

Preparation of porous hafnium oxide in the presence of a cationic surfactant

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A thermally stable mesostructured hafnium oxide is synthesized for the first time.

Shortly after the discovery of M41S mesoporous materials,¹ the supramolecular templating approach was extended to the synthesis of non-silica based materials.² Stucky and coworkers^{2,3} synthesized a variety of oxides of Pd, W, Mo and Fe, but obtained only a limited number of three-dimensional mesostructures. However, the surfactants in these materials could not be removed without the collapse of the structure. Recently, Antonelli *et al.*^{4–6} successfully synthesized mesoporous niobium and tantalum oxides using a ligand-assisted templating approach. The surfactant was removed by solvent extraction using a mixture of nitric acid and isopropyl alcohol. Mesoporous alumina has also been obtained by using either non-ionic polymer surfactants⁷ or long-chain carboxylic acids⁸ as templates.

Hexagonal mesoporous zirconium oxide has been synthesized by Sayari and coworkers.^{9,10} While the as-synthesized material was not stable upon removal of the surfactant, it was successfully stabilized by a post-synthesis treatment with potassium phosphate. After air calcination, a Zr–P oxide with a surface area as high as 500 m² g⁻¹ was obtained. Independently, Ciesla *et al.*¹¹ reported similar results. In addition, they obtained a pure zirconium oxide with a surface area of 280 m² g⁻¹ using zirconium isopropoxide in the presence of large amounts of ammonium sulfate and hydrochloric acid.

Hafnium oxide is useful for the preparation of strong acid catalysts similar to sulfated zirconia.¹² Here, we report the first synthesis of porous hafnium oxide, using the surfactant templating approach. In a typical synthesis, 2.68 g of HfCl₄ was hydrolysed in 10 g of water. To this solution, 0.82 g of

cetyltrimethylammonium bromide (CTAB) in 8 g of water was added followed by a solution of 4.4 g of (NH₄)₂SO₄ in 24 g of water. After stirring for 10 min, the pH of the solution was adjusted to 2.1 by adding 1.4 g of 30 mass% ammonia. The gel was then stirred for 30 min before being transferred to a Teflon-lined autoclave and heated statically for 24 h at 373 K. The solid was recovered by filtration and washed with large amounts of water, followed by drying at room temperature for 24 h.

X-Ray powder diffraction was performed on a Siemens D5000 diffractometer. The XRD pattern of the solid shows an intense peak at a low angle ($d \gg 4.0$ nm) along with a shoulder [Fig. 1(a)]. This pattern is characteristic of a mesophase with a pore system lacking long-range order. Fig. 2(a) shows the transmission electron microscopy (TEM) image of the as-synthesized material. As seen, the pore structure has no long-range order which is consistent with the XRD data. This is reminiscent of HMS¹³ and MSU¹⁴ mesoporous materials.

FTIR and EDX showed that the material calcined in air at 773 K for 2 h was carbon free. Its surface area as determined from N₂ adsorption isotherm (Fig. 1, insert) was 204 m² g⁻¹. Taking the molecular mass difference between HfO₂ and ZrO₂ (104 vs.

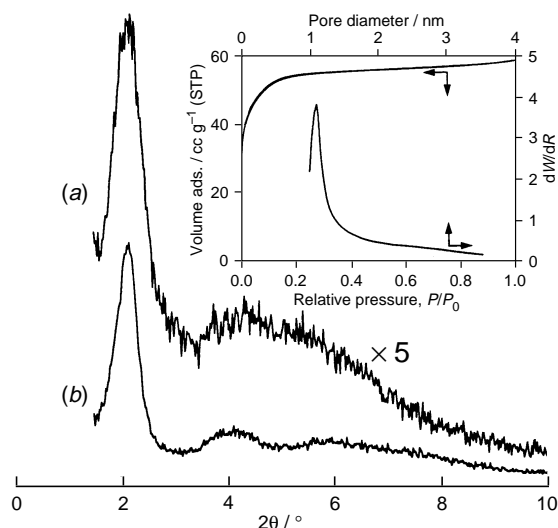


Fig. 1 Powder X-ray diffraction patterns of mesostructured hafnium oxide prepared at (a) 373 K and (b) room temperature. Insert: nitrogen adsorption-desorption isotherm and pore size distribution for the sample prepared at 373 K.

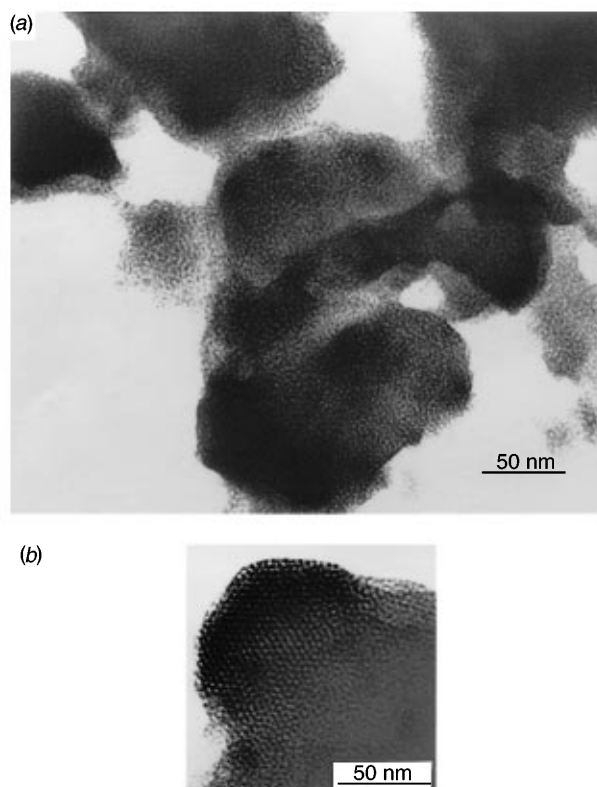


Fig. 2 Transmission electron micrographs of as-synthesized samples prepared at (a) 373 K and (b) room temperature

72) into account, this surface area is comparable to that obtained for pure zirconium oxide ($280 \text{ m}^2 \text{ g}^{-1}$).¹¹ The pore diameter calculated from the adsorption isotherm using the Horvath–Kawazoe model¹⁵ was *ca.* 1.1 nm (Fig. 1, insert). This is also comparable to the pore diameter of ZrO_2 .⁹ An extensive contraction of the inorganic structure took place during the removal of the surfactant at high temperature.

The effects of pH and synthesis temperature on the final morphology were also investigated. It was found that a pH higher than 1.5 is essential for the formation of the mesostructure. Mesostructured HfO_2 can also be prepared at room temperature. In one synthesis, 2.68 g of HfCl_4 was hydrolysed in 10 g of water. A solution of 0.82 g of CTAB in 8 g of water was added followed by 4.4 g of $(\text{NH}_4)\text{SO}_4$. The mixture was stirred for 10 min before adding 1.2 g of 30 mass% ammonia. After stirring for 30 min, 30 g of water was added and the gel was stirred for 10 min. The pH of the final mixture was around 1.6. As inferred from XRD data [Fig. 1(b)] and confirmed by TEM [Fig. 2(b)], this mesostructure is much more ordered and the hexagonal pore structure can be easily seen. However, the materials thus obtained were found to be thermally unstable. This indicates that hydrothermal treatment at 373 K or a higher pH of the synthesis gel enhances the polymerization of the inorganic species and improves the stability.

In conclusion, we have for the first time synthesized a thermally stable porous hafnium oxide. The high surface area of this material would be useful for the preparation of strong acid catalysts.

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