

MOLECULAR APPROACH TO MESOPOROUS METAL SULFIDES

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ABSTRACT

We have synthesized metal-sulfide/surfactant nanocomposite materials by cooperative assembly of molecular precursors in a aqueous medium. The template-mediated synthetic approach is applicable to metals sulfides that exhibit aqueous thiometallate chemistry. The products are lamellar and have a bilayers or interdigitated layers of surfactant molecules sandwiched between metal sulfide layers. The layers of anionic metal sulfide molecules are not completely condensed in the nanocomposites, which results in a negative charge on the metal sulfide layers. The materials are stable at room temperature in water, methanol, 1 M HCl, 30 wt% NH₃, and 1 M NaOH. The materials do not dissolve at 80 °C in water and are stable to at least 180 °C in air. The nanocomposites exhibit ion exchange of smaller surfactants, alkali-metal ions, and divalent metal ions.

INTRODUCTION

Porous materials are grouped into three general categories based on the average diameter of their pores¹: microporous (< 20 Å), mesoporous (20 to 500 Å), and macroporous (500 Å). The former two are the most interesting for separation, catalysis, sensing, and exchange of ions, molecules, and small macromolecules. Periodic microporous oxides² and sulfides³ and periodic mesoporous oxides^{4,5,6} are made by the use molecular precursors and organic templates in water. The synthesis of periodic mesoporous metal sulfides that contain accessible porosity remains an outstanding challenge to the synthetic chemist. However, periodic lamellar nanocomposites have been synthesized by intercalation routes for more than 20 years⁷, and two lamellar tin(IV) sulfide nanocomposites have been reported recently.^{8,9} The synthetic route and the materials described here represent a significant step toward metal sulfide phases that possess accessible mesoporosity.

EXPERIMENTAL

Synthesis

Surfactant solutions were prepared from water, cosolvent (methanol), and cetyltrimethylammonium bromide (CTAB) or similar surfactants. To this solution a 16.5 wt% aqueous solution of Na₂S was added with vigorous stirring. Aqueous solutions of metal salts (Mo, W, Co, Fe, Zn, Ga, Sn, Sb) were added to these solutions. Finally concentrated (28-30 wt%) HCl was added to reduce the pH. Reactions were performed at room temperature or 80 °C. Products typically formed within 10 seconds of addition of the metal salt solution or, for acidic metal ions, within 10 seconds of the addition of HCl. Products were recovered by vacuum filtration

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and were washed with water and methanol. Products were generally yellow or brown and pasty (even when dried in air at room temperature). Many compositions were examined; an example of molar ratios of reagents that gave ordered periodic products (for W, Mo, and Sn) is 1M : 4S : 0.16 CTAB : 100 to 500 H₂O.

Characterization

Powder X-ray diffraction was performed on all samples with Scintag PAD V or Siemens D5000 diffractometers. Peak positions were fit, and the diffraction patterns were indexed to determine unit cell parameters. Typically sets of *00l* reflections were observed for each phase. Chemical analyses for C, H, N, S, Na, and Sn, W, Mo, or Ga were performed by Galbraith Laboratories. Thermal analyses with the sample in flowing air were obtained by the use of a Omnitherm STA 1500 dual thermogravimetric/differential thermal analyzer. Transmission electron microscopy was performed on crushed samples with a JEOL 1200 STEM. Chemical stability was determined by placing 35 to 45 mg of sample in 15 mL of deionized water, methanol, 1 M HCl, 30 wt% aq NH₃, and 1 M NaOH solution and stirring for 3 d at room temperature. Ion exchange was performed in an aqueous solution that contained a 100-fold excess of ions to replace those in the nanocomposite (dodecyltrimethylammonium, Na⁺, Cd²⁺, Pb²⁺).

RESULTS

The synthetic method described above is applicable to metal ions that exhibit aqueous thiometallate chemistry, which include Cr, Mo, W, Mn, Fe, Co, Ni, Cu, Ag, Zn, Cd, Hg, Ga, In, Tl, Sn, Pb, As, and Sb.³ Eight systems (outlined above) are examined in this study. Detailed information is presented for the W-S-H₂O-methanol-CTAB system. Figure 1 shows that the tungsten sulfide products are lamellar and have interlayer spacings of approximately 41 Å (interdigitated), 63 Å (90° bilayer), and 47 Å (tilted bilayer or staged). The interdigitated and 90° bilayer phases exhibit only *00l* Bragg peaks. The 47 Å phase can be indexed on an orthorhombic unit cell with $a = 7.336$ (4), $b = 23.741$ (3), $c = 47.00$ (7) Å. The a and b cell constants are 4 and 13 times the radius of a sulfide atom (1.84 Å),¹⁰ which indicates a possible 4 x 13 intralayer ordered arrangement of nonclosest-packed sulfide ions. Figure 2 depicts the three structures. Transmission electron microscopy generally shows grains with no regular order. In one case where the sample had proper orientation and thickness, a series of parallel lines can be seen. No TEM evidence for an MCM-41-type phase^{4,5} (1-d hexagonal pore system) has been found.

The interdigitated phase is predominant at low pH. A mixture of the three phases is present at neutral and higher pH. The 90° bilayer is predominant at very high pH. Kinetics and precise synthetic conditions govern the phase assemblies observed. The solvent system also affects the assembly of phases present in a given preparation. For example, addition of up to 20 wt% methanol to the surfactant solution (in a W-S-H₂O-methanol-CTAB preparation) decreases the 90° bilayer phase relative to the interdigitated and 47 Å phases. In marked contrast to nanocomposites formed by intercalation of guests into lamellar metal sulfide hosts,⁷ no Bragg peaks characteristic of the intralayer M-S scattering are observed for the interdigitated and 90° bilayer phases (i.e. no *hkl* reflections).

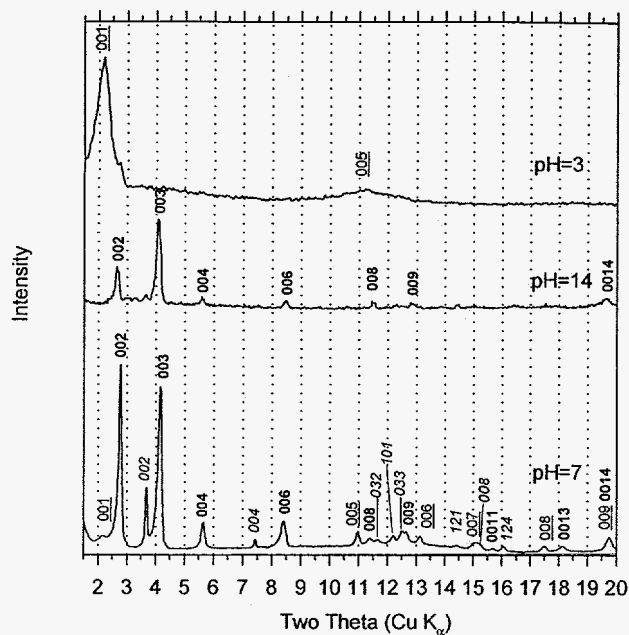


Figure 1. Powder X-ray diffraction pattern of W-S-CTAB prepared at different pH values. **Bold** indicates lamellar 90° bilayer phase; underline indicates interdigitated phase; *italics* indicates tilted bilayer or staged compound.

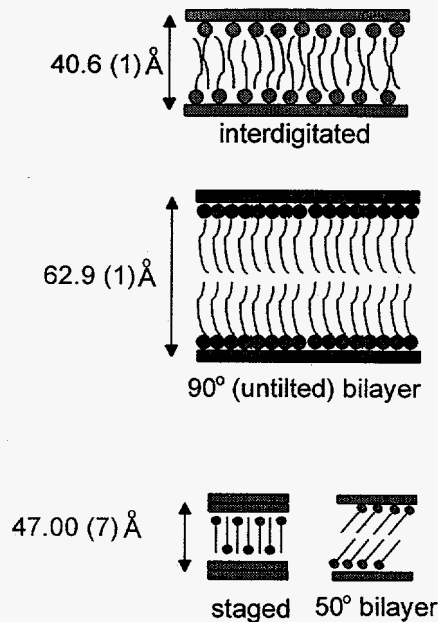


Figure 2. Proposed structures of the interdigitated, 90° bilayer, and 47 Å phases.

Chemical analyses of tin, tungsten, and molybdenum sulfide/CTAB nanocomposites show a sulfide to metal ratio greater than 2 to 1. The S to M ratio for seven Sn, Mo, and W materials prepared at pH values ranging from 3 to 14 spans a narrow range from 2.50 to 1 up to 2.95 to 1. The S to M ratio greater than 2.0 indicates – assuming tetravalent metal ions – a charge of -1.0 to -1.9 per metal atom in each metal sulfide layer. Other ranges of ratios (relative to the metal ion) are CTA^+ - 0.16 to 1.59, Na^+ - 0.01 to 0.42, H^+ - 0.00 to 1.32, and water - 0.00 to 4.7. In general, the surfactant to proton ratio increases with increasing pH. Two specific examples in the from the W-S-H₂O-methanol-CTAB system are: $\text{WS}_{2.81}^{1.62-} \cdot 0.01 \text{H}^+ \cdot 1.59 \text{CTA}^+ \cdot 0.02 \text{Na}^+ \cdot 0 \text{H}_2\text{O}$ (pH = 13, 100% water, 4 to 1 mixture of 90° bilayer and interdigitated), and $\text{WS}_{2.5}^{1.00-} \cdot 0.00 \text{H}^+ \cdot 0.82 \text{CTA}^+ \cdot 0.24 \text{Na}^+ \cdot 0 \text{H}_2\text{O}$ (pH = 7, 80/20 water/methanol, 1 to 1 to 1 mixture of 90° bilayer, interdigitated, and 47 Å phases). Thermogravimetric analyses show that samples with no interlayer water begin to lose weight at or above 180 °C when heated in air; see Figure 3. X-ray diffraction of tungsten TGA products shows that the sulfide is converted to WO_3 below 1000 °C.

$\text{WS}_{2.87}^{-1.73} \text{CTA}_{1.73}^+$ (initially formed in 70/30 water/methanol and stirred 55 minutes before recovery) exhibits excellent chemical stability over a 3 day period at room temperature when stirred in water, methanol, 1M HCl, 1M NaOH, and 30 wt% NH_3 . The XRD patterns of the materials recovered after 3 days are shown in Figure 4. TGA of the recovered material indicates that 84, 86, 84, 76, and 77% of the CTA^+ is removed owing to condensation of the metal sulfide framework and charge compensation of the anionic framework by cations in solution. XRD indicates the treated materials do not dissolve or decompose, although the higher order reflections are attenuated or absent, which indicates less well ordered materials. The samples treated in HCl and in water show the appearance of the 47 Å phase. The same $\text{WS}_{2.87}^{-1.73} \text{CTA}_{1.73}^+$ sample treated in 90 °C deionized water dissolves/ decomposes. The same $\text{WS}_{2.87}^{-1.73} \text{CTA}_{1.73}^+$

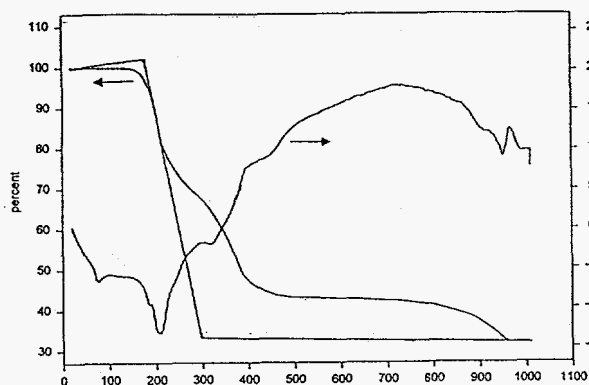


Figure 3. Thermogravimetric and differential thermal analyses of $WS_{2.87}^{-1.73}CTA_{1.73}^{+}$ performed in flowing air.

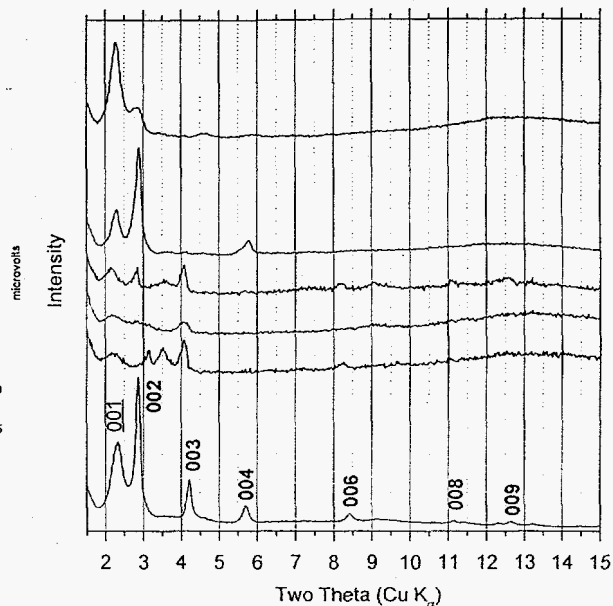


Figure 4. Powder X-ray diffraction patterns of $WS_{2.87}^{-1.73}CTA_{1.73}^{+}$ (bottom) and $WS_{2.87}^{-1.73}CTA_{1.73}^{+}$ stirred at room temperature for 3 days in a solution of (from bottom to top) 1M HCl, methanol, water, 30 wt% NH_3 , and 1 M NaOH.

sample also shows the ability to exchange smaller surfactant ions, alkali metal ions, and divalent metal ions at room temperature in a 100-fold molar excess of exchange ions relative to CTA^+ . The diffraction pattern of the dodecyltrimethylammonium exchanged materials exhibits four $00l$ reflections that can be indexed on a $c = 56.5$ (9) cell in addition to peaks from the parent and the 47 Å phase. The diffraction pattern of the sodium exchanged sample shows a nearly complete absence of the 90° bilayer phase, presence of the 47 Å, and interdigitated phases, and two new peaks that - along with the first peak in the pattern - can be indexed as the 001 , 110 and 002 of a hexagonal unit cell; $a = 44.3$ (5) Å.

DISCUSSION

The synthetic method outlined here represents a general method to make mesophase nanocomposites without the use of slow, high temperature, environmentally hazardous (because of solvents typically used) intercalation routes.⁷ Some of the nanocomposites (Mo, W, Sn) are structurally similar to those made by one- or two-step intercalation routes⁷ and some (Fe, Ga) cannot be accessed by intercalation routes because the initial metal sulfide is not lamellar.¹¹ All of the products represent new compositions of matter (with the possible exception of the tin(IV) sulfides previously reported).^{8,9} The high sulfide to metal ratios and residual negative charge on the M-S layers have not been achieved by any other reported method. Other advantages are that the method is a 1-pot synthesis that can be done in water at room temperature in a matter of seconds. Finally, the method holds the promise of new structures and, through judicious choice of the organic and inorganic precursors employed, exquisite control of structure and properties of the final product.

The nanocomposites show limited chemical and thermal stability. It is possible to remove up to 86% of the organic material from the nanocomposite through condensation of the framework and/or charge balance by cations introduced in the template removal process. Access to porosity should be improved if the materials can be pillared with robust inorganic units. Questions exist about the molecular chemistry, the existence and ability to make pure MCM-41 type hexagonal phases, and about the electrical and optical properties of the nanocomposites. These aspects of the materials are currently under investigation.

As a result of the structural, chemical, and physical properties of the materials, they may be useful in acid catalysis, chemically specific filtration, as new host for large molecules, and perhaps in optical or electronic applications. The synthetic method also shows similarity to biomimetic approaches to materials, although it lacks the rigid spatial control imparted by anchoring the organic template to a substrate.

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