

Sonochemically Prepared Nanostructured Amorphous Molybdenum Sulfide

Submitted by Annabeth Ryder and Kenneth Suslick

School of Chemical Sciences, University of Illinois at Urbana-Champaign

ABSTRACT

A sonochemical preparation of nanostructured amorphous molybdenum sulfide is described.^[1] A slurry of elemental sulfur and molybdenum hexacarbonyl in isodurene is irradiated with high-intensity ultrasound (20 kHz, $\sim 80 \text{ W/cm}^2$) under Ar, then filtered and washed with pentane to yield a black powder. This product is heated under vacuum to remove residual solvent and any unreacted precursor. Elemental analysis results indicate an atomic S:Mo ratio of 2.0, with carbon content less than 2 weight percent. X-ray powder diffraction and electron microscopy analysis reveal that the MoS₂ is amorphous and nanostructured.

CLASSIFICATION

form:	amorphous, nanostructured fine powder
function:	hydrodesulfurization catalyst, lubricant
preparation:	sonochemical synthesis
composition:	MoS ₂
extraordinary issues:	—

INTRODUCTION

Molybdenum sulfide is a layered material and the standard catalyst for industrial hydrodesulfurization (HDS) of petroleum and other fuel stocks.^[2] HDS catalysis by MoS₂, however, originates only from the exposed Mo atoms on the edges of the layers. A logical strategy to improve its catalytic activity would thus be to increase the relative amount of exposed edge sites. By making MoS₂ (i) nanostructured to increase surface area, and (ii) largely amorphous to decrease the length scale over which MoS₂ layers are ordered, this can be achieved. Sonochemically synthesized materials have been shown to exhibit both nanostructure and amorphous character;^[3, 4] it follows that developing a procedure for sonochemical synthesis of MoS₂ creates a facile route to enhancing the catalytic activity of MoS₂.^[1]

Ultrasonic cavitation (the formation, growth, and implosive collapse of gas-filled cavities (bubbles) in a liquid) is ultimately responsible for the unique properties of materials made using high-intensity ultrasound. In the presence of ultrasound, bubbles expand and contract with the sound field. During the rarefaction phase, volatile species surrounding the bubble diffuse inside to compensate for an increase in volume and decrease in pressure. This is possible since the time scale of expansion is relatively long (microseconds). However, the time scale for rapid, final compression is much shorter (nanoseconds) such that the resulting decrease in volume cannot be compensated for by

mass and energy diffusion out of the bubble. As a result, extreme temperatures and pressures are achieved within the bubble (on the order of 5000 K and 300 bar)^[5, 6], as well as cooling rates well above 10¹⁰ K/s. These unique and severe conditions can be used to drive chemical reactions within the bubble; one result is the synthesis of nanostructured, amorphous materials.

Metal carbonyls have high vapor pressures and low bond strengths, which make them an excellent choice as precursors for sonochemical reactions. Low vapor pressure solvents are also appropriate choices, as the solvent content within the bubble is minimized. This avoids extensive cushioning of bubble collapse, in turn resulting in higher achievable temperatures, pressures, and quenching rates.

MATERIALS

- Sulfur (99%) purchased from Strem, used as received
- Mo(CO)₆ (98%) purchased from Strem, used as received
- Isodurene purchased from Aldrich, dried and distilled over Na, and degassed
- Pentane purchased from Aldrich, dried and distilled over Na/benzophenone, and degassed
- Ar, purified through molecular sieve and charcoal traps; the tank should have a stainless steel tubing connection to the regulator for connection to the reaction cell
- VCX750 power supply (750W) and CV33 transducer purchased from Sonics & Materials (other sources: www.sigmaldrich.com, www.aceglass.com, www.coleparmer.com)
- Ti horn with groove for o-ring, threaded end with removable tip, 1/2" diameter (Ace Glass product # 9814-25)
- Stainless steel tubing connected to a needle valve and 1/4" Swagelok nut/Teflon[®] ferrule fitting for attachment to side arm on glass cell
- Threaded Teflon[®] collar and o-ring for attachment of horn to glass cell
- Glass cell with threads matching plastic collar and two 1/4" OD side arms for gas inlet and outlet
- Cooling bath
- 60 mL fine frit
- Glove box, < 0.5 ppm O₂
- Sealable glass container for sample, with connection to vacuum line

PROCEDURE

Preparation in Glove Box

In a glove box or other inert atmosphere apparatus, add 2.5 g Mo(CO)₆, 0.75 g sulfur, and 35 mL isodurene to the glass cell used for sonochemical synthesis. Slide the plastic collar and then the o-ring onto the Ti horn, and hand tighten the collar into the threading of the glass cell until it no longer turns (it should be air tight). To one side arm attach the valved tubing with Swagelok fitting, making sure the valve is closed. Seal the other sidearm such that air cannot penetrate the cell.

Reaction in Fume Hood

Remove the cell from the glove box and connect the horn to the CV33 transducer. Connect the tubing on the side arm to a continuous flow of Ar, turn it on, and open the valve on the tubing connected to the glass cell side arm. Connect the gas outlet sidearm to a bubbler to monitor the Ar flow. Place the glass cell/horn/transducer assembly in a constant temperature bath (set to 60 °C) to a depth such that only the glass cell is immersed. Turn the power box on, making sure the transducer is connected to it; set the timer for 90 minutes. Slowly turn the power output up to $\approx 80 \text{ W/cm}^2$ (the transducer can be calibrated calorimetrically to determine its actual power output at a given setting) and turn on the transducer. When 90 minutes have passed, seal the gas outlet and inlet.

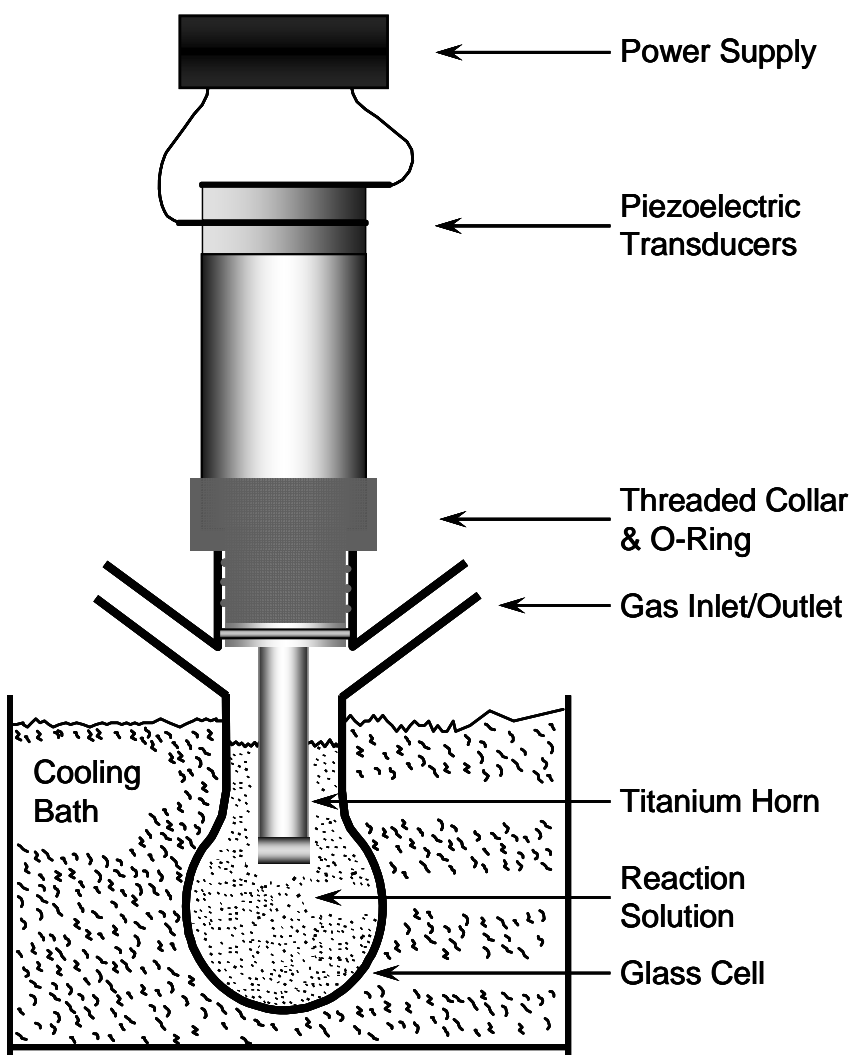


FIGURE 1. Schematic of reaction cell and setup

Product Recovery in Glove Box

Turn off the power supply and remove the horn/cell assembly from the transducer. Take this as well as filtering supplies and pentane (distilled and degassed) into the glove box.

Filter the black slurry and wash it with six 30 mL aliquots of pentane. Transfer the black powder to a sealable container suitable for heating to 80 °C and connecting to a vacuum line for 3 hours. Move the sample to a fume hood with a vacuum line.

Product Drying in Fume Hood

Hook up the sample container to a vacuum line, and apply heat at 80 °C. Open the connection to vacuum very slowly, as the sample is a very fine powder and can easily be lost if the connection is opened too quickly. After three hours, remove the heat source and cool while maintaining the vacuum connection. When the sample has cooled to room temperature, close the connection to vacuum and fill the sample container with Ar to achieve atmospheric pressure. Make sure the sample container is sealed and store it in a glove box or other appropriate vessel.

Characterization

Elemental Analysis was conducted with a CHN Analyzer CE440 by Exeter Analytical, Inc. and Inductively Coupled Plasma (ICP) OES Optima 2000 DV by Perkin Elmer.^[7] Scanning electron microscopy (Hitachi S800) and x-ray powder diffraction (Rigaku D-max diffractometer, Cu K α radiation)^[8] are used to verify the nanostructured and amorphous nature of the sample, respectively; representative data are shown in Figures 2 and 3.

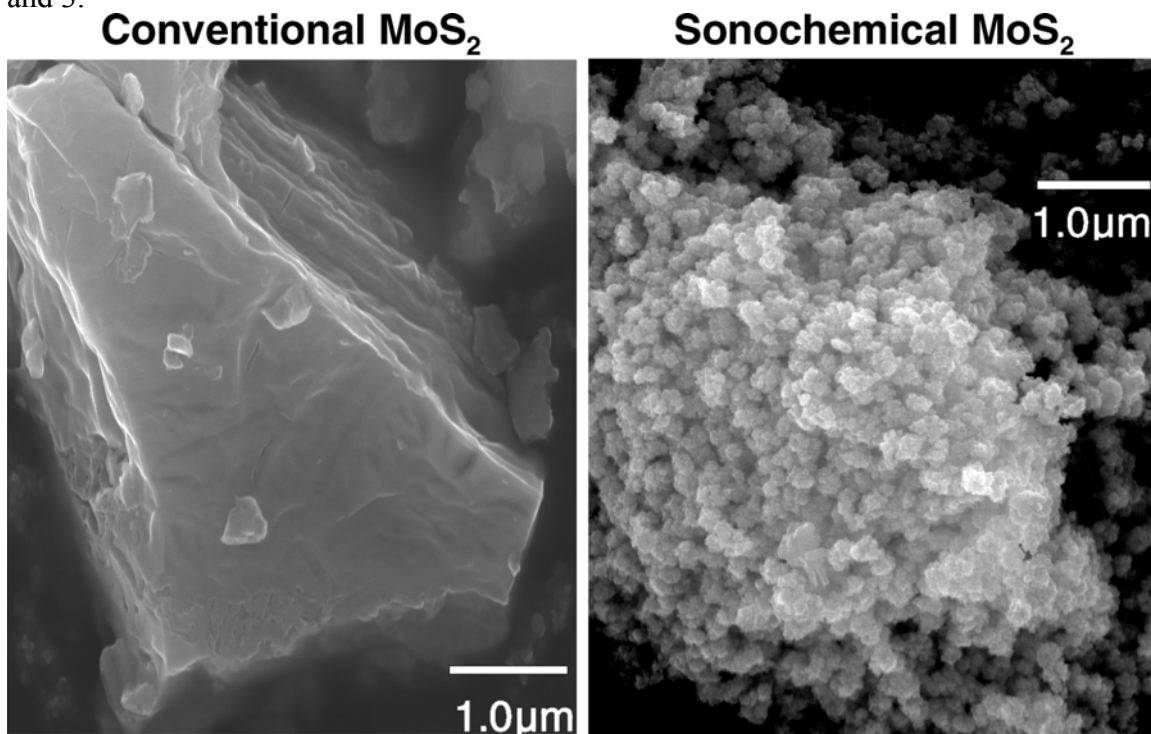


FIGURE 2. SEM of sonochemically prepared MoS₂ compared to conventional MoS₂^[1]

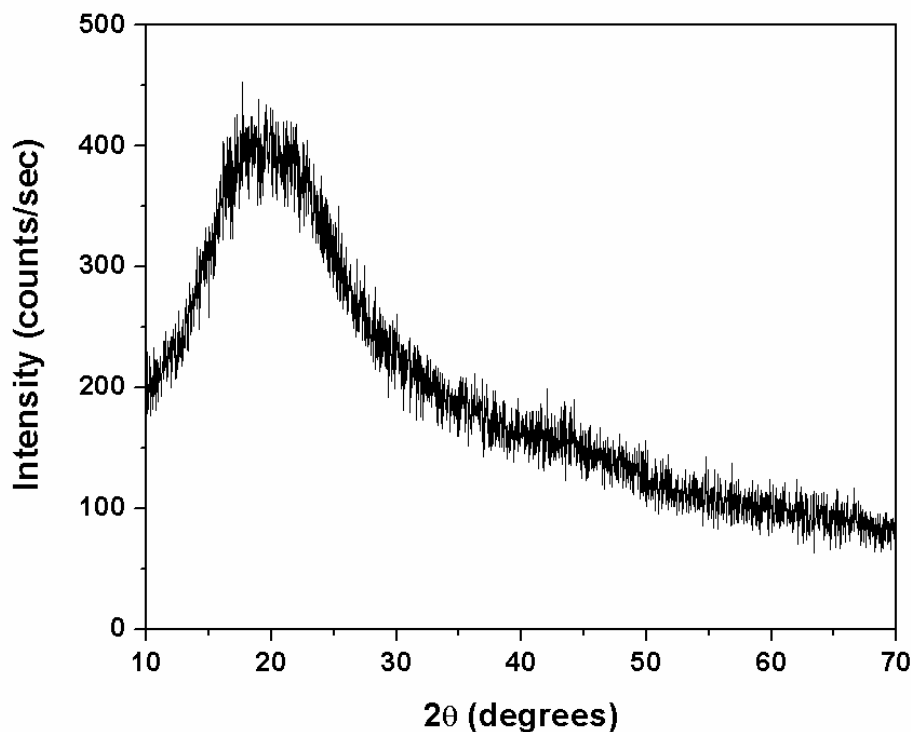


FIGURE 3. XRD powder pattern of sonochemically prepared molybdenum sulfide. The broad peak is from the glass slide on which the sample is mounted.

Safety

Always handle $\text{Mo}(\text{CO})_6$ in a fume hood. Never touch the ultrasonic horn when the ultrasonic processor is in use. Use a solid Ti horn (rather than one with a removable tip) when processing low surface tension liquids to avoid infiltration of solvent into the threaded portion of the tip; on occasion this can loosen the tip and cause damage to both horn and glassware.

Comments

- (1) Chemicals may be purchased from a different supplier provided the purity is equivalent.
- (2) The synthesis may be performed inside a glove box rather than a fume hood if the appropriate gas connections and cooling apparatus exist within the glove box.
- (3) When tightening the Swagelok nut connection to the glass cell sidearm, wrenches should be used; hand tightening will result in an air leak. Care should be taken not to over tighten, however, as this will result in cracking the cell.

(4) After sonication for 90 minutes, the reaction yield is approximately 40%. While increasing sonication time will increase the overall yield, this time should not exceed 90 minutes as ultrasonic decomposition of the solvent will lead to increased carbon contamination.

[1] Millan M. Mdleleni, Taeghwan Hyeon, Kenneth S. Suslick, Sonochemical Synthesis of Nanostructured Molybdenum Sulfide. *Journal of the American Chemical Society* **1998**, 120, 6189-6190.

[2] Gates, Bruce G., *Catalytic Chemistry*. John Wiley & Sons, Inc.: New York, 1992.

[3] Kenneth S. Suslick, Seok-Burm Choe, Andrzej A. Cichowlas, Mark W. Grinstaff, Sonochemical Synthesis of Amorphous Iron. *Nature* **1991**, 353, 414-416.

[4] Taeghwan Hyeon, Mingming Fang, Kenneth S. Suslick, Nanostructured Molybdenum Carbide: Sonochemical Synthesis and Catalytic Properties. *Journal of the American Chemical Society* **1996**, 118, 5492-5493.

[5] Edward B. Flint, Kenneth S. Suslick, The Temperature of Cavitation. *Science* **1991**, 253, 1397-1399.

[6] William B. McNamara III, Yuri T. Didenko, Kenneth S. Suslick, Pressure During Sonoluminescence. *Journal of Physical Chemistry B* **2003**, 107, 7303-7306.

[7] Elemental analysis is provided by the UIUC School of Chemical Sciences Microanalytical Laboratory.

[8] SEM and XRD analyses are carried out in the UIUC Center for Microanalysis of Materials, which is supported by the DOE (DEFG0291ER45439). This work was supported by the NSF (0315494).