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ORDERED MESOPOROUS SILICAS AND ZIRCONIAS: CONTROL ON LENGTH SCALES BETWEEN NANOMETER AND MICROMETER

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ABSTRACT

Surfactant-controlled condensation of inorganic solution species can be used to prepare mesostructured phases of silica, zirconia, and titania with structures on a length scale of 1 to 10 nm. If the surfactant can be removed from the composite, a mesoporous structure with a highly regular and ordered pore system is left. If oil soluble inorganic precursors, such as tetraethoxysilane, are used, the organization of the material on a longer scale is also possible. Under favorable circumstances, the inorganic/organic interface in the emulsions, created by mixing the appropriate compounds, controls the shape of the resulting particles, which are structured as well on the nanometer scale. The resulting materials could have several different applications in catalysis, separation technology, or possibly even drug delivery. *© 1999 Elsevier Science Ltd*

KEYWORDS: A. inorganic compounds, A. microporous materials, A. nanostructures, B. sol-gel chemistry, D. crystal structure

INTRODUCTION

Interfaces can play a crucial role in almost any area of physics, chemistry, and biology. Interfaces govern the properties of semiconductor devices, control reaction pathways, and

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rates in heterogeneous catalysis and are necessary to create the different compartments in cells, control material flux between the compartments, or provide nucleation sites for the formation of inorganic materials in living organisms. They can also be used to shape materials, as in epitaxy of semiconductors, in controlling shapes in micellar or reverse micellar systems [1–4], or in biomineralization [5–9]. These processes can be important on an atomic scale, such as in epitaxial growth, or on a more macroscopic scale, such as in particle growth control by micellar systems.

The synthesis of ordered mesoporous oxides introduced in 1992 by scientists of the Mobil Oil Corporation [10] uses a related principle, although here it is not a preformed interface, which controls the assembly process, but a cooperative self-organization of organic surfactant molecules and inorganic solution species. In addition, the boundary between the organic and the inorganic part of the resulting assembly is not an interface in the thermodynamic sense (boundary between two phases) [11] as in the systems mentioned above, because the whole mesophase itself is a thermodynamic phase. However, several of the properties of the boundary are similar to the properties of a real interface. This synthetic approach was developed first for silica, but subsequently several other inorganic materials have been structured following such or related synthetic principles [12–19]. From some of these materials the surfactant molecules could be removed to obtain mesoporous oxides [14–17,19].

Although several partly related mechanisms have been presented to explain the formation of such mesostructured organic/inorganic composite materials [20–23], it appears that the cooperative interactions between the components of the system is the key factor driving the assembly [21,24]. Depending on the exact conditions used, there might be differences with respect to the exact pathway by which the final product is reached, but the process as a whole is controlled by the interaction at the boundary between the surfactant part and the inorganic part of the composite. If reaction conditions are chosen such that no or very limited condensation occurs in the inorganic part of the composite, the process will be governed by the thermodynamics of the composite liquid crystal formation, which is essentially dominated by the surfactant behavior [25]. Thus, different well-known phases from surfactant chemistry, such as the hexagonal, the lamellar, and the gyroid cubic phase, can form, but now include inorganic oligomers in the liquid crystal. Since these systems are not condensed in the inorganic part, switching back and forth between the phases by changing a control parameter, such as temperature, is possible. If, on the other hand, condensation in the inorganic part is predominant, the nature of the final product will be primarily controlled by the inorganic species and the transformations between phases are mostly irreversible, and if reversible then only slowly by partially depolymerizing the inorganic framework.

The porous oxides resulting from such synthetic procedures have remarkable properties, if the surfactant can be successfully removed without structural collapse. Since the pore structure of the materials is defined by the regular liquid crystalline assembly during the synthesis, the pore system is usually highly regular with sharp pore size distributions centered around 2–8 nm, depending on the surfactant and auxiliary organic components used, and a width of less than 1 nm. The pore volumes can exceed 1 ml/g, and the surface areas are about 1000 m^2/g, if they can be reliably determined. Due to the regular arrangements of pores and pore walls, XRD patterns with Bragg peaks reflecting the regularity of the walls were observed. Honeycomb-like patterns, which result from the hexagonal pattern of the pores, were observed in TEM experiments.

However, this high degree of order present on the nanometer scale usually is not translated to larger scales. If the synthesis is performed in the manner described in the original literature

[10,20], a powder consisting of very fine particles is obtained, with primary particle sizes well below 1 μm and usually rather ill-defined particle shapes. The notable exception is boron-containing materials synthesized by the Geis group [26]. For many possible applications, however, it would be desirable to control the morphology of mesostructured oxides. For this purpose, control on another length scale, i.e., the μm to cm scale, is necessary. Three pathways for such a morphological control have been developed recently, which all use interfaces in the strict sense of the word: Yang et al. [27] and Aksay et al. [28] used the solid/liquid interface to grow oriented mesostructured silica on different solid support materials, where some sort of epitaxy seems to occur. In addition, Yang et al. [29] observed the formation of thin films of ordered mesostructured silica at the air/water interface. We have chosen a third kind of interface, a liquid-liquid interface, to structure mesophase organic/inorganic composites on a length scale above the micrometer range [30–32]. We report the possibilities and limitations of this approach with respect to the systems that can be structured.

EXPERIMENTAL

Syntheses. Syntheses of the mesostructured silicas followed the acidic procedure developed by Huo et al. [33]. In this synthesis, tetraethoxysilane (TEOS) is used as the silica precursor, which is hydrolyzed with aqueous HCl in the presence of a surfactant, typically cetyltrimethylammoniumbromide (CTAB). To create an emulsion, a hydrocarbon such as hexane, benzene, trimethylbenzene, or toluene is added to the system. Most experiments were performed with hexane or trimethylbenzene. In a typical preparation, 4.74 g of CTAB were dissolved in 250 ml of water and 34 ml of concentrated HCl were added. To this solution, a mixture of 7 g of the hydrocarbon and 4 g of TEOS were added slowly over 30 min while stirring. The stirring conditions are important in controlling the morphology of the resulting particles.

The zirconias were synthesized following a method similar to that developed by Ciesla et al. [17], but modified (as discussed in the previous paragraph) to use zirconium alkoxides as precursor and auxiliary organics. Propoxide, butoxide, and octoxide were used as alkoxides; mesitylene was used in all cases to create the two-phase system. In a typical synthesis, 2.5 g of the surfactant, in most cases CTAB, were dissolved in 115 g of water. To the solution, 20.1 g of concentrated HCl and 2.04 g of $(NH_4)_2SO_4$ were added. 12.8 mmol of the zirconium alkoxide (6 g for the propoxide) were dissolved in 5 g of mesitylene. This solution was slowly added to the surfactant solution under stirring. After 1 h, the mixture was heated to the desired final temperature (between room temperature and 90°C); at this temperature, the solution was stirred overnight. The resulting solid was filtered, dried at 90°C, and calcined at 500°C for 4 h after heating at a rate of 1 K/min.

Characterization. The materials were characterized by X-ray diffraction using Cu Kα radiation, with a Stoe Stadi P diffractometer in transmission geometry. Nitrogen adsorption was performed at 77.35 K on a Micromeritics ASAP 2010 sorption instrument after activation at 250°C for at least 6 h. The morphology of the particles during the synthesis was analyzed by optical microscopy after removing a droplet of solution with a pipette from the synthetic solution and placing it on a glass slide. The morphology of the final product was analyzed with an Atomica scanning electron microscope without sputtering of the samples.

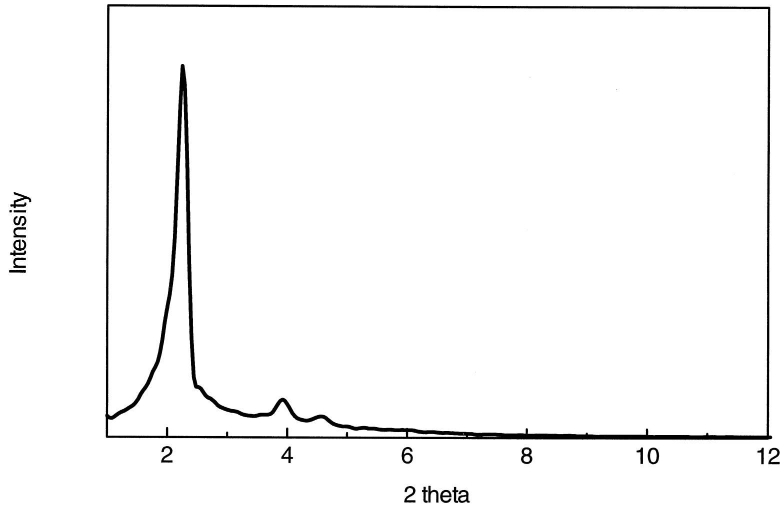


FIG. 1
X-ray diffraction pattern of a calcined siliceous material resulting from a synthetic mixture as described in the experimental section. Such a concentration of mesitylene results in a mesostructured silica with a d-spacing of about 7 nm under alkaline conditions.

Transmission electron micrographs were recorded on a Philips CM 200 TEM on selected samples.

RESULTS AND DISCUSSION

In the synthesis of mesostructured silica under acidic conditions, in contrast to the results obtained under alkaline conditions, added auxiliary organics do not have a drastic influence on the d-spacing and thus on the pore size of the resulting materials. Irrespective of the concentration of the auxiliary organic component, the d-spacing in syntheses performed as described above was always about 4.5 nm. A typical diffraction pattern of a material prepared with mesitylene at a concentration that would lead to an increase in d-spacing to about 8 nm under alkaline conditions is presented in Figure 1.

On the other hand, the addition of the auxiliary organic component helps to control the morphology of the resulting material, since the reaction does not proceed in a one-phase system, but rather in an emulsion. Figure 2 shows the morphology of particles isolated from the system after stirring the synthetic emulsion with a butterfly stirrer in a 400 ml beaker for 1 h at different stirring speeds. Obviously, different secondary morphologies of the resulting particles can be prepared. The fibers obtained at low stirring speeds, shown in Figure 2a, are not completely homogeneous, but consist of smaller primary particles, which results in an intertwined, rope-like morphology (Fig. 3). However, these primary particles seem to be aligned with respect to each other, as TEM data indicate that the pores seem to be oriented mainly parallel to the fiber axis in the different particles building up the fiber. Better-defined, optically transparent fibers have been prepared recently [32] using a modified technique at a static interface. This technique can also lead to the formation of thin films of mesostructured

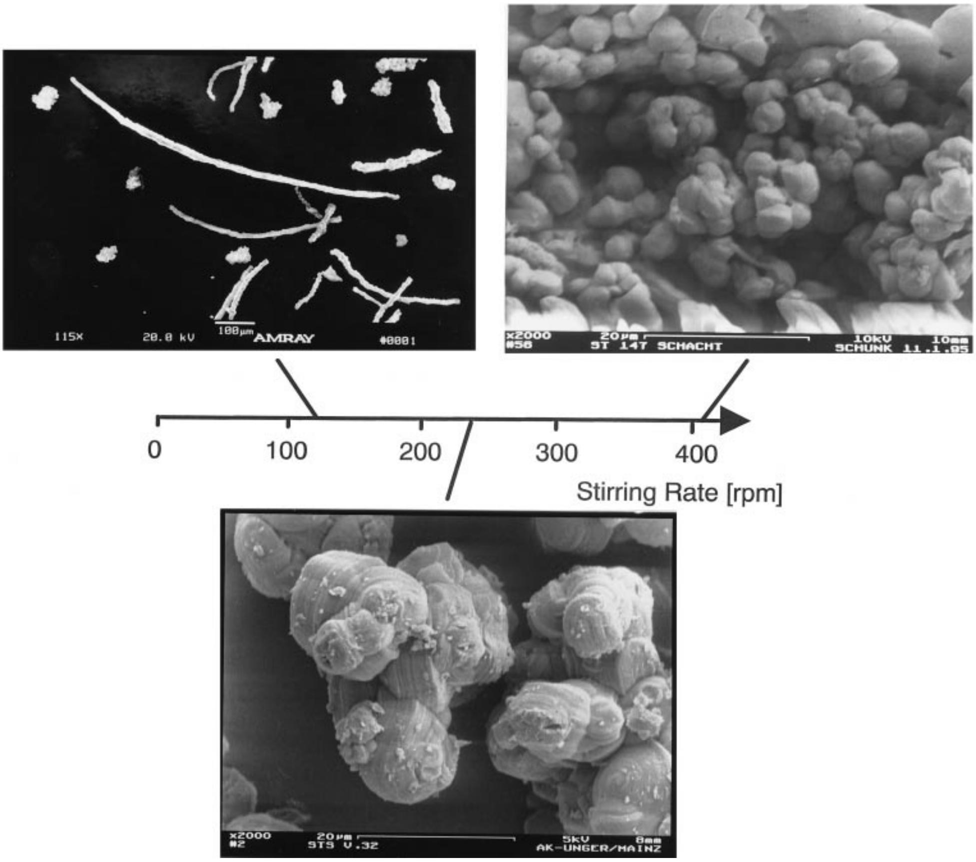


FIG. 2
Dependence of secondary morphology on stirring rate for the mesostructured silica system. Synthetic mixture as described in the experimental section.

silica [30]. If the stirring speed is increased, the fiber morphology is no longer obtained, but rather spherical particles form, the size of which depends on the stirring speed (Fig. 2). The faster the system is stirred, the smaller the particles become. Since initially a fairly unstable emulsion is formed on mixing the TEOS and the surfactant solution, the stirring determines the size and shape of the emulsion droplets and the contact between the individual oil droplets, at the surface of which the TEOS is hydrolyzed.

If the concentration of the auxiliary organics is sufficiently high and the stirring rate is approximately 200 rpm, the spherical particles are hollow [30]. This is due to the fact that the TEOS is hydrolyzed at the oil-water interface in the emulsion and immediately condenses there under the influence of the surfactant, which is enriched in this part of the system. As a result, a “silica skin” forms that has the mesostructure observed for the materials normally obtained from the acidic synthesis of mesostructured oxides [30]. When all the TEOS has been hydrolyzed and condensed to the mesoporous silica, the oil droplet is covered by a silica skin. If this skin is sufficiently stable and the material (synthesized as described in the experimental section) is carefully filtered, dried, and calcined, the mesoporous silica is

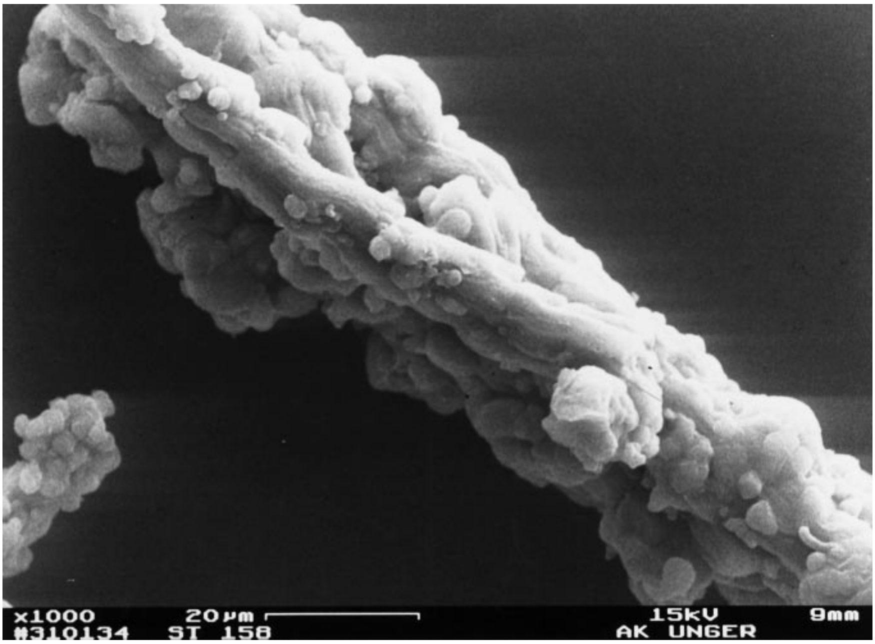


FIG. 3
Fiber-type morphology from Figure 2 at higher magnification. The rope-like structure with particles grown on it is clearly visible.

obtained in the form of hollow aggregated spheres. However, if the system is diluted by a factor of about 10 by adding the emulsion to a high volume of water after the completion of sphere formation has been detected in the optical microscope, fairly well-isolated spherical particles can also be prepared (Fig. 4). Independent of the conditions of the emulsion synthesis, the physicochemical characteristics of the materials, such as XRD, TEM and sorptive behavior, did not change significantly from those produced by the original acidic synthesis. If no auxiliary organic component is used, but instead a less water-soluble alkoxysilane such as butoxide is used, hard, optically transparent mesoporous spheres are formed as a result of the complete hydrolysis of the TBOS droplet [31]. In such cases, the whole oil droplet of the emulsion is converted to silica.

It was shown that the synthetic principle developed for silica can be transferred to zirconia [17] and, to a lesser extent, also to titania. The titania is obtained in a somewhat more disordered form, but if it is stabilized with phosphoric acid, as was done for the zirconia, a calcinable mesostructured titania results which is related to the silica and the zirconia; this can be seen, for instance, from the adsorption isotherm. However, the XRD pattern only shows one peak for these materials, and the TEM data show relatively disordered pores, but with a relatively narrow size distribution, as is suggested by the isotherm. As is possible for the silica, inorganic/organic composites resembling other surfactant structures can be prepared with zirconia. If other surfactants are used that favor the formation of the cubic *Ia*3*d* phase, this phase can be synthesized with zirconia as the inorganic part of the composite. Figure 5 shows the XRD pattern of such a material prepared with benzyl-dimethyl-stearylammoniumbromide. Although the diffraction pattern is not sufficient to unambiguously assign

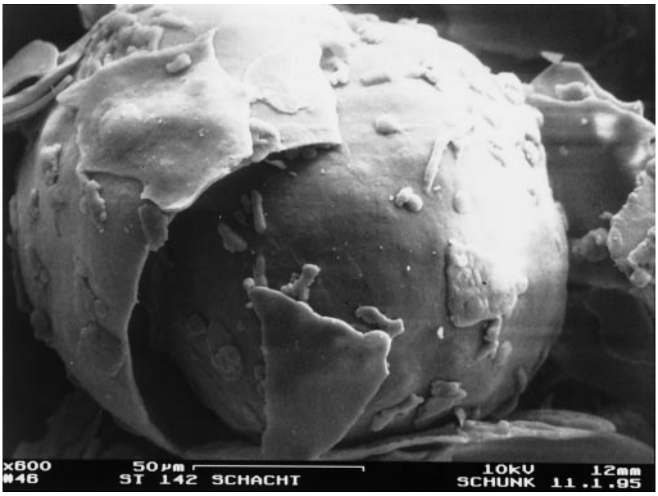
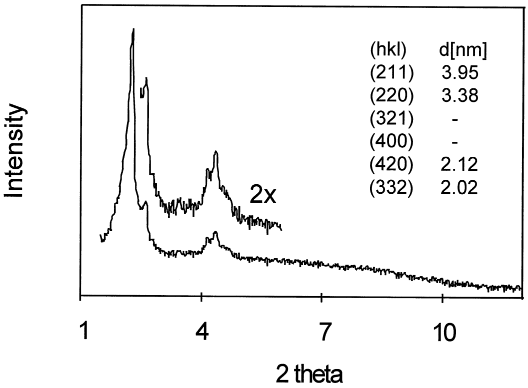


FIG. 4
Isolated hollow silica sphere resulting from a diluted synthesis as described in the text.

space group Ia3d, the similarities to the silica synthesized with the same surfactant, which exhibits enough peaks for indexing, are obvious. It is thus highly probable that the zirconia/surfactant composite exists in *Ia*3*d* structure.

Since the general principle of structuring the inorganic material by the use of surfactants can be transferred from silica to transition metal oxides, it should also be possible to apply the approach to long-scale structuring by emulsion chemistry to the preparation of other mesostructured oxides like the zirconia. Also, in this case, alkoxides, which have a low solubility in water, can be used as the precursors. We therefore attempted to use a similar



(hkl)	d[nm]
(211)	3.95
(220)	3.38
(321)	-
(400)	-
(420)	2.12
(332)	2.02

FIG. 5
X-ray diffraction pattern of a cubic surfactant-zirconia mesophase prepared with benzyl-dimethyl-stearyl-ammoniumbromide as surfactant. Synthetic mixture: 12.8 mmol $Zr(SO_4)_2 \cdot 4H_2O$ in 1.4 mol H_2O added to 6.87 mmol surfactant in 4.7 mol H_2O under stirring, heated for 2 days at 90°C.

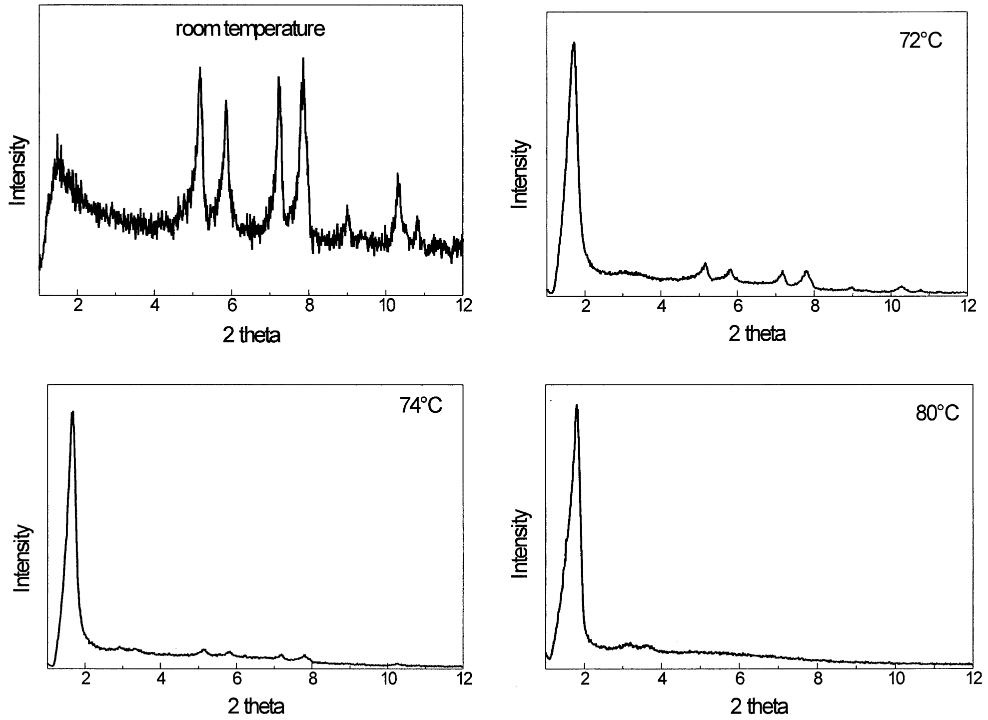


FIG. 6
Structure development dependent on temperature for the zirconia emulsion system. Synthetic mixture as described in the experimental section.

synthetic procedure for the preparation of zirconias structured on the micrometer-to-millimeter scale by utilizing the oil-water interface in an emulsion. However, this system is more complicated than that in the silica case in two respects. First, there is one more key component in the mixture to obtain a mesophase, i.e., sulfate ions usually introduced as $(NH_4)_2SO_4$. These ions are necessary to produce suitable oligomers in solution that can interact with the surfactant [17]. Second, so far this synthetic procedure had only been performed successfully at elevated temperature, normally at 90°C, and was relatively slow [17]. At such high temperatures, the emulsion is a very dynamic system, and there could be insufficient time to form a stable zirconia-surfactant composite skin at the surface of the oil droplets.

We attempted to establish a lower-temperature threshold for the formation of the hexagonal mesophase in the presence of mesitylene. The powder XRD patterns given in Figure 6 summarize the results of these studies. At room temperature, the hexagonal MCM-41 analogous structure cannot be formed from the system described in the experimental section. The material recovered after 10 h reaction time shows several peaks in the range below 10° (2θ). The identification of the phase formed was not possible, however, and calcination resulted in the loss of any structure detectable by X-ray diffraction. At elevated temperatures, the low-angle reflection characteristic of the mesophase grew in intensity with respect to the peaks present in Figure 6a and a pure mesophase, which was also calcinable and retained its

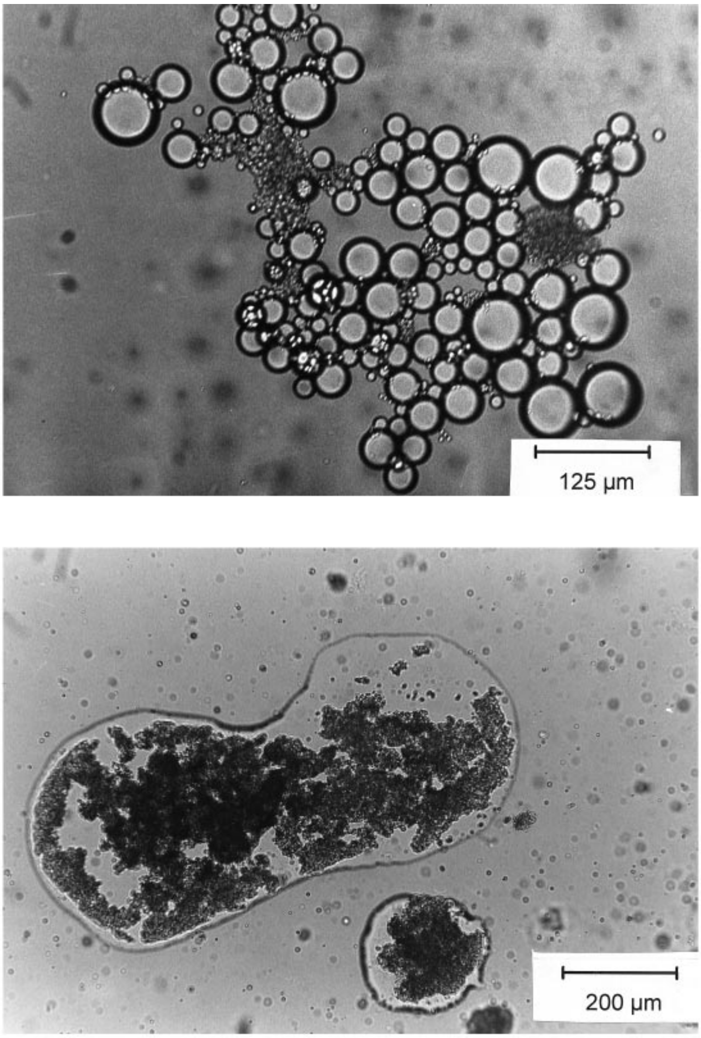


FIG. 7
Optical micrographs of samples from the emulsion synthesis of zirconia. (a) 15 min after mixing, no particles of zirconia have formed. (b) 20 min after mixing, mesostructured zirconia particles are visible, but no large-scale structure has formed.

structure after calcination, was obtained at about 75°C (Fig. 6b–d). However, at such temperatures the dynamics in the emulsion seems to be too rapid for the formation of a well-developed morphology. The resulting products were highly intergrown and consisted of relatively small primary particles well below 1 μm in size.

The development of this morphology was followed by optical microscopy (Fig. 7a and b). After 15 min reaction time at 75°C, no solid product was formed, but small oil droplets existed in the aqueous matrix. For the silica system at room temperature, the formation of the silica skin started after about 15 min and was completed for individual droplets within

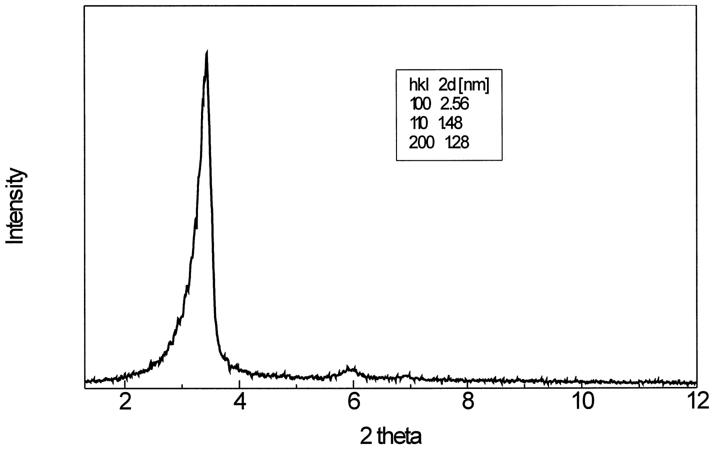


FIG. 8
X-ray diffraction pattern of a mesostructured S^-I^+ composite from zirconia and sodium-dodecyl-benzenesulfonate. The pattern can be indexed analogous to MCM-41 assuming hexagonal symmetry. Synthetic mixture as described in the experimental section with zirconium tetrapropoxide and sodium-dodecyl-benzenesulfonate as surfactant but without ammonium sulfate.

approximately 1 min. After about 20 min, the first solid particles appeared at the oil-water interface in the zirconia system, but did not form a dense skin. Figure 7b shows the system after 30 min reaction time. It is obvious that only loosely connected particles have formed, probably due to the low stability of individual droplets. Afterwards, no further fundamental change was observed; the fraction of the precipitate increased, but no long-scale structures were formed. Changing the zirconia precursor to the tetrabutoxide or the tetraoctoxide, which should result in an increase of the solubility of the precursor in the oil phase, did not result in any improvement. On the contrary, syntheses with the tetraoctoxide did not result in the formation of solid products but produced a highly viscous oil.

To check whether the high temperature or the depletion of sulfate near the oil-water interface, which is necessary for the formation of the mesostructure, is responsible for the lack of success in the macroscale structuring, a sulfate headgroup surfactant (sodium dodecyl-benzenesulfonate) was used. It was expected that the surfactant would bind favorably to positively charged solution species (S^-I^+) [33] directly at the oil-water interface. The ammoniumsulfate normally added to the synthetic mixture to produce the negatively charged oligomers, which can then crosslink, was not added in these experiments. In this system, oil droplets form at room temperature, but a solid mesostructured product was obtained only by heating at 90°C overnight. The X-ray pattern of the material was fairly well developed (Fig. 8) and can be indexed assuming a hexagonal structure. This is one of the few examples where a hexagonal mesostructure can be formed in the charge-reversed situation, i.e., from an anionic surfactant and a cationic solution species; the other examples are a relatively ill-defined lead oxide [33] and titania prepared by Antonelli and Ying [14]. However, the material prepared from zirconium propoxide and sodium dodecyl-benzenesulfonate in the presence of mesitylene was obtained as a fine powder; no macroscale structuring has as yet been possible following this approach. The possible lack of sulfate near the interface thus does not seem to be the main cause for the problems in creating mesostructured zirconia, because even a sulfate-containing surfactant does not lead to the formation of spherical zirconia-based particles.

The variation of other reaction parameters—concentration, temperature programs, and reaction times—also did not result in the formation of mesostructured zirconias with well-defined macrostructure. The system is thus much more difficult to control than the silica system. It might be possible to tune the system by using additional emulsifiers to stabilize the emulsion even at elevated temperatures. However, the influence of these additives on the properties of the mesostructure is not yet clear.

CONCLUSION

These investigations show that it is possible to create mesostructured silicas and zirconias that are structured on the nanometer scale. Structuring on the micrometer-to-millimeter scale, however, proved to be more difficult. In the silica system, more complex morphologies could be created by using the oil/water interface of an emulsion. This approach was not successful for zirconias. Possible reasons for this include the higher synthetic temperature and the slower condensation kinetics in the zirconia system. Before a stable macroscale structure, which should be molded on the emulsion droplets, can form, the dynamics in the emulsion at higher temperature destroys the developing structure. Attempts to control the mesostructured zirconia morphology on the micrometer scale resulted instead in the formation of a dodecylsulfate-zirconia composite. This is one of the few examples of a well-developed hexagonal composite being prepared following the S^-I^+ route.

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