Synthesis and characterization of a novel mesostructured layered tin(IV) sulfide

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A novel mesostructured lamellar tin(IV) sulfide with a basal spacing of 25.5 Å is prepared at room temperature in the presence of the cationic cetyltrimethylammonium surfactant.

Recently there has been increasing interest in the synthesis of open novel sulfide structure types. Bedard *et al.*[1,2] reported a new class of microporous substituted germanium and tin sulfides using the hydrothermal technique for the synthesis of the aluminosilicate zeolites and molecular sieves by adding an organic amine as template into sulfide slurries. Jiang *et al.*[3,4] and Parise *et al.*[5,6] published the synthesis of layered tin sulfides, denoted R-SnS-*n* (R = organic amine), by using various reactants.

Much work has been done on the mesostructured silica-based M41S family including the hexagonal MCM-41, cubic MCM-48 and lamellar MCM-50 materials obtained in the presence of long-chain surfactant species.[7,8] Also the preparation of a novel lamellar tin sulfide with cetyltrimethylammonium bromide (C_{16}TMABr) was mentioned;[8] however, no detailed information was provided. In the present paper, the synthesis and characterization of a lamellar tin(IV) sulfide with a basal spacing of 25.5 Å is reported. This is designated C_{16}TMA-SnS-L in keeping with the nomenclature adopted by Bedard *et al.*[1]

A typical starting molar composition was $7.2Na_2S:4.0C_{16}$-$TMABr:3.0SnCl_4:1500H_2O$. First, an aqueous solution of sodium sulfide was added into a solution of tin(IV) chloride and a gold–yellow precipitate of tin sulfide was formed, then, cetyltrimethylammonium bromide was added under stirring. A NaOH or HCl solution was used to adjust the pH of the mixtures to 12.3 and crystallization was carried out at room temperature for 19 days. The product was filtered, washed with water and ethanol, and air-dried. Calcination of the material under argon leads to the collapse of the structure at 330 °C.

X-Ray powder diffraction was performed on a STOE STADI-P diffractometer using monochromated Cu-Kα_1 radiation. The powder was contained in a capillary. Scanning electron micrographs were obtained on an XL30 Philips electron microscope using conventional sample preparation and imaging techniques. Thermogravimetric analysis (TG) and differential thermal analysis (DTA) were used to obtain an insight into the decomposition of the organic species occluded in the structure; measurements were performed on a Mettler 1 Thermoanalyser and BDL-Setaram M2 Microanalyser respectively. The samples were heated in air or argon with a heating rate of 4 °C min^{-1} for TG and 10 °C min^{-1} for DTA. ^{119}Sn MAS NMR spectra were recorded on a Bruker MSL300 spectrometer using $SnMe_4$ as the chemical shift reference.

The XRD pattern of C_{16}TMA-SnS-L obtained by room-temperature synthesis for 19 days (pH = 12.3) is shown in Fig. 1. A number of basal reflections corresponding to a highest *d* value of 25.5 Å are observed beside weaker reflections. The basal reflections alone are observed in the reflection mode on a flat sample (Philips PW1800 diffractometer), thus leading to the conclusion that the material is indeed layered. The spectrum is indexable on the basis of a monoclinic unit cell with a = 25.88(6), b = 18.56(3), c = 10.81(2) Å, β = 100.99(9)°. The chemical composition determined by bulk elemental analysis is $C_{19}H_{42}NSnS_{2.5}$ [calc. (mass%): Sn, 24.58; S, 16.58; C, 47.24; N, 2.90; found Sn, 24.53; S, 16.13; C, 46.94; N, 2.96]. No sodium, oxygen, chlorine or bromine was detected by EDX analysis. The composition of the inorganic part of C_{16}TMA-SnS-L is different from those of TPA-SnS-3,[3] TEA-SnS-1[4]

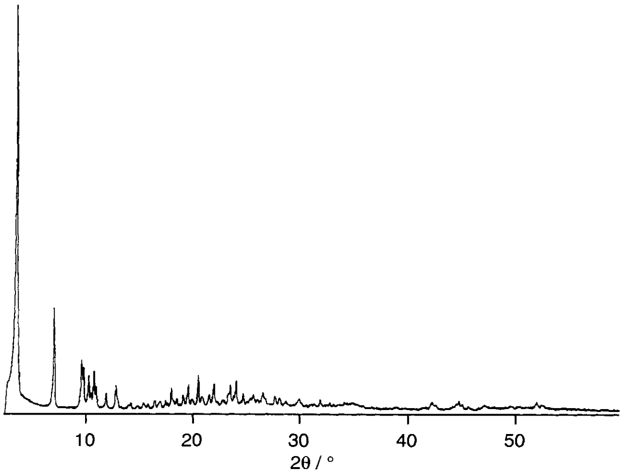

Fig. 1 XRD pattern (Cu-Kα_1) of C_{16}TMA-SnS-L

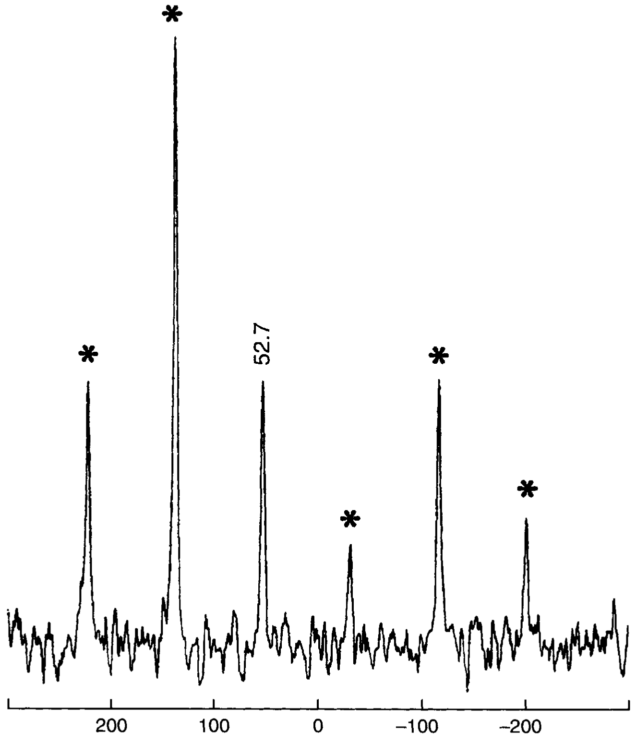

Fig. 2 ^{119}Sn MAS NMR spectrum of C_{16}TMA-SnS-L (spinning rate 9 kHz, * spinning side-bands) and Dab-SnS-SB1,[5] whose overall compositions are $[NPr^n_4]_2Sn_4S_9{\cdot}H_2O$, $[NEt_4]_2Sn_3S_7$ and $Sn_5S_{12}(N_2C_4H_{11})_2(N_4C_{10}H_{24})$ respectively. This indicates the versatility of the tin(IV) sulfide based frameworks.

It is well known that the reaction conditions, especially the temperature, play a key role in the synthesis of mesostructured silica-based materials.[9] The highest crystallinity for C_{16}TMA-SnS-L was obtained for a synthesis temperature of −2 °C. The increase of the temperature well above room temp. was not favourable for the formation of C_{16}TMA-SnS-L, a decrease of crystallinity being observed. When the reaction temperature reached 110 °C, a layered material was no longer observed and an unknown phase with a single diffraction peak of low intensity at d = 39.1 Å was formed. A new layered material with a basal spacing of 10.24 Å was obtained when the reaction temperature was raised to 150 °C.

The ^{119}Sn MAS NMR spectrum of C_{16}TMA-SnS-L given in Fig. 2 comprises several lines. Variation of the spinning rate showed that one single type of tin site seems to be present in the material (δ 52.7). ^{119}Sn MAS NMR is a powerful tool to determine the oxidation state, ligand type and coordination number of tin. The chemical shift for tetrahedral tin(IV) in Na_4SnS_4 occurs at δ 62.6, for octahedral tin(IV) in SnS_2 at δ −764 and for octahedral tin(IV) in SnO_2 at δ −603 (relative to $SnMe_4$).[3] It thus appears that the single line observed for C_{16}TMA-SnS-L at δ 52.7 may be best assigned to tetrahedrally coordinated Sn^{IV}.

In summary, a novel mesostructured lamellar tin(IV) sulfide material has been synthesized at low temperatures. Detailed characterization of this material described here will be reported elsewhere. We believe that other mesostructured metal sulfide materials can be obtained.

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References

1 R. L. Bedard, L. D. Vail, S. T. Wilson and E. M. Flanigen, *US Pat.*, 4 880 761, 1989.

2 R. L. Bedard, S. T. Wilson, L. D. Vail, J. M. Bennett and E. M. Flanigen, in *Zeolites: Facts, Figures, Future. Proceedings of the 8th International Zeolite Conference*, Elsevier, Amsterdam, 1989, p. 375.

3 T. Jiang, G. A. Ozin and R. L. Bedard, *Adv. Mater.*, 1994, **6**, 860.

4 T. Jiang, G. A. Ozin and R. L. Bedard, *Adv. Mater.*, 1995, **7**, 166.

5 Y. Ko, C. L. Cahill and J. B. Parise, *J. Chem. Soc., Chem. Commun.*, 1994, 69.

6 J. B. Parise, Y. Ko, J. Rijssenbeek, D. M. Nellis, K. Tan and S. Koch, *J. Chem. Soc., Chem. Commun.*, 1994, 527.

7 Q. Huo, D. I. Margolese, U. Ciesla, P. Feng, T. E. Gier, P. Sieger, R. Leon, P. M. Petroff, F. Schüth and G. D. Stucky, *Nature*, 1994, **368**, 317.

8 Q. Huo, D. I. Margolese, U. Ciesla, D. G. Demuth, P. Feng, T. E. Gier, P. Sieger, A. Firouzi, B. F. Chmelka, F. Schüth and G. D. Stucky, *Chem. Mater.*, 1994, **6**, 1176.

9 D. Zhao and D. Goldfarb, *J.Chem. Soc., Chem. Commun.*, 1995, 875.

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