

Effect of Templates on the Structure and Stability of Ti-TMS

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Abstract: Pure Mesoporous TiO₂ molecular sieves (Ti-TMS) were synthesized with different templates for the first time and the templates can be successfully removed by refluxing the samples in the EtOH/H₂O/KOH solution. The XRD pattern and TEM confirm that the uniformity and stability of Ti-TMS2 synthesized with dodecylamine as template is obviously inferior to that of Ti-TMS1 prepared with dodecylphosphate and hexadecylphosphate as templates. Furthermore, after the templates were removed, the mesostructure of Ti-TMS1 was preserved to a great degree than that of Ti-TMS2.

Keywords: TiO₂; mesoporous molecular sieves; template.

Mesoporous materials are of great interest to catalysis because of their large and uniform pore size (20~100Å), which allow stereo-hindered molecules facile diffusion to internal active sites. Although recent effects have suggested that it should be possible to synthesize mesoporous materials from transition metal oxide by molecular self-assembly of organic templating agents and inorganic oxides¹, but there are few reports of this technique successfully generating such materials which could maintain a stable mesoporous structure upon removal of the organic micelles^{2,3}. Recently, Antonelli *et al* reported that a hexagonally packed purely mesoporous TiO₂ material (Ti-TMS) was accomplished through a usual modified sol process. The strategy was just successful with tetradecyl-phosphate surfactants⁴. Herein we first report some studies with other surfactants.

In our experiments, two approaches to the synthesis of Ti-TMS have been adopted. One method involved a modified method described by Antonelli *et al*. We employed acetylacetone to slow down the condensation of the titanium alkoxide precursor, thus allowing the titanium to interact with dodecyl- and hexadecylphosphate templates before the metal alkoxide formed an insoluble titanate. The templates was first removed at pH=9 in the EtOH/H₂O solution. The second method we developed just relied on the formation of a discrete covalent bond between the titanium alkoxide and the dodecyl-amine prior to hydrolysis. All samples were characterized by low-angle XRD and TEM. The results clearly display the hexagonal array of the mesopores.

Figure 1 indicated that two samples showed typical XRD of Ti-TMS1. The d-spacing for the (100) reflection appears at about 35Å, the secondary (110), (200), (210)

reflections appear between of 4° and $7^\circ 2\theta$. Our experiments showed that the length of the hydrocarbon tail of the alkylphosphate can be used to vary the pore size of Ti-TMS1 and the longer the hydrocarbon tail of the alkylphosphate are, the better the structure and uniformity are. There is a considerable increasing in the intensity and sharpness of the patterns for our samples after removal of hexadecylphosphate by reflux in EtOH/H₂O mixture at pH=7 for 24h, as compared to the XRD patterns of the samples reported by Antonelli *et al.*, in which the template was removed by calcination at 350°C for 4h. This suggested that there is loss of structure and reduction in crystalline domain size on calcination more than on reflux with solution. From **Figure 2**, we can conclude that Ti-TMS2 are synthesized successfully. After removal of the template with EtOH/H₂O mixture at pH=7, the intensity and stability are increased. But compared **Figure 1** with **Figure 2**, we also found that the stability and uniformity of the pure TiO₂ mesostructure with alkylamine surfactant is obviously not as good as the one with alkylphosphate surfactant.

Figure 1. XRD patterns of Ti-TMS1 prepared by: a) hexadecylphosphate after the template removal, b) hexadecylphosphate before the template removal, c) dodecylphosphate before the template removal

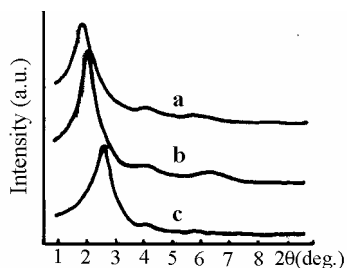
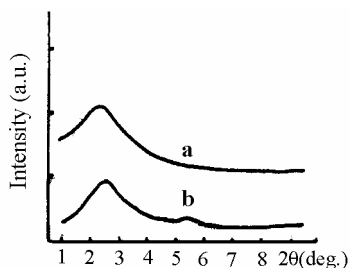


Figure 2. XRD patterns of Ti-TMS2 prepared by: a) dodecylamine after the template removal, b) dodecylamine before the template removal.



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