

## Effects of templates on the structure, stability and photocatalytic activity of mesostructured TiO<sub>2</sub>

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### Abstract

Using long-chain alkylphosphate and alkylamine surfactants as templates, two kinds of purely mesoporous TiO<sub>2</sub> molecular sieves (Ti-TMS) were prepared by hydrolysis of titanium isopropoxide under completely different conditions. The templates can be successfully removed by refluxing the samples in an EtOH/H<sub>2</sub>O/HNO<sub>3</sub> solution. Properties of the samples were characterized by means of SEM, FT-IR, DR-UV, TEM, XRD and TG-DTA techniques. XRD patterns and TEM images confirm that the uniformity and stability of Ti-TMS1 synthesized with dodecylphosphate, hexadecylphosphate, or octadecylphosphate as templates is superior to that of Ti-TMS2 prepared with dodecylamine. Furthermore, after the removal of the templates, the stability and the structure of the mesoporous Ti-TMS1 are better than that of Ti-TMS2. Effects of other factors on the structure and stability of Ti-TMS are discussed. The photocatalytic activities of Ti-TMS were also investigated by using polychlorophenol (TCP) and reactive red dye (X-3B) solutions as model pollutants. It was found that the amount of the templates greatly affects the photoactivity of these kind of mesoporous materials. © 2002 Published by Elsevier Science B.V.

**Keywords:** TiO<sub>2</sub>; Mesoporous materials; Photocatalysis; Pollutants

### 1. Introduction

TiO<sub>2</sub> nanoparticles, among the most popular photocatalysts, have long been investigated in water treatment [1]. However, in most cases the photocatalytic activity is not sufficient for commercial application. Increasing attention has been focused on surfactant-mediated mesoporous materials since Mobil's scientists [2] succeeded in the synthesis of a novel mesoporous silicate called MCM-41, which exhibited highly organized hexagonal packing of cylindrical channel of 20–100 Å in diameter. Since mesoporous molecular sieves also have the properties of nanopores similar to those of nanoparticles, it is likely that the syntheses of these kind of materials can provide useful information for efficient photocatalytic degradation of pollutants. Synthesis and photocatalytic properties of microporous silicates incorporating crystalline TiO<sub>2</sub> in its channels or with a Ti-doped framework, Ti-doped silicate-based hexagonal mesoporous molecular sieves, lamellar mesoporous TiO<sub>2</sub>

have been reported recently [3,4]. These reports suggest that pure titanium-based hexagonal mesoporous molecular sieves (Ti-TMS) may be very promising for wastewater treatment.

Most attempts aimed at synthesizing hexagonal mesoporous materials from transition metal oxides by molecular self-assembly of organic templating agents and inorganic oxides have led to lamellar phase in which the surfactant and metal oxide phases are layered and the resulting structure easily collapses upon the removal of templates [5]. However, recent reports on the syntheses of mesoporous materials from transition metal oxides [6–11], including TiO<sub>2</sub> by molecular self-assembly of organic templating agents and inorganic oxides have indicated the formation of certain stable materials.

The successful synthesis of stable mesoporous TiO<sub>2</sub> involved the application of tetradecylphosphate surfactant as a template and removing it by calcinations [6]. For such systems, no other surfactants or other methods for removal of the templates, nor tests for the photocatalytic activity in the degradation of pollutants have been reported so far.

The present work concerns the investigation of different surfactants as templates for the synthesis of Ti-TMS. We studied alkylphosphate with different chain lengths and alkylamine as templates, using an alternative method for re-

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removal of the templates. The effect of the template on the photocatalytic activity is reported here for the first time.

## 2. Experimental

### 2.1. Materials

TCP (99%) was purchased from Aldrich. Dodecyl-, hexadecyl-, and octadecylphosphate were synthesized according to the modified procedures described by the typical way. Their structures were confirmed by elemental analysis and infrared spectroscopy. Other chemicals were reagent grade and used as received.

### 2.2. Experimental methods

The first approach to the synthesis of Ti-TMS1 with alkylphosphate as templates: in a typical preparation, dodecylphosphate (14.6 g, 0.005 mol) was dissolved in 73 ml KOH (1.4 g, 0.025 mol) solution and the pH was adjusted to 5.0 with 12.5 M HCl. In a separate beaker, titanium isopropoxide (14.6 g, 0.05 mol) was treated with acetylacetone (5.7 ml, 0.05 mol). The solution was cooled and added to the surfactant solution with vigorous stirring. The thick yellow meringue was then aged at ambient temperature for 2 h and then at 80 °C for 5 days. The resulting fawn powder was then collected by filtration, washed with water (3 × 100 ml) and subsequently dried overnight. The as-synthesized sample was then refluxed in EtOH/H<sub>2</sub>O to give a mesoporous sample of Ti-TMS1. The experimental procedures for the synthesis of Ti-TMS1 with hexadecyl- and octadecylphosphate as templates were similar to that described above.

The second approach [12] to the synthesis of Ti-TMS2 with alkylamine as a template: in a typical procedure, dodecylamine (4.4 g, 0.024 mol) was dissolved in titanium isopropoxide (13.5 g, 0.046 mol). To get a homogeneous solution, ethanol (15 ml) and water (45 ml) were then added under stirring, which caused the immediate precipitation of a white solid. This mixture was then left overnight at ambient temperature and further aged at 80 °C (1 day), 100 °C (1 day) and 180 °C (7 day), separately. The product was collected by suction filtration and washed with three 50 ml portions each of water, ethanol, and ether. After drying in a vacuum oven at 100 °C, the surfactant was removed by refluxing with 70% nitric acid at pH = 2 in ethanol for 24 h.

### 2.3. Characterization

The SEM was recorded on a Hitachi S-450 instrument. The framework vibration IR spectra of the samples were investigated on a Nicolet 5DX FT-IR instrument with KBr wafer technique. The DR-UV spectra were recorded with Shimadzu 240 UV spectrophotometer. TEM images were obtained on a JEOL 100CX transmission electron microscope operated at 160 kV. XRD were recorded on a Rigaku

D/max-γA with a rotating anode using Cu Kα radiation ( $\lambda = 1.54059 \text{ \AA}$ ). TGA curves were recorded by Simultaneous SDT2960 system.

### 2.4. Photocatalytic experiments

Photocatalytic activity of various catalysts was evaluated by measuring the loss of TCP. Prior to commencing illumination, a suspension containing 40 mg Ti-TMS1 catalyst and 50 ml of 1.33 mM TCP was stirred for 1 h. The reactions were carried out with continuous stirring in a glass flask. Samples were irradiated with UV light from a 300 W high-mercury lamp enclosed a quartz glass cooled by water circulation to 25 °C during the experiments. In comparison runs, total irradiation time was 80 min for each sample. Samples of 2 ml were withdrawn by syringe from the irradiated suspension every 10 or 20 min, and filtered through a Millipore filter membrane (0.45 μm in pore size). GC-MS and HPLC were used for analysis. Comparative studies were carried out using TiO<sub>2</sub> (P<sub>25</sub>). In order to further examine the effects of the mesostructure of Ti-TMS1 and the amount of its template on the photocatalytic degradation of organic pollutants, another substrate dye X-3B was also selected as a model wastewater. During the reaction, the concentration of X-3B and Ti-TMS1 was the same as that of TCP and Ti-TMS1. The results were recorded by Shimadzu UV 2201 spectrophotometer. Other conditions are also similar to that described above.

## 3. Results and discussion

### 3.1. General physical–chemical properties of samples

The morphology of the as-synthesized Ti-TMS was observed by SEM, which shows the typical shapes of the small crystallites, as seen in Fig. 1 (12 kV, ×1.000K, 30 μm). A

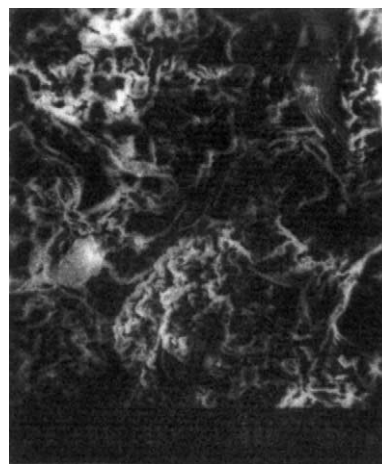


Fig. 1. SEM of as-synthesized sample of Ti-TMS1 templated by hexadecylphosphate.

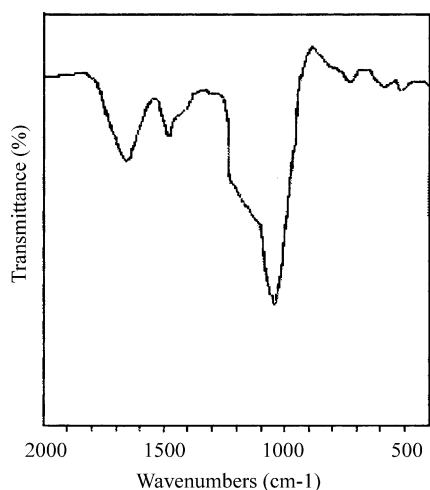


Fig. 2. FT-IR spectrum of Ti-TMS1 templated by hexadecylphosphate.

series of other experiments were conducted to determine the molar ratio of surfactant, molar ratio of acetylacetonate, and optimal pH in the synthesis of Ti-TMS. The parameters that seemed most critical were the acetylacetonate concentration and the surfactant-to-Ti ratio. The effect of the pH was not dramatic in the precursor composition. Details about the original synthesis and characterization of this kind of mesostructured materials were discussed before in the previous paper [13].

### 3.2. Ti-skeleton of Ti-TMS framework

After removal of the template, FT-IR spectra of Ti-TMS1 (Fig. 2) are similar to that of Ti-MCM-41 [14]. The IR band at about  $960\text{ cm}^{-1}$  is usually taken as evidence at the relevant concentration of Ti-skeleton [10]. This band was also observed ( $\sim 970\text{ cm}^{-1}$ ) in the framework IR spectra. The intensity of this band increases with the increase in Ti content of Ti-TMS, which indicates that all the Ti of Ti-TMS1 may be incorporated into the channel wall. The DR-UV spectra of the samples (Fig. 3) also support the result from

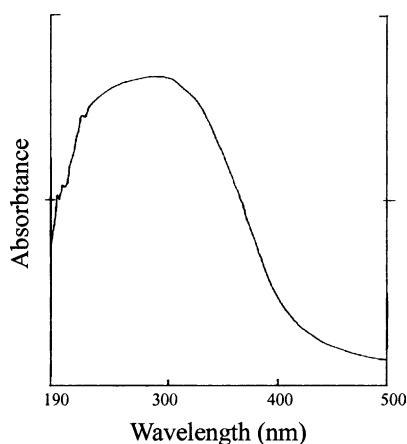


Fig. 3. DR-UV spectrum of Ti-TMS1 templated by hexadecylphosphate.

IR spectra. The Ti-TMS sample was examined by using a DR-UV photospectrometer, which is equipped with a Praying Mantis (light collector). This technique has been used extensively for the characterization of the nature and coordination of  $\text{Ti}^{4+}$  ions in molecular sieves [15]. In Fig. 3, the strong broad band observed from 220 to 380 nm, indicates the existence of Ti-skeleton in the structure of the sample.

### 3.3. Formation mechanism of Ti-TMS by liquid crystal templating of surfactant micelles

MCM-41 is synthesized using a micelle-based liquid crystal templating method at varying of pH values from a source of silica and a cationic trimethylammonium bromide surfactant at concentrations under which micelle formation of the organic phase is favorable [16]. This approach relies on the coulombic attraction between the inorganic phase, consisting of polysilicate anions and the organic template [17]. Early attempts to prepare transition metal oxide analogs of MCM-41 employed this approach to successfully synthesize mesostructured tungsten, lead, antimony, and iron oxides [18] as well as a vanadyl phosphate structure [19]. Recognizing that this micelle template route relied on the existence of soluble inorganic anions, which would have electrostatic interaction with the cationic template, we anticipated that this would not be generally applicable to the synthesis of early transition metal oxides. This is due to the large ionic radius of the early transition metal oxides, which favors the formation of insoluble oxide oligomers, and is therefore unable to interact sufficiently with the template to form the desired mesostructures. Under this assumption two different routes were attempted in order to make mesostructured  $\text{TiO}_2$ . The hexagonal pore structures were confirmed by TEM studies. Fig. 4 shows that the first approach was successful in the synthesis of Ti-TMS1 templated by hexadecylphosphate. Fig. 5(a) shows the TEM of Ti-TMS2 synthesized from alkylamine and (b) shows the TEM of Ti-TMS2 synthesized under the same conditions but with a different aging time. Comparing Fig. 5(a) and (b), it is obvious that the sample prepared under the latter conditions appears to be either mixed phases or a single phase

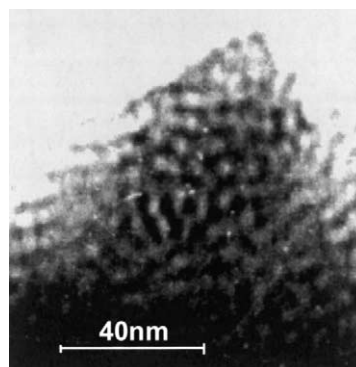


Fig. 4. TEM image of Ti-TMS1 templated by hexadecylphosphate.

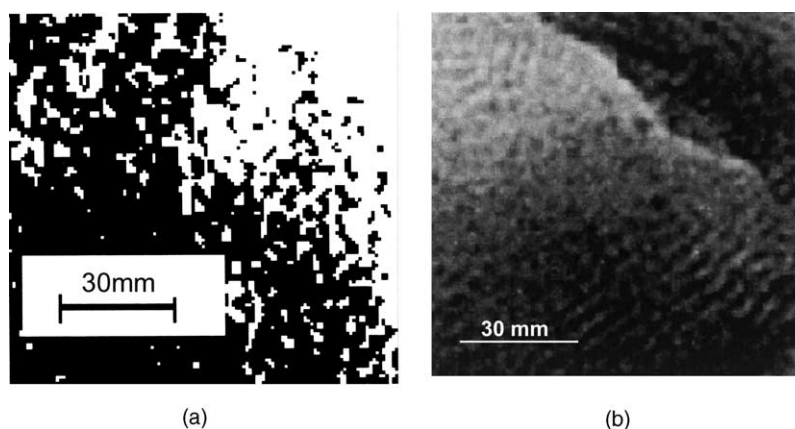


Fig. 5. TEM image of Ti-TMS2 templated by dodecylamine: (a) sample aged for 7 days; (b) sample aged for 1 day.

which is less well crystallized than that obtained under the former conditions. This strongly suggests that the process of formation of the mesopore structures may involve the transformation from layer phase to hexagonal phase.

#### 3.4. Effect of variation of templates

In order to determine the ideal surfactant as template for the synthesis of Ti-TMS, a cationic surfactant had also been tried as the template at the beginning of our experiments besides the anionic and neutral surfactants that described above. As shown in Fig. 6(a), an as-synthesized Ti-TMS1 templated by hexadecylphosphate exhibits a series of XRD peaks in good order at  $d$  spacing of 100 (4.2 nm), 110, 200, 210, which is characteristic of the MCM-41 related hexagonal mesophase templated by the surfactant [20]. No peak was observed at  $2\theta > 10^\circ$ , excluding any ordinary crystalline phase of the surfactant or titanium species. Nevertheless, as shown in Fig. 6(b), an as-synthesized Ti-TMS2

obtained with dodecylamine shows only one peak which has broader humps around  $2\theta = 3^\circ$  in the XRD pattern, which was attributed to the lower hexagonal order of the channels. It also indicates that the uniformity and stability of Ti-TMS2 templated by alkylamine as template is obviously inferior to those of Ti-TMS1 templated by alkylphosphate as templates. Similar results are also concluded from comparison of the two TEM images in Figs. 4 and 5(a). In addition, a product obtained with cetyltrimethylammonium bromide and that without surfactant showed no peak at all, as seen in Fig. 6(c) and (d).

#### 3.5. Effect of the different chain lengths of the template

Fig. 7 shows the XRD patterns of Ti-TMS templated by three alkylphosphates of different chain length (dodecyl-, hexadecyl- and octadecylphosphates). From this figure, we noted that the length of the hydrocarbon tail of the alkylphosphate could be used to vary the pore size of hexagonally

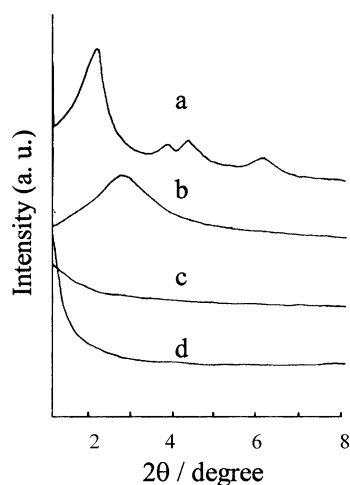


Fig. 6. XRD patterns of the samples templated by: (a) hexadecylphosphate; (b) dodecylamine; (c) no surfactant; (d) cetyltrimethylammonium bromide.

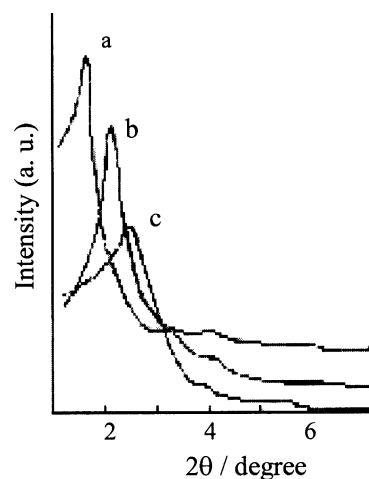


Fig. 7. XRD patterns of Ti-TMS1 templated by: (a) octadecylphosphate; (b) hexadecylphosphate; (c) dodecylphosphate.

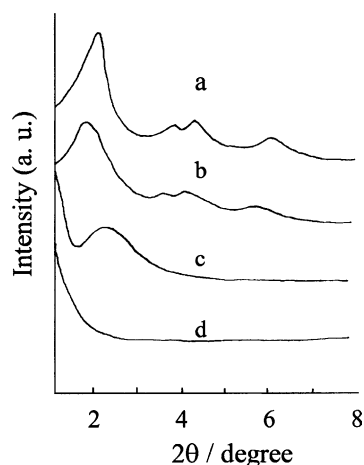


Fig. 8. XRD patterns of: (a) the as-synthesized sample templated by hexadecylphosphate; (b) the sample with solution method to remove the template; (c) the Ti-TMS [6] with calcination method to remove the template; (d) the sample with calcination method to remove the template.

packed mesostructure. This is indicated by the fact that the intensity of the diffraction peaks increased with the increase of the chain length. The power HRTEM pictures (not shown here) clearly displayed the hexagonal array of Ti-TMS1 with different pore sizes 27, 38 and 44 Å, and almost no amorphous or layered phases were observed in these materials. From these images, it can be concluded that increasing the length of the alkylphosphate will lead to the increase of the pore size of Ti-TMS.

### 3.6. Removal of the template

As shown in Fig. 8(a) and (b), there is a considerable increase in the intensity and sharpness of the XRD patterns for the samples after the removal of the template by solvent extraction. Comparing the reported XRD patterns of Ti-TMS (see Fig. 8(c)) with that of the sample we made, it indicates a degradation of structure and reduction in crystalline domain size upon calcination more than upon reflux with solution. Thus the solution extraction was screened as the main method for the removal of the template. However, in order to compare the two methods for the removal of the template, we also conducted the calcination method to remove the template, but this strategy often led to structural collapse, seen in Fig. 8(d).

### 3.7. Refluxing time on the removal of the template

Intensive washing of these materials with an extraction solvent system containing at least one cation donor and one polar solvent was applied to remove the template. Fig. 9 shows the thermogravimetric analysis curves of Ti-TMS1, which indicates the stronger interactions of the associated template with titanium groups. The trend indicates that as the washing times were increased, the amount of the re-

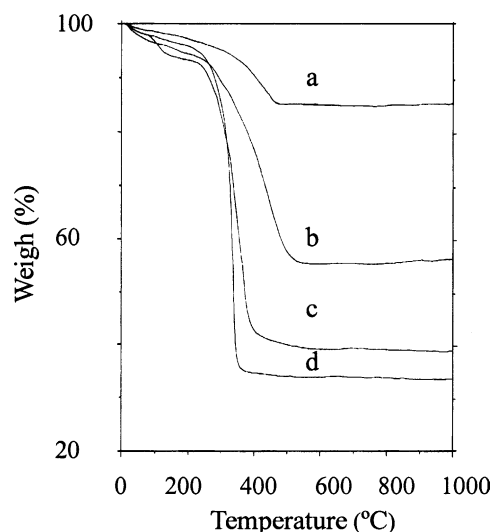


Fig. 9. TGA of samples 1–4 after washing with the EtOH/H<sub>2</sub>O/HNO<sub>3</sub>: (a) 7 days; (b) 5 days; (c) 1 day; (d) 0 day.

moved templates in Ti-TMS1 also increased. We used a solvent/cation system which consisted of ethanol and nitric acid at pH 2 for the removal of the hexadecylphosphate in the as-synthesized samples. Fig. 9(d) also indicates the template associated with titanium groups can be removed by heating the sample in air up to 350 °C. The observed continuous weight loss of this sample below 300 °C may be due to a constant loss of water with increasing temperature.

### 3.8. Effect of the residual template in Ti-TMS on degradation of TCP

The photocatalytic results of Ti-TMS1 templated by hexadecylphosphate over TCP are given in Fig. 10. It shows that the photocatalytic degradation of TCP over the Ti-TMS1 occurs at a higher rate than that of TiO<sub>2</sub>. The more the

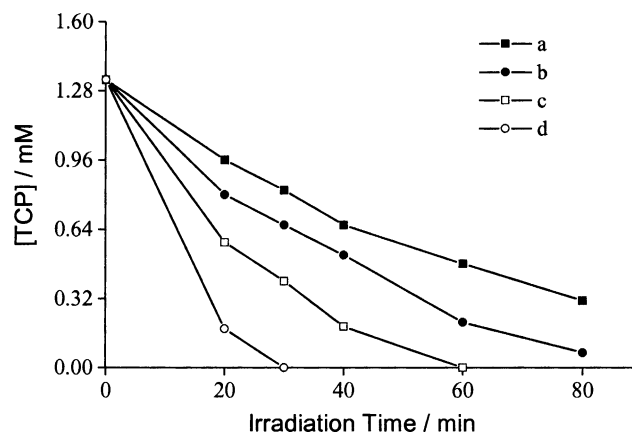


Fig. 10. Dependence of TCP photocatalytic degradation rate on various catalysts: (a) TiO<sub>2</sub> (P<sub>25</sub>); Ti-TMS1 with the template removal of: (b) 13%; (c) 30%; (d) 100%.

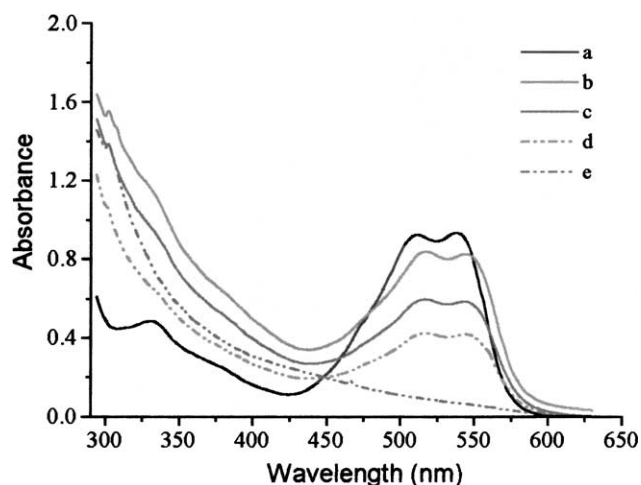


Fig. 11. Adsorption spectra of 1.33 mM X-3B with 64 mg Ti-TMS1 with template removal of 13% as photocatalyst recorded at: (a) 0h; (b) 1h; (c) 2.5h; (d) 3h; (e) 4.5h, following the UV-photolysis.

template in Ti-TMS1 was removed, the faster the degradation rate. The degradation rate was highest when the template in Ti-TMS1 was almost removed. This effect is easily understood since the increase in Ti-TMS1 surface area and internal active sites will increase with the removal of the template, therefore, the photocatalytic activity increases. Fig. 11 shows the absorbance of dye X-3B almost completely disappeared following the photocatalysis, indicating complete degradation of X-3B although the template of Ti-TMS1 was only removed 13%. The observation of increased absorbance in the 200–460 nm region at short illumination time is attributed to the formation of reaction intermediates. These observations are similar to the absorption peaks corresponding to TCP [21]. As shown in Fig. 12, the photocatalytic activity of the Ti-TMS1 with template removal of 13% is obviously

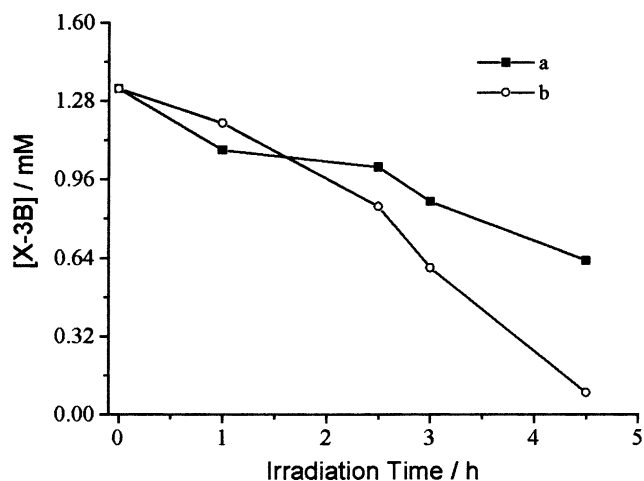


Fig. 12. Dependence of X-3B photocatalytic degradation rate on different kinds of catalysts: (a) as-synthesized Ti-TMS1; (b) Ti-TMS1 with template removal of 13%.

higher than that of the as-synthesized sample, in which all the templates were remained. The photocatalytic degradation of X-3B over Ti-TMS1 occurs at a little slower rate than that of the as-synthesized samples in the beginning of the reaction. A possible explanation is that the opening of Ti-TMS1 allows the internal surface area of this material accessible to molecules and therefore enhances the photocatalytic activity.

#### 4. Prospects

The effects of the templates of pure TiO<sub>2</sub> mesoporous molecular sieves on the mesostructure and stability were studied as well as the effect of the template on the photocatalytic activity of Ti-TMS. TCP and X-3B were used as the model systems for wastewater degradation. The results show pronounced improvement compared to the relevant reported results [6,22], however, it is still difficult to remove the organo-phosphates completely by calcination or other methods, including the method introduced in this work because of strong binding to the molecular sieve. This effect may prevent commercial application for photocatalytic detoxification. Note that the relatively low photocatalytic activity of Ti-TMS may be attributed to the poisoning of the catalytic surface sites by the residual phosphorus in calcination [22]. More work is being carried out in our laboratory in order to improve the photocatalytic activity by appropriate choice of templates for pure mesoporous TiO<sub>2</sub>. It is known that the non-ionic polyoxyethylene alkyl ether surfactants are relatively inexpensive and biodegradable. Complete removal of the templates can be achieved by simple extraction. The synthesis of mesoporous silica has recently attracted particular attention due to their interesting physico-chemical properties. We are studying how to introduce such kind of templates into the synthesis of mesoporous TiO<sub>2</sub>. Our preliminary work on a polyoxyethylene tridecylether (C<sub>13</sub>EO<sub>6</sub>) as the template suggests its use in a simple effective route for synthesizing high surface area and thermally stable mesoporous TiO<sub>2</sub>. Tests using XRD, TEM, TG-DTG and nitrogen adsorption-desorption analysis show that the surfactant/titanium molar ratio has a strong effect on the surface areas, pore diameters and thermal stabilities. Under the current conditions [23], the N<sub>2</sub>-adsorption isotherm reveals the existence of mesoporosity in this titanium dioxide with a type IV typical mesoporous material and a BET surface area 413 m<sup>2</sup> g<sup>-1</sup>, pore distribution is a quite narrow and centered at 4.4 nm, as well as the materials are thermally stable up to 630 °C. Optimization of the synthesis of mesoporous TiO<sub>2</sub> templated by C<sub>13</sub>EO<sub>6</sub> and research of its synthesis mechanism and other poly(oxyethylene) alkyl ethers as templating agents for the synthesis of better structure, larger pore mesoporous TiO<sub>2</sub> materials as well as their photocatalytic activities are in progress. It is supposed that such kind of new mesoporous TiO<sub>2</sub> may make a breakthrough in the application of photocatalysis.

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