

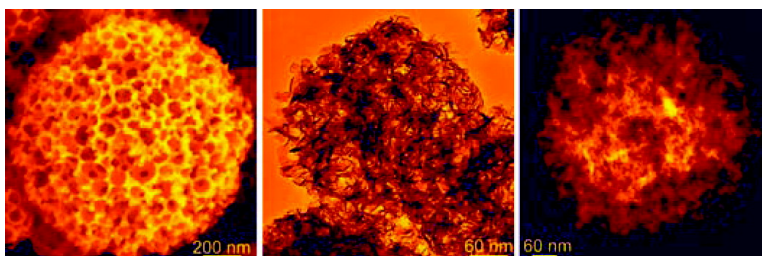
Communication

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J. Am. Chem. Soc., **2005**, 127 (28), 9990-9991 • DOI: 10.1021/ja051654g • Publication Date (Web): 25 June 2005

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Porous MoS₂ 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 mandate² 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 supported⁴ and unsupported⁵ catalysts of different chemical compositions have been prepared by a variety of synthetic techniques. Here, ultrasonic spray pyrolysis⁶ (USP) has been used to synthesize porous, nanostructured MoS₂, 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 MoS₂ so produced has exceptionally high HDS activity.

Porous MoS₂ was prepared by USP using colloidal silica as a sacrificial template, with (NH₄)₂MoS₄⁸ as a MoS₂ 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 SiO₂/MoS₂ composite. Material is collected and treated with HF, leaving a MoS₂ network, whose porosity and surface area can be controlled by changing the size and concentration of the template.

For comparison, conventional MoS₂ and nontemplated USP MoS₂ were prepared by thermal decomposition of (NH₄)₂MoS₄. SEMs¹⁰ of the conventional layered, platelike MoS₂ (Figure 1A) contrast dramatically with the porous networks of the templated USP MoS₂ (Figure 1C,D). TEMs of the USP product before and after leaching are shown in Figure 1E,F. Before leaching, both colloidal SiO₂ and MoS₂ can be seen, and the SiO₂ and MoS₂ are woven within each other. This suggests MoS₂ formation occurs within the crevices created as the SiO₂ spheres compact during solvent evaporation. After HF leaching, the MoS₂ is network-like, but retains the lattice fringes of the MoS₂ interlayer spacings (0.42 ± 0.01 nm, Figure 1F), similar to that of conventional MoS₂.

The XRD patterns of heat-treated USP and conventional MoS₂ 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-MoS₂.¹⁰ The average *c*-stacking height, calculated from the {002} reflection, was 37 Å for conventional MoS₂ and 35 Å for nontemplated USP MoS₂, but only 25 Å for 20 nm silica-templated MoS₂. When larger diameter SiO₂ templates are used, the *c*-stacking increases to that of conventional MoS₂.

The electronic states of Mo and S in the heat-treated USP MoS₂ 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 MoS₂.¹⁰ Analysis of the Mo(3d) and S(2p) peak intensities gave a S/Mo atomic ratio slightly less than 2 for all samples.

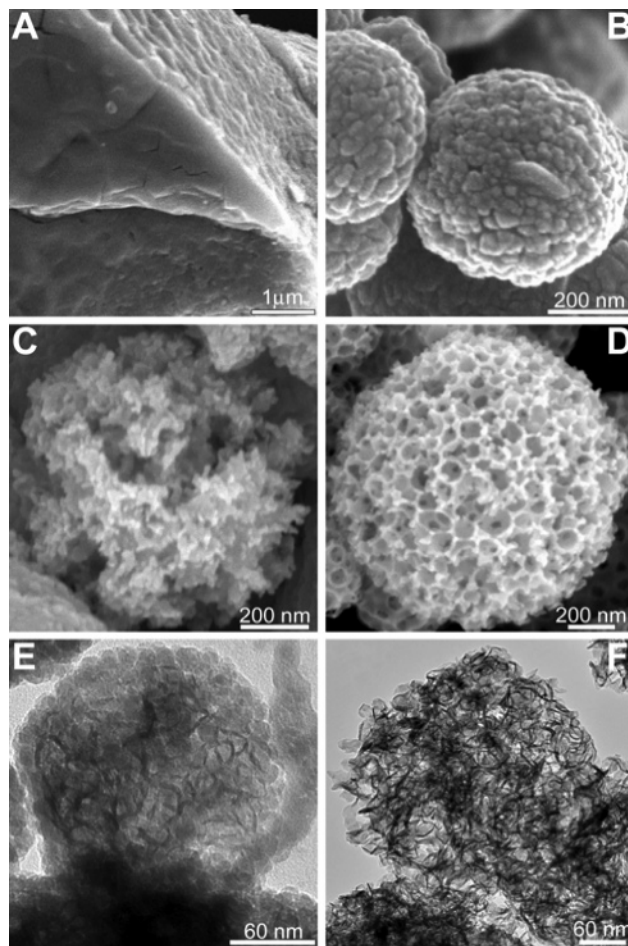


Figure 1. Electron micrographs of conventional and USP-derived MoS₂. (A) SEM of conventional MoS₂. (B) SEM of USP MoS₂ without templating material. (C) SEM of 20 nm silica-templated USP MoS₂, after leaching of the colloidal silica. (D) SEM of 80 nm silica-templated USP MoS₂, after leaching of the colloidal silica. (E) TEM of USP SiO₂/MoS₂ composite (prior to leaching, 20 nm SiO₂ template). (F) TEM of 20 nm silica-templated USP MoS₂, after leaching of the colloidal silica.

Figure 2 shows complete N₂ adsorption–desorption isotherms for several USP preparations and, for comparison, conventional MoS₂ with total surface areas, determined by BET analysis.¹⁰ Without templating, low surface area MoS₂ is obtained (20–40 m²/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 SiO₂ is used as a template, the USP MoS₂ 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 m²/g), but the MoS₂ itself is acting as the dispersion phase rather than a separate support material. The USP products display no plateau region in the N₂ isotherms; this, in

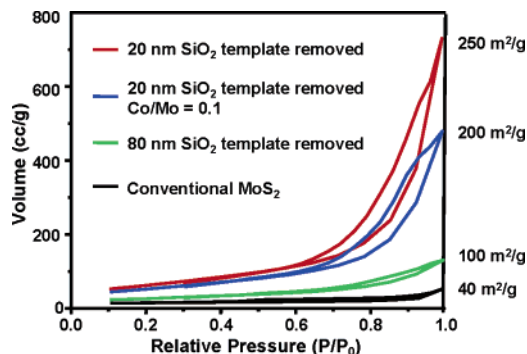


Figure 2. N₂ adsorption–desorption isotherms for various catalysts and corresponding BET surface areas.

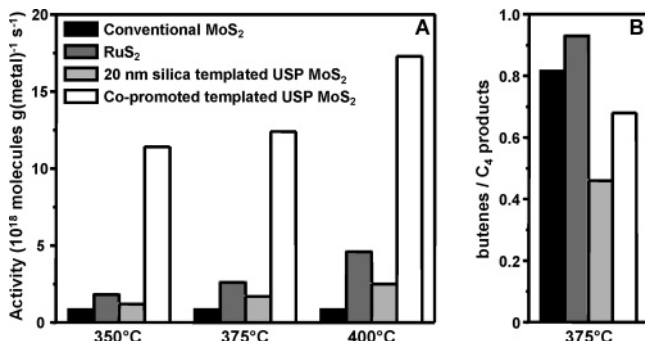


Figure 3. (A) Catalytic activities of various catalysts for thiophene HDS as a function of temperature after 12 h of catalysis, which is necessary to reach steady-state activity for these catalysts; initial rates show larger temperature differences, as expected. (B) Fraction of butenes in C₄ hydrocarbon 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 MoS₂ samples was examined with a single-pass microreactor at 1 atm (Figure 3).¹² Of the USP samples, the 20 nm silica-templated MoS₂ obtained the greatest HDS activities.¹³ Additionally, cobalt-promoted USP MoS₂ 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, Co₉S₈, were observed. These samples were compared to conventional catalysts of MoS₂ and RuS₂ (60 m²/g); RuS₂ 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 MoS₂ 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 MoS₂ was more active than conventional MoS₂ and is attributed to the enhanced dispersion of the HDS active phase achieved by this technique. Upon cobalt incorporation, the activity of the USP MoS₂ is well above that even of RuS₂.

Figure 3B shows the mole fraction of butenes in the total product mixture of C₄ hydrocarbons at 375 °C. No butadiene or tetrahydrothiophene were observed. The nonpromoted USP MoS₂ had an increased percent butane compared to that of conventional MoS₂, reflecting the higher activity of USP MoS₂. The selectivity for butenes increased upon cobalt incorporation, as expected.¹⁷

In summary, a high surface area MoS₂ network can be synthesized by USP by using a sacrificial colloidal silica template. The resulting highly porous MoS₂ network has higher thiophene HDS activity than that of conventional MoS₂ and when promoted with cobalt, higher even than RuS₂. By controlling the template size and concentration, a unique micro- and macroporous form of MoS₂ can be prepared that may provide enhanced diffusion rates and decreased residence times, requirements for improved HDS catalysts.

Acknowledgment. We thank Dr. Y. Didenko for helpful advice. These studies were supported by the NSF (CHE0315494). Microscopic analysis, XRD, and XPS were carried out in the Center for Microanalysis of Materials, University of Illinois, which is partially supported by the U.S. Department of Energy under Grant DEFG02-91-ER45439.

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>.

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- (9) In a typical synthesis, a 0.04 M (NH₄)₂MoS₄ aq. solution containing colloidal SiO₂ (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 (NH₄)₂MoS₄ decomposition is observed in the atomization cell. SiO₂ was leached with 10% HF in C₂H₅OH for 24 h, confirmed by e.a. and EDS. Samples were treated with 5% H₂S/45% H₂/50% He (30 cm³/min) at 450 °C for 12 h. E.A. shows nearly stoichiometric MoS₂ 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.
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- (12) Thiophene vapor at 56.25 Torr in H₂ flow (27.5 cm³(STP)/min). Analysis by GC–MS with a 30 m carbon PLOT column.
- (13) MoS₂ 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 × 10¹⁸ molecules g(metal)⁻¹ s⁻¹, respectively.
- (14) Co(NO₃)₂·6H₂O dissolved in acetone was added in the appropriate stoichiometry to the solid catalyst, which was then dried and heat treated.
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JA051654G