Sonochemical Synthesis of Nanostructured Molybdenum Sulfide

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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,5,6 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).

MoS2 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 preparations of MoS2 were 55 and 32 m2/g, respectively, as determined by Brunauer–Emmett–Teller (BET) N2 adsorption isotherms.

The X-ray diffraction (XRD)15 pattern of the initial amorphous powder sonochemically prepared shows ill-defined, extremely thin planes are seen as dark fringes with interlayer spacings of 0.62 nm, the same as those for conventional MoS2
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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/cm2; 1 cm2 titanium horn; Sonics & Materials VCS600) 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 deagassed, distilled pentane inside an Ar-filled glovebox (Vacuum Atmospheres, <0.5 ppm O2). The washed powder was then heated at 80 °C for 3 h under vacuum to remove any untreated molybdenum hexacarbonyl. Any excess sulfur was removed by heating the amorphous product at 450 °C for 10 h under He flow (30 cm3/min), which also leads to crystallization of the initially amorphous MoS2. (b) Prasad, T. P.; Diemann, E.; Müller, A. J. Inorg. Nucl. Chem. 1973, 38, 1895.
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 \(\text{Å}\) corresponding to the {002}, {100}, {103}, and {110} reflections of hexagonal MoS\(_2\) (6.16, 2.67, 1.58, and 1.22 \(\text{Å}\)), 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 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 Mo3d\(_{5/2}\), Mo3d\(_{3/2}\), 3d\(_{x2-y2}\), and S2p\(_{3/2}\), 2p\(_{1/2}\) doublets at binding energies of 20.6, 19.6 eV, respectively,\(^{19}\) the same as that for conventional MoS\(_2\).\(^{20}\) Analysis of the Mo3d\(_{5/2}\) and S2p\(_{3/2}\) 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 MoCo, 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.

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) > MoCo (sonochemical) > 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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