Mesostructured iron sulfides

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The synthesis and characterization of the first mesostructured iron sulfides are reported: the first is a disordered hexagonal structure prepared *via* a neutral template route; the other, formed using an ionic template, is a relatively ordered phase which represents the first hexagonal mesostructured transition metal sulfide.

Since the first synthesis of mesoporous silicates, much activity has focussed on self-assembled inorganic/surfactant composites[1–5] due to their potential applications as catalysts and absorbents. The best known member of this family, MCM-41, possesses a hexagonal array of channels while the atomic arrangement in the channel walls is disordered. Following this, many different types of surfactants have been used to prepare numerous mesostructured oxides, primarily in the silicate family. A liquid crystal templating mechanism[1] and a self-assembly process involving electrostatic interaction between the inorganic ions in solution and the charged surfactant head group[2,3] were proposed for the mechanism of formation. Using a neutral template, formation of a mesoporous silicate containing a disordered arrangement of channels was explained on the basis of hydrogen bonding and self-assembly between neutral primary amine micelles and neutral inorganic precursors.[4] Neutral surfactants have also been used to prepare mesoporous transition metal oxides with a high specific surface area.[5]

Compared with oxygen, sulfur has a far richer coordination chemistry due to its low-lying d orbitals. The lack of thermodynamic stability of sulfides in the presence of oxygen has made synthesis of mesostructured sulfides more difficult, however, and hence only a few have been reported. These include primarily the main group family, namely mesolamellar and pseudo-hexagonal phases of Group IV (Sn,[6] Ge[7]), and Group II (Cd,[8] Zn[9]). As metal sulfides are generally semiconductors, while many metal oxides are insulators, open-framework metal sulfides may be potentially useful for different applications. Iron sulfides are particularly interesting since they play an important role in life's beginning.[10] The catalytic formation of complex organic molecules from simple precursors is considered to take place on the surface of iron monosulfide or pyrite as a result of redox reactions between FeS and FeS_2.[11] Furthermore, bulk iron(II) and iron(III) sulfides have shown potential applications as cathodes,[12] high refractive index materials[13] and catalysts for coal liquefaction.[14] Herein we report the first mesostructured phases based on iron sulfides, prepared *via* different routes.

Mesostructured iron(II) sulfide [denoted DDA-FeS-M (DDA = dodecylamine)] was formed in the system dodecylamine–iron(II) sulfate–sodium sulfide–ethanol–H_2O at room temperature. Use of the two solvent system improved the solubility of dodecylamine. Fig. 1(*a*) shows the resulting XRD pattern: One peak is evident with a *d*-spacing of 33.8 Å, similar to the value observed for HMS.[4] The presence of a single broad peak is considered an indication of randomly ordered pores.[4,15] A very broad, low intensity line at about 20° (2θ), similar to that of MCM-41 and HMS-type materials, also observed in the XRD pattern, suggests that the inorganic wall is amorphous as expected.[1–4,15] We have found that DDA-FeS-M is formed at an optimum H_2O/ethanol ratio of 7.7: at lower ratios the material is not formed at all. An unknown impurity phase was found in the product when the ethanol was increased, or the amount of iron sulfate and sodium sulfide was increased in the reactant mixture. The impurity phase therefore is minimized under slightly acidic conditions.

The presence of DDA in the material was confirmed by thermal gravimetric analysis (TGA). The TGA curve (under N_2) shows an initial weight loss of about 3.6% below 135 °C due to the desorption of water. Weight loss (48.7%) above this temperature corresponds to the loss of organic material and also some sulfur species. The corresponding differential thermal analysis (DTA) curve in air shows two exothermic peaks at low temperature attributable to reaction with oxygen that result in a weight gain of about 4.4 wt%, evident from the TGA trace. Two exothermic peaks between 250 and 500 °C correspond to combustion of the surfactant. The total weight loss corresponding to the loss of surfactant and transformation from iron(II) sulfide to iron(III) oxide is about 61.5%, translating into an empirical composition of $FeS(DDA)_{0.6}\cdot 0.4H_2O$. This material displayed a very disordered structure in its TEM image, similar to HMS.[4]

Employment of an ionic surfactant hexadecyltrimethylammonium hydroxide/chloride as a structure-directing agent,

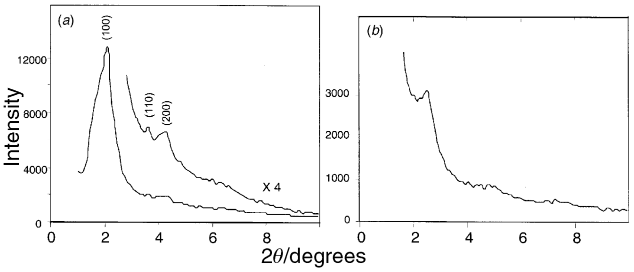

Fig. 1 (*a*) Powder X-ray diffraction patterns (Siemens D-500; Cu-Kα radiation) of DDA-FeS-M; (*b*) XRD pattern of $C_{16}TMA\text{-}Fe_2S_3\text{-}M$. Inset shows scale expansion of the 3–10° 2θ range showing the weak 110 and 200 reflections. Values for the experimental and calculated *d*-spacings, respectively for the hexagonal unit cell where a = 48.4 Å are (100), 41.92, 41.89 Å; (110), 24.25, 24.19 Å; (200), 20.59, 20.94 Å.

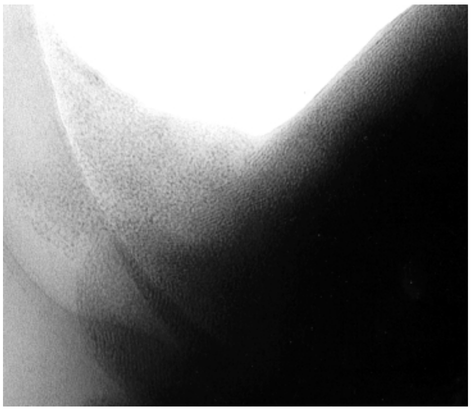

Fig. 2 Transmission electron micrograph image (Phillips, CM20, 200 keV) of mesostructured $C_{16}TMA\text{-}Fe_2S_3\text{-}M$ (1 cm = 74 nm).

Table 1 Influence of reaction composition on the formation of $C_{16}TMA\text{-}Fe_2S_3\text{-}M$

Sample No.	Molar ratio			Crystallization time/h	Products
	$Fe_2S_3/CTMA$	$H_2O/CTMA$	$(NH_4)_2S/CTMA$		
f	0.50	100	0.0	23	Fe_2O_3
g	0.50	150	0.0	12	$C_{16}TMA\text{-}Fe_2S_3\text{-}M + Fe_2O_3$
h	0.50	200	0.0	23	$Fe_2O_3 + FeS_2$
i	0.50	150	0.5	15	$C_{16}TMA\text{-}Fe_2S_3\text{-}M$
j	0.75	150	0.5	8.5	$C_{16}TMA\text{-}Fe_2S_3\text{-}M$
k	1.00	150	0.5	8.5	$C_{16}TMA\text{-}Fe_2S_3\text{-}M$
l	0.50	150	0.5 S[a]	24	$C_{16}TMA\text{-}Fe_2S_3\text{-}M + Fe_2O_3$

[a] Elemental sulfur was used in place of $(NH_4)_2S$

and an amorphous iron(III) sulfide,[16] as iron and sulfur sources yielded $C_{16}TMA\text{-}Fe_2S_3\text{-}M$ after hydrothermal synthesis at 110 °C for 16 h. Fig. 1(*b*) shows the resultant XRD pattern in which three reflections are observed, consistent with diffraction from a poorly ordered hexagonal phase with a = 48.4 Å. Moreover, a broad peak at $2\theta \approx 20°$ is also evident in the XRD pattern, which indicates the inorganic wall is amorphous as previously described. The TEM image (Fig. 2) is in accord with the XRD pattern, in that a poorly organized phase is evident with no long range order apparent. The material is clearly not lamellar, however. The instability of the material in the beam precludes any further detailed TEM study.

Table 1 shows the influence of reaction composition on the products. The molar ratio of $H_2O/C_{16}TMA$ plays a key role in the formation of $C_{16}TMA\text{-}Fe_2S_3\text{-}M$, as it influences the basicity of the reactant mixture. For example, Fe_2O_3 was formed when the basicity was higher in the reactant mixture, while a mixture of Fe_2O_3 and FeS_2 was obtained when the basicity was lower. Our experiments also show that the addition of a small amount of ammonium sulfide in the reactant mixture can effectively prevent the formation of iron(III) oxide and result in formation of pure $C_{16}TMA\text{-}Fe_2S_3\text{-}M$. Addition of elemental sulfur cannot inhibit the formation of iron(III) oxide under the same conditions, however. Bulk chemical analysis results indicate that S/Fe molar ratio is about 1.5, with a C/N ratio close to 20.[17] This indicates that the inorganic component is amorphous iron(III) sulfide, and suggests the aliphatic surfactant chains remain intact during the formation of $C_{16}TMA\text{-}Fe_2S_3\text{-}M$.

Confirmation of the presence of intact surfactant was obtained by FT-IR. The spectrum of $C_{16}TMA\text{-}Fe_2S_3\text{-}M$ shows several absorption bands, which may be assigned to occluded $[C_{16}H_{33}N(CH_3)_3]^+$ at: 2960(sh), $\nu_{as}(CH_3)$; 2920, $\nu_{as}(CH_3)$; 2850, $\nu_{as}(CH_2)$; 1467, $\delta_s(CH_2)$.[7a,18] The absorption band at 334 cm^{-1} is assigned to Fe–S.[19] The bands at about 3400 and 1635 cm^{-1} are due to water adsorbed in the pores of the material. Thermal gravimetric analysis confirms that surfactant is present in the material. The TGA curve under N_2 showed that physisorbed water was removed at about 40 °C, corresponding to a weight loss of 3.1%. The DTA curve in air revealed an exothermic peak at 85 °C and a corresponding weight gain in the TGA of 7.8%, assigned to an oxidation reaction. Subsequent weight loss between 150 and 700 °C, arising from the loss of H_2O and combustion of the surfactant was 71.3% corresponding to a composition of $C_{16}TMA\text{-}Fe_2S_3\text{-}M$ as $0.8C_{16}TMA\cdot Fe_2S_3\cdot 0.4H_2O$. The surfactant/inorganic element ratio of about 1/2 is in accord with previous reports for MCM-41 obtained at higher synthesis pH ($CTMA/SiO_2$ molar ratio = 0.44).[20] and mesoporous tin(IV) sulfide ($0.5\ C_{16}TMA\cdot SnS_2\cdot 0.75\ H_2O$).[21] Similar to bulk iron(III) sulfide,[22] $C_{16}TMA\text{-}Fe_2S_3\text{-}M$ is very unstable towards oxidation and therefore attempts to remove the surfactant were not successful.

Two probe electrical conductivity measurements indicated that whereas amorphous Fe_2S_3 is a poor semiconductor (σ = 5.4×10^{-8} S cm^{-1}), as-synthesized $C_{16}TMA\text{-}Fe_2S_3\text{-}M$ is an insulator. This is probably the result of the large surfactant content and poor electronic transport along the confined dimensions of the amorphous wall. Other factors which would contribute to low conductivity include the possibility of incomplete polycondensation in the inorganic component which would lead to defects, and grain boundary effects.

In summary, two different synthetic routes provide new mesostructured iron sulfide phases, including the first hexagonal transition metal sulfide phase. Their lack of thermodynamic stability with respect to oxygen inhibits ready removal of the surfactant. Controlled oxidation of this material may provide a facile route to a hitherto unknown mesostructured or mesoporous iron oxide.

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