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Porous MoS_2 Synthesized by Ultrasonic Spray Pyrolysis

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The catalytic removal of oxygen, nitrogen, and sulfur from organic molecules is an important step in petroleum processing.[1] A recent EPA mandate[2] requires a further reduction of such heteroatoms from petroleum, making improved hydrotreating catalysts essential. Specifically, more efficient catalysts for the hydrodesulfurization (HDS) of refractory thiophene-based compounds and residual fuel fractions are urgently needed.[3] To address this, both supported[4] and unsupported[5] catalysts of different chemical compositions have been prepared by a variety of synthetic techniques. Here, ultrasonic spray pyrolysis[6] (USP) has been used to synthesize porous, nanostructured MoS_2, a typical HDS material. Unless modified,[7] USP produces low surface area powders, undesirable for catalysis. The technique described herein provides a general aerosol route to high surface area materials. We find that the highly porous MoS_2 so produced has exceptionally high HDS activity.

Porous MoS_2 was prepared by USP using colloidal silica as a sacrificial template, with $(NH_4)_2MoS_4$[8] as a MoS_2 precursor. The precursor solution is ultrasonically nebulized into microdroplets,[9] which are carried by a gas flow into a furnace where solvent evaporation and precursor decomposition occurs, producing a SiO_2/MoS_2 composite. Material is collected and treated with HF, leaving a MoS_2 network, whose porosity and surface area can be controlled by changing the size and concentration of the template.

For comparison, conventional MoS_2 and nontemplated USP MoS_2 were prepared by thermal decomposition of $(NH_4)_2MoS_4$. SEMs[10] of the conventional layered, platelike MoS_2 (Figure 1A) contrast dramatically with the porous networks of the templated USP MoS_2 (Figure 1C,D). TEMs of the USP product before and after leaching are shown in Figure 1E,F. Before leaching, both colloidal SiO_2 and MoS_2 can be seen, and the SiO_2 and MoS_2 are woven within each other. This suggests MoS_2 formation occurs within the crevices created as the SiO_2 spheres compact during solvent evaporation. After HF leaching, the MoS_2 is network-like, but retains the lattice fringes of the MoS_2 interlayer spacings (0.42 $\pm$ 0.01 nm, Figure 1F), similar to that of conventional MoS_2.

The XRD patterns of heat-treated USP and conventional MoS_2 samples showed four broad peaks with *d* spacings of 6.4, 2.7, 1.6, and 1.2 Å, corresponding to the {002}, {100}, {103}, and {110} reflections, respectively, of poorly crystalline, nanostructured 2H−MoS_2.[10] The average *c*-stacking height, calculated from the {002} reflection, was 37 Å for conventional MoS_2 and 35 Å for nontemplated USP MoS_2, but only 25 Å for 20 nm silica-templated MoS_2. When larger diameter SiO_2 templates are used, the *c*-stacking increases to that of conventional MoS_2.

The electronic states of Mo and S in the heat-treated USP MoS_2 samples were determined by X-ray photoelectron spectroscopy (XPS), which showed spin-coupled Mo($3d_{5/2}$, $3d_{3/2}$) and S($2p_{3/2}$, $2p_{1/2}$) doublets at the binding energies of conventional MoS_2.[10] Analysis of the Mo(3d) and S(2p) peak intensities gave a S/Mo atomic ratio slightly less than 2 for all samples.

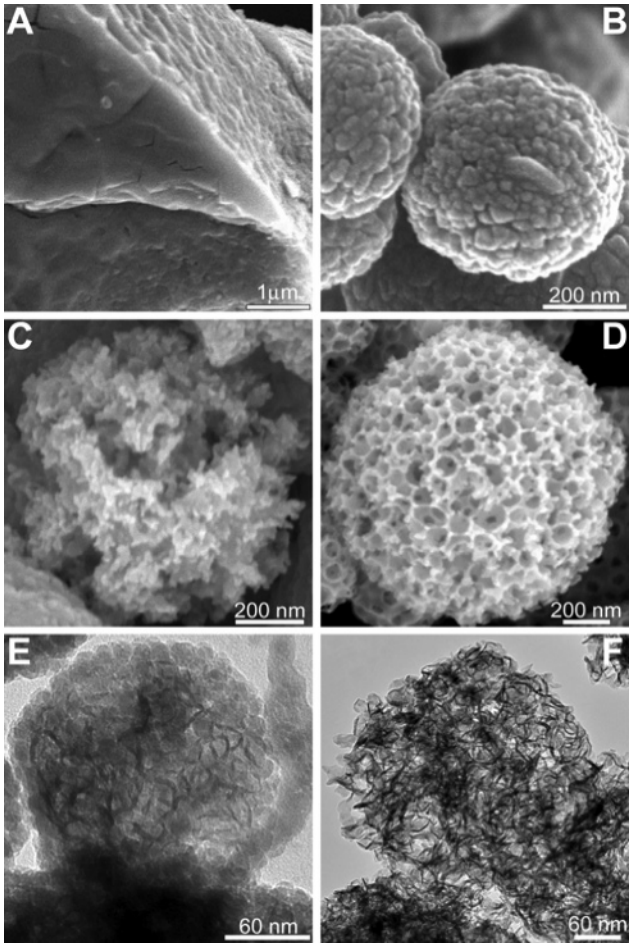

Figure 1. Electron micrographs of conventional and USP-derived MoS_2. (A) SEM of conventional MoS_2. (B) SEM of USP MoS_2 without templating material. (C) SEM of 20 nm silica-templated USP MoS_2, after leaching of the colloidal silica. (D) SEM of 80 nm silica-templated USP MoS_2, after leaching of the colloidal silica. (E) TEM of USP SiO_2/MoS_2 composite (prior to leaching, 20 nm SiO_2 template). (F) TEM of 20 nm silica-templated USP MoS_2, after leaching of the colloidal silica.

Figure 2 shows complete N_2 adsorption−desorption isotherms for several USP preparations and, for comparison, conventional MoS_2 with total surface areas, determined by BET analysis.[10] Without templating, low surface area MoS_2 is obtained (20−40 m^2/g) by USP, which is comparable to conventional preparations; however, with templating, the surface area can be controlled and substantially enhanced. In fact, when 20 nm SiO_2 is used as a template, the USP MoS_2 has a surface area comparable to that of a commercial catalyst support (e.g., Crosfield 465 1:20 Co−Mo on γ-alumina is 210 m^2/g), but the MoS_2 itself is acting as the dispersion phase rather than a separate support material. The USP products display no plateau region in the N_2 isotherms; this, in

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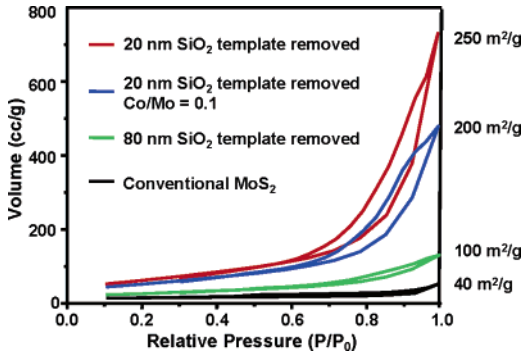

Figure 2. N_2 adsorption−desorption isotherms for various catalysts and corresponding BET surface areas.

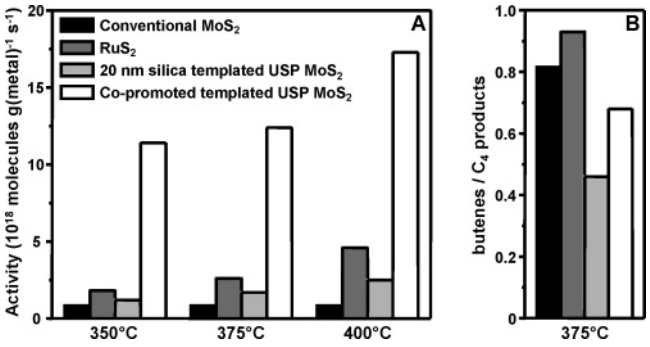

Figure 3. (A) Catalytic activities of various catalysts for thiophene HDS as a function of temperature after 12 h of catalysis, which is necessary to reach steady-state activity for these catalysts; initial rates show larger temperature differences, as expected. (B) Fraction of butenes in C_4 hydrocarbon product mixture observed during thiophene HDS at 375 °C.

conjunction with the high surface area, is characteristic of both micro- and macroporosity.[11] Such a combination is potentially ideal for the HDS of fuel residua.

The catalytic activity of thiophene HDS for the heat-treated USP MoS_2 samples was examined with a single-pass microreactor at 1 atm (Figure 3).[12] Of the USP samples, the 20 nm silica-templated MoS_2 obtained the greatest HDS activities.[13] Additionally, cobalt-promoted USP MoS_2 samples were prepared by salt impregnation;[14] maximum activity was achieved with a Co/Mo ratio of 0.1. At higher Co/Mo ratios, a decrease in catalytic activity and the formation of a separate cobalt sulfide phase, Co_9S_8, were observed. These samples were compared to conventional catalysts of MoS_2 and RuS_2 (60 m^2/g); RuS_2 is the most intrinsically active metal sulfide for HDS, but too expensive to be used industrially.[15] The results are shown in Figure 3A; catalyst activities are reported on a per gram of metal basis because HDS activity of MoS_2 does *not* scale with total surface area due to the different reactivity of edge and basal planes and Co promotion of edge sites.[16] The nonpromoted templated USP MoS_2 was more active than conventional MoS_2 and is attributed to the enhanced dispersion of the HDS active phase achieved by this technique. Upon cobalt incorporation, the activity of the USP MoS_2 is well above that even of RuS_2.

Figure 3B shows the mole fraction of butenes in the total product mixture of C_4 hydrocarbons at 375 °C. No butadiene or tetrahydrothiophene were observed. The nonpromoted USP MoS_2 had an increased percent butane compared to that of conventional MoS_2, reflecting the higher activity of USP MoS_2. The selectivity for butenes increased upon cobalt incorporation, as expected.[17]

In summary, a high surface area MoS_2 network can be synthesized by USP by using a sacrificial colloidal silica template. The resulting highly porous MoS_2 network has higher thiophene HDS activity than that of conventional MoS_2 and when promoted with cobalt, higher even than RuS_2. By controlling the template size and concentration, a unique micro- and macroporous form of MoS_2 can be prepared that may provide enhanced diffusion rates and decreased residence times, requirements for improved HDS catalysts.

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Supporting Information Available: Additional electron micrographs, XPS spectra, and XRD data. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Furimsky, E. *Appl. Catal. A* **1998**, *171*, 177−206. (b) Grange, P. *Catal. Rev. Sci. Eng.* **1980**, *21*, 135−181.
(2) *Federal Register*, August 4 2002, *65* (151), 48057−48105.
(3) (a) Raseev, S. *Thermal and Catalytic Processes in Petroleum Refining*; Suciu, G. D., Ed.; Marcel Dekker: New York, 2003. (b) Speight, J. G. *The Desulfurization of Heavy Oils and Residua*, 2nd ed.; Heinemann, H., Ed.; Chemical Industries; Marcel Dekker: New York, 2000.
(4) (a) Dhas, N. R.; Ekhtiarzadeh, A.; Suslick, K. S. *J. Am. Chem. Soc.* **2001**, *123*, 8310−8316. (b) Zdrazil, M. *Catal. Today* **1988**, 3, 269−361.
(5) (a) Mdeleni, M. M.; Hyeon, T.; Suslick, K. S. *J. Am. Chem. Soc.* **1998**, *120*, 6189−6190. (b) Afanasiev, P.; Xia, G. F.; Gilles, B.; Jouguet, B.; Lacroix, M. *Chem. Mater.* **1999**, *11*, 3216−3219.
(6) (a) Messing, G. L.; Zhang, S. C.; Jayanthi G. V. *J. Am. Ceram. Soc.* **1993**, *76*, 2707−2726. (b) Patil, P. S. *Mater. Chem. Phys.* **1999**, *59*, 185−198. (c) Kodas, T. T.; Hampden-Smith, M. *Aerosol Processing of Materials*; Wiley-VCH: New York, 1999. (d) Okuyama, K.; Lenggoro, I. W. *Chem. Eng. Sci.* **2003**, *58*, 537−547. (e) Tsai, S. C.; Long, Y. L.; Tsai, C. S.; Yang, C. C.; Chiu, W. Y.; Lin, H. M. *J. Mater. Sci.* **2004**, *39*, 3647−3657.
(7) (a) Iskandar, F.; Mikrajuddin; Okuyama, K. *Nano Lett.* **2002**, *2*, 389−392. (b) Xia, B.; Lenggoro, W.; Okuyama, K. *Adv. Mater.* **2001**, *13*, 1579−1582. (c) Iskandar, F.; Mikrajuddin; Okuyama, K. *Nano Lett.* **2001**, *1*, 231−234.
(8) (a) Berntsen, N.; Gutjahr, T.; Loeffler, L.; Gomm, J. R.; Seshadri, R.; Tremel, W. *Chem. Mater.* **2003**, *15*, 4498−4502. (b) Vasudevan, P. T.; Zhang, F. *Appl. Catal. A* **1994**, *112*, 161−173.
(9) In a typical synthesis, a 0.04 M $(NH_4)_2MoS_4$ aq. solution containing colloidal SiO_2 (e.g., 5-fold molar excess 20 nm LUDOX HS-40 or 80 nm SNOWTEX-ZL) was nebulized using a *Sunbeam* Ultrasonic Humidifier (2.7 MHz), carried in an Ar flow (2 cfh) through a furnace (700 °C) and collected in bubblers. No $(NH_4)_2MoS_4$ decomposition is observed in the atomization cell. SiO_2 was leached with 10% HF in C_2H_5OH for 24 h, confirmed by e.a. and EDS. Samples were treated with 5% H_2S/45% H_2/50% He (30 cm^3/min) at 450 °C for 12 h. E.A. shows nearly stoichiometric MoS_2 with trace (<2 wt %) carbon and oxygen.
(10) Hitachi S-4700 SEM with Oxford INCA EDS; Philips CM-12 TEM; Rigaku D-MAX diffractometer; Physical Electronics PHI 5400 XPS; Quantachrome Instruments Nova 2200e Surface Area and Pore Analyzer.
(11) Gregg, S. J.; Sing, K. S. *Adsorption, Surface Area, and Porosity*; Academic Press: New York, 1967.
(12) Thiophene vapor at 56.25 Torr in H_2 flow (27.5 cm^3(STP)/min). Analysis by GC−MS with a 30 m carbon PLOT column.
(13) MoS_2 prepared by USP without a template and with 80 nm silica template (after leaching of the silica) shows thiophene HDS activities at 350 °C of 0.4 and 1.6 × 10^{18} molecules $g(metal)^{-1}$ s^{-1}, respectively.
(14) $Co(NO_3)_3 \cdot 6H_2O$ dissolved in acetone was added in the appropriate stoichiometry to the solid catalyst, which was then dried and heat treated.
(15) Pecoraro, T. A.; Chianelli, R. R. *J. Catal.* **1981**, *67*, 430−445.
(16) (a) Tauster, S. J.; Pecoraro, T. A.; Chianelli, R. R. *J. Catal.* **1980**, *63*, 515−519. (b) Chianelli, R. R.; Daage, M. *J. Catal.* **1994**, *149*, 414−427. (c) Topsøe, H. *J. Catal.* **2003**, *216*, 155−164. (c) Inamura, K.; Prins. R. *J. Catal.* **1994**, *147*, 515−524.
(17) Hatanaka, S.; Yamada, M.; Sadakane, O. *Ind. Eng. Chem. Res.* **1997**, *36*, 5110−5117.

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