

The Synthesis of MoS₂ Nanoparticles Using Ultrasonic Cavitation

E. Sekreta, H. Ichitsubo*, Y. Kuriki, K. Shimada, K. Uchida, S. Yoda, A. Kawai,
S. Oshima, M. Yumura and F. Ikazaki

National Institute of Advanced Industrial Science and Technology

1-1 Higashi 1-chome, AIST Tsukuba Central 5, Tsukuba, Ibaraki 306-8565, JAPAN

FAX 81-298-61-4454 e-mail: ikazaki-fumikazu@aist.go.jp

*National Institute of Radiological Sciences

4-9-1 Anagawa, Inage, Chiba 263-8555, JAPAN

Using molybdenum carbonyl and sulfur containing compounds, we have sonochemically synthesized material containing sulfur and molybdenum that is a precursor to MoS₂ formation and which contains MoS₂ particles. This material is primarily amorphous but can crystallize into MoS₂ particles when heated. When this is done in an oxygen free environment, the MoS₂ formed has a stacking height relative to crystal length that is lower than MoS₂ particles synthesized by conventional methods.

The bent strand-like MoS₂ prepared by heating sonochemically produced Mo₂C with sulfur has much higher hydrogenation activity than vibrating milled MoS₂, and with less hydrogen consumption as high an activity as in-situ pyrolysis product of Mo(CO)₆ with sulfur.

Key words sonochemically synthesized, MoS₂, heat treatment, hydrogenation, 1-methylnaphthalene

1. Introduction

MoS₂ has a layered structure composed of alternating molybdenum and sulfur layers and crystallizes in several different forms. The structure of MoS₂ influences its properties, and there have been several investigations synthesizing nanocrystalline MoS₂¹⁾. Recently, several nanostructured catalysts have been synthesized by taking advantage of the high pressures and temperatures that can be generated in cavitating bubbles²⁾. It has been shown that the dissociation of metal carbonyls with ultrasonic cavitation is a useful route for producing amorphous metal. With ultrasound, the synthesis of Mo₂C from Mo(CO)₆ has been previously reported³⁾. Using the same method, we have irradiated solutions of Mo(CO)₆ together with various sulfur containing compounds.

The object of our work is to investigate whether or not novel forms of MoS₂ can be prepared in this manner and the catalytic activity using hydrogenation of 1-methylnaphthalene (1-MN).

2. Experimental Method

Solutions of Mo(CO)₆ and (CH₃)₂S₂, CS₂, or H₂S in tetradecane were irradiated with a Branson 450 sonifier using a sound intensity between 25 and 35 W/cm². The solutions were degassed with argon or a 70% by volume Ar/H₂S mixture. Experiments were performed with 20 ml solutions contained in a cell under a continuous flow of argon. Because the solubility of Mo(CO)₆ was very low (approximately 10⁻² g/ml), an excess amount of Mo(CO)₆ was added to the solutions. This amount gradually dissolved as

the Mo(CO)₆ reacted over the course of several hours. The concentration of (CH₃)₂S₂ or CS₂ used in the experiments was between 1 and 0.1 M. Irradiation of the solutions generated particles which were then filtered and washed with THF. In some cases the particles were separated from the solvent by evaporating the solutions in a ceramic oven. Another experiment was conducted to prepare MoS₂ by heating sonochemically produced Mo₂C with sulfur.

The powder was examined with a JEOL JEM-2000FX11 transmission electron microscope and X-ray measurements were obtained with a Phillips 1800 X-ray diffractometer employing Cu K α radiation. To measure the elemental content of the material, samples were pyrolyzed, reacted with nitrogen or oxygen, and detected with a calibrated gas chromatograph.

3. Results

When separated from the solution, the material synthesized was always dark brown or black. The yield of powder was roughly 0.1 g per hour of sonication time. As shown below, features in the X-ray spectra of the synthesized material showed a dependence on the starting material. Heating the powder also strongly affected the crystallinity of the material.

The X-ray spectrum of material formed by irradiating solutions of Mo(CO)₆ and H₂S followed by filtering and washing the product is shown in Fig. 1A. This spectrum shows a main feature which consists of overlapped several broad bands indicating the material is fairly amorphous. As shown in Fig. 1B, a very broad feature is also present along

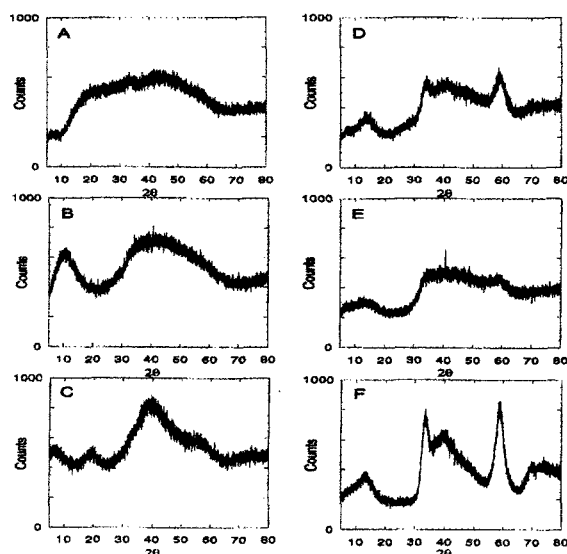


Fig. 1. X-ray spectrum of powder formed:

A) by irradiating solutions of Mo(CO)₆ and H₂S followed by filtering and washing the product. B) Same as A except that (CH₃)₂S₂ is used instead of H₂S. C) Same as A except that CS₂ is used instead of H₂S. D) Same as A except that the product was also baked at 300°C under a flow of argon for 1 hour. E) Same as B except that the product was also baked at 300°C under a flow of argon for 1 hour. F) X-ray spectrum of powder formed by irradiating solutions of Mo(CO)₆ and (CH₃)₂S₂ directly followed by heating the product at 300 °C under a flow of argon for 1 hour.

with a sharper, low angle band in the X-ray spectrum of material formed using solutions of Mo(CO)₆ and (CH₃)₂S₂. This spectrum is very similar to that exhibited by mixtures of MoS₂ and Mo₂S₃ formed from molybdate solutions⁹. The broad band is attributed to the presence of amorphous Mo₂S₃ and the sharper band at low angles is caused by reflections from the basal plane of MoS₂. In our case the sharper band is slightly shifted towards low angle from the expected position of the peak in the X-ray spectrum of pure crystalline hexagonal MoS₂. This may indicate that the layer spacing of the MoS₂ in the synthesized material is slightly larger than that of MoS₂ produced by conventional methods.

The X-ray diffraction spectrum of material formed from solutions containing Mo(CO)₆ and CS₂ is shown in Fig. 1C. This spectrum is different from that of material formed using H₂S or (CH₃)₂S₂. The features at high angle (2θ = 40) match the X-ray spectrum of Mo₂C formed by irradiating hydrocarbon solutions containing Mo(CO)₆. The peak at 2θ = 20 degrees may be due to MoC. Figs 1D and 1E show the X-ray spectrum of material formed by irradiating Mo(CO)₆ solutions containing H₂S and (CH₃)₂S₂ respectively that was filtered and then heated at 300 °C under a flow of argon for 1 hour. As compared to Figures 1A and 1B, the

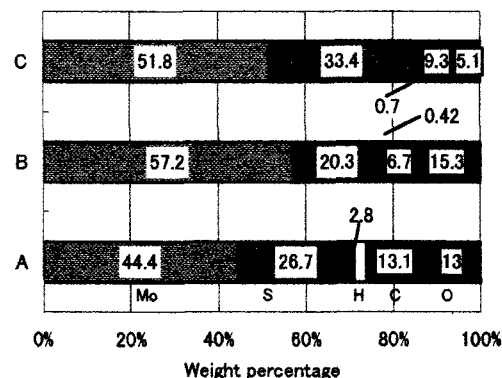


Fig. 2. Weight percentage of molybdenum, sulfur, carbon, oxygen and hydrogen in material formed by irradiating solutions of Mo(CO)₆ and (CH₃)₂S₂. A) Material that was filtered and washed. B) Same as A except that the material was baked at 300 °C under a flow of argon for 1 hour C) Material that was baked at 300°C under a flow of argon for 1 hour without exposure to oxygen.

application of heat has a strong effect on the crystal structure of the synthesized material. Several features in the spectra shown in Fig. 1D and 1E are similar to that of a very broadened band profile of hexagonal MoS₂. In particular, the 002 band at 2θ = 14, the 100 band at 2θ = 33, the 103 band at 2θ = 40 and the 110 band at 2θ = 58 can be observed in Fig. 1D. Additional heating for longer time or at a higher temperature of 440 °C did not significantly affect the crystallinity of the material. It is possible that MoS₂ formed in our experiments partially oxidizes when filtered and washed.

To avoid exposure to oxygen, a solution containing Mo(CO)₆ and (CH₃)₂S₂ was irradiated and then heated directly at 300 °C for 9 hours under a flow of argon to evaporate the solvent and the excess (CH₃)₂S₂. The X-ray diffraction spectrum of material treated this way is shown in Fig. 1F. Compared to the spectra shown in Figs 1D and 1E, the spectrum shown in Fig. 1F contains sharply defined 100 and 110 bands as well as diffuse 002 and 103 bands. The 110 band and the 002 band occur in uncongested areas of the spectrum and have a breadth of approximately 2θ = 2 and 5 respectively. This information can be used to estimate average crystallite depth and length. Using the Sherrer formula, this results in average crystal dimensions approximately 2 nm in height and 5 nm in length. The broadness of the bands in the X-ray spectra points to the condition that our synthesized material does not consist purely of MoS₂.

In order to specifically examine chemical content, elemental analysis was performed on several samples. As an example, Fig. 2 shows the weight percentage of molybdenum (Mo),

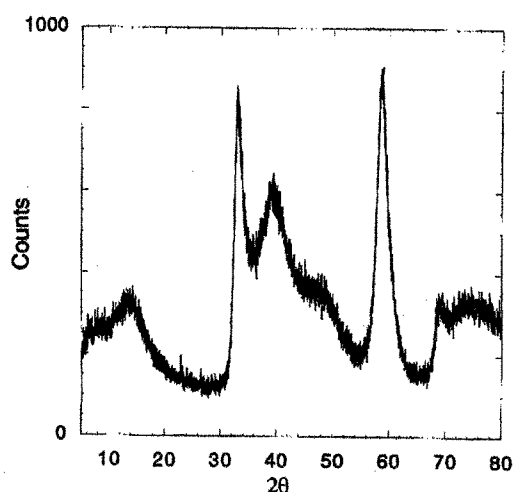


Fig. 3. X-ray diffraction spectrum of MoS_2 formed from Mo_2C and sulfur that was heated at 325°C for 24 hours under a flow of argon.

sulfur(S), carbon(C), oxygen(O), and hydrogen(H) in the material formed by irradiating solutions of $\text{Mo}(\text{CO})_6$ and $(\text{CH}_3)_2\text{S}_2$. Fig. 2A depicts the weight percent of the material that was not heated whose X-ray spectrum is shown in Fig. 1B. This material contains 26.7 % S and 44.4 % Mo, relative amounts similar to the 40:60 stoichiometric ratio in MoS_2 . However, there is a substantial amount of O, C and H in the material. Fig. 2B shows that when the material is baked, the amount of C and H decreases, most likely due to the evaporation of residual solvent in the material. Furthermore, the amount of S also substantially decreases due to evaporation. This gives an indication that some of S in the unbaked sample is not complexed to Mo to form MoS_2 . Fig. 2C shows the content of the material baked without exposure to oxygen whose X-ray spectrum is shown in Fig. 1F. In this case there is a substantial increase in the amount of S and the ratio of the amounts of S and Mo matches that found in MoS_2 . The amount of O and H is the lowest of the three samples. These observations account for the fact that the X-ray spectrum of this sample exhibits the highest degree of crystallinity.

To check whether MoS_2 crystallites could be formed via a secondary reaction, a slurry of $\text{Mo}(\text{CO})_6$ and sulfur powder was irradiated under similar conditions as the above experiments. In this case, the low vapor pressure of sulfur was expected to result in a negligible concentration of sulfur inside the cavitating bubbles. Using TEM, crystallites were not observed in the material indicating that MoS_2 is not formed by secondary reactions in solution.

Warzinski and Bockrath⁵⁾ have found that MoS_2 can be formed by heating $\text{Mo}(\text{CO})_6$ in the presence of H_2S gas. Using a similar scheme, we found that MoS_2 could be formed



Fig. 4. TEM image of MoS_2 formed from Mo_2C and sulfur that was heated at 325°C for 24 hours under a flow of argon.

by heating Mo_2C (formed sonochemically) with sulfur. Fig. 3 shows the X-ray diffraction spectrum of MoS_2 formed by sonicating a solution of $\text{Mo}(\text{CO})_6$ to form Mo_2C , mixing the solution with sulfur powder, and evaporating the solvent by heating the mixture at 325°C for 24 hours under an argon flow (the material thus formed is hereafter called as $\text{MoS}_2\text{-HS}$). This X-ray spectrum, which shows a very broad 002 peak and more sharply defined 110 ($2\theta = 58$) and 100 ($2\theta = 33$) peaks, is very similar to the spectrum depicted in Fig. 1F. As shown in Fig. 4, the TEM image of this material indicates that the MoS_2 consists of strands several nanometers long with not much layering. Several strands appear bent due to a lack of rigidity. When material formed in this way was reheated at 400°C for 24 hours, not much change was observed in the X-ray diffraction spectrum.

The catalytic activity of the material ($\text{MoS}_2\text{-HS}$) whose X-ray spectrum is shown in Fig. 3 has been measured and compared to other forms of MoS_2 . Fig. 5 shows the conversion of 1-methylnaphthalene (1-MN), and weight percent of 1-methyltetralin (1-MTL), 5-methyltetralin (5-MTL), 1-methyldecalin (1-MD) and others produced from the reaction of 1-MN at 350°C , using a 3 % weight of catalyst, a reaction time of 1 hour, and a hydrogen pressure of 8 Mpa. In this figure, the total weight percent of products is the conversion of 1-MN. From this figure, using $\text{MoS}_2\text{-HS}$, the

conversion is very high compared to commercially available MoS₂(Aldrich) and vibrating milled MoS₂. However, the material formed from in-situ pyrolysis of Mo(CO)₆ with sulfur in the reactor has as high a catalytic activity as the MoS₂-HS. The MoS₂-HS, however, consumes less hydrogen than the in-situ pyrolysis product.

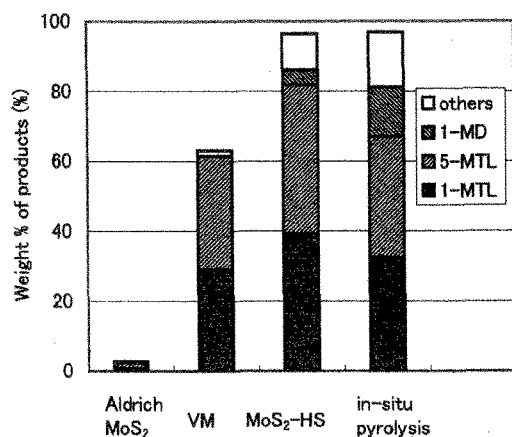


Fig.5 Hydrogenation of 1-methylnaphthalene(1-MN) using various catalysts: VM= vibrating milled Aldrich MoS₂ for 90 hour; MoS₂-HS= heating sonochemically produced Mo₂C with sulfur; in-situ pyrolysis= in-situ pyrolysis of Mo(CO)₆+S in the reactor

4. Discussion

When (CH₃)₂S₂ or H₂S is used as a source of sulfur in our experiments, MoS₂ and/or Mo₂S₃ most likely are components of the material that is formed. This material is fairly amorphous, contains significant amounts of carbon, oxygen and hydrogen, and has too little sulfur to match the stoichiometric amounts of sulfur in MoS₂. When this material is heated, the MoS₂ that exists remains primarily non crystalline. As shown in Fig. 1F and Fig. 3, it seems that MoS₂ with the highest crystallinity can be produced by limiting the sample's exposure to oxygen before it is sintered. One reason why this can effect crystallinity involves the free sulfur trapped in the material and its reaction to form SO₂. If there is no oxygen available, then SO₂ formation becomes impossible when the sample is heated and more sulfur becomes available to generate MoS₂. The source of molybdenum originates from the Mo₂C generated from Mo(CO)₆. The X-ray diffraction spectra of MoS₂ formed from (CH₃)₂S₂ and Mo(CO)₆ or from Mo₂C and sulfur that was heated without exposure to oxygen shows a very short, wide 002 peak relative to a well defined 110 peak (Fig. 1F and Fig. 3). This indicates that the stacking height of the crystals is

short compared to their length and is consistent with the TEM image shown in Fig. 4. The ratio of height to length is very different from MoS₂ formed by other methods. The reason why the MoS₂ particles formed in our experiments have such a low stacking height is probably due to the amount of carbon and oxygen contaminants in the samples studied. Impurities may lie on the surface or between layers of MoS₂ and may impede the stacking process leading to longer crystals with short stacking heights. For the same reason, large concentrations of sulfur may also enhance the formation of long crystals.

The much higher hydrogenation activity of MoS₂ prepared by heating sonochemically produced Mo₂C with sulfur (MoS₂-HS) is attributed to bent basal planes and very tiny crystals as reported by Iwata et al⁶⁾

5. Conclusion

Using molybdenum carbonyl and sulfur containing compounds, we have sonochemically synthesized material containing sulfur and molybdenum that is a precursor to MoS₂ formation and which contains MoS₂ particles. This material is primarily amorphous but can crystallize into MoS₂ particles when heated. When this is done in an oxygen free environment, the MoS₂ formed has a stacking height relative to crystal length that is lower than MoS₂ particles previously synthesized by other methods.

The bent strand-like MoS₂ prepared by heating sonochemically produced Mo₂C with sulfur (MoS₂-HS) has much higher hydrogenation activity than vibrating milled MoS₂, and with less hydrogen consumption as high an activity as in-situ pyrolysis product of Mo(CO)₆ with sulfur.

References

- 1) M.W. Peterson, M. T. Nenadovic, T. Rajh, R. Herak, O. I. Micic, J.P. Goral and A.J. Nozik, *J. Phys. Chem.*, **92**, 1400(1988)
- 2) K. S. Suslick, S. Choe, A. A. Cichowlas, M. W. Grinstaff, *Nature* **353**, 414(1991).
- 3) T. Hyeon, M. Fang, K. S. Suslick, *J. Am. Chem. Soc.* **118**, 492 (1996).
- 4) H. W. Wang, P. Skeldon, G. Thompson, G. C. Wood, *J. Mat. Sci.* **32**, 497(1997).
- 5) R. P. Warzinski, B.C. Bockrath, *Energy & Fuels* **10** 612 (1996)
- 6) Y. Iwata, K. Sato, T. Yoneda, Y. Miki, Y. Sugimoto, A. Nishijima and H. Shimada, *Catalysis Today*, **45**, 353(1998)

(Received December 21, 2001; Accepted January 30, 2002)