

Aerosol Spray Synthesis of Porous Molybdenum Sulfide Powder

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ABSTRACT

Highly porous, nanostructured MoS₂ spheres have been prepared by ultrasonic spray pyrolysis (USP), an aerosol synthesis technique.^[1] An aqueous solution of ammonium tetrathiomolybdate, (NH₄)₂MoS₄, and colloidal silica, SiO₂, was ultrasonically nebulized using a household humidifier; the resulting aerosol droplets are heated in a furnace where solvent evaporation and precursor decomposition occurs, yielding a MoS₂/SiO₂ composite. Leaching of the colloidal SiO₂ with hydrofluoric acid, HF, results in a porous, high surface area MoS₂ network. The resulting material is a highly active hydrodesulfurization catalyst.

CLASSIFICATION

Form:	porous, fine powder
Function:	hydrodesulfurization catalyst
Preparation:	aerosol spray, pyrolysis
Composition:	MoS ₂
Extraordinary issues:	-

INTRODUCTION

Aerosol syntheses and processing are common in materials science because of their ability to be scaled-up for industrial applications.^[2] USP is an attractive aerosol technique because it provides researchers with control over a wide range of experimental conditions. Fig. 1 shows a typical, laboratory-scale USP apparatus that is inexpensive and easily assembled. The process involves the

atomization of one or more precursor solutions. Aerosol droplets are then carried by a gas (inert or reactive) into a furnace where solvent evaporation and precursor decomposition occurs. The product is collected in bubblers, and by-products either remain dissolved in the collection solvent or are flushed out of the system by the carrier gas.

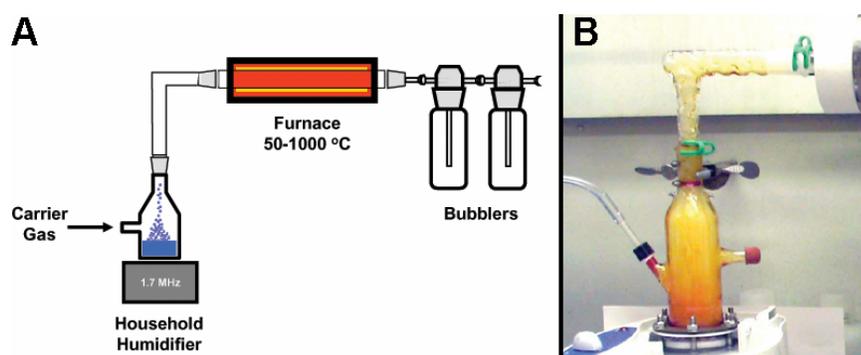


FIGURE 1. (a) Typical laboratory-scale USP apparatus. (b) Photograph of atomization cell and base.

The droplets are individual micro-reactors: the size and morphology of the resulting material can be controlled by the size of and chemistry within the droplets. Eq. 1 shows the parameters that dictate droplet size, D_d . By changing the frequency of atomization or solvent/solution properties, droplet size can be controlled. Additionally, the final particle size, D_p , can be tuned by changing the concentration or the composition of the precursor solution, as indicated by Eq. 2. Typically, micron-sized particles are obtained; however, by adding surfactants or template material, particle morphology and porosity can be greatly altered. Here, two syntheses are presented. The first synthesis presents methodology for the production of micron-sized MoS_2 spheres of relatively low surface area ($\sim 40 \text{ m}^2 \text{ g}^{-1}$) through the thermal decomposition of $(\text{NH}_4)_2\text{MoS}_4$. The second synthesis incorporates a template, SiO_2 , which upon chemical removal, yields high surface area ($100\text{-}250 \text{ m}^2 \text{ g}^{-1}$), porous MoS_2 . Both powders contrast greatly with MoS_2 synthesized by conventional techniques (Fig. 2A).

$$D_d = 0.34 \left(\frac{8\pi\sigma}{\rho f^2} \right)^{1/3} \quad \begin{array}{l} D_d = \text{droplet diameter} \\ \sigma = \text{surface tension} \\ \rho = \text{density} \\ f = \text{atomization frequency} \end{array} \quad (1)$$

$$D_p = \left(\frac{MD_d^3 C_s}{1000\rho} \right)^{1/3} \quad \begin{array}{l} D_p = \text{particle diameter} \\ M = \text{molecular weight} \\ C_s = \text{molar concentration} \\ D_d = \text{droplet diameter} \\ \rho = \text{density} \end{array} \quad (2)$$

The production of high surface area, porous MoS₂ is important because of its use as the standard hydrodesulfurization catalyst in the petroleum industry.^[3] MoS₂ has a layered structure with a repeating motif of S-Mo-S sandwiched layers. Hydrodesulfurization, however, only occurs at the exposed edges of these layers.^[4] Thus, the desulfurization activity of MoS₂ is greatly affected by the synthetic technique employed in its production. By using USP to prepare MoS₂, the catalytically active edge sites are increased substantially, improving the desulfurization properties.

MATERIALS

- Ammonium tetrathiomolybdate (NH₄)₂MoS₄ from Aldrich (99.97%); used as received.
- SNOWTEX® ZL colloidal silica (~80 nm) 40 wt% solution in water; used as received.
- 49% HF diluted to 10% with ethanol (reagent grade).
- Deionized water.
- Ar gas (purity ≥ 99.99%).

SAFETY AND DISPOSAL

Safety and handling instructions for the chemicals are found in the corresponding materials safety data sheets (MSDS). Pyrolysis of (NH₄)₂MoS₄ generates hydrogen sulfide, H₂S; a bubbler of bleach or concentrated sodium hydroxide (aq) should be attached to the end of the product collection bubblers. The experiments should be conducted in a well-ventilated fume hood. Extra caution should be employed while handling HF to avoid contact with skin.

PROCEDURES

The USP apparatus shown in Fig. 1A consisted of a household *Sunbeam*TM Ultrasonic humidifier base (model #696, 1.7 MHz) filled with water as a coupling medium. The base of the atomization cell has a 52 mm diameter opening with O-ring groove (ChemGlass #CG-138-02), over which a polyethylene membrane (2 mils, cut from a zip-lock plastic bag) was clamped between a Teflon donut and the O-ring (Fig 1B). The atomization cell had both a gas inlet and solution-addition arm. The atomization cell was placed directly above the humidifier transducer, and the glassware assembled as in Fig. 1. The flow tube through the furnace was 25 mm quartz, which permits the use of high furnace temperatures. A single zone furnace with a total heated region of ~30 cm was employed. Four collection bubblers (each 200 mL volume) were used in series and each was filled ~25% with deionized water. A final scrubber bubbler filled with either bleach or aqueous sodium hydroxide was placed at the end of the bubbler series.

A. Preparation of low-porosity MoS₂

To 25 ml of deionized water, 0.25 g (NH₄)₂MoS₂ was added and dissolved. The solution was sparged with Ar for 30 min and then added to the atomization cell through the solution-addition arm. The USP system was flushed with Ar prior to solution addition and was continuously flushed with Ar while the furnace was heated to 700 °C. Once temperature was reached, the Ar flow was set to 940 ml min⁻¹ (monitored with a calibrated rotometer) and the humidifier was turned on. A fine orange-red mist is observed and black powder deposits on the cooler furnace tube outlet as well as in the collection bubblers.

The contents of the collection bubblers were combined into tubes and centrifuged. The supernatant was decanted off the powder. The powder was then re-suspended in ethanol and transferred to a round bottom flask. The ethanol was removed by rotary evaporation, and the powder collected.

Characterization

Elemental analysis: Samples were vacuum dried at 110 °C for 24 h prior to analysis. The total weight percent of carbon, hydrogen, and nitrogen contaminants together was below 1%. Oxygen was below 2% (calculated by difference). The molybdenum to sulfur mole ratio was 2.0±0.1.

XRD: Four broad peaks were observed with d-spacings 6.35, 2.70, 2.54, and 1.57 Å which correspond to the [002], [100], [103], and [110] reflections of poorly crystalline hexagonal MoS₂. Spectra were obtained with a Rigaku D-MAX

diffractometer using Cu K α ; crystallite sizes were determined using the Jade X-ray analysis software package. C-stacking height, calculated with the Scherrer equation using the [002] reflection, was ~ 36 Å.

BET surface area: N₂ isotherms (at 77 K) and surface area measurements were obtained with Quantachrome Instruments Nova 2200e Surface Area and Pore Analyzer. Three point analysis gave a surface area of 20 to 40 m²g⁻¹.

SEM (Fig. 2): Hitachi S-4700 SEM operating at 10 kV.

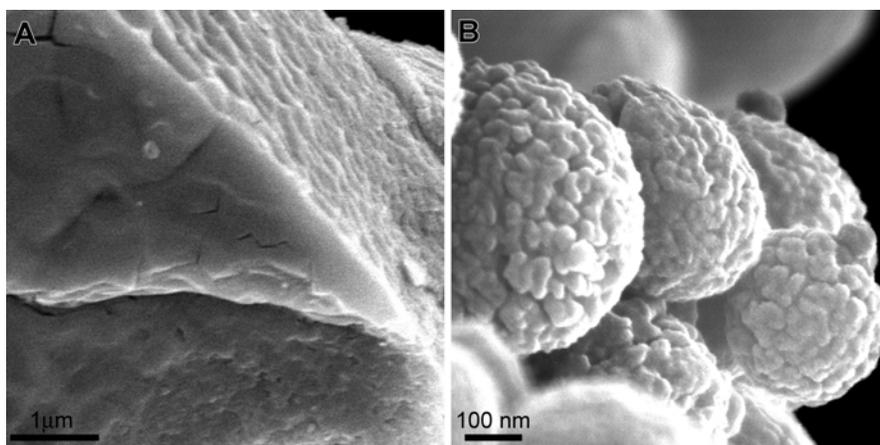


FIGURE 2. (a) SEM image of conventional MoS₂. (b) SEM image of USP generated MoS₂ spheres.

B. Preparation of porous MoS₂

To 25 ml of deionized water, 0.25 g (NH₄)₂MoS₄ and 1.20 g of SNOWTEX-ZL was added. The remainder of the synthesis and the powder collection was followed as described in part A.

Composite Etching

The collected powder was transferred to a plastic, HF resistant, centrifuge tube. Ca. 30 ml of 10% HF was added to the tube, the tube was sealed and spun on a Barnstead/Thermdyne Labquake® Rotisserie for 24 h. The HF was then decanted off after centrifugation; the powder was re-suspended in water, centrifuged, and supernatant was removed. This procedure was repeated until a neutral pH was obtained (~ 5 times). The powder was re-suspended in ethanol and transferred to a

round bottom flask; the ethanol was removed by rotary evaporation, and the powder collected.

Characterization

Elemental analysis, XRD and SEM (Fig. 3): Same as in part A.

BET surface area: Same as in part A. Three point analysis gave a surface area of $100 \text{ m}^2 \text{ g}^{-1}$.

TEM (Fig. 3): Philips CM-12 TEM operating at 120 kV.

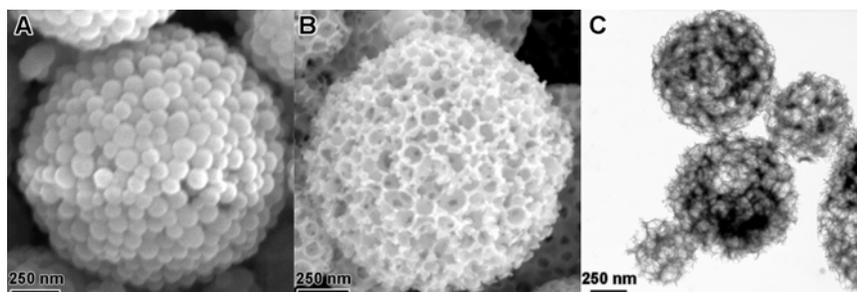


FIGURE 3. (a) SEM image of $\text{MoS}_2/\text{SiO}_2$ composite made by USP. (b) SEM image of USP product after leaching of template SiO_2 with HF acid. (c) TEM image of USP product after leaching of template SiO_2 with HF acid.

Comments

- (1) If poor atomization of solution is observed, it is likely due to air bubbles in the coupling water that are trapped under the polyethylene membrane. A syringe may be used to remove these.
- (2) If a quartz furnace tube is unavailable, the furnace temperature should not exceed 450°C with a Pyrex tube. The MoS_2 can be prepared even at 400°C ; the XRD powder pattern of such material, however, may show peaks of elemental sulfur. Such sulfur can be removed by subsequent heating under an inert atmosphere.
- (3) Custom bubblers, composed of ball and socket joints, were used in our apparatus. If standard bubblers are employed and connected via Tygon tubing, the weight percent carbon in the final samples was found to increase slightly.
- (4) Colloidal silica is readily available in many sizes. This procedure can be modified by changing the size of the colloidal silica being used. This

provides the researcher with the ability to modify the porosity and morphology of the MoS₂ to meet their specific application. MoS₂ surface areas of 250 m²g⁻¹ can be achieved. For different sized colloidal silica, the ratio of (NH₄)₂MoS₄ to silica may require optimization to prevent MoS₂ network collapse.

- (5) The use of colloidal silica as a sacrificial template in aerosol syntheses can be extended to many other materials, resulting in unique morphologies and pore structures.^[5]
- (6) The base of a *Sunbeam*TM Model 696 Ultrasonic Humidifier was used in this study; however, other household humidifiers can be used without changing the properties of the resulting material significantly, so long as the ultrasonic frequency remains ~2 MHz. Fortunately, many commercially available ultrasonic humidifiers are similar. For example, successful results have been obtained with *Vicks*TM Model V5100 Ultrasonic Humidifier, *Sunbeam*TM Model 696 and 701 Ultrasonic Humidifiers, and *Holmes*TM Model HM461 Ultrasonic Humidifier.

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