Surfactant Controlled Preparation of Mesostructured Transition-metal Oxide Compounds

Ulrike Ciesla,[a] Dirk Demuth,[a] Rosa Leon,[b] Pierre Petroff,[b] Galen Stucky,[c] Klaus Unger[a] and Ferdi Schüth*[a]

[a] *Institut für Anorganische und Analytische Chemie, Johannes Gutenberg-Universität, 55099 Mainz, Germany*
[b] *Materials Department, University of California, Santa Barbara, California, 93106, USA*
[c] *Department of Chemistry, University of California, Santa Barbara, California, 93106, USA*

The use of surfactants as templates allows the synthesis of mesostructured transition-metal oxides by a cooperative, interface controlled condensation process.

The preparation of inorganic mesoporous materials has attracted considerable attention because of their possible use in catalysis and sorption, as well as in host–guest chemistry. One of the most intensively investigated mesoporous compounds is the silicate species, designated MCM-41 by scientists of the Mobil Oil Corporation.[1] Previous studies concerning the synthesis and characterisation[2–4] and the mechanism of MCM-41 formation[5] have been published. Based on the synthesis mechanism the idea was developed to design mesostructured transition-metal oxides. The MCM-41 analogous transition-metal oxide would have a regular array of uniform mesopores, the channel diameter of which could be controlled by variation of the synthesis parameters. Such a material could have a possible use as a high surface area catalyst, especially in partial oxidation reactions, and as a host for quantum sized materials. A different approach to the synthesis of related compounds is the swelling of layered oxides with surfactants and subsequent pillaring which was described also by scientists of the Mobil Oil Corporation.[6]

A suitable transition-metal oxide should have the following characteristics: according to the formation mechanism the ability to form polyanions allows a multidentate binding to the surfactant, which has template function. Silicate oligomers perform the analogous function in the synthesis of MCM-41. In addition, the transition-metal oxide polyanions have to condense to build up stable walls. Finally, a charge density matching between the surfactant and the transition-metal oxide is necessary to control the formation of a certain phase. These requirements could, for instance, be met by molybdates and tungstates. If it is possible to create mesostructured phases from an anionic transition metal oxide/cationic surfactant system, as in the case of the silicate MCM-41, it should also be feasible using the reversed system: The combination of transition-metal polycations with anionic surfactants should result in similar materials. As polycation forming metal oxides we used lead and iron. Here we present examples for both pathways, which are successful in the design of mesostructured transition-metal oxides.

In the system anionic transition-metal oxide/cationic surfactant the best results were obtained using tungstate in the presence of quaternary ammonium surfactants. The tungsten oxide–surfactant samples were prepared as follows: An aqueous solution of hexadecyltrimethylammonium chloride was combined with an aqueous solution containing commercial ammonium metatungstate $(NH_4)_6H_2W_{12}O_{40}$. The pH of this solution was adjusted by addition of aqueous NH_3 or aqueous HCl. The mixture was stirred and then heated at 90 °C. The solid white product was recovered by filtration. The as-synthesised product contains 33 wt% of the surfactant, as determined by TG/DTA. This corresponds to a molar ratio of surfactant to WO_3 of 1 : 3, which in the silicate case is around 1 : 7.

Fig. 1 shows the XRD pattern of the tungstate surfactant compound with an almost pure hexagonal phase. The XRD pattern shows reflections only in the narrow angle range $2 < 2\theta < 8°$. The first intense reflection corresponds to a *d*-spacing of 3.9 nm, which agrees with that of MCM-41 using the same surfactant. Most of the peaks below 5° (2θ) can be indexed assuming a hexagonal phase (P_6). However, there is a difference in the total number of reflections in comparison to the silicate species. The XRD pattern of MCM-41 shows only four reflections, whereas there are usually more in the case of the tungsten oxide surfactant. This may be due either to the presence of a lamellar phase, another impurity phase, or to a periodic structure of the walls which are amorphous in the silicate case. The fact that the amorphous peak is missing in the tungstate compound, which is present in the XRD pattern of MCM-41 at 20–25° (2θ), may be an indication of wall crystallinity in the tungstate compound. Transmission electron microscopy shows the regular hexagonal array of uniform channels with a *d*-spacing of 4.0 nm of the hexagonal phase (Fig. 2). This value is in excellent agreement with the results from the XRD pattern. Recording of the micrographs proved to be relatively difficult, since the tungstate compound forms (in contrast to the silicate) needle-like crystals with the

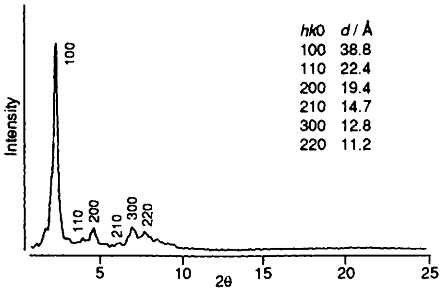

Fig. 1 XRD pattern of the hexagonal phase of tungsten oxide surfactant indexed on a hexagonal unit cell with $a = b = 4.5$ nm. All XRD data were collected with an automatic divergence slit (ADS) but transformed to a fixed slit configuration for the representation.

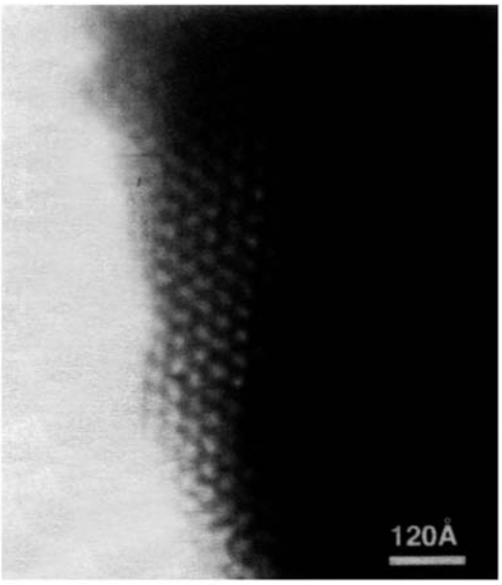

Fig. 2 Transmission electron micrograph of the hexagonal phase of the tungsten oxide surfactant showing a *d*-spacing of 4.0 nm

channels along the needle axis. Thus, in most cases the tubes can only be seen sideways, appearing like a layer.

The optimum pH for the synthesis of the hexagonal phase is 4–8, but mostly these products also contain a lamellar phase. A typical XRD pattern containing the hexagonal as well as the lamellar phase is shown in Fig. 3, region (*b*). At the extremes of the pH scale, mainly layers were obtained. At high pH (>9) two layers can be identified with a *d*-spacing of 2.8 and 3.0 nm together with another phase exhibiting a larger *d*-spacing (Fig. 3).

In contrast to MCM-41, it is not possible to calcine the tungsten oxide surfactant by thermal treatment at 500 °C. Degradation of the mesostructure occurs, and the thermodynamically more stable yellow WO_3 is obtained. This is probably due to intermediate reduction of the W^{VI} by the surfactant at elevated temperatures. Removal of the template by extraction in different solvents (diethyl ether–HCL, ethanol, ethanol–HCl or DMSO) was unsuccessful, possibly due to the strong interaction in the pores. In all cases the TG/DTA analysis shows that the surfactant was completely retained by the pore system. Investigations into template removal by oxygen plasma calcination and supercritical fluid extraction are under investigation.

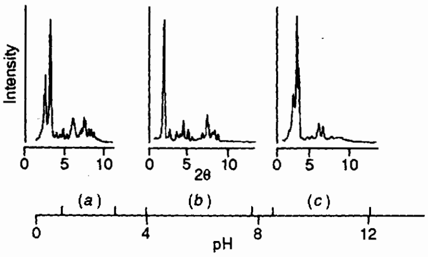

Fig. 3 Dependence of the product composition on the pH with corresponding typical XRD patterns of the tungsten oxide surfactant using alkyltrimethylammoniumchloride as surfactant

Table 1 Effect of the surfactant chain length on the *d*-spacing in the molybdenum oxide system

Surfactant chain length $C_nH_{2n+1}NMe_3$ *n*	*d*(001)/nm	*d*(002)/nm
12	2.07	1.04
14	2.25	1.13
16	2.44	1.23
18	2.55	1.30

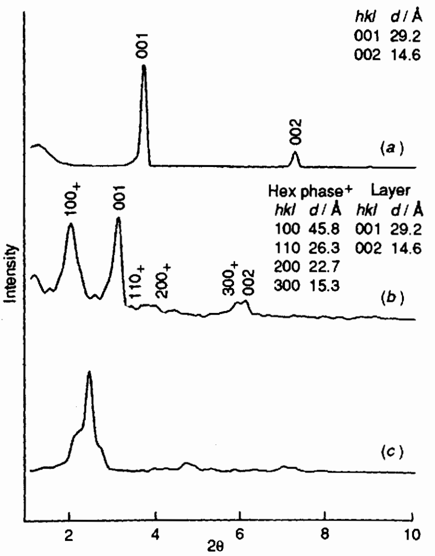

Fig. 4 XRD patterns of the Mo-oxide surfactant (*a*), the lead oxide surfactant (*b*) and the iron oxide surfactant (*c*). The intensities are not equal for the different compounds. Indexing of the iron oxide surfactant was not possible so far.

Using molybdenum polyanions only a layer structure was obtained, despite varying the pH of the synthesis solution over the pH range from 1 to 13. The commercial product ammonium molybdate tetrahydrate $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ was used for the molybdenum polyanion. The *d*-spacings of the layers can be controlled by variation of the surfactant alkyl chain length. A shorter chain length was shown to give a lower *d*-spacing and *vice versa* (Table 1). Since only (001)-reflections were observed, there is no periodic structure in the layers [Fig. 4(*a*)].

In the transition-metal and metal polycations/anionic surfactant system the use of iron and lead polycations proved to be successful in the formation of mesostructured materials. Hexadecylsulfonic acid was used as the anionic surfactant. The surfactant solution was combined with an aqueous solution of $Pb(NO_3)_2$ or $FeCl_2\cdot 4H_2O$. The reaction temperature for the synthesis of the lead oxide surfactant compound was 90 °C whilst the synthesis of the iron oxide surfactant was carried out at room temperature to prevent precipitation of amorphous material.

The XRD pattern of the lead oxide surfactant shows two coexisting phases [Fig. 4(*b*)]. The first *d*-spacing of 4.6 nm results from the hexagonal phase, which can be indexed on a hexagonal unit cell with $a = 5.3$ nm ($2d_{100}/\sqrt{3}$). In addition, a layer with a *d*-spacing of 2.9 nm is noticeable. The TG/DTA analysis indicates a ratio of surfactant to PbO of 1:6. The XRD pattern for the iron oxide surfactant synthesised with $FeCl_2$ might also indicate formation of a hexagonal structure [Fig. 4(*c*)]. The first intense reflection at 3.75 nm is comparable with the (100)-reflections of the other oxide surfactant compounds. The TG/DTA analysis shows a template content of over 80 wt%. This corresponds to a ratio of surfactant to FeO of 1:2. From this it follows that the structure should be unstable and thus a removal of the template by extraction has so far proved to be unsuccessful.

The experiments reported here prove that it is possible to generalise the mechanism described in ref. 3 to other oxides than silica. Detailed characterisation of the materials described here are under way. It can be expected that many other compositions will be synthesised following the procedure lined out here, and that applications of the mesostructured transition-metal oxides might lead to a new generation of highly active oxidation catalysts.

This work was supported by the FCI, the DFG (Schu 744/6-1) the Office of Naval Research, and the MRL Program of the NSF. We would like to thank C. Weidenthaler for valuable discussions.

Received, 17th January 1994; Com. 4/00266K

References

1 C. T. Kresge, M. E. Leonowicz, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710.

2 J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T.-W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins and J. L. Schlenker, *J. Am. Chem. Soc.*, 1992, **114**, 10834.

3 O. Franke, G. Schulz-Ekloff, J. Rathousky, J. Starek and A. Zukal, *J. Chem. Soc., Chem. Commun.*, 1993, 724.

4 P. J. Branton, P. G. Hall and K. S. W. Sing, *J. Chem. Soc., Chem. Commun.*, 1993, 1257.

5 A. Monnier, F. Schüth, Q. Huo, D. Kumar, D. Margolese, R. S. Maxwell, G. D. Stucky, M. Krishnamurty, P. Petroff, A. Firouzi, M. Janicke and B. F. Chmelka, *Science*, 1993, **1261**, 1299.

6 M. E. Landis, B. A. Aufdembrink, P. Chu, I. D. Johnson, G. W. Kirker and M. K. Rubin, *J. Am. Chem. Soc.*, 1991, **113**, 3189.