

Effect of Surfactant on the Physical Properties of Hierarchically Macro–Mesoporous Metal Oxides

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Hierarchically macro–mesoporous titania and alumina were prepared by simply dropwise addition of titanium and aluminum alkoxides to an ammonia solution in the presence or absence of surfactant molecules, cetyltrimethylammonium bromide (CTAB). The textural, morphological, and crystalline phase features of the prepared and calcined samples were characterized by N₂ adsorption–desorption, SEM, and XRD analysis. It was found that the surfactant molecules had a significant effect on the physical properties of the hierarchically porous metal oxides.

Recently, hierarchically macro–mesoporous metal oxides, such as alumina, titania, and zirconia, attract much attention due to their unique pore structures, i.e., the monolithic macropores and the hierarchical structures, which make them high potential supports and catalysts.^{1–3} The key factors that influence the textural properties of hierarchically porous metal oxides include hydrolysis temperature and time, pH value of the solvent, and surfactant.^{2,4–7} Among these factors, the effects of surfactant molecules on the physical properties of the metal oxides bring about discrepancy. Some researchers found that the surfactant influenced the stability of microphase-separated interfaces, i.e., the surface areas, pore volume, and mesopore size.^{5,6} But others believed that surfactant molecules served as the self-assembled templates for the formation of the macroporous structure.⁷ Moreover, to the best of our knowledge, very few have reported the effect of surfactant on the crystalline phase of the prepared metal oxide. Here, alumina and titania with a hierarchically macro–mesoporous structure were prepared in the presence and absence of CTAB, and the effects of CTAB on the physical properties of the metal oxides are disclosed and highlighted.

In a typical surfactant-assisted synthesis of alumina, a 0.8 wt % (mass percent) micellar solution was prepared by dissolving CTAB into a mixture of 35 mL of twice-distilled water and 15 mL of ethanol (pH 12, adjusted by ammonium hydroxide) with moderate stirring (350 r/min) at room temperature. Aluminum tri-*sec*-butoxide was added dropwise. After reaction for 1 h, the precipitates formed were separated by centrifugation, washed with ethanol by a Soxhlet extractor for 30 h, and dried in air for 24 h. The as-prepared samples were finally calcined at 600 and 800 °C for 5 h, respectively. The surfactant-free synthesis was similar except that no CTAB was added in the mixture solution, and correspondingly, the extraction step was omitted. The hierarchically porous titania was synthesized by a very similar method, and detailed information is provided in the Supporting Information.⁸

Table 1 summarizes the preparation conditions and the physical properties of all the alumina and titania samples. Sample a1 was aluminum oxide, which was prepared in the presence of CTAB and without calcination. Samples a2, and a3 were the calcination counterparts of sample a1 at 600 and 800 °C, respectively. Corresponding to samples a1, a2, and a3, the Al₂O₃ prepared in the absence of CTAB were labeled as a4, a5, and a6, respectively. Similarly, the TiO₂ samples prepared with and without CTAB were labeled as t1–t6.

An interesting result is the effect of CTAB on the textural properties of the metal oxide samples. Note that no difference appears between macropore sizes of the samples prepared with and without CTAB, implying that the formation of the macroporous channels is not affected by surfactant molecules. On the contrary, the mesopore size, the surface area, and the pore volume are influenced to some extent by CTAB. In both cases, the prepared samples with CTAB (a1 and t1) exhibit larger

Table 1. Preparation conditions and physical properties of the alumina and titania samples

No.	CTAB /g	Temperature ^a /°C	$S_{\text{BET}}^{\text{b}}$ /m ² g ⁻¹	Pore volume /cm ³ g ⁻¹	Macropore size ^c /μm	Mesopore size ^d /nm	Crystalline phase
a1	0.4	None	514.1	0.81	0.45	5.1	boehmite
a2	0.4	600	211.1	0.64	0.55	9.4	γ-Al ₂ O ₃
a3	0.4	800	126.4	0.51	0.50	12.1	δ-Al ₂ O ₃
a4	0	None	403.5	0.39	0.60	3.2	boehmite, bayerite
a5	0	600	206.6	0.39	0.67	6.2	γ-Al ₂ O ₃
a6	0	800	108.0	0.38	0.43	10.9	θ-Al ₂ O ₃
t1	0.4	None	320.5	0.17	0.75	3.8	amorphous
t2	0.4	500	29.04	0.08	0.94	8.4	anatase, rutile
t3	0.4	650	5.44	0.05	1.14	16.7	rutile
t4	0	None	305.1	0.13	0.75	3.3	amorphous
t5	0	500	42.5	0.07	1.00	4.9	anatase
t6	0	650	18.7	0.07	0.90	18.6	anatase

^aCalcination temperature. ^bBET surface area. ^cAverage macropore diameter obtained from analysis of the image. ^dBJH pore diameter determined from the desorption branch.

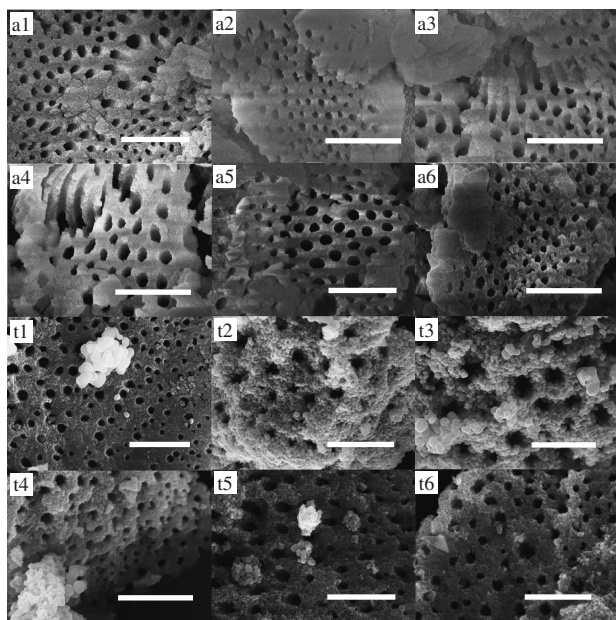


Figure 1. SEM images of hierarchically macro-mesoporous Al_2O_3 and TiO_2 . Scale bar: 5 μm .

mesopore size, surface area, and pore volume than those of CTAB-free samples (a4 and t4).⁸

As shown in Figure 1, all the alumina and titania samples exhibit uniform macroporous structures, i.e., the macroporous channels are of one-dimensional orientation, parallel to each other and perpendicular to the tangent of the outer surface of the particle. Closer inspection of Figure 1 further shows that the walls separating the macrochannels are formed by aggregates of tiny particles, indicating that the mesoporosity of the samples likely results from both interparticle and intraparticle porosity.

The generation of the macrochannels in the CTAB-assisted or CTAB-free synthesis implies that the surfactant molecules have no effect on the formation of macropores. A spontaneous self-assembly mechanism can explain the formation of this structure.^{2,3,5,9} When an alkoxide droplet is added to a solution, a semipermeable membrane is formed simultaneously at the outer surface of the droplet, which makes the reaction front move inwardly. Meanwhile, hydrolysis/condensation reactions produce the microphase-separated regions of the solid phase (alumina nanoparticles) and the liquid phase (water and alcohol), which finally generate the macrochannel structure.

Another interesting result is the effect of CTAB on the crystalline phase of the metal oxide. The crystalline phases of the above samples are shown in Table 1 and Figure S5.⁸ It can be seen that the CTAB-assisted samples exhibit different crystalline phases in comparison with those without the aid of CTAB. As far as the aluminum oxide is concerned, the as-prepared alumina sample with CTAB (a1) only exhibits the boehmite phase (JCPDS 21-1307), while the sample without CTAB (a4) shows a mixture of boehmite and bayerite (JCPDS 20-0011). After calcination at 600 °C, both samples display the γ - Al_2O_3 phase (JCPDS 10-0425). However, the 800 °C calcined samples show different crystalline phases, depending on whether or not surfactant molecules are added. The sample with CTAB

(a3) and without CTAB (a6) exhibits δ - Al_2O_3 (JCPDS 16-0394) and θ - Al_2O_3 (JCPDS 11-0517), respectively.

Besides the XRD measurements, the difference in the crystalline phase for samples a1 and a4 can also be reflected by the SEM images. As shown in Figure S6,⁸ sample a1 prepared with CTAB consists of much smaller particles than that of sample a4 prepared without CTAB. In addition, the former has a more homogeneous microstructure than the latter. This result is reasonable taking into account the formation of bayerite as a well-developed crystallite in sample a4 (relatively low surface area), which consequently causes the inhomogeneous microstructure of sample a4.

Similarly to Al_2O_3 , the surfactant also has an effect on the crystalline phase of the titanium oxide samples. The as-prepared TiO_2 without CTAB (t4) was in an amorphous phase, and the calcination samples at 500 (t5) and 650 °C (t6) show the anatase phase (JCPDS 21-1272). However, the 500 °C calcined TiO_2 with CTAB (t2) exhibits a mixture of anatase and rutile (JCPDS 12-1276), and the 650 °C calcined samples (t3) only displays the rutile phase. This result implies that the addition of CTAB facilitates the phase transition of TiO_2 from anatase to rutile. Similar results were also reported by other researchers.^{10,11} Therefore, the presence of surfactant molecules is a key factor that influences the crystallization and growth of the crystallite of the macro-mesoporous metal oxides after thermal treatment.

In conclusion, we have prepared hierarchically macro-mesoporous alumina and titania in the presence and absence of surfactant molecules. Addition of CTAB does not direct the formation of macropores but affects the mesopore size, the surface area, and the pore volume. In addition, the CTAB surfactant can effectively direct the crystal growth and influence the intrinsic crystal structure of the metal oxides.

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