

# Mesoporous zirconia obtained with anionic templates

G. Pacheco,<sup>a</sup> E. Zhao,<sup>a</sup> A. Garcia,<sup>c</sup> A. Sklyarov<sup>b</sup> and J. J. Fripiat<sup>\*a</sup>

<sup>a</sup> Department of Chemistry and Laboratory for Surface Studies, and <sup>b</sup> Advanced Analysis Facility, University of Wisconsin-Milwaukee, PO Box 413, Milwaukee, WI 53211, USA

<sup>c</sup> Materials Department, Instituto Polytechnico Nacional, Zacatenco, Lindavista, CP 07300, Mexico, DF, Mexico

## Mesoporous zirconia is synthesized with anionic templates.

The success of Mobil scientists in the surfactant-assisted synthesis of mesoporous molecular sieves<sup>1,2</sup> with hexagonal or cubic ordering of the pore system and high temperature stability has been followed by an enormous amount of research worldwide. An array of cationic surfactants (such as quaternary alkylammonium) with chains containing, typically, twelve carbon atoms interact with an inorganic anionic or cationic oligomer (or polymer) to form a solid in which small-angle X-ray scattering reveals the existence of an ordered system of pores.

The basic principles of these syntheses have been reviewed by Huo *et al.*<sup>3</sup> who have distinguished the interaction between cationic or anionic surfactant with anionic or cationic metal oligomers on the basis of studies involving a large variety of metals other than silicon. Three kinds of structures have been characterized by their X-ray patterns, namely, hexagonal, lamellar and cubic. A high spacing reflection is easily observed in the range  $2\theta$  2–4°, whereas the other Bragg reflections, on which the differentiation between the structures is based, are more difficult to observe because of their intrinsic lower intensity and the broadening due to disorder. Removal of the surfactant does not necessarily keep the hexagonal or cubic structure intact, as desirable for producing high-area solids.

The incorporation of titanium<sup>4</sup> and of zirconium<sup>5</sup> in hexagonal mesoporous silica has been proposed to circumvent the lack of stability of mesoporous titania or zirconia. However, hexagonally packed transition-metal mesoporous molecular sieves of pure niobium, titanium or tantalum oxide have been synthesized with octadecylamine by Antonelli and Ying.<sup>6,7</sup> The preparation of pure mesoporous zirconia with surface area of ca. 300 m<sup>2</sup> g<sup>−1</sup> at 500 °C has been achieved by Knowles and Hudson<sup>8</sup> using tetramethyl alkylammonium surfactants and zirconyl chloride. Starting from Zr sulfate or propoxide, Schüth<sup>9</sup> and Ciesla *et al.*<sup>10</sup> have obtained a hexagonal mesoporous zirconia of a quality corresponding to that of the silica analogue using alkyl tetramethylammonium surfactants as templates. Reddy and Sayari<sup>11</sup> obtained either hexagonal or lamellar phases of templated zirconia using either quaternary ammonium surfactants or acidified primary alkylamine, respectively. Sachtler and coworkers<sup>12</sup> have used a primary acidified (C<sub>16</sub>) alkylamine. The ordering of the pores was far from perfect but the sulfation of the 'as-synthesized precursor' remarkably stabilizes the structure. After sulfation the X-ray diagram characteristic of tetragonal ZrO<sub>2</sub> appears at about 600 °C.

Except in this latter work, the formation of structurally 'ordered' walls has not drawn much attention. Since the stability of tetragonal ZrO<sub>2</sub> appears to be driven by particle size,<sup>13,14</sup> the onset of crystallization of the wall in the monoclinic phase could give information on the thickness of the walls between pores. At 500 °C, particles with diameters > 16 nm undergo the tetragonal to monoclinic transformation.<sup>15</sup>

Here, we report on the synthesis of mesoporous zirconia using two anionic surfactants. As far as we know such synthesis has not been achieved up to now and it may be that the

elimination of this category of surfactants could be easier. The preparation was as follows. The source of zirconium was a 70% m/m solution of zirconium propoxide in propanol. The two 'straight alkyl chain' surfactants were: C<sub>12</sub>H<sub>25</sub>OP(OH)<sub>2</sub> (*M* = 266), abbreviated P<sub>12</sub> and C<sub>12</sub>H<sub>25</sub>OSO<sub>3</sub>Na (*M* = 288), abbreviated S<sub>12</sub>, respectively. The P<sub>12</sub> solution was left at pH = 3, namely, the original pH of the solution. The initial pH of the S<sub>12</sub> solution was adjusted by HCl at about 3. The propanolic zirconium alkoxide solution was added slowly to the surfactant solution until the molar ratio S/Zr was 0.16. The mixture was transferred into a hydrothermal bomb where it was heated between 90 and 120 °C for about 12 h. The products of the reaction, called, in short, either P<sub>12</sub> or S<sub>12</sub> solids, were dried at 140 °C or calcined at 500 °C.

Low-angle X-ray scattering in the range  $2\theta$  0.8–10° was obtained with a Scintag  $\Theta$ – $\Theta$  X-ray diffractometer (Cu-K $\alpha$ ) fitted with a solid-state detector and the following set of slits: 0.5, 0.3, 0.2 and 0.07°. For medium-angle X-ray scattering (2–70°), the slits were 3, 2, 0.5 and 0.3°. Fig. 1 shows a diffraction line corresponding to spacing at about 47 Å after drying at 140 °C. After calcination at 500 °C, the spacing generally increases, but sometimes, as observed for the S<sub>12</sub> solid, the ordering disappears.

The N<sub>2</sub> adsorption–desorption isotherms were obtained with an automated physisorption instrument operated in a static mode (Omnisorp 100, Coulter Co.). All measurements were performed after outgassing at 150 °C under vacuum down to a residual pressure better than 10<sup>−4</sup> Torr. During calcination in air at 500 °C, all organics were burned as proved by the analysis of residual carbon (Table 1). The typical shape expected for mesoporous solids is observed in Fig. 2(a), namely, for the S<sub>12</sub> and P<sub>12</sub> solids dried at 140 °C. The *t*-plot specific surface area is in excess of 500 m<sup>2</sup>. A broad maximum in the porosity distribution function dV/dr vs. *r*, the radius of the pore, is observed at *2r* ca. 35 Å. As shown in Table 1, for these solids over 70% of the porous volume is in pores with diameters between 10 and 100 Å, even in P<sub>12</sub> calcined at 500 °C, in spite of a ca. 50% loss in mesoporosity [Fig. 2(b)]. The qualitative agreement between the small-angle X-ray scattering data is

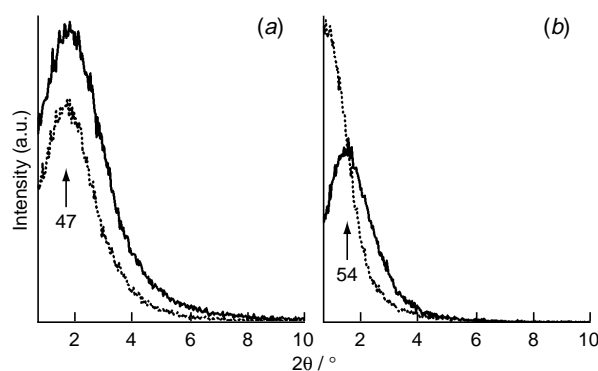
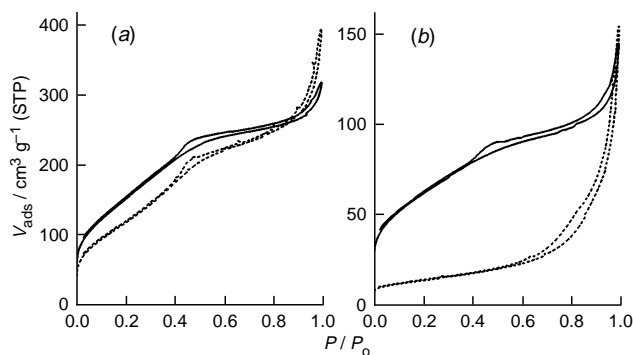


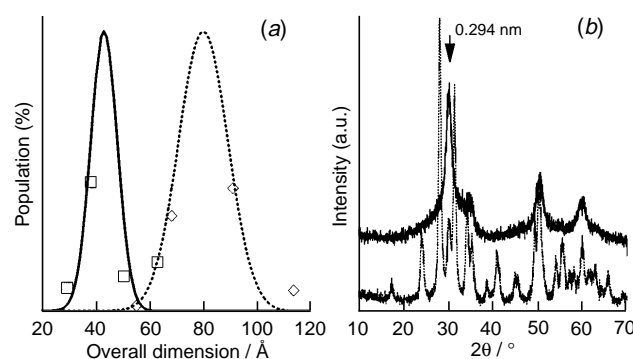
Fig. 1 Small-angle XRD reflections for the P<sub>12</sub> (—) and S<sub>12</sub> (---) solids (a) dried at 140 °C or (b) calcined at 500 °C

**Table 1** Chemical and physical characteristics of mesoporous zirconias obtained from templating with P<sub>12</sub> or S<sub>12</sub> surfactants. The solids are dried at 140 °C or calcined at 500 °C. S/Zr: surfactant to zirconium molar ratio. Porous volume (ml liquid N<sub>2</sub> g<sup>-1</sup>) in pores with diameter,  $\phi$  < 10 Å or between 10 and 100 Å. N<sub>2</sub> desorption branch is used

	S/Zr	Pore volume		% Pore volume 10 ≤ $\phi$ ≤ 100
		$\phi$ < 10	10 ≤ $\phi$ ≤ 100	
P <sub>12</sub> , 140	0.12	0.007	0.538	89.0
S <sub>12</sub> , 140	0.13	0.028	0.577	74.2
P <sub>12</sub> , 500	0	0.006	0.225	81.3
S <sub>12</sub> , 500	0	0.001	0.093	37.5



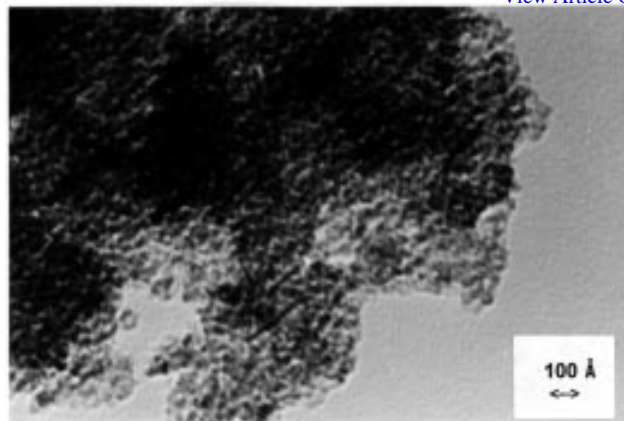
**Fig. 2** N<sub>2</sub> adsorption-desorption isotherms for mesoporous zirconia obtained from templating with P<sub>12</sub> (—) and S<sub>12</sub>(---); (a) samples dried at 140 °C or (b) samples calcined at 500 °C



**Fig. 3** (a) Gaussian-fitted distribution of the dimension (Å) of the hexagons observed in the HRTEM pictures of the P<sub>12</sub> and S<sub>12</sub> solids dried at 140 °C (□, maximum at ca. 43 Å). The distribution with maximum at ca. 80 Å is observed for P<sub>12</sub> calcined at 500 °C (◇). (b) XRD obtained for P<sub>12</sub> (—) or for S<sub>12</sub>(---) solids calcined at 500 °C. The reflection at 2.94 Å is characteristic of the trigonal structure.

striking, particularly when comparing the development of macroporosity due to the sintering of S<sub>12</sub> at 500 °C.

The materials were examined with high-resolution transmission electron microscopy (HTREM, 200 kV). On a microphotograph (Fig. 4) obtained with P<sub>12</sub> dried at 140 °C, a network of more or less organized pseudo-hexagonal pores is observed. In Fig. 3(a), the measured distribution of the overall dimension (Å) of the pseudo-hexagonal pores in P<sub>12</sub> or S<sub>12</sub> is fitted to a Gaussian distribution with a maximum at ca. 44 Å and a width of 7 Å. Upon calcining P<sub>12</sub> at 500 °C, the maximum of the distribution shifted towards 80 Å while the width doubled. Again, this is in qualitative agreement with the low-angle scattering data in Fig. 1(b) and the isotherms shown in Fig. 2(b). The loss of mesoporosity in solid S<sub>12</sub> calcined at 500 °C is supported by the disappearance of the network of pseudo-hexagons in the corresponding HRTEM picture (not shown). The comparison [Fig. 3(b)] of the X-ray scattering data of P<sub>12</sub>



**Fig. 4** HRTEM picture of mesoporous zirconia obtained with P<sub>12</sub> template

and S<sub>12</sub> solids calcined at 500 °C provides some insight into the sintering observed for S<sub>12</sub>, since in this sample the phase transformation from a tetragonal to monoclinic structure is evident while P<sub>12</sub> is at the onset of crystallization. The thickness of the walls between pseudo-hexagons increases from approximately 10 Å to ca. 20 Å (HRTEM). <sup>31</sup>P NMR spectroscopy shows that the phosphate remains in the solid after calcination at 500 °C.

Scanning electron microscopy revealed that P<sub>12</sub> and S<sub>12</sub> consist mainly of a collection of polygonal particles, of diameter 4–10 μm. Spherical particles in this range of dimensions appear upon sintering S<sub>12</sub> at 500 °C.

Thus, it may be concluded that mesoporous zirconia can be prepared by hydrolysing the zirconium propoxide in the presence of anionic surfactants (alkyl-phosphate and -sulfate) and subsequent ageing.

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