Mesoporous phases based on SnO₂ and TiO₂

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A hexagonal mesoporous phase based on SnO₂ is synthesized for the first time by using an anionic surfactant; hexagonal phases of TiO₂ are prepared with neutral amine surfactants.

There has been intense research activity in the synthesis and characterization of non-siliceous mesoporous solids based on metal oxides, since the discovery of mesoporous silica of the MCM-41 type.[1–3] Thus, Huo et al.[4] and Ciesla et al.[5] attempted to synthesize mesostructured materials of tungsten, molybdenum, iron and lead oxides, and had definitive success in obtaining a hexagonal mesoporous phase in the case of tungsten oxide. The surfactant (alkyltrimethylammonium salt), however, could not be removed thermally or by the use of different solvents. Stein et al.,[6] on the other hand, obtained a nonporous CTMA–tungsten oxide composite (CTMA = cetyltrimethylammonium) from hydrothermal synthesis. Abe et al.[7] have reported vanadium phosphate-based hexagonal mesoporous phases by employing alkyltrimethylammonium chlorides as surfactants, but were unable to remove the surfactants from the pores. A hexagonal mesoporous phase based on vanadium oxide has also been prepared by using CTMA, again with the surfactant remaining in the pores.[8] We have explored ways of synthesizing mesoporous solids based on tin and titanium oxides for some time. We have been able to prepare hexagonal mesoporous phases of TiO₂ by using Ti(OPrⁱ)₄ and neutral amine surfactants, but have since noticed the work of Antonelli and Ying[9] reporting a hexagonal phase with alkyl phosphate surfactants. We have however succeeded in preparing a hexagonal phase of SnO₂, for the first time, by using an anionic surfactant.

Having failed to obtain a mesoporous phase of SnO₂ with cationic and neutral surfactants, we employed anionic surfactants such as sodium lauryl sulfate, sodium stearate and aerosol OT (sodium dioctylsulfosuccinate, AOT). It is indeed known that Snᴵᴵ and Snᴵⱽ occur as cationic species in solution and polymerize to a tin–oxygen network between pH 4 and 8.5.[10] In order to prepare the mesophase of SnO₂, compositions corresponding to molar ratios of 1 SnO₂ : 1–2 AOT : 1000–2000 H₂O were prepared by adding the AOT solution to SnCl₄. This resulted in a white thick mass which settled quickly on standing. The supernatant water was periodically decanted and the solid allowed to age in water for 24 h. The resulting material was filtered off and washed with acetone, and air dried. The X-ray diffraction pattern of the solid showed a single intense peak at a low angle (d ca. 3.2 nm) characteristic of mesoporous materials [Fig. 1(a)]. We could not obtain a mesoporous phase when we used sodium lauryl sulfate or sodium stearate as the surfactant [Fig. 1(b)].

The IR and ¹³C NMR spectra of the SnO₂–AOT composite showed the known features of AOT confirming the presence of the surfactant in the pores. Thermogravimetric analysis of the composite showed the loss of the water below 420 K and surfactant loss starts at ca. 513 K and was completely removed at ca. 670 K. Based on the mass loss, the composition of the starting material was (SnO₂·2H₂O)₄·AOT. Calcining the composite at ca. 700 K in air for 12 h results in the collapse of the mesoporous structure [Fig. 1(c)], giving the dense cassiterite

form of SnO₂. Attempts to remove the surfactant by extraction with solvents including acetonitrile or dimethyl sulfoxide were unsuccessful, resulting in the collapse of the mesophase structure. Further efforts to remove the surfactant are in progress.

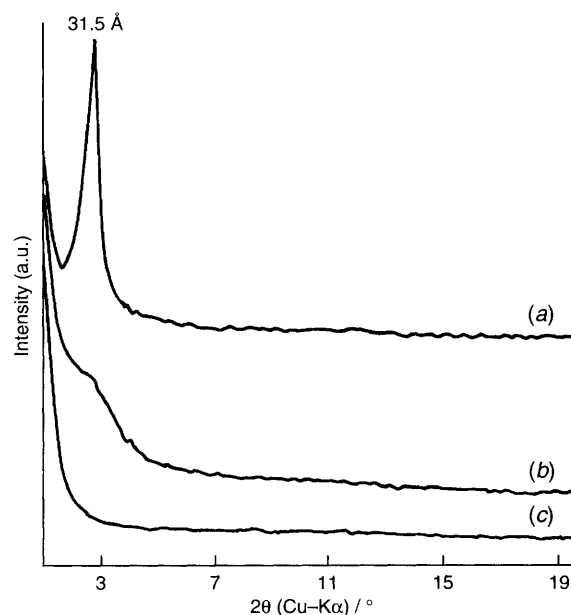Transmission electron microscope images of the SnO₂–AOT composite (using a JEOL JEM 3010 instrument) confirm the

Fig. 1 X-Ray diffraction patterns of (a) the mesoporous SnO₂–AOT, (b) material obtained using lauryl sulfate and (c) of SnO₂–AOT calcined at 700 K
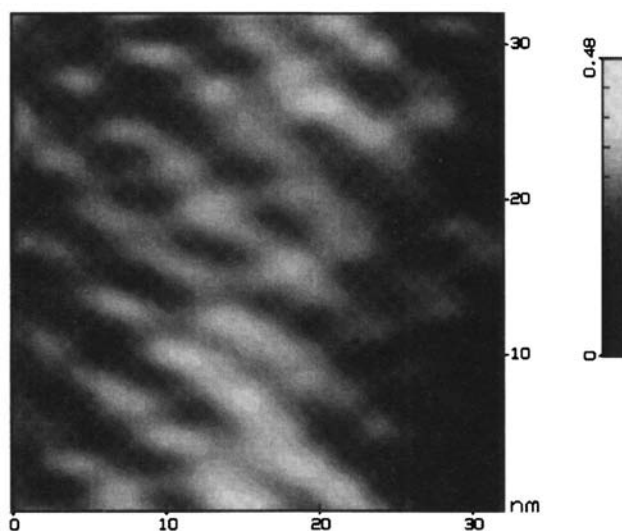

Fig. 2 Atomic force microscope image of SnO₂–AOT showing pores of ca. 3 nm diameter

presence of hexagonal channels with a pore size of *ca.* 3 nm. Atomic force microscope images (obtained with a Nanoscope II instrument) also show pores of *ca.* 3 nm (Fig. 2). The ^{119}Sn MAS NMR spectrum of SnO_2–AOT shows a signal at δ −629, close to the chemical shift of SnO_2 (δ −604), suggesting that the coordination around tin in the mesoporous material is octahedral, as in SnO_2. The resonance from the mesoporous material is however broader than that of SnO_2, indicating the presence of some local disorder around the tin site.

Since we were unsuccessful in obtaining the hexagonal phase of TiO_2 by employing cationic or anionic surfactants, we used titanium alkoxide in combination with decylamine or hexadecylamine. In a typical preparation, 0.6 mmol of the amine was dispersed in 20 mmol of isopropyl alcohol and 2 mmol of $Ti(OPr^i)_4$ was added to the mixture. Addition of 60 mmol of water to this solution resulted in a pale yellow slurry which was
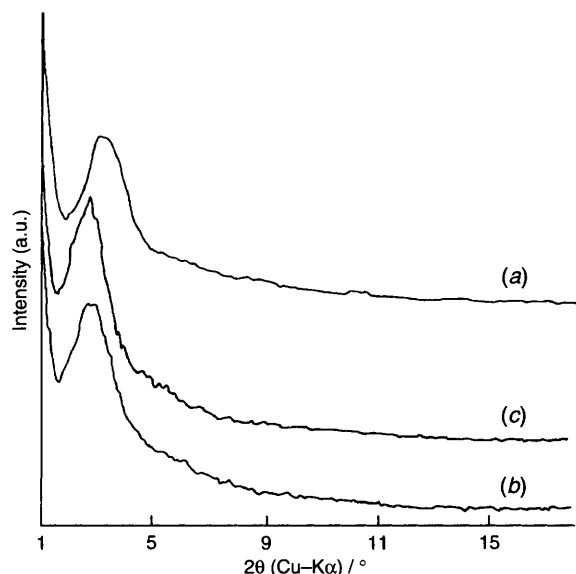

Fig. 3 X-Ray diffraction patterns of mesoporous TiO_2 prepared with amine surfactants: (*a*) decylamine at room temperature, (*b*) hexadecylamine at room temperature and (*c*) hexadecylamine under hydrothermal conditions

aged at room temperature for 18 h in one experiment and subjected to hydrothermal treatment at 363 K for 18 h in another. The product obtained from either procedure after washing and drying at 373 K was mesoporous as revealed by X-ray diffraction. The pore sizes were 2.9 and 3.2 nm, with decylamine and hexadecylamine as surfactants, respectively (Fig. 3). Thermogravimetric analysis showed the loss of the amine at *ca.* 700 K. The observed mass loss suggests the composition of the mesoporous amine adduct to be $(TiO_2)_{3.5}$·$2H_2O$·amine. The oxide obtained after the removal of the surfactant by calcination has the anatase structure. Removal of the amine from the pores thermally or by the use of solvents generally destroys the mesoporous structure. Leaching of the amine in an acidified dilute alcohol medium, however, appears more promising. It should be noted that Antonelli and Ying[9] could partially remove alkyl phosphate from the pores with the phosphate units being retained in the oxide phase.

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