# High Photocatalytic Activity of Pure $TiO_2$ Mesoporous Molecular Sieves for the Degradation of 2,4,6-Trichlorophenol

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Pure $TiO_2$ mesoporous molecular sieves, Ti-TMS, were first synthesized using alkylphosphate surfactant with different chain length. A high photocatalytic activity for the degradation of pollutant over these materials was first presented here. The Preliminary results are reported of an investigation into the photodegradation of 2,4,6-trichlorophenol, TCP, in the presence of suspended Ti-TMS solution, compared with $TiO_2$ nanoparticles under the same conditions.

2,4,6-trichlorophenol(TCP), a major pollutant produced by paper mills, is a good model of environmental pollutant. As we know, halogenated aromatic compounds are common environmental pollutants because of their halogen content. Many of these compounds are extremely persistent in the environment because of their slow degradation by reductive or oxidative enzymatic pathways. Systems that can remove halogen substituents from aromatics may produce compounds that can be more easily biodegraded. Efficient chemical catalysts are needed that can oxidatively degrade halogenated phenols, especially industrial effluents that include a large amount of chemicals that can overload the transformation capacity of microorganisms.[1] $TiO_2$ nanoparticles, one of the most popular photoactive chemical catalysts, has long been investigated in water treatment. Recent studies on the photocatalytic degradation of chloroorganic compounds in water show possibilities that the photocatalytic systems could be applied to the actual water treatment.[2] For this purpose, however, it is still necessary to develop the catalyst exhibiting higher photocatalytic activities and the more efficient photocatalytic systems than ever.

Mesoporous molecular sieves have large and uniform pore size from about 10~100 Å which allow sterically-hindered molecules facile diffusion to internal active sites, they are of more and more interest to catalysis. Today, they have been found great utility as titanium-doped silicate-based hexagonal mesoporous materials, and these materials also have nanopore properties similar to those of nanoparticle properties.[3] There is no doubt that it exists a strong incentive to synthesize pure titanium-based mesoporous molecular sieve (Ti-TMS) and therefore to become useful catalyst especially in the field of photocatalytic degradation of pollutant. Up to now, the only reported example of a hexagonally packed purely mesoporous $TiO_2$ material is the one through a usual modified sol process reported by J.Y.Ying research group.[4-6] Their strategy was successful using tetradecylphosphate surfactant as template removed by calcination, but no alkylphosphate surfactants with other chain length as templates and other method of removal of templates were reported.

In this paper, one method was successful in the synthesis of Ti-TMS and involved a modified method described by J.Y.Ying research group which employed acetylacetone to slow down the condensation of the titanium alkoxide precursor, thus allowing the titanium to interact with dodecyl-, hexadecyl-, and octadecylphosphate templates before the metal alkoxide formed an insoluble titanate, i.e., $TiO_2$ nanoparticles. The samples were first prepared at pH=5 with alkylphosphate-titanium molar ratio of 1:1 after four days aging at 80 ℃ and refluxed to remove the templates at pH=9 in $EtOH/H_2O$ solution.

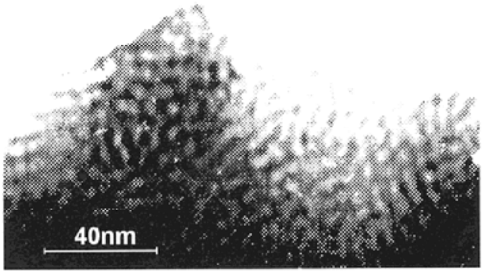

**Figure 1.** TEM image of Ti-TMS prepared from hexadecylphosphate and refluxed in $EtOH/H_2O$ mixture (pH=9) for 24 h.

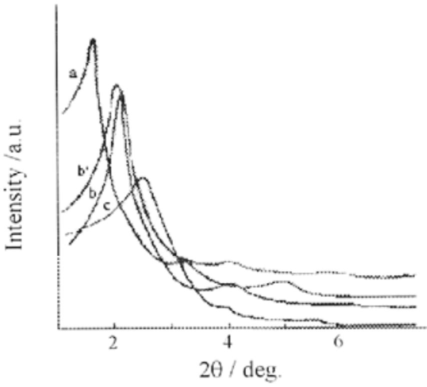

**Figure 2.** XRD patterns of Ti-TMS prepared with alkylphosphate as templates: a) octadecylphosphate before the surfactant removal; b) hexadecyl phosphate before the surfactant removal; b') hexadecylphosphate after the surfactant removal; c) dodecylphosphate before the surfactant removal.

The power transmission electron microscopy (TEM) clearly displayed the hexagonal array of Ti-TMS with different pore sized in the range of 27~44 Å (27, 38 and 44 are for the samples synthesized from dodecyl-, hexadecyl-, and octadecylphosphate, respectively.), almost no amorphous or layered phases were observed in these materials. Figure 1. is the TEM picture of Ti-TMS templated by hexadecylphosphate. It shows that the pore size is about 38 Å (The pore size of Ti-TMS from TEM reported by J.Y.Ying research group using tetradecylphosphate as template was 32 Å). Figure 2 also indicated that the XRD of hexagonal Ti-TMS prepared with dodecyl-, hexadecyl- and octadecylphosphate as templates. Our experiments showed that the length of the hydrocarbon tail of the alkylphosphate can be used to vary the pore size of hexagonallly packed meso-structure and the longer of the hydrocarbon tail of alkylphosphate, the better the structure and uniformity.[7] There is a considerable increase in the intensity and sharpness of the XRD patterns of our samples after the removal of hexadecylphosphate by refluxing in EtOH/$H_2O$ mixture at pH=7 for 24 h, as compared with the XRD patterns of the samples reported by J.Y.Ying et al in which the template was removed by calcination. This suggested that there is a more loss of structure and reduction in crystalline domain size upon calcination than that upon reflux.

Concerning the best photocatalytic activity of Ti-TMS itself for the degradation of pollutant, here we typically select Ti-TMS as catalyst which was synthesized using hexadecylphosphate as template and was refluxed to remove the template (Ti-TMS1 was remove 10% of the template and Ti-TMS2 was removed about 30% of the template). TCP was used as a model degraded substrate. The reactions were conducted in a stirred glass flask by irradiation with UV light from a 300w high Hg lamp at room temperature. For comparison, $TiO_2(P_{25})$ was also investigated under the same conditions.

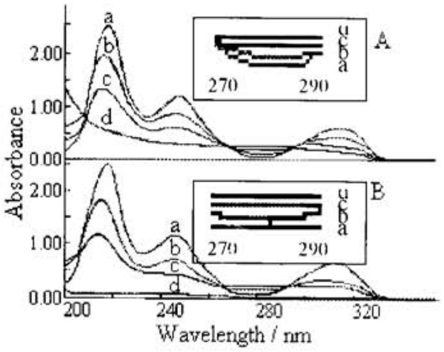

**Figure 3**. Adsorption spectra of 1.33 mM TCP (pH=9) in (A) 0.8 g/l slurry of $TiO_2$ (P25); (B) 0.8 g/l slurry of Ti-TMS, recorded at (a) o; (b)20; (c) 40; (d) 80 min. following the UV-photolysis.

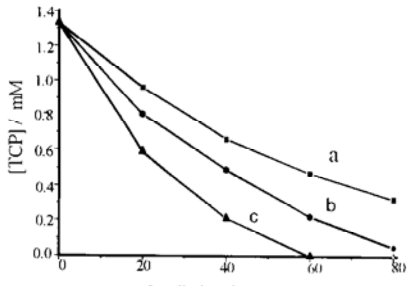

**Figure 4.** Dependence of TCP photocatalytic degradation rate on the kinds of catalysts. (a) $TiO_2$(P25); (b) Ti-TMS1; (c)Ti-TMS2. The difference between Ti-TMS1 and Ti-TMS2 is the amount of removed templates of Ti-TMS during refluxing.

The reaction results are given in Figure 3 and 4. (B) in Figure 3. showed the absorption peaks corresponding to TCP disappear completely following the photolysis, indicating complete disappearance of TCP. The observation of increased absorbance in the 270-290 nm region at short illumination time is attributed to the formation of reaction intermediates.[8] These observations are similar to those observed in Figure 3. (A), but the catalytic activity of Ti-TMS is much higher than that of $TiO_2$ nanoparticles. A possible explanation is that the opening of Ti-TMS allows the internal surface area of this material accessable to molecules and therefore enhances their catalytic activity. The intermediates detected by GC-MS during the course of the degradation were chloromaleic acid, chlorofumaric acid, maleic acid and fumaric acid. The substrate conversions were monitored by HPLC (ultraviolet detection at 248 nm), and were summarized in Figure 4. It is evident that the photocatalytic degradation of TCP over Ti-TMS occurs at a faster rate than that over $TiO_2$. The more the surfactant was removed, the faster the degradation rate was. This is explained by increase of Ti-TMS surface area and internal activity enhancing its catalytic activity with the decrease of the amount of the surfactant in Ti-TMS. At present, the photocatalytic degradation using Ti-TMS completely template-removed and other further consideration are being studied.

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## References and Notes

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