Meso-Macroporous Metal Oxides

Hierarchically Mesoporous/Macroporous Metal Oxides Templated from Polyethylene Oxide Surfactant Assemblies**

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Surfactant templating techniques based on electrostatic, hydrogen-bonding, covalent, and van der Waals interactions between organic and inorganic species have been developed for the synthesis of materials with a narrow mesopore size distribution and controlled pore structure.[1,2] The use of block copolymers was recently shown to extend the pore sizes of ordered mesoporous oxides up to ten nanometers.[3,4] In addition, macroporous materials with pore sizes ranging from 100 nm to 1 μm can be obtained using latex spheres as templating agents.[5–8] The fabrication of hierarchically ordered structures at multiple length scales has attracted much interest from both a fundamental and practical viewpoint.[9,10] The combination of surfactant and colloidal crystal templating methods, together with microfabrication techniques allows the construction of hierarchical micro/meso/macroporous architectures.[10–15] In this report, hierarchical mesoporous metal oxides with a novel macroporous architecture were synthesized in one step by single-surfactant templating without the need for polymeric spheres to act as a template that generates the macroporous structure. Polyethylene oxide (PEO) surfactants were used, which have been shown to efficiently organize mesoporous materials with structures of disordered wormhole-like MSU-type[16–18] and ordered SBA-*n*[19] and CMI-1[20] materials.

The occurrence of pores with a bimodal pore-size distribution in mesoporous materials is important and useful for both catalysis and the engineering of pore systems.[21] Mesoporous metal-oxide molecular sieves with macroporous structures are of interest as potential catalysts and sorbents, partly because the textural mesopores and intrinsic interconnected pore systems of macrostructures should efficiently transport guest species to framework binding sites. Biomimetic vesicular structures can be formed when the ionic strength of the nonionic surfactant solution is raised from that of the pure aqueous solution through the modification of PEO–H_2O hydrogen bonding; one kind of bimodal mesoporous silica has been synthesized by adding dilute electrolytes during PEO-templating.[22] Spongelike silica membranes with three-dimensional meso-macrostructures (that is, materials composed of mesopores of 2–50 nm in diameter, and macropores with diameters of between 50 nm and several micrometers) were synthesized from an electrolyte phase of a block copolymer/silica system, though inorganic salt crystals inevitably grew together with the silica membrane.[23] Meso-macroporous niobium oxides have also been prepared by adding NaCl to a ligand-assisted templating mixture of niobium ethoxide and amine surfactants; the salt was emphasized as being necessary for macropore (vesicle) formation.[24] We have used a simple method to prepare mesoporous metal oxides, such as TiO_2 and ZrO_2, with macroporous hierarchical structure by the cooperative assembly of nonionic alkyl-PEO surfactants and inorganic precursors derived from metal alkoxides. The synthesized materials exhibit both wormhole-like mesochannels and a funnel-like macrostructure with more accessible pores and a very high internal surface area, which should be significant in processes involving large molecules.

$C_{16}(EO)_{10}$ and $C_{13}(EO)_6$ surfactants were employed as structure-directing agents, and zirconium *n*-propoxide and titanium isopropoxide were used as inorganic precursors. Hydrothermal treatment was performed in a teflon-lined autoclave at 60–80 °C for one to two days. Almost all of the surfactant species in the product channels could be removed by ethanol extraction (as confirmed by IR measurements),

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[**] This work has been carried out within the framework of the Belgian Federal Government PAI-IUAP-5/01 project. A.L. is a FRIA fellow. Z.Y.Y. is a PAI-IUAP research fellow. A.K.C. is the International Francqui Chair holder of Belgium (2000–2002).

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

DOI: 10.1002/ange.200250816

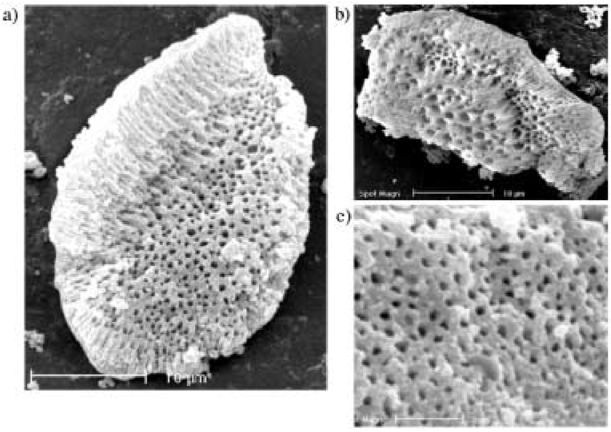

Figure 1. Representative SEM images of mesoporous zirconium oxides showing a novel macroporous structure.

which avoids possible structural collapse caused during high-temperature calcination to free the pores. Figure 1 shows several representative scanning electron microscopy (SEM) images of the synthesized macro-mesoporous zirconia materials, while Figure 2 displays transmission electron microscopy (TEM) images of the zirconia meso-macrostructures viewed along various directions of the macropores. Almost all of the obtained zirconia particles exhibit macroscopic network structures with relatively homogenous macropores of 300–600 nm in dimension, revealed by both SEM and TEM micrographs. A closer observation (Figure 2a) shows some regularity in the macropore array of the oxides formed using single-surfactant templating. Moreover, the macrochannels are arranged parallel to each other and perpendicular to the tangent of the surface of the particle; the pores are funnel-like (tapered towards the center) in shape. TEM images also revealed that the oxide macroporous framework is composed of accessible mesochannels with a wormhole-like array (Figure 2d).

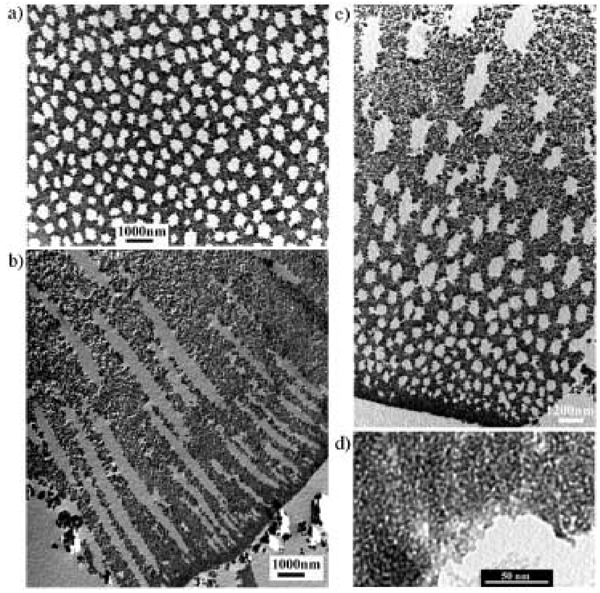

Figure 2. TEM images of ultrathin sections of the macro-mesoporous zirconias. a–c) Low-magnification images of the macropores viewed parallel, perpendicular, and side-on to the pores, respectively; d) a higher magnification image of the macropore walls showing the wormhole-like mesophase.

X-ray diffraction shows that the zirconia frameworks possess amorphous walls. One diffraction peak is present in the small-angle region, which is indicative of a disordered mesostructure (see Figure S1 of the Supporting Information). Representative nitrogen adsorption–desorption isotherms and the corresponding Barrett–Joyner–Halenda (BJH) pore-size distributions (obtained from an analysis of the adsorption branch of the isotherm) are shown in Figure 3. A strong uptake of N_2 as a result of capillary condensation is observed in a relative pressure (P/P_0) range of 0.14–0.40 and reaches a plateau at 0.80. This kind of isotherm indicates that the final materials belong to the mesoporous family, with pore sizes close to 2.0 nm. The analysis of pore-size distributions confirms this tendency; the maximum in the BJH pore-size distribution curve is centered at about 1.8 nm. The existence of openings with a pore-diameter distribution located in this range can also be displayed using the Horvath–Kawazoe (HK) method. For relative pressures greater than 0.85, the adsorbed volume of nitrogen increased significantly, rather than remaining constant, because of saturation, which suggests that the material contains an appreciable amount of secondary porosity. Therefore, TEM and SEM observation and N_2 adsorption analysis have revealed that the materials

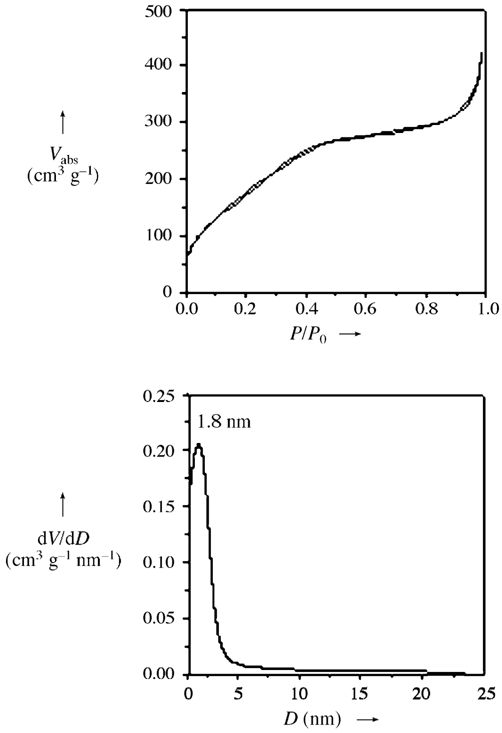

Figure 3. N_2 adsorption–desorption isotherm (left) and the corresponding BJH pore-size distribution curve (right) of macro-mesoporous zirconia. The pore-size distribution was determined from the adsorption branch of the isotherm.

exhibit a bimodal pore-size distribution, and are truly meso-macroporous systems. A very high surface area of 550–700 m^2g^{-1} can be obtained from these materials when synthesized with different surfactant to zirconium ratios. An increase in mesopore size up to 2.6 nm could arise from the increase of hydrothermal temperature or time, though no evident change was observed on the macroporous structure.

Synthesis was carried out at surfactant weight percentages that, according to the phase diagram, afford the existence of micelles in solution (for instance, 10 wt % $C_{16}(EO)_{10}$). The surfactant micellar solution reacted with the metal-oxide species hydrolyzed from the transition-metal alkoxide precursors. Mesostructured surfactant/metal oxide compounds were formed by a well-known neutral surfactant-templating pathway[16,17] through cooperative assembly of hydrolyzed inorganic species and amphiphilic PEO-surfactants. The condensation rates of metal alkoxides in aqueous solutions are normally faster than those of silicon alkoxides, while for zirconium *n*-propoxide, the precipitation rate is very fast when the ratio between the concentration of water and zirconium is higher than four.[25] In this study, the ratio of water to zirconium is located in a range from 20 to 300. Thus, hydrolysis and condensation occurred as soon as $[Zr(OC_3H_7)_4]$ was added to the micellar solution, and the mesostructured surfactant/zirconia nanoparticles are formed with a large number of surface hydroxyl groups, as a result of incomplete condensation. These particle surfaces can be regarded as hydrophilic or polar.

Those surfactant molecules that are not consumed in solution can generally be adsorbed onto hydrophilic solid surfaces, and can then self-assemble at the solid/solution interface following a two-step mechanism.[26–30] Firstly, single molecules are bound through head-group adsorbent interactions. Further adsorption is then strongly promoted by hydrophobic interactions between the tail groups. As a result of the fixation at the solid substrate, the process of surface aggregation takes place at critical aggregate concentrations much lower than the bulk-phase critical micelle concentration. This indicates that the aggregates are truly self-assembled on the surface, and that they are not micelles that are formed in the bulk which then get adsorbed on the surface. An aggregative adsorption process appears to be a cooperative process involving strong lateral interactions between surfactants and weak interactions with the solid surface. Amphiphilic self-assembled aggregates can have a variety of geometrical shapes.[31] Nonionic PEO-surfactants have been observed to form either globular aggregates or continuous bilayer structures on hydrophilic silica.[29] In the present work, the adsorption and self-assembly of surfactant molecules on the external surfaces of zirconia/surfactant nanocomposites occurs to form surface aggregates (otherwise known as "hemi-micelles"[32]) during the formation of internal mesostructures. These primary aggregates can attract more individual surfactant micelles to form "supermicelles". Hydrothermal treatment may play an important role in the formation of supramicellar aggregates, since temperature has a significant effect on the supramolecular organization of surface-active species in aqueous solution.[33] Under static autoclaving, the aggregates may develop following the defined direction (which is perpendicular to the external surface of monolith particles) through micellar coalescence, which generates threadlike (or conical) supermicellar aggregates with the lengths in the micrometer range and diameters in the submicrometer range. Thus, hierarchical monolithic particles form during the aggregation of surfactant/zirconia nanocomposites and these supermicelles should interlink successfully with the surfactant micelles in mesochannels. The removal of the surfactant by ethanol extraction results in the presence of hierarchical mesoporous–macroporous structures with conical (tapered towards the center) parallel macropores. Figure 4 illustrates the proposed formation mechanism of such an architecture. The meso-macrostructured oxide network with open and accessible pores can be successfully preserved after calcination at 500 °C, which indicates a high thermal stability (see Supporting Information). It is expected that meso-macrostructured materials with different macropore shapes could be synthesized by tuning the morphology of supermicelles by varying the experimental parameters, such as pH value, surfactant concentration, hydrothermal temperature, and reaction time.

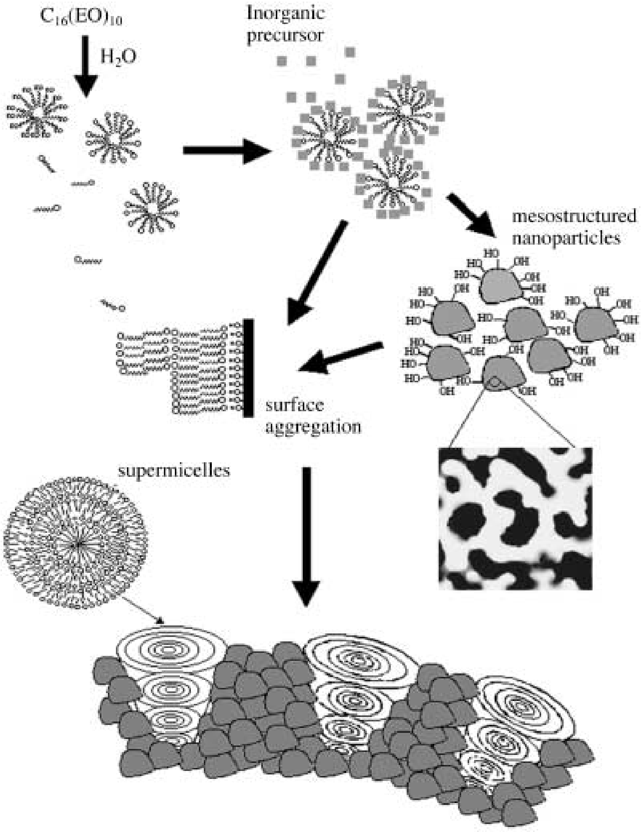

Figure 4. Proposed mechanistic scheme for the formation of macro-mesostructured metal oxides.

It is known that the microemulsion droplets induced by stirring can be used to template the macropores. However, these macropores are generally nonuniform or spherical, whereas the macroporous structure in our materials is ordered, regular, and shaped, which compares favorably with the well-known liquid-crystal phase behavior of surfactant micelles. Moreover, it was found that the stirring rate did not affect the formation of the macropore structure, and the macropores were even found to be present in the zirconia particles. These were synthesized without stirring the mixture of the Zr precursor and surfactant solution, in which emulsified droplets were not present. A significant amount of C_3H_7OH is generated during the condensation process, and one might expect that this is related to macropore formation. However, further study has shown that propanol has no significant effect on the macropore formation.

The macroporous structure of mesoporous titania has also been obtained by this simple surfactant-templating method. The structure is similar to that of the zirconia materials, but has a larger macropore size (up to about 5 μm) and wormhole-like mesopores of 5 nm dimensions (see Supporting Information). This synthetic strategy can be successfully applied to other metal oxides, such as Nb_2O_5, Ta_2O_5, Al_2O_3, and CeO_2, to prepare macroporous–mesoporous hierarchical structures. The experimental results indicate that the present method is versatile and can be generalized for the formation of macro-mesostructured metal oxides.

In summary, one kind of novel mesoporous metal oxide with funnel-like macroporous structures has been synthesized by a simple surfactant-templating process, which has important implications for use in catalysis, molecular separations, and biological-cell encapsulation. This kind of material can be employed to design inorganic membranes that may be applied in various domains such as process filtration, cell culture, or laboratory filtration. Functionalization of these materials by chemical modifications of their internal pore surface may lead to more practical applications. Additionally, these three-dimensional open structures can also be used as templating materials for the inverted synthesis of new advanced porous materials.

Experimental Section

A micellar solution (5–30 wt%) of decaoxyethylene cetyl ether ($C_{16}(EO)_{10}$) or of polyoxyethylene(6)tridecyl ether ($C_{13}(EO)_6$) was prepared by dissolving the surfactant at room temperature in an aqueous solution for 3 h. Zirconium *n*-propoxide ($[Zr(OC_3H_7)_4]$, 70 wt% in 1-propanol) or titanium isopropoxide ($[Ti(OC_3H_7)_4]$, 97%) was added dropwise to the above medium, followed by further stirring for 3 h at room temperature. The obtained mixture was then transferred to a teflon-lined autoclave and heated under static conditions at 60 °C for 48 h for zirconia, or 80 °C for 24 h for titania. The product was filtered and washed by soxhlet extraction over ethanol for 48 h to remove the surfactant species. X-ray diffraction was carried out on a Philips PW1820 diffractometer using $Cu_{K\alpha}$ radiation. N_2 adsorption and desorption isotherms were determined on a Micromeritics ASAP 2010 sorptometer at −196 °C. Scanning electron microscopy and transmission electron microscopy were carried out on Philips XL-20 (15 keV) and Philips TECNAI-10 (100 kV) microscopes, respectively. The specimen for TEM observation was prepared by epoxy-imbedded microsection and by being mounted on a copper grid.

Received: December 20, 2002
Revised: April 9, 2003 [Z50816]

Keywords: macroporous materials · mesoporous materials · self-assembly · titanium · zirconium

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