Synthesis and Characterization of Nano-Sized Hydrodesulfurization Catalyst

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Introduction

The effect of burning transportation fuels on the environment is now gaining global attention. In addition to CO_2, sulfur is also an issue. Sulfur removal is crucial because it also poisons catalysts during petroleum refining processes. The new regulations will likely limit S to low ppm (almost zero) levels in fuels.

We previously reported synthesis of unsupported nano-phase MoS_2 catalysts using sonolysis (Mahajan et al., 2004). We are now further investigating this reaction. This work explores a reliable technique for nanoparticle synthesis. For characterization, in addition to X-ray Diffraction (XRD), the Computed Microtomography (CMT) technique is used, for the first time, to show 2-D and 3-D images of the material.

Experimental

An experimental apparatus was an ultrasonic liquid processor Model XL2020, from MISONIX, Inc., with a variable power output of up to 550 W, at a frequency of 20 kHz. The actual sonolysis took place at the probe tip of 0.5 inch diameter. The entire apparatus was placed in sound-absorber containment. The sonicator was programmed. The reaction vessel was a borosilicate glass four-neck flask that was made air-tight with a series of O-rings and standard ground-glass joints during sonication. The gas evolved during sonolysis was collected and metered in an inverted measuring cylinder in a water bath. The extent of reaction could be calculated from these data.

Hexacarbonylmolebdenum ($MO(CO)_6$) (>99% purity), sulfur powder (99.9%) and hexadecane (99%, anhydrous) were purchased from Aldrich. N_2 gas was obtained from Scotts Specialty Gases. All manipulations were carried out in a well-ventilated fume hood. $Mo(CO)_6$ (10 mmol) and 25 (or 50) mmol S were added to hexadecane solvent (70 mL). The resulting off-white slurry was degassed with N_2 for 15-20 minutes. The sonication was performed in the 4-second/1-second on/off mode. The gradual appearance of a black slurry in the reaction vessel was evident within minutes indicating metal carbonyl decomposition.

$$Mo(CO)_6 + 2S \xrightarrow{)))} MoS_2 + 6CO^{\uparrow}$$

At STP, 60 mmols of CO accounts for 1.36 L. The CO evolution was recorded as a function of time until CO volume exceeded 1.23 L which corresponded to ~90% metal carbonyl decomposition.

The slurry work-up produced air-stable black particles of MoS_2. The slurry was centrifuged and the upper hexadecane solvent layer was decanted to separate the product. The remaining black solid was washed and centrifuged three times with hexane (10 ml) to remove residual hexadecane. The collected solid was dried in vacuum and then stored in a gas-tight vial to avoid any sample oxidation. Samples of the isolated solid were used for characterization.

SEM images of MoS_2 were obtained using Leo 1550 Field Emission SEM unit. For Computed Microtomography (CMT) analysis, at the Beamline X-2B, National Synchroton Light Source (NSLS), Brookhaven National Laboratory (BNL), an X-ray beam with energy 15 keV is produced with a bending magnet that was used for the CMT analysis. The 5X lens used in this analysis provided 4-micron resolution. A polypropylene syringe was filled with the sample from the $Mo(CO)_6$/S (1/:2.5 molar ratio) and subjected to analysis. The 1200 images were taken with 4000 msec exposure for each image at every 1.5° increment from 0 to 180°. The output file, filename.prj contained all 1200 tomographic image slices, each composed of a rectangular array of reconstructed linear attenuation coefficient values and corresponding to a specific voxel of the sample. A reconstruction of 300 slices from the assembled file in a tomogram and their conversion into a stack of jpegs was performed using IDL tomography software. The vertical axis was optimized for each reconstruction to reduce artifacts in the images.

Results and Discussion

Figure 1 shows a first-order plot for $Mo(CO)_6$ decomposition in ~50 hours in the presence of S. Two runs were conducted with varying S/Mo molar ratio of 2.5/1 and 5/1 (Figure 1).

1. XRD Data

Recently published XRD patterns of 150-200 nm and ~100 nm sized MoS_2 particles revealed a characteristic 002 peak at $2\theta = 14.5$ to be broad (Pourabbas and Jamshidi, 2008). The peaks for the 100 nm sample were broader than those completely disordered ribbon-like stacking of S-Mo-S layers confirmed with TEM.

The XRD pattern of the product derived from sonication of $Mo(CO)_6$ and S in 2.5/1 and 5/1 molar ratios are shown in Figures 2 and 3, respectively. A broad peak at $2\theta = 40^o$ is very analogous to previously presented literature on nano-sized MoS_2 especially by Xu et al. (1996). The broad peak at $2\theta = 40^o$ may be a combination of peaks at $2\theta = 32.7^o$and 39.5^o which are assigned to the (100), and (103)

lattice planes of MoS_2 respectively. The peak at $2\theta = 58^o$ corresponding to (110) is also broad. The widened peaks confirm the absence of MoS_2 crystallites with high defect densities. The XRD pattern of the product from the 5/1 ratio of S/$Mo(CO)_6$ appears to have broadened effects of all peaks at 32.7^o, 39.5^o, and 58^o.

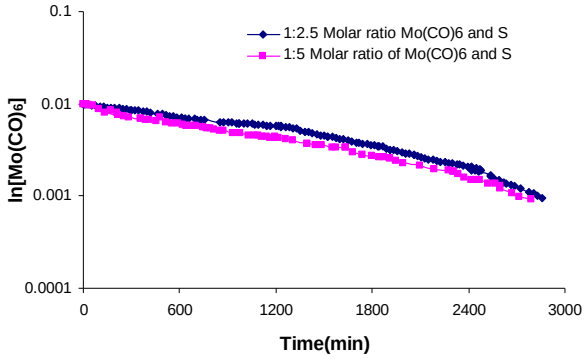

Figure 1. A first-order plot for sonolysis-assisted $Mo(CO)_6$ decomposition with sulfur in hexadecane at T ~50^oC, using pulsed sonication.

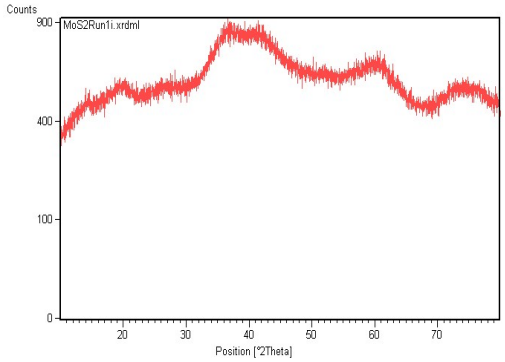

Figure 2. XRD pattern of MoS_2 particles derived from sonication of $Mo(CO)_6$ and S in a 1:2.5 molar ratio

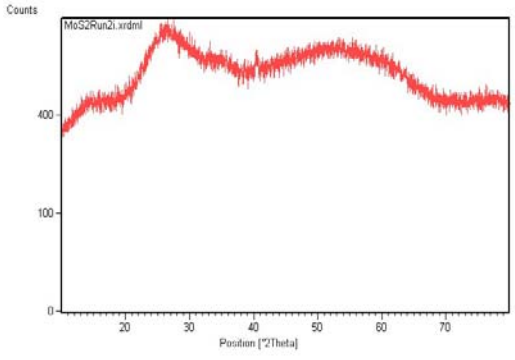

Figure 3. XRD pattern of MoS_2 particles derived from sonication of $Mo(CO)_6$ and S in a 1:5 molar ratio

2. Scanning Electron Microscopy (SEM) and EDAX Elemental Analysis

Figure 4 shows the SEM image, at 100 KX magnification, of MoS_2 that was obtained from $Mo(CO)_6$ and S in a 1:2.5 molar ratio. The product appears porous with dark and light areas representing heavy and light portions of the elements, respectively. The cluster-like nature of the MoS_2 is also obvious. The particles are not distinguishable, possibly due to their small size.

The EDAX elemental analysis showed a strong peak between 2.0-2.5, corresponding to S and Mo peaks (Figure 5). The peaks at 0.2, 0.3, 0.5 corresponding to Mo, C, and O, respectively indicate the presence of residual CO, unreacted $Mo(CO)_6$ and an oxidized product.

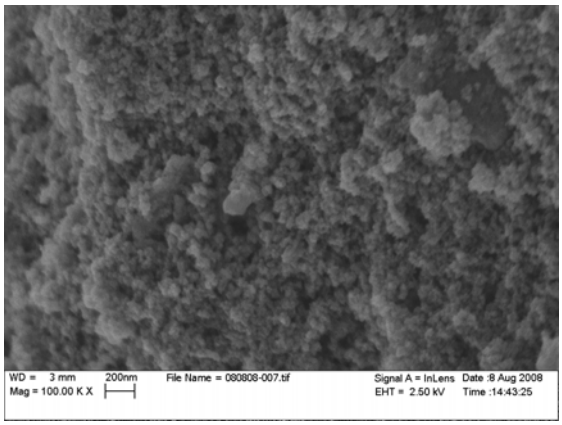

Figure 4. SEM of the product from the $Mo(CO)_6$ and S (1/2.5 molar ratio) reaction.

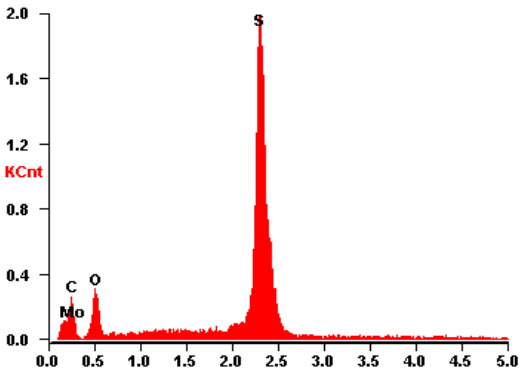

Figure 5. EDAX analysis of the product from the $Mo(CO)_6$ and S (1/2.5 molar ratio) reaction.

Figure 6 shows the SEM image of the MoS_2, obtained from the $Mo(CO)_6$/S (1/5 molar ratio) reaction, at 100 KX magnification. The image shows the same pattern of cluster-like porous material with dark and light areas.

The EDAX pattern (Figure 7), however, is somewhat different. There are noticeably smaller peaks for C and O, compared to the previous sample. This could indicate that increasing the concentration of S enhances the conversion of $Mo(CO)_6$.

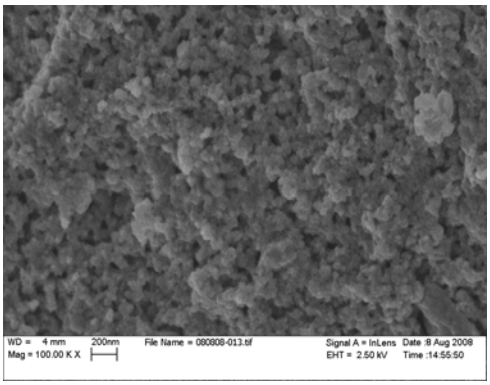

Figure 6. SEM of the product from the $Mo(CO)_6$ and S (1/5 molar ratio) reaction.

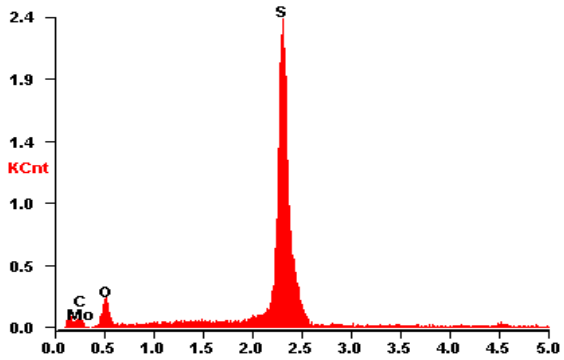

Figure 7. EDAX analysis of product from the $Mo(CO)_6$/S (1/5 molar ratio) reaction.

3. X-ray Computed Microtomography (CMT) Analysis

Figure 8 shows an X-ray CMT image of the sample taken with 4000 msec exposure. All 1200 angular images were reconstructed to get horizontal cross-section shown in Figure 9. A 3-D volume (not shown here) was created from the stack of images using a volume rendering software, Drishti (Limye, 2006). The 2-D image shows an uneven size of the product. The absence of histogram peak corresponding to air within sample may be due to nano-sized particles resulting into even smaller air pathways to get detected in the X-ray beam. The CMT 2-D and 3-D images confirmed that the synthesized particles of MoS_2 are indeed nano-sized.

Figure 8. An X-ray CMT image of a sample from the $Mo(CO)_6$/S (1/2.5 molar ratio) reaction.

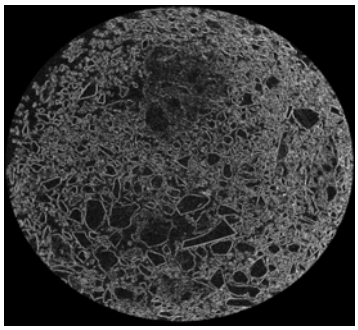

Figure 9. Reconstructed 2-D cross-section (7mm diameter) of sample from Figure 8.

6. Conclusions

The sonolysis product of $Mo(CO)_6$ and S in both 1/2.5 and 1/5 molar ratios, exhibited cluster-like aggregates without distinguishable nano-particles. The EDAX analysis of both products confirmed the presence of Mo, S, C and O in variable concentrations. Increasing the sulfur concentration enhanced $Mo(CO)_6$ conversion. The XRD pattern of the product showed a broad peak at $2\theta = 40^o$ which may be a combination of peaks at $2\theta = 32.7^o$and 39.5^o, which are assigned to the (100) and (103) lattice planes of MoS_2, respectively. Moreover, another broad peak at $2\theta = 58^o$ corresponding to (110) and the CMT 2-D and 3-D images confirmed the synthesis of nano-sized particles and the absence of MoS_2 crystallites.

Acknowledgements

This work was performed at Brookhaven National Laboratory under contract No. DE-AC02-98CH10886 with the U.S. Department of Energy. ID thanks the Summer Undergraduate Laboratory Internship (SULI) program, administered by the Office of Science, U.S. Department of Energy, for summer fellowship. We also thank Mr. Prasad Kerkar for the CMT analysis of the samples.

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