

Preparation of mesostructured lamellar zirconia

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Mesostructured lamellar zirconia is synthesized by using anionic surfactants under hydrothermal conditions.

Since the discovery by scientists at Mobil of the mesoporous aluminosilicate (MCM-41),^{1,2} much attention has been paid not only to mesoporous aluminosilicates, but also to mesoporous oxides of other metals. Many mesoporous transition-metal oxides have been obtained. Huo *et al.*³ and Ciesla *et al.*⁴ report the syntheses of mesostructured oxides of Fe, Mn, Zn, Co, Ni, Al, Sb, W by interaction of a soluble metal solution and an anionic surfactant. Unfortunately, attempts to remove the template used for synthesis, either by leaching or by calcination, have led to the collapse of the mesostructure. Recently the syntheses of mesoporous TiO₂, Nb₂O₅ and ThO₂ with hexagonal pore arrangements and amorphous pore walls have been reported.^{5–7} As for mesostructured zirconia, several papers report that this material can only be obtained with amorphous walls^{8,9} and irregular pore arrangement. The mesoporosity is, however, lost upon crystallization of the zirconia. Another paper claims the synthesis of mesoporous zirconia with regular pore arrangement based on small-angle XRD.¹⁰ Mesoporous lamellar zirconia was also prepared by a route using neutral amines, but the mesostructure was lost when the samples were calcined to remove the surfactant.¹¹ The synthesis of mesoporous zirconia using a neutral amine template that was subsequently extracted with ethanol has been reported by us; although no regular pore structure has been obtained, the mesoporosity of this material can be maintained up to 700 °C if the tetragonal modification of zirconia is stabilized by sulfation. Here, we report the synthesis of mesostructured lamellar zirconia, by using soluble zirconium chloride and an anionic surfactant.

Lamellar zirconia is obtained by hydrothermal reaction. In a typical synthesis process, 1.5 g ZrOCl₂ was first dissolved in 10 ml water. 1.26 g of sodium 1-hexadecanesulfonate (*n*-C₁₆H₃₃SO₃Na) was then dissolved in 10 ml water and mixed with the ZrOCl₂ solution under stirring. The surfactant/zirconium molar ratio is *ca.* 0.5 and the mixture has a pH of *ca.* 6. Stirring was continued for 30 min; the mixture was then sealed in a polyethylene bottle and heated at 90 °C for 48 h before final filtering, washing and drying in air.

Besides sodium 1-hexadecanesulfonate, 1-hexadecanesulfonyl chloride (*n*-C₁₆H₃₃SO₂Cl) was also used as surfactant for the synthesis of mesostructured zirconia, using the same procedure. In some cases, some Pt(NH₃)₄(NO₃)₂ was added to a zirconyl chloride solution before mixing it with the surfactant solution. The Pt loading is *ca.* 1 mass% based on the amount of ZrO₂.

The materials have been characterized by small-angle XRD and TEM. Fig. 1(a) and (b) show the small-angle XRD patterns of mesostructured zirconias synthesized using either the surfactant *n*-C₁₆H₃₃SO₃Na or *n*-C₁₆H₃₃SO₂Cl. Their XRD patterns are very similar. The peak at $2\theta = 2^\circ$ clearly indicates the existence of some mesostructure. The peaks at higher diffraction angles are not well resolved. In view of the inaccuracy of the XRD pattern, a *d* value of *ca.* 40 Å is estimated for the first peak.

Though many authors use small-angle XRD to determine the symmetry of the mesostructure, this procedure sometimes leads

to inaccurate results. Schüth has shown that a highly resolved XRD pattern can be consistent with a chaotic structure.¹² Therefore, the present work mainly employs TEM to identify the structure of the materials. Fig. 2 shows the TEM image of mesostructured zirconia obtained by using *n*-C₁₆H₃₃SO₃Na surfactant. The lamellar structure is clearly visible. The distance between two layers is estimated to be *ca.* 41 Å. This is consistent with the value obtained from XRD.

The same lamellar TEM image is found with material obtained using *n*-C₁₆H₃₃SO₂Cl as the template. Incorporation of Pt does not change the mesostructure of the materials.

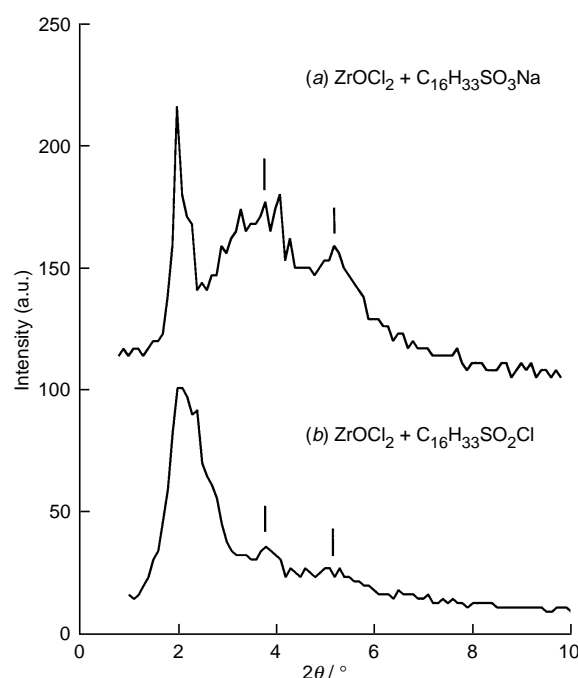


Fig. 1 Small-angle XRD patterns of mesostructured zirconia synthesized by using surfactant *n*-C₁₆H₃₃SO₃Na (a) and *n*-C₁₆H₃₃SO₂Cl (b)

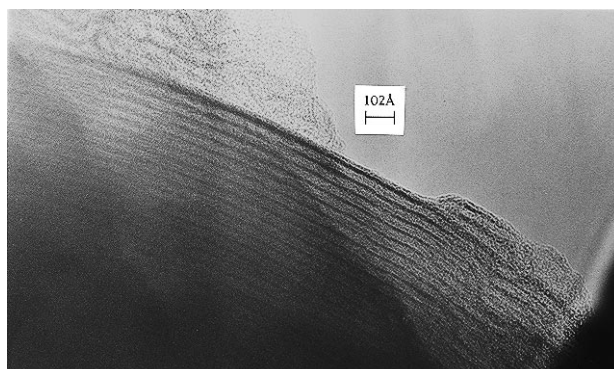


Fig. 2 TEM image of mesostructured zirconia synthesized with *n*-C₁₆H₃₃SO₃Na

The materials were also analysed by thermal gravimetry (TG). As shown in Fig. 3, the surfactant is oxidized in an O₂ atmosphere at ca. 275 °C. A strong exothermic effect is observed at that temperature. The total mass loss is due to desorption of occluded materials in addition to oxidation of the surfactant. The mass loss corresponding to the oxidation of surfactant is about 50% of the total mass. Based on the TG results, a Zr/surfactant molar ratio of 1.5 is estimated. This is higher than expected for the charge balance of ZrO₂⁺ with *n*-C₁₆H₃₃SO₃⁻. Apparently considerable quantities of water and other species are included in the material.

As *n*-C₁₆H₃₃SO₃Na is dissolved in water, the negative *n*-C₁₆H₃₃SO₃⁻ ion is formed. The anion can also be formed by hydrolysis of *n*-C₁₆H₃₃SO₂Cl. The surfactant anion will react with the ZrO₂⁺ cation to form a 'cation-anion composite

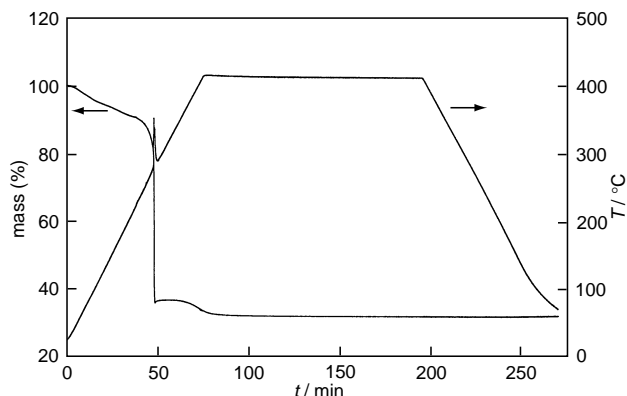


Fig. 3 TG profile of mesostructured zirconia synthesized with *n*-C₁₆H₃₃SO₃Na registered in a flow of oxygen of 20 ml min⁻¹

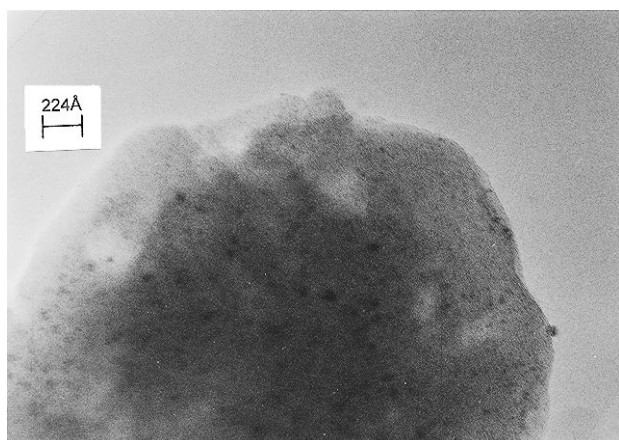


Fig. 4 TEM image of Pt containing mesostructured zirconia by using *n*-C₁₆H₃₃SO₃Na as surfactant, after calcination at 300 °C in a flow of oxygen of 100 ml min⁻¹

molecule'. This composite molecule has a low solubility in water and tends to reassemble, forming an ordered structure.

Although considerable effort was made to maintain the mesostructure by cautiously removing the surfactant, these attempts failed. Leaching of the material synthesized from *n*-C₁₆H₃₃SO₃Na with an ammonia-ethanol mixture did not work either, whereas such treatment with the material from *n*-C₁₆H₃₃SO₂Cl leads to the gelation of the original material.

Calcination of the materials in air at 500 °C for 6 h results in the collapse of the lamellar structure and the formation of tetragonal zirconia. The characteristic small-angle diffraction peak is lost. Upon calcining these materials in a flow of oxygen (100 ml min⁻¹) at 300 °C for 2 h at low ramping rate (0.5 °C min⁻¹), XRD analysis shows that the lamellar structure collapses and amorphous zirconia is obtained. TEM confirms that the material contains mainly amorphous zirconia particles and some small particles of tetragonal zirconia. In the case of the Pt-containing materials, highly dispersed Pt metal particles are formed. Fig. 4 shows rather uniform Pt particles dispersed on zirconia.

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Footnote

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