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Sonochemical Synthesis of Nanostructured Molybdenum Sulfide

Millan M. Mdleleni, Taeghwan Hyeon, and
Kenneth S. Suslick*

School of Chemical Sciences
University of Illinois at Urbana-Champaign
601 South Goodwin Avenue, Urbana, Illinois 61801

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There is growing interest in nanostructured inorganic materials, in large part because they often exhibit properties distinct from those of the bulk that can prove useful in various applications, including heterogeneous catalysis.[1−4] The established methods for the preparation of nanostructured inorganic materials include metal evaporation,[5] reduction of metal salts,[6,7] and thermal decomposition and laser pyrolysis of organometallic compounds.[8,9] In addition, the sonochemical reaction of volatile organometallics is a recent and general synthetic approach to nanophase transition metal powders, alloys, carbides, and colloids.[10−13] We report here a simple sonochemical synthesis of nanophase, high-surface-area molybdenum sulfide and the examination of its catalytic activity for thiophene hydrodesulfurization (HDS).

MoS_2 was prepared by irradiating a slurry of molybdenum hexacarbonyl and sulfur in 1,2,3,5-tetramethylbenzene (isodurene) with high-intensity ultrasound (20 kHz) under Ar.[14a] Elemental analysis of the purified powder indicates a stoichiometric molybdenum sulfide (S/Mo atomic ratio of 2.0) with a trace amount (<2 wt %) of carbon contamination. For comparison, a conventional molybdenum sulfide sample was also prepared by thermally decomposing ammonium tetrathiomolybdate (Aldrich) under helium.[14b] Surface areas of the thermally treated sonochemical and conventional MoS_2 were 55 and 32 m^2/g, respectively, as determined by Brunauer−Emmett−Teller (BET) N_2 adsorption isotherms.

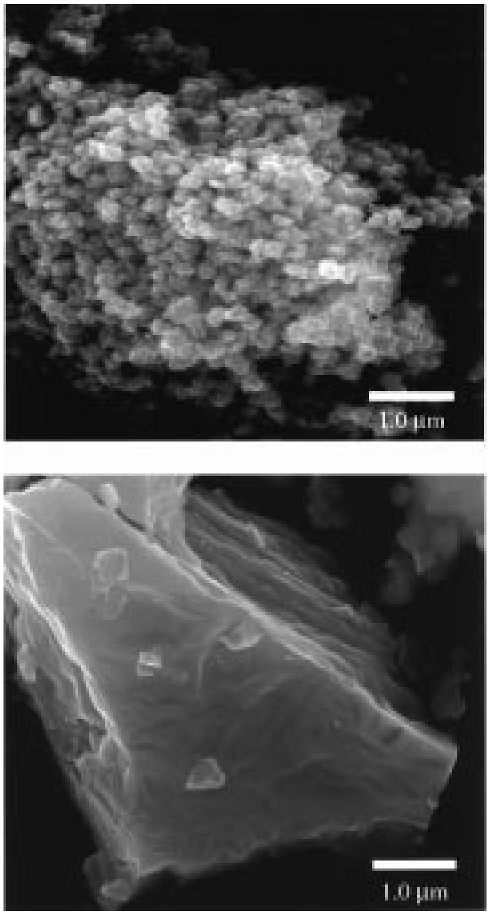

Figure 1. SEM micrographs of (a, top) sonochemical and (b, bottom) conventional preparations of MoS_2.

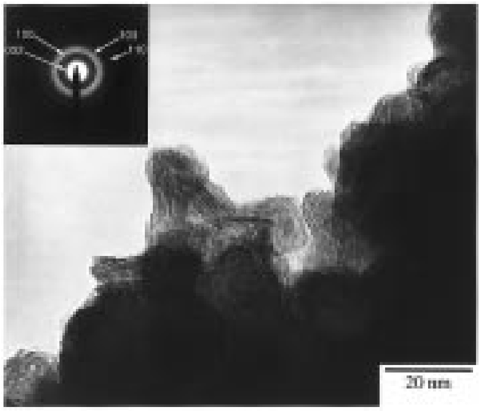

Figure 2. TEM micrographs of sonochemically prepared MoS_2. Basal planes are seen as dark fringes with interlayer spacings of 0.62 ± 0.01 nm, the same as those for conventional MoS_2.

The X-ray diffraction (XRD)[15] pattern of the initial amorphous powder sonochemically prepared shows ill-defined, extremely

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(14) In a typical preparation, a slurry of molybdenum hexacarbonyl (2.5 g, 9.5 mmol) and sulfur (0.75 g, 23 mmol) in 35 mL of 1,2,3,5-tetramethylbenzene was irradiated with high-intensity ultrasound (20 kHz, ≈80 W/cm^2, 1 cm^2 titanium horn; Sonics & Materials VCX600) for 1.5 h at 80 °C under Ar. The resulting black powder (yield: 0.6 g, 40% theoretical; longer sonication increases yield but also C contamination) was filtered and washed several times with degassed, distilled pentane inside an Ar-filled glovebox (Vacuum Atmospheres, <0.5 ppm O_2). The washed powder was then heated at 80 °C for 3 h under vacuum to remove any unreacted molybdenum hexacarbonyl. Any excess sulfur was removed by heating the amorphous product at 450 °C for 10 h under He flow (30 cm^3/min), which also leads to crystallization of the initially amorphous MoS_2. (b) Prasad, T. P.; Diemann, E.; Müller, A. *J. Inorg. Nucl. Chem.* **1973**, *35*, 1895.

(15) XRD: Rigaku D-max diffractometer using Cu Kα radiation. SEM: Hitachi S800. TEM: Philips CM-12. PES: Phi-540 spectrometer using Mg Kα radiation.

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broad peaks. After thermal treatment under He, however, the MoS_2 exhibits sharper peaks with corresponding *d* spacings of 6.30, 2.68, 1.57, and 1.22 Å corresponding to the {002}, {100}, {103}, and {110} reflections of hexagonal MoS_2 (6.16, 2.67, 1.58, and 1.22 Å), respectively.[16] An average crystallite size of ~1.6 nm was estimated from the {002} peak width.[17]

Scanning electron micrographs of sonochemically and conventionally prepared MoS_2 are shown in Figure 1. The sonochemical MoS_2 exists as a porous agglomeration of clusters of spherical particles with an average diameter of 15 nm, which are themselves aggregates of smaller particles. Energy dispersive X-ray (EDX) analysis performed on these particles gave a S/Mo atomic ratio of 2.06, identical within experimental error to that from bulk chemical analysis. In contrast, the conventional MoS_2 shows a platelike morphology typical for such layered materials. Despite the morphological difference between the sonochemical and conventional MoS_2, the transmission electron microscopy (TEM) images (Figure 2) of these sulfides both show lattice fringes with interlayer spacings of 0.62 ± 0.01 nm, the same as those for conventional MoS_2.[18] The sonochemically prepared MoS_2, however, shows much greater edge and defect content, as the layers must bend, break, or otherwise distort to fit the outer surface of the 15-nm particle size (Figure 2).

The electronic states of Mo and S in the sonochemically prepared MoS_2 were determined by X-ray photoelectron spectroscopy (XPS), which showed well-defined spin-coupled Mo($3d_{5/2}$, $3d_{3/2}$) and S($2p_{3/2}$, $2p_{1/2}$) doublets at binding energies[19] the same as that for conventional MoS_2.[20] Analysis of the Mo(3d) and S(2p) peak intensities (corrected with sensitivity factors based on Scofield cross sections)[21] gave a S/Mo atomic ratio of 2.03, in agreement with the EDX and chemical analysis results.

Molybdenum sulfide is an excellent high-temperature lubricant, but more importantly, it is also the predominant HDS catalyst.[22] It is well established that the activity of MoS_2 is localized at the edges and not on the flat basal planes.[22] Given the inherently higher edge concentrations in nanostructured materials, the catalytic properties of our sonochemically prepared MoS_2 become especially interesting. To this end, the catalytic activity and selectivity for thiophene HDS by sonochemically prepared MoS_2 was examined in a single-pass microreactor.[23] Conventional MoS_2, sonochemical Mo_2C, commercial ReS_2 (Gallard-Schlesinger Ind., Carle Place, NY), and RuS_2 (Gallard-Schlesinger) were also investigated under the same conditions for comparison. For conventionally prepared sulfides, ReS_2 and RuS_2 are inherently more reactive than MoS_2[24] but are too expensive to be generally used. Given the difference in edge versus basal surface activity, catalytic activity does not correlate with total surface area[24] and therefore comparisons must be made on a catalyst mass basis.

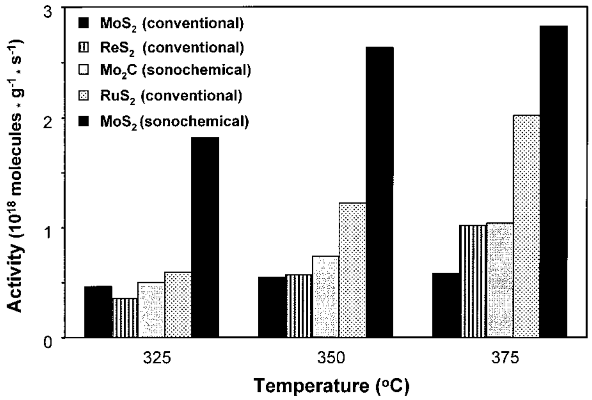

Figure 3. Catalytic activities of various catalysts in thiophene HDS as a function of temperature.

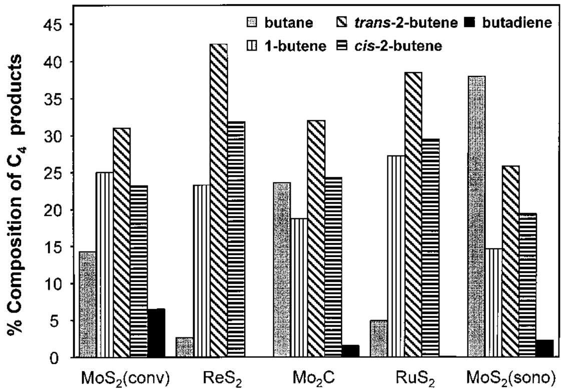

Figure 4. Distribution of C_4 hydrocarbon products observed during thiophene HDS with various catalysts at 375 °C.

The observed turnover frequencies as a function of temperature for these catalysts are shown in Figure 3. The principal products detected by GC were the C_4 hydrocarbons butadiene, 1-butene, *trans*-2-butene, *cis*-2-butene, and butane. No partially hydrogenated thiophenes were detected, and lighter (C_1−C_3) hydrocarbons accounted for less than 1% of the reaction products. The observed HDS activity order is MoS_2 (sonochemical) > RuS_2 (conventional) > ReS_2 (conventional) ~ Mo_2C (sonochemical[11]) > MoS_2 (conventional). Catalytic activity of the sonochemically prepared samples decreased initially somewhat (<50% over 20 h), so the activities reported here were measured *after* 20 h of use. The product selectivities, expressed as percent of total C_4 hydrocarbons, observed at 375 °C are shown in Figure 4. All of the catalyst studied show high selectivity for butenes with the exception of the sonochemical MoS_2, which gives more butane due to its higher activity. The accepted mechanism for thiophene HDS involves initial hydrogenolysis of the C−S bonds to give butadiene, followed by rapid hydrogenation to 1-butene, which is subsequently hydrogenated to butane or isomerized to a thermodynamic mixture of *cis*- and *trans*-2-butenes.[22,25]

In summary, high-surface-area nanostructured MoS_2 can be generated sonochemically from molybdenum hexacarbonyl and sulfur. It is morphologically distinct from its conventional counterpart and catalyzes thiophene HDS with higher activities than those of the most active materials. Further studies on the use of the sonochemically prepared MoS_2 as supported and Co- or Ni-promoted heterogeneous catalysts are underway.

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[19] For sonochemically prepared MoS_2: Mo($3d_{5/2}$) and Mo($3d_{3/2}$) at 228.5 and 232.16 eV, respectively; S(2s) at 226.16 eV, characteristic of S^{2-}; S($2p_{3/2}$) and S($2p_{1/2}$) at 161.65 and 162.82 eV, respectively.

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