture was continuously shaken in a shaking bath with a speed of 120 r/min at 25 °C until equilibrium was reached (typically 8 h). After adsorption, an aliquot was centrifuged at 4000 r/min for 5 min, and the phenol concentration in the clear supernatant was analyzed by a high performance liquid phase chromatograph (Agilent 1100) using a C18 reversed phase column with UV detection (UV 6000 diode array detector, Thermo Finnigan). A reverse phase C18 column and water/acetonitrile (40/60) were employed. The concentration of phenol was determined from the absorbance at 225 nm. The separated catalyst loaded with phenols was dried at 50 °C overnight under vacuum. The photocatalytic degradation of phenol was initiated by irradiating the phenol-loaded catalyst mixture with a commercial 300 W xenon lamp. The light source was located 10 cm from the solid surface. UV light with wavelengths less than 420 nm was removed by a Pyrex glass filter. After a fixed time (normally 8 h), the lamp was turned off. This was one adsorption-photocatalysis cycle. The reacted mesoporous composite catalyst was placed in the above clear supernatant containing residue phenol for re-adsorption and then illumination by visible light for photocatalysis for more cycles until the phenol was completely removed.

To explore the procedure of the above cycles, 0.10 g of OMC-TiO₂ was suspended in 100 ml of aqueous solution containing 50 mg/L of phenol to reach equilibrium adsorption (the adsorbed amount was monitored as a function of time), separated from the solution, and subjected to irradiation under artificial visible light. Before the light was switched on, the catalyst was washed with 20 ml acetone. The eluted adsorbed phenol was counted as the initial concentration (C_0). After an interval of irradiation, the light was turned off, and the catalyst

was eluted with 20 ml of acetone. The difference between the initial and final eluted phenol amount was counted as the degraded concentration (C). After the first adsorption-photocatalysis run, the solid catalyst was dried and reused for adsorption in 100 ml of fresh aqueous solution containing 50 mg/L of phenol and then used for the second adsorption-photocatalysis run. In some selected runs, before and after illumination, elution was performed in water with assistance of ultrasonic treatment to measure the total organic carbon (TOC) value by a TOC analyzer (TOC-VCSH, Shimadzu). For the phenol degradation in solution, 0.05 g of powder catalyst was suspended in 50 ml of aqueous solution containing phenol (20 mg/L). Before illumination, the suspension was stirred magnetically for 60 min to ensure complete adsorption of phenol. The photocatalytic reaction was initiated by irradiating the system with 300 W xenon lamp located 10 cm away from the reaction solution. UV light with wavelengths less than 420 nm was removed by a Pyrex glass filter. During a run, samples (approximately 1.0 ml) of the reaction solution were taken at fixed time intervals. Each sample was filtered through a Millipore membrane filter (0.22 mm pores). The degradation rate of phenol was monitored by HPLC. Tests demonstrated a good linear relationship between light absorbance and pollutant concentration. Less than 2% pollutant was decomposed after reaction for 2 h under the same condition in the absence of either the catalyst or light irradiation, and this can be neglected in comparison with the phenol degraded by photocatalysis.

The adsorption-photodegradation cycle for methylthionine chloride included adsorption of dye with an initial concentration of 400 mg/L for 24 h in dark, separation of the catalyst, drying at 40 °C overnight under vacuum, and irradiation of the dye-loaded catalyst with a commercial 300 W xenon lamp for 2 h. The dye concentration in the clear supernatant was determined spectrophotometrically by measuring the absorbance of the solution at 664 nm with UV-Vis spectroscopy (UV-7502PC).

Batch mode adsorption studies for phenol and methylthionine chloride were carried out by agitating 0.10 g of mesoporous catalysts in 100 ml of polluted aqueous solution. Then the mixture was continuously shaken in a shaking bath with a speed of 120 r/min at 25 °C until equilibrium was reached (typically 24 h). After adsorption, an aliquot was centrifuged at 4000 r/min for 5 min, and the phenol or dye concentration was analyzed.

3. Results and discussion

3.1. Structure and composition of ordered mesoporous carbon-anatase

The Raman spectrum of the ordered mesoporous carbon-anatase composite (OMC-TiO₂) showed lines at 153, 416, 518, and 634 cm⁻¹ (Fig. 1(a)), which is similar to those of bulk and mesoporous anatase (MTiO₂) except for their frequency blue shift and line width increase [22,23]. These lines can therefore be assigned as the Eg, B1g, A1g or B1g, and Eg modes of the anatase phase. The strongest Eg mode at 153 cm⁻¹ from the external vibration of the anatase structure was well resolved, indicating the formation of the anatase phase with a

Fig. 1. Raman spectra for titania (a) and carbon (b) in ordered mesoporous carbon-titania (OMC-TiO₂) and ordered mesoporous anatase (MTiO₂).

long range order to some extent. The blue shift of the line and shape change for the low frequency mode have been studied and interpreted as due to phonon confinement effects in small-sized nanocrystals and non-stoichiometry due to oxygen deficiencies [24] or disorder induced by minor phases, e.g., non-metal doping in the lattice and the hybridization on the surface of TiO₂ [25–27]. Therefore, the Raman line shift from 144 cm^{-1} in bulk anatase to 153 cm^{-1} in the C-TiO₂ composite catalyst and the line broadening probably originated from the phonon confinement effect in the tiny anatase nanocrystals and the oxygen vacancies and/or defects induced by the non-metal doping in the lattice. The doping of carbon into the anatase lattice probably originated from the chelating between hydroxyl groups and titanium ions from the strong intermolecular hydrogen bonding interaction in the synthesis, and the subsequent crystallization and carbonization accompanied with the formation of a large number of TiO₂ nanoparticle precipitates

and the cleavage of Ti–O–C bonds [28,29]. The titania relaxation intensity of OMC-TiO₂ was, however, much lower than that of commercial titania P25. A possible reason is the significant fraction of light being absorbed and partly transformed into separated charges in the carbon-TiO₂ hybrid material [30].

UV-Vis and XPS spectra were used to further investigate the titania structure. The C-TiO₂ catalyst showed enhanced absorption over the whole UV to visible region (data not shown here), which may be attributed to the composite structure [31]. The nanocrystals did not aggregate in the pores. The light absorption of anatase was therefore shielded by carbonized substances [16,32,33]. A combustion step was adopted to remove free carbon support in the mesoporous C-TiO₂ composite (the elimination of free carbon was confirmed by TG analysis; data not shown here). The TiO₂-cal product, which showed the typical XRD pattern for anatase, with a particle size of 5.5 nm showed enhanced absorption in the visible region as compared with commercial P25 (Fig. 2(a)). A plot of the modified Kubelka-Munk function versus the energy of exciting light gave band gap energies of 2.99 and 3.15 eV for TiO₂-cal and P25, respectively [34,35]. The band gap narrowing of TiO₂-cal was further evidence of element C introduction into the TiO₂ lattice [9,36,37]. It should be mentioned that TiO₂-cal is not exactly the same as the anatase nanoparticles in the composite, e.g., the nanocrystals can grow bigger on heating. However, combustion at 350 °C does not significantly affect the carbon dopant because the TiO₂ lattice doping with carbon has been reported to be very stable [30]. The XPS spectrum (Fig. 2(b)) for the OMC-TiO₂ composite showed spectral Ti 2p_{3/2} and Ti 2p_{1/2} values comparable to bulk anatase, but the spin-orbital splitting was 5.6 eV, slightly lower than that of the latter (5.8 eV) [38]. This observation has also been reported for non-metal doped anatase [29], further corroborating carbon atom introduction into the anatase crystal lattice [16].

The FT-IR spectrum for OMC-TiO₂ (Fig. 3) clearly showed bands at 3400, 1642, 1444, and 1114 cm^{-1} . This was different from the carbon catalyst (OMC-900) where most of the vibrations due to an organic substance in the range of 3000–1000 cm^{-1} did not appear. This was evidence that the present catalyst is composed of organic carbonaceous substances and inorganic titania due to the use of low temperature and rapid crys-

Fig. 2. Diffuse reflectance UV-Vis spectra (a) for TiO₂-cal and P25, and XPS spectra (b) for OMC-TiO₂. Inset (a) is the modified Kubelk-Munk function.

Fig. 3. FT-IR spectra for OMC-TiO₂ and the catalyst in the adsorption-photocatalysis cycles: after adsorption of methylthionine chloride (OMC-TiO₂-ad), one adsorption-photocatalysis cycle of adsorption in dark for 24 h, separation of solid and photocatalysis under UV-Vis light for 2 h (OMC-TiO₂-1), and 20 adsorption-photocatalysis cycles (OMC-TiO₂-20). For comparison, the FT-IR spectrum for mesoporous carbon carbonized at 900 °C (OMC-900) is also given.

tallization. The bands at ~ 3400 cm⁻¹ can be assigned to the -OH stretching from both organic and inorganic components, i.e., phenolic -OH group, and not cross-linked benzyl alcohol and surface hydroxyl groups. The broadness of the absorption is due to intermolecular H bonding. The presence of carbonaceous substances was shown by the bands at 1642, 1444, and 1114 cm⁻¹, which appeared in the spectrum of fresh OMC-TiO₂. The band of 1642 cm⁻¹ can be attributed to the C=O stretching, 1444 cm⁻¹ to the C=C stretching of 1,2,4- and 1,2,6-tri-substituted tetra-substituted benzene rings and C-C bond of phenyl-alkyl ether-type substituted aromatic ring structures [39], and 1114 cm⁻¹ to the C-O stretching of resin. However, the Raman spectrum showed two strong and wide bands near 1582 and 1357 cm⁻¹ (Fig. 1(b)), which is different

from the typical spectrum of a weak and broad band from 700 to 2000 cm⁻¹ from the polymeric structure of the phenolic resin. The mode at 1582 cm⁻¹, often referred to as the G mode, was assigned to "in plane" displacement of the carbon strongly coupled in the hexagonal sheets. Its shifts and line width variations are indications of defects in the lattice. It has also been suggested that the spectrum of well-crystallized graphite in the form of a small grain size (polycrystalline) has a band near 1357 cm⁻¹. This mode is usually called the disorder-induced or D mode [40]. The D band, which has a low intensity in graphite and well-organized materials, becomes as intense or even more intense than the G band for more disordered solids. Maeng and co-workers [41] have reported a similar phenomenon. Below 400 °C, there were no carbon structures visible in the Raman spectra analysis, and this was indicative of a polymer structure. Above 600 °C, the original resin structures disappeared completely. The G and D bands appeared for the sample cured at 500 °C, suggesting a carbonized resin. Accordingly, it was concluded that the present OMC-TiO₂ composite also possessed a carbonized framework. The observations that the G-band shifted to 1587 cm⁻¹ and the line width was broaden in addition to that the D-band had a high intensity implied a disordered structure for the carbonized solids. The TG and DTA curves (data not shown here) showed a loss of 8.6% in the low temperature range attributed to the physisorption of water, and another loss of 37.1% accompanied with a distinct exothermic peak in the temperature range of 200–550 °C attributed to the combustion of carbonaceous material. The catalyst is therefore composed of carbonized resin and anatase with the weight content ratio of 40:60.

The XRD patterns for the ordered mesoporous carbon-titania catalyst showed typical diffraction peaks of an ordered 2-D hexagonal mesostructure with a cell parameter of 10.9 nm and anatase and amorphous carbonaceous substances (Fig. 4(a)) [16,17]. From the line width of the (101) reflection and the Scherrer formula, the average crystallite anatase size

Fig. 4. XRD patterns (a) for fresh (1) and used (2) OMC-TiO₂ after successive adsorption-photodegradation cycles in treating phenol with an initial concentration of 200 mg/L. Inset (a) shows small angle XRD patterns. TEM images in low (b) and high (c) resolution viewed along the (001) direction for fresh OMC-TiO₂.

Fig. 5. N₂ sorption isotherms (a) and pore size distribution (b) for fresh OMC-TiO₂ (1) and this catalyst after saturated adsorption of phenol with an initial concentration of 200 mg/L (2), after successive adsorption-photodegradation cycles in treating phenol (3), saturated adsorption of methylthionine chloridew with an initial concentration of 400 mg/L (4), and one adsorption-photodegradation cycle for treating dye (5).

for the catalyst was estimated to be 4.2 nm. The particle size is smaller than the domain size of the mesostructure, implying the high dispersion of tiny anatase particles in the mesoporous framework. TEM images (Fig. 4(b) and (c)) showed typical hexagonally arranged pores, confirming the ordered 2-D hexagonal mesostructure. A large number of well-dispersed nanoparticles can be clearly observed inside the pore walls, in good agreement with the XRD patterns. No nanocrystals were found aggregated outside the pores. The N₂ adsorption isotherms of the mesoporous solid OMC-TiO₂ displayed Type IV curves with a sharp capillary condensation step at middle relative pressures, suggesting highly uniform mesopores (Fig. 5). The hysteresis loops belonged to the H2 type, suggesting roughly cylindrical pores. The BET specific surface area, pore volume, and pore size were calculated to be 348 m²/g, 0.30 cm³/g, and 4.3 nm, respectively. Therefore, the mesopore walls were constructed by the anatase nanocrystals, which were randomly “glued” together by amorphous carbonaceous substances [42–46]. Pore blockage by inorganic particles was probably not serious, leaving large enough space for adsorption inside the straight channels.

Fig. 6. Residue concentration of phenol in water with different initial concentrations during successive adsorption-photodegradation cycles over OMC-TiO₂. White: adsorption in dark; shaded: illumination in visible light.

3.2. Photodegradation of phenol

Adsorption-photodegradation cycles were adopted to eliminate phenol with a high concentration of 200 mg/L from water, which included saturated adsorption on OMC-TiO₂ in dark (normally 8 h), separation of the solid catalyst, and photodegradation of phenol by direct illumination of the phenol-loaded catalyst with artificial visible light.

Figure 6 shows the residue phenol concentrations in water with different initial concentrations after successive adsorption-photodegradation cycles. With a high concentration of 200 mg/L, about 26.2 mg of phenol can be removed from 100 ml of polluted water in the first adsorption-photodegradation run. Then the catalyst was used to adsorb from the residue polluted water and again illuminated by light. After 10 cycles, phenol was almost undetectable in the water. When the initial concentration was decreased to 50 mg/L, the treatment can be reduced to 3 cycles. Because photosensitization contribution by phenol to the photodegradation can be ignored, these results give evidence of the highly active photocatalyst of OMC-TiO₂ under visible light. The present adsorption-catalysis cycles pave the way for the treatment of contaminated water with a high concentration of phenol.

To confirm photodegradation in the adsorption-photodegradation cycles, the illumination process was studied. Here, C_0 represents the phenol concentration inside the pores, which can be eluted by acetone. The adsorbed phenol cannot be completely extracted, reflecting elution efficiency about 80%. After an interval of time, the light was turned off and the catalyst was washed with acetone. The difference between the initial and eluted phenol amount was counted as the degradation concentration. It should be mentioned that this estimate is rough because of the incomplete elution by acetone. Despite this, the efficiency can still reflect relative activity in visible light-driven degradation (Fig. 7). With the prolonging of the illumination time, the degradation efficiency dramatically increased, reflected in that the residue phenol in the pores decreased. After 8 h, the efficiency reached 99%. Almost no phenol, which could be extracted by acetone, was present. At that time, oxidized

Fig. 7. Adsorption amounts (a) and visible light-driven photodegradation efficiency monitored as the normalized concentration change (b) for phenol on fresh ordered mesoporous OMC-TiO₂ catalyst (1) and used OMC-TiO₂-1 catalyst (2) as a function of the contacting or irradiation time. Inset (b) is kinetic curves with transformed linear graphs of $\ln(C_0/C)$ versus irradiation time. The adsorption conditions are 0.10 g of OMC-TiO₂ and 100 ml of aqueous solution containing 50 mg/L of phenol.

intermediates such as benzoquinone, hydroquinone, catechol, and oxalic acid were undetectable by HPLC. Water was also used to extract organic substances from OMC-TiO₂ with the assistance of ultrasonic treatment. At the beginning, the elution efficiency was as low as 40%. Negligible TOC concentration could be detected in the decant water at the end of the reaction. The analysis is rather rough because water is not a good elution solvent for use to extract organic substances from OMC-TiO₂. Here we cannot completely exclude the formation of oxidized large molecules but at least, they were not easily eluted by water. A pseudo-first order reaction was observed for OMC-TiO₂, with a phenol reduction reaction constant of 0.627 min⁻¹. Some parallel experiments were also carried out. The first one was turning off the light in the illumination step. The catalyst with adsorbed phenol, which was placed for 8 h under dark, was subjected to further adsorption of phenol. The additional adsorption amount was as low as 0.4 mg/g. The second experiment was to change the catalyst to a titania-free material, i.e., mesoporous carbon OMC. This material exhibited an adsorption capacity of 48.5 mg/g. After illumination under visible light for 8 h, the additional adsorption amount was only 2 mg/g. The adsorbed phenol can be eluted by acetone, implying the presence of most of the adsorbed phenol inside the mesopores after illumination. These observations illustrated that the phenol adsorbed in ordered mesoporous carbon-titania was mineralized by TiO₂ nanoparticles under light. Phenol that cannot be extracted by acetone was also not oxidized by anatase.

The white TiO₂-cal catalyst without the carbon support showed a much higher reduction rate than commercial P25 in degrading phenol (20 mg/L) under visible light irradiation, further indicating that the anatase nanoparticles were the active catalyst. Negligible oxidation intermediates were detected after the complete reaction over TiO₂-cal. The anatase doped with carbon was thus responsible for the high photoactivity under visible light. The change of the surface electric charge of the oxide in the carbon-titania composite catalyst probably led to modifications of the fundamental process of electron/hole

pair formation under visible irradiation, which enhanced the photocatalytic performance under visible light [38,47,48]. In addition, the adsorption-catalysis cycle separated the adsorption and photocatalysis steps. This avoided mass transfer problems inside the mesopores during photodegradation and the full accessibility of the anatase nanoparticles to facilitate the degradation of phenol [18]. The high adsorption capability of the mesostructure adsorbed the toxic intermediates, which were not released into the air atmosphere and/or in solution phase and thereby preventing secondary pollution by the intermediates.

Once the phenol in pores was mineralized, the occupied pores become empty and can provide more adsorption. The adsorption amount for phenol in the used catalyst was slightly less than the fresh one, but the elution efficiency by acetone was higher (about 94%). The result implied that some phenol molecules adsorbed inside the pores were inaccessible and remained in the pores. The degradation under visible light was repeated over OMC-TiO₂-1 loaded with phenol. A similar time versus conversion plot with that of the fresh catalyst was obtained, implying the similar initial reaction rate and degradation efficiency over the fresh and used catalysts. Therefore, the catalyst can be easily reused. In fact, after the adsorption-photodegradation cycles were carried to eliminate 200 mg/L phenol from water, the used catalyst was analyzed with XRD and N₂ sorption isotherms. Similar results with those of the fresh catalyst were observed, indicating the stability of the mesostructure and preservation of the anatase nanoparticles after light illumination. The high stability was probably due to the presence of the carbonized framework, which both showed stability in the reaction and performed the “glue” role for the anatase nanoparticles. The particles were confined by the carbonized resin pore walls, which inhibited aggregation to large particles, so that the mesostructure was preserved. Therefore, the carbon-titania composite has large advantages in stabilizing anatase nanoparticles as compared to activated carbon supported TiO₂ catalysts, in which particle aggregation is a serious

problem [45].

FT-IR spectra were also used to study the adsorption-photodegradation cycle. After the adsorption of phenol, the FT-IR spectrum was quite similar with that for the fresh OMC-TiO₂ catalyst, so phenol was not used for this study. Therefore, the adsorption-photodegradation cycles for dye over OMC-TiO₂ were followed by FT-IR (Fig. 3). The catalyst was first used to adsorb methylthionine chloride with an initial concentration of 400 mg/L. The adsorption amount was 171.5 mg/g. The FT-IR spectrum showed the vibrations for the catalyst retain, and several bands at 3000–2800, 1737, 1268, and 848 cm⁻¹ appeared, which can be attributed to the C–H, C=S, and C=N stretchings, and substituted benzene rings of methylthionine chloride. After photodegradation, the vibrations due to methylthionine chloride were undetectable, and the spectrum for the used catalyst was almost the same as the fresh one, suggesting the elimination of large organic molecules. Then the catalyst was used to adsorb dye again, and a similar adsorption capacity can be achieved. These observations showed that the adsorbed dye was mineralized by irradiation. The adsorption-degradation cycle was repeated 20 times. The final used catalyst displayed a similar FT-IR spectrum with that of the fresh catalyst, indicating the high activity in mineralizing dyes and high stability of the catalyst.

Here we noticed that the adsorption amount of phenol over OMC-TiO₂ was quite low. Figure 8 plots the equilibrium adsorption isotherms of phenol and methylthionine chloride on OMC-TiO₂. The isotherms are Type I curves characteristic of the Langmuir isotherm. However, the equilibrium adsorption amount for phenol (27.4 mg/g, 0.291 mmol/g) was much lower than for methylthionine chloride (170 mg/g, 0.531 mmol/g). The occupied pore volumes were 0.08 and 0.21 cm³/g by phenol and dye, respectively, which were estimated by the simple calculation of the molecular volume on the basis of a Newtonian ball and spring model. The pore occupation was similar to that over pristine mesoporous carbon (75%) [20]. Although the estimate is rough, it is clear that: (1) pore blockage of carbon by anatase is not serious because of the large adsorption capacity for largemolecule dye and (2) the adsorption performance for phenol over OMC-TiO₂ was somewhat inhibited. N₂ sorption isotherms (Fig. 3) for the catalysts after the adsorption of phenol were Type IV curves with

capillary condensation at middle relative pressures. The calculated BET surface area and pore volume were 112 m²/g and 0.07 cm³/g, respectively. Partial occupations of the pores by phenol took place. In contrast, capillary condensation almost disappeared in the N₂ sorption isotherms for the dye loaded OMC-TiO₂. As a result, the BET surface area and pore volume were as low as 14 m²/g and 0.02 cm³/g, respectively. These results further confirmed the above conclusion. The inhibition of the adsorption of phenol inside the pores was mainly due to the pore surface of the carbon-anatase composite, and not pore blockage.

Results from Ania et al. [49] and Zhang et al. [50] demonstrated that the adsorption of phenol over carbon is more influenced by the surface chemistry of the adsorbent than by its porosity although the surface area and porosity distribution of the carbon adsorbents play important roles in the adsorption capacity in most cases, for example, for dyes [51]. The postulate is that the adsorption of phenol is mostly influenced by the interaction of the aromatic ring with the surface of the activated carbon through the formation of donor-acceptor complexes. This mechanism involves carbonyl oxygen groups acting as an electron donor, and the aromatic ring of phenol acting as an acceptor. Other oxygen functionalities like carboxyl and hydroxyl inhibit the adsorption of phenol [52,53]. In the OMC-TiO₂ catalyst, the presence of abundant surface hydroxyl and carboxyl groups in the carbonized resin would inhibit the adsorption of phenol and increase the affinity of the carbon towards water, therefore leading to the rather low adsorption capacity.

It should be noted that upon further reaction with the light turned on, the typical Type IV isotherms of the fresh catalysts were recovered with only a slight reduce in BET surface area and pore volume (Fig. 3), independent of the adsorbed substances, further demonstrating the adsorption inside the pores and the mineralization of the contaminant.

4. Conclusions

The ordered mesoporous C-TiO₂ catalyst has high efficiency in degrading phenol in water with a high phenol concentration. This water treatment used adsorption-photocatalysis cycles comprising adsorption in dark and irradiation under visible light (> 420 nm). The high activity in eliminating phenol is due to the nanocomposite structure of the catalyst, in which anatase nanocrystals with a size of 4.2 nm were “glued” by carbonized substances, the uniform mesopores produced in the catalyst, in which the pollutants were adsorbed and accessible to the anatase photocatalyst, and carbon doping of the anatase lattice, which reduced the titania band gap and enhanced visible light absorption. Although the adsorption of phenol was inhibited on the carbonized resin surface, the mineralization can be achieved by visible light irradiation. Polluted water with 200 mg/L phenol can be eliminated by 10 adsorption-photocatalysis cycles. The results indicate promising applications of the mesoporous photocatalyst in environmental remediation, especially in treating relatively high concentrations of non-biodegradable organic substances.

Fig. 8. Adsorption isotherms with phenol and methylthionine chloride on OMC-TiO₂.

Graphical Abstract

Chin. J. Catal., 2013, 34: 1066–1075 doi: 10.1016/S1872-2067(12)60567-1

Ordered mesoporous carbon-based titania as a reusable adsorbent-catalyst for removing phenol from water

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An effective combination of adsorption and visible light-driven photocatalysis to remove high concentration phenol using mesoporous carbon-anatase is described.

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可重复使用的有序介孔碳-氧化钛吸附-光催化剂用于去除水中苯酚

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摘要: 制备了有序介孔碳-氧化钛吸附-光催化剂, 利用可见光高效降解水中苯酚. 为去除水中高浓度苯酚, 设计了吸附-光催化循环, 即暗条件吸附8 h, 分离催化剂和将固体催化剂置于可见光下辐照8 h. 经过10次循环, 水中高浓度苯酚(200 mg/L)几乎可被完全降解. 详细讨论了TiO₂晶格中非金属掺杂、介孔碳壁对TiO₂纳米颗粒聚集的阻抑作用、介孔孔道吸附苯酚性能等因素对吸附-光催化剂性能的影响. 有序介孔碳-氧化钛复合体有效地结合了物理吸附和光化学降解技术, 有望用于降解水中难生物降解的高浓度有机污染物.

关键词: 苯酚; 可见光; 二氧化钛; 碳掺杂; 介孔光催化剂

收稿日期: 2013-02-06. 接受日期: 2013-02-25. 出版日期: 2013-06-20.

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基金来源: 国家重点基础研究发展计划(973计划, 2013CB934102); 长江学者和创新团队发展计划(IRT1269); 国家自然科学基金(21073122, 21173149); 高等学校博士学科点专项科研基金(20123127110004); 上海市科委和教委基础研究计划(11JC1409200, S30406, DZL123); 霍英东教育基金(121013).

本文的英文电子版由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).

《催化学报》第四届编委会新增成员简介

为了适应期刊国际化的发展需求, 经部分编委推荐, 《催化学报》第四届编委会现增补万颖教授为编委.

万颖, 上海师范大学教授、博士生导师、教育部环境功能材料创新团队带头人. 主要从事面向绿色碳科学的新型介孔催化材料研究工作. 近期的研究方向包括: (1) 基于介孔碳载体的纳米金属和氧化物催化材料生长、稳定化、电子化学和表面化学; (2) 氯苯偶联、醇选择性氧化、CO₂转化等反应中纳米金属催化剂尺寸和电子化学等与催化反应活性、选择性的构效关系和调变规律, 为能源、环境相关的催化技术提供理论基础.

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