Available online at www.sciencedirect.com

SCIENCE DIRECT

ELSEVIER

Microporous and Mesoporous Materials 88 (2006) 187–190

MICROPOROUS AND MESOPOROUS MATERIALS

www.elsevier.com/locate/micromeso

# Mesostructured cobalt and nickel molybdenum sulfides

Pantelis N. Trikalitis [1], Tracy A. Kerr, Mercouri G. Kanatzidis *

*Department of Chemistry, Michigan State University, East Lansing, MI 48824, USA*

Received 8 August 2005; received in revised form 6 September 2005; accepted 6 September 2005
Available online 2 November 2005

**Abstract**

We report the synthesis of mesostructured cobalt and nickel molybdenum sulfides prepared by reacting $MoS_4^{2-}$ anions with $Co^{2+}$ and $Ni^{2+}$ in formamide solution in the presence of alkyl-pyridinium surfactant molecules acting as template. These systems represent the first examples of templated mesostructured Co–Mo–S and Ni–Mo–S type materials.

*Keywords:* Molybdenum sulfide; Mesostructured sulfides; Hydrodesulfurization

The catalysts of choice for hydrodesulfurization (HDS) of crude oils for many decades have been cobalt and nickel promoted molybdenum sulfides [1,2]. In these systems the active sites are referred to as "Co(Ni)MoS" phases. It is generally a challenge to generate such phases, while excluding the formation of separate non-active binary Co(Ni) sulfides. Active HDS CoMoS phases can be prepared using $MoS_4^{2-}$ as precursor. Despite numerous studies, the development of highly active Co–Mo–S and Ni–Mo–S catalysts continues to be desirable [3–5]. For this reason new ways of combining these elements to generate nanostructured Co–Mo–S and Ni–Mo–S compositions is still of considerable interest.

Recent advances in the field show that mesoporous oxidic materials such as Ti-HMS and Al-HMS are excellent supports for "Co(Ni)MoS" active phases because of their high specific surface area, large pore size and pore volume [6]. In comparison with traditional microporous supports such as $\gamma$-$Al_2O_3$ and various zeolites, they allow for higher dispersion of the active phases and accessibility to large S-containing molecules such as dialkyl dibenzothiophenes. The removal of the later is of paramount importance to achieve deep hydrodesulfurization of the crude oil in order to meet the allowable limit on diesel sulfur which in the near future will be restricted to 50 wppm in most advanced countries due to stringent environmental regulations [7–9].

It would be particularly attractive if Co–Mo–S and Ni–Mo–S compositions were single phase and mesoporous because it could lead to more effective and improved HDS catalysts. Such systems would combine the necessary porosity and metal active sites in one material. A promising synthetic approach that to our knowledge has not been exploited is the use of organic templates to construct open framework mesostructured materials based on $MoS_4^{2-}$ and $Co^{2+}$ or $Ni^{2+}$ building units. This route has been applied successfully for the construction of other mesostructured metal sulfides and selenides [10–12]. Here we describe a new set of surfactant templated mesostructured cobalt and nickel molybdenum sulfides.

The cobalt and nickel mesostructured phases were synthesized in formamide (FM) by the simultaneous addition of a solution of $Co^{2+}$ (or $Ni^{2+}$) cations, and a solution of $MoS_4^{2-}$ anions into a solution of supramolecularly organized alkyl-pyridinium surfactant molecules ($C_nPyBr$, $n = 12$, 14, 16, 18 and 20) in 80 °C FM. In a typical experiment 4 g surfactant were dissolved in 20 ml warm FM. Upon addition of the $(NH_4)_2MoS_4$ (1.9 mmol/10 ml) and the transition metal salts (1.3 mmol/10 ml) precipitation

---

* Corresponding author. Tel.: +1 517 355 9715; fax: +1 517 353 1793.
*E-mail addresses:* ptrikal@chemistry.uoc.gr (P.N. Trikalitis), kanatzid@cem.msu.edu (M.G. Kanatzidis).

[1] Present address: Department of Chemistry, University of Crete, Heraklion 71409, Greece.

1387-1811/$ - see front matter © 2005 Elsevier Inc. All rights reserved.
doi:10.1016/j.micromeso.2005.09.004

of a black ($Co^{2+}$) or dark brown ($Ni^{2+}$) solid occurred immediately. The mixtures were aged overnight at 80 °C, filtered, washed with warm FM, and dried under vacuum. These phases are denoted as $C_n$PyMMoS (M = Co, Ni). We also performed reactions that included the addition of $S^{2-}$ anions in order to observe if this extra building block could impart better ordering on the mesostructures. The experimental procedure for making these $C_n$PyMMoS/$S^{2-}$ phases was the same as outlined above using molar quantities of $Co^{2+}/(Ni^{2+}):MoS_4^{2-}:S^{2-}$ 1:1:1. The $S^{2-}$ (as $K_2S$/FM) was added to the surfactant solution prior to the other precursors.

The elemental and C, H, N analysis results coupled with thermal gravimetric analyses (TGA) gave the chemical formulae $[C_nPy]_{2-2x}M_xMoS_4$ ($0.64 < x < 0.70$), and $[C_nPy]_{2x}MMoS_{4+x}$ ($0.91 < x < 1.05$) for the mesophases phases with $K_2S$ added. This suggests that the materials contain anionic M–Mo–S frameworks charge balanced by surfactant cations.

Powder X-ray diffraction (XRD) patterns of all phases exhibit a strong reflection in the low angle region $2° < 2\theta < 4°$ (similar to other mesostructured sulfides), with *d*-spacing indicative of an uniform pore–pore separation in the material. Fig. 1 shows the typical patterns from the $C_{18}$PyMMoS (M = Co, Ni) phases. The presence of a broad and weak higher order harmonic is visible in the $4° < 2\theta < 6°$ region of the diffraction patterns suggesting lamellar ordering or regions of short range ordering of pores in a otherwise wormhole-type arrangement within the mesostructures [13]. The more narrow reflection of the $C_{18}$PyNiMoS/$S^{2-}$ phase (Fig. 1b) suggests the formation of a material with a longer coherence length when $K_2S$ is added. In contrast the cobalt phases are not as well ordered as their nickel counterparts as indicated by the broader first peaks in the diffraction pattern (Fig. 1c). As in all mesostructured materials reported todate the inorganic framework walls are amorphous as indicated by the lack of Bragg peaks at high angles (>10°) of the powder pattern. Furthermore, no crystalline binary Co(Ni) sulfides were present in these materials.

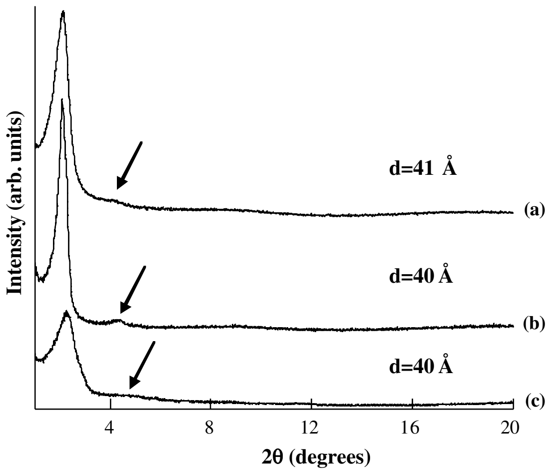

Fig. 1. X-ray diffraction patterns of (a) $C_{18}$PyNiMoS, (b) $C_{18}$PyNiMoS/$S^{2-}$, and (c) $C_{18}$PyCoMoS/$S^{2-}$.

The pore–pore separation represented by the *d*-spacing of the low angle Bragg peak is readily adjustable and increases with increasing surfactant chain length. Fig. 2 shows the XRD patterns of $C_n$PyNiMoS ($n = 16$, 18 and 20) solids where the pore distance increases with chain length in the range 37.9–43.1 Å.

Comparison of the differential scanning calorimetry (DSC) results for the $C_{18}$PyBr surfactant and the mesophased $C_{18}$NiMoS material (Fig. 3) show that for the latter there are no thermal events in the region of the surfactant melting transition (~72 °C) that are typically observed in lamellar phases [14]. This is attributed to the lack of conformational changes or rearrangement of the long surfactant alkyl chains and is due to their confinement in an interconnecting three-dimensional M–Mo–S (M = Co, Ni) environment that hinders this motion. This suggests that the mesophases have a three-dimensional inorganic framework creating a rigid wormhole-like pore structure.

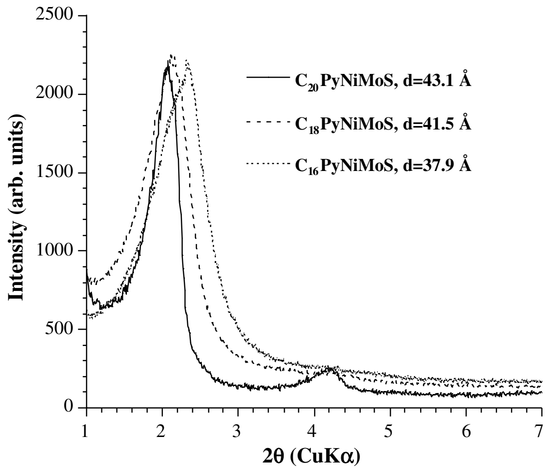

Fig. 2. X-ray diffraction patterns of $C_{16}$PyNiMoS, $C_{18}$PyNiMoS and $C_{20}$PyNiMoS materials.

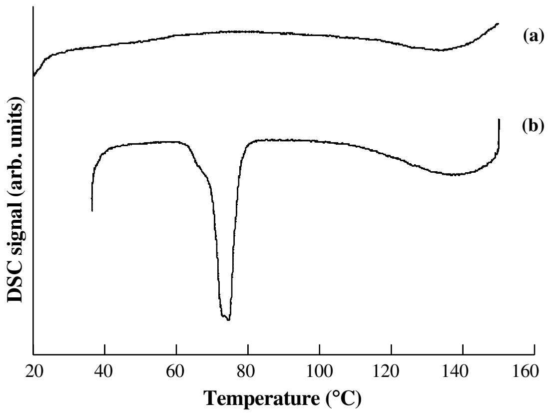

Fig. 3. Differential scanning calorimetric traces of (a) $C_{18}$PyNiMoS/$S^{2-}$ compared with that of (b) the $C_{18}$PyBr surfactant. Heating rate 5 °C/min.

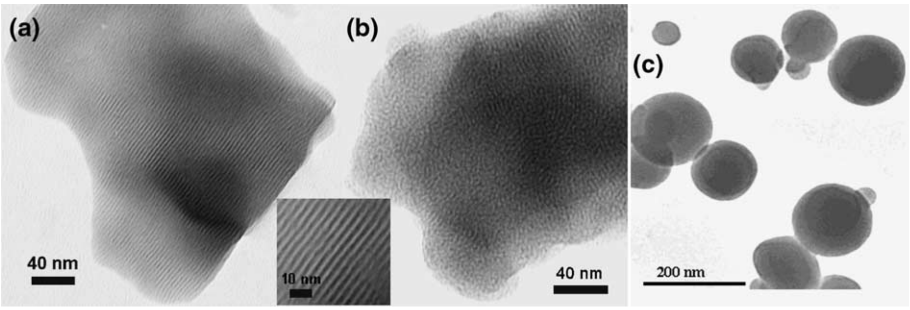

Fig. 4. Transmission electron micrographs of (a) $C_{20}PyNiMoS/S^{2-}$, (b) $C_{16}PyNiMoS/S^{2-}$, and (c) $C_{16}PyNiMoS/S^{2-}$ from $NiCl_2 \cdot 6H_2O$.

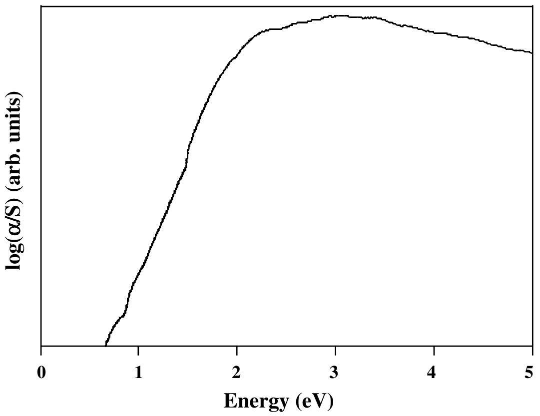

Fig. 5. Optical absorption spectrum of $C_{16}NiMoS$.

Similar phases have been identified in mesoporous silicas where the layers are stabilized by pillaring or electrostatic interactions [15].

Transmission electron microscopy (TEM) images demonstrate that $C_{20}PyNiMoS/S^{2-}$ (Fig. 4a) shows lamellar-like morphology. The long straight parallel lines clearly shown in the inset of Fig. 4 are characteristic and typical of a lamellar structure. The wall–wall spacing measured from the micrographs is in good agreement with those obtained from the X-ray diffraction data. In contrast, the TEM image of the $C_{16}PyNiMoS/S^{2-}$ phase (Fig. 4b) exhibits local lamellar or wormhole order. Remarkably, in the case of $C_{16}PyNiMoS$ made from the $NiCl_2 \cdot 6H_2O$ precursor, the particles are spherical in shape and are dispersed [16] with relatively narrow size distribution (see Fig. 4c), while in all other samples the particle morphology was nondescript. The spheres are essentially transparent in the TEM micrographs suggesting that they do not consist of hard cores of inorganic material, but rather are hollow with the mesophase encompassing them. Scanning electron micrographs of the material also demonstrate the spherical shape of the particles, and show that all remain totally intact without any defects to allow observation of the interior of the spheres.

Optical absorption spectroscopy of the mesostructured sulfides show well-defined energy gaps of 0.5 eV $C_{16}CoMoS$ and 0.8 eV for $C_{16}NiMoS$ (Fig. 5) respectively, indicating that these are narrow gap semiconductors. The thermal stability was investigated with thermogravimetric analysis (TGA). The compounds shows no appreciable weight loss up to 200 °C, consistent with the fact that solvent molecules are not present. Between 200 and 450 °C, weight loss occurs due to surfactant decomposition. The X-ray powder diffraction pattern of the product taken after thermal decomposition at 450 °C do not show any Bragg peak indicating the collapse of the mesostructured framework and the formation of an amorphous solid. At 700 °C the corresponding XRD pattern shows the presence of few broad and weak reflections at $2\theta > 30°$ characteristic of totally exfoliated $MoS_2$ phase [17].

The $C_nPyMMoS$ (M = Co, Ni) materials are the first solids composed of same ingredients that define the most active industrial HDS catalysts to have mesostructural order. Future work will focus on exploring the ion-exchange properties and pore accessibility of these systems as well as their possible utility as catalytic HDS agents.

## Acknowledgement

Financial support from the National Science Foundation CHE-0211029, is gratefully acknowledged.

## References

[1] H. Topsøe, B.S. Clausen, F.E. Massoth, in: J.R. Anderson, M. Boudard (Eds.), Catalysis—Science and Technology, vol. 11, Springer, Berlin, 1996.
[2] R. Prins, V.H.J. Debeer, G.A. Somorjai, Catal. Rev.—Sci. Eng. 31 (1989) 1.
[3] N.A. Dhas, A. Ekhtiarzadeh, K.S. Suslick, J. Am. Chem. Soc. 123 (2001) 8310.
[4] Y. Okamoto, S.Y. Ishihara, M. Kawano, M. Satoh, T. Kubota, J. Catal. 217 (2003) 12.
[5] K.A. Carrado, C.L. Marshall, J.R. Brenner, K. Song, Micropor. Mesopor. Mater. 20 (1998) 17.
[6] T.A. Zepeda, J.L.G. Fierro, B. Pawelec, R. Nava, T. Klimova, G.A. Fuentes, T. Halachev, Chem. Mater. 17 (2005) 4062.
[7] C. Song, Catal. Today 77 (2002) 17.
[8] Shyamal K. Bej, Samir K. Maity, Uday T. Turaga, Energy Fuels 18 (2004) 1227.
[9] K. Segawa, K. Takahashi, S. Satoh, Catal. Today 63 (2000) 123.
[10] P.N. Trikalitis, K.K. Rangan, T. Bakas, M.G. Kanatzidis, J. Am. Chem. Soc. 124 (2002) 12255.
[11] P.N. Trikalitis, K.K. Rangan, M.G. Kanatzidis, J. Am. Chem. Soc. 124 (2002) 2604.

[12] P.N. Trikalitis, K.K. Rangan, T. Bakas, M.G. Kanatzidis, Nature 410 (2001) 671.

[13] T.R. Pauly, Y. Liu, T.J. Pinnavaia, J.L. Billinge, T.P. Rieker, J. Am. Chem. Soc. 121 (1999) 8835.

[14] (a) F. Bonhomme, M.G. Kanatzidis, Chem. Mater. 10 (1998) 1153;
(b) M. Wachhold, M.G. Kanatzidis, Chem. Mater. 12 (2000) 2914;
(c) M. Wachhold, K.K. Rangan, M. Lei, M.F. Thorpe, S.J.L. Billinge, V. Petkov, J. Heising, M.G. Kanatzidis, J. Solid State Chem. 152 (2000) 21.

[15] (a) J.-O. Barth, J. Kornatowski, J.A. Lercher, J. Mater. Chem. 12 (2002) 369;
(b) Y.J. He, G.S. Nivarthy, F. Eder, K. Seshan, J.A. Lercher, Micropor. Mesopor. Mater. 25 (1998) 207.

[16] (a) R.I. Nooney, D. Thirunavukkarasu, Y.M. Chen, R. Josephs, A.E. Ostafin, Chem. Mater. 14 (2002) 4721;
(b) J.L. Blin, A. Leonard, B.L. Su, Chem. Mater. 13 (2001) 3542;
(c) B. Pauwels, G. Van Tendeloo, C. Thoelen, W. Van Rhijn, P.A. Jacobs, Adv. Mater. 13 (2001) 1317;
(d) M. Grun, K.K. Unger, A. Matsumoto, K. Tsutsumi, Micropor. Mesopor. Mater. 27 (1999) 207.

[17] P. Afanasiev, G.F. Xia, G. Berhault, B. Jouguet, M. Lacroix, Chem. Mater. 11 (1999) 3216.