

## Characterization of Catalysts from Molybdenum Naphthenate

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### INTRODUCTION

Molybdenum naphthenate has been shown to be a highly active catalyst precursor for coal conversion in both coal processing and coal liquefaction (1-3). This catalyst precursor has also been effective for producing highly upgraded end products (4-6). Molybdenum naphthenate, a metal salt of the organic acid, is thermally decomposed releasing the metal at liquefaction conditions. Subsequent reaction of the metal to the sulfide occurs if sulfur is present. This *in situ* sulfided catalyst has been shown to have a different selectivity for hydrogenation and heteroatom removal reactions than commercial hydrotreating catalysts (7) at liquefaction conditions.

Chianelli and coworkers (8-10) have prepared bulk molybdenum sulfides having surface areas up to 50 m<sup>2</sup>/g by reacting MoCl<sub>4</sub> with Li<sub>2</sub>S in a tetrahydrofuran solvent. The precipitated sulfide was then treated with acetic acid to remove residual Li<sub>2</sub>S. It was then treated with H<sub>2</sub>S/H<sub>2</sub> at 400°C. Line broadening analysis of X-ray diffraction peaks suggested that the average size of the crystalline regions was 28Å in the perpendicular direction and 78Å in the lateral direction. Crystallites of these dimensions would, however, give larger surface areas. This discrepancy was resolved by TEM which indicated that the lateral extent of the MoS<sub>2</sub> crystallites was several thousand angstroms (9-10). The authors described the structure as having a "rag morphology" (10).

The purpose of our study was to prepare and characterize the active catalytic species generated from molybdenum naphthenate and excess sulfur under conditions similar to those used in coal liquefaction and coprocessing. Several catalytic hydrogenation reactions were performed using model compounds having structures representative of those present in coal or petroleum residuum. The model systems used were naphthalene, indene, benzofuran, indole, and benzothiophene dissolved in hexadecane. Molybdenum naphthenate which is oil soluble was added directly into the solvent as was sulfur which was introduced in excess. After reaction, the active catalytic species was recovered from the product solution and characterized by a number of analytical techniques to ascertain its composition and surface properties.

### Experimental

Hydrogenation Reactions.--Hydrogenation reactions were conducted in horizontal stainless steel tubing bomb reactors of ca. 56 cm<sup>3</sup>. The reactor was charged with 11.2g of reactant solution composed of 2 weight percent naphthalene or 1 weight percent of the other model species, molybdenum naphthenate at 3000 ppm Mo per total charge and excess elemental sulfur. Three different amounts of elemental sulfur, 0.067, 0.201, and 0.269g, were charged; these levels corresponded to three, nine, and twelve times the amount of sulfur required to convert Mo to MoS<sub>2</sub>. Reactions were conducted at 380°C for 30 minutes with H<sub>2</sub> introduced at 1250 psig at ambient temperature. The reactors were agitated at 550 cpm. The reactors were quenched in water immediately after reaction.

Chemicals.--The model reactants, naphthalene (99%), indene (99%), benzofuran (99.5%), indole (99%), and benzothiophene (97%), were obtained from Aldrich Chemical Company. Molybdenum naphthenate containing 6 weight percent Mo was obtained from Shepard Chemical Company.

Analysis.--After the reaction, the recovered product solution was separated into a liquid fraction and a black solid. The solid was washed with tetrahydrofuran, dried in a vacuum desiccator for three days and stored in a vial. The total weight of the black solid recovered from three equivalent reactions was approximately 0.19g.

The liquid products were analyzed by gas chromatography using a 30m DB-5 fused silica capillary column of 0.32mm inner diameter from J&W Scientific and FID detection. Para-xylene was used as the internal standard. Selected solid samples were characterized using X-ray diffraction, surface area (BET using N<sub>2</sub>), and scanning and transmission electron microscopy (SEM and TEM). The X-ray diffraction patterns were measured using a Scintag PAD V powder diffractometer using samples mounted on double-sided adhesive tape with curve deconvolution to remove the tape signal. Surface area was measured using a Digisorb-2600. SEM and TEM scans were made using JOEL-840A and Philips-400T instruments.

### Results and Discussion

Reactions Using Molybdenum Naphthenate and Excess Sulfur.--The reactions using molybdenum naphthenate and excess sulfur were performed with naphthalene, indole, benzofuran, indene, and benzothiophene. The product distributions obtained at two different levels of excess sulfur are given for each reactant in Table 1. For naphthalene, the major product was tetralin for both sulfur levels. At the higher sulfur level, slightly more hydrogenation to decalin was observed. The partially saturated hydrocarbon, indene, was readily hydrogenated to indan; however, further hydrogenation to the fully saturated hexahydroindan was limited. Only a small amount, 2%, of hydrogenolysis to methylcyclohexane occurred. The higher sulfur level again showed a higher level of hydrogenation of indene.

The oxygen containing species, benzofuran, was the least reactive of the heteroatomic species used in this study. Benzofuran was completely converted to a product slate containing primarily o-ethylphenol, ethylbenzene, and ethylcyclohexane. The higher sulfur level was detrimental to deoxygenation and nearly doubled the amount of ethylphenol present in the products. Both indole and benzothiophene underwent total heteroatom removal. However, the primary product from indole was ethylcyclohexane, and that from benzothiophene was ethylbenzene. In both cases the higher sulfur levels resulted in slightly higher levels of hydrogenation. However, the effect on indole, because of its high degree of hydrogenation, was small.

Characterization of Catalyst Solids. --Selected samples of reactor solids were analyzed for carbon hydrogen and nitrogen contents. Some samples were also subjected to pyrolysis using a thermogravimetric unit with nitrogen. The results given in Table 2 indicate that adsorbed or trapped hexadecane remained on the catalyst solids; some indole was adsorbed in those two runs. Mass spectrometric analyses confirmed this conclusion.

The results of surface area determinations are given in Table 3. Even though the solids were dried at 250°C under vacuum, not all of the solvent was stripped in all cases. The BET surface area results were low until this material was removed. Final surface areas were in the range of 150 to 200 m<sup>2</sup>/g.

SEM microphotographs taken at X25,000 indicated that the solids were composed of irregular clusters of rounded particles which ranged from about 500 to 2500Å in diameter. A typical SEM microphotograph is given in Figure 1. Subsequent TEM microphotographs of five selected solid samples (1A, 2A, 4A, 4B, 5A; see Table 3) showed that the solids were similar in appearance and were composed of "needle-shape" crystallites; see Figure 2. The shape was consistent with the "rag morphology" of Chianelli et al. (8-10)

X-ray diffraction analyses indicated that the solids were MoS<sub>2</sub> crystallites as a rhombohedral polymorph, and no excess sulfur was found. A low angle peak at about 13 degree's, after tape correction, corresponded to the diffraction perpendicular to the layers of MoS<sub>2</sub>. From peak width broadening, a spacing of 26Å (4 layers) was indicated. A peak at 59 degree's, corresponding to the diffraction parallel to the layers, indicated that a lateral dimension of 45Å existed with additional indications of longer elements.

#### Summary

When molybdenum naphthenate was added as a feed with model compounds for reactions at coal liquefaction conditions, the hydrogenation of naphthalene, indene, benzothiophene, and indole was enhanced by introducing a high level of sulfur. Indole, which had the highest degree of hydrogenation in the product slate, showed the least effect of sulfur level. Benzofuran was the least reactive of the three heteroatomic species having the same molecular skeletal structure. Deoxygenation was

inhibited by the higher amount of sulfur in the system. Molybdenum naphthenate reacted in situ to form rhombohedral MoS<sub>2</sub>. The resulting catalyst particles were of small size, 26A in the perpendicular direction and about 45A, or larger, in the lateral direction. These solids had higher surface areas, 150 to 200 m<sup>2</sup>/g, than previously reported.

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Table 1. Catalytic Hydrogenation of Model Compounds Using Molybdenum Naphthenate and Excess Sulfur

## 1. Naphthalene

Sulfur Amount*	Product Distribution (mole %)			
	Naphthalene	Tetralin	Decalin	Butylbenzene
3	1.3±0.2	89.7±0.7	7.9±0.5	1.1±0.1
9	0.9±0.1	87.0±0.2	10.7±0.1	1.1±0.3

## 2. Indene

Sulfur Amount*	Indene	Product Distribution (mole %)			
		Indan	cis-Hexahydro indan	trans-Hexahydro indan	Methyl cyclohexane
3	0	89.1±0.2	7.1±0.2	3.0±0.2	0.7±0.1
12	0	83.7±0.4	9.5±0.4	4.9±0.1	1.9±0.2

## 3. Benzofuran

Sulfur Amount*	Benzofuran	Product Distribution (mole %)					
		Dihydro benzofuran	o-Ethyl phenol	Ethyl benzene	Ethyl cyclohexene	Ethyl cyclohexane	Methyl cyclohexane
3	0	0	15.4±0.4	53.8±0.3	0.2±0.2	30.2±0.2	0.6±0.1
12	0	0	29.5±0.9	35.8±0.6	0.8±0.0	33.1±0.3	0.9±0.1

## 4. Indole

Sulfur Amount*	Indole	Product Distribution (mole %)					
		Indoline	o-Ethyl aniline	Ethyl benzene	Ethyl cyclohexene	Ethyl cyclohexane	Methyl cyclohexane
3	0	0	0	8.9±0.1	0.9±0.1	86.5±0.1	3.8±0.1
12	0	0	0	7.8±0.1	0.9±0.1	88.2±0.1	3.1±0.2

## 5. Benzothiophene

Sulfur Amount*	Benzo thiophene	Product Distribution (mole %)					
		Dihydro benzothiophene	o-Ethylthio phenol	Ethyl benzene	Ethyl cyclohexene	Ethyl cyclohexane	Methyl cyclohexane
3	0	0	0	93.8±0.2	0	5.7±0.2	0.5±0.1
12	0	0	0	89.7±0.2	0	9.4±0.2	0.9±0.1

\* Multiples of the stoichiometric amount of sulfur in MoS<sub>2</sub>

\*\* Each reaction was triplicated.

Table 2. Weight Loss and Carbon & Hydrogen Analyses of Recovered Catalysts

1. Naphthalene

<u>Sulfur Amount</u>	<u>% Loss TGA/N</u>	<u>Carbon</u>	<u>Hydrogen</u>	<u>Nitrogen</u>
3	----	12.6	2.3	----
9	19	14.7	2.6	----

2. Indene

<u>Sulfur Amount</u>	<u>% Loss TGA/N</u>	<u>Carbon</u>	<u>Hydrogen</u>	<u>Nitrogen</u>
3	20	11.0	2.3	----
12	----	----	----	----

3. Benzothiophene

<u>Sulfur Amount</u>	<u>% Loss TGA/N</u>	<u>Carbon</u>	<u>Hydrogen</u>	<u>Nitrogen</u>
3	15	10.1	1.9	----
12	----	----	----	----

4. Indole

<u>Sulfur Amount</u>	<u>% Loss TGA/N</u>	<u>Carbon</u>	<u>Hydrogen</u>	<u>Nitrogen</u>
3	29	24.0	4.3	0.5
12	18	14.1	2.4	0.4

5. Benzofuran

<u>Sulfur Amount</u>	<u>% Loss TGA/N</u>	<u>Carbon</u>	<u>Hydrogen</u>	<u>Nitrogen</u>
3	17	13.4	2.5	----
12	----	----	----	----

Table 3. Areas and Pore Volumes of Recovered Catalysts

1. Naphthalene

<u>Sulfur Amount</u>	<u>% Loss Drying*</u>	<u>Surface Area, M<sup>2</sup>/g</u>	<u>Pore Volume CC/g</u>
3	9.4	158	0.28
9	12.8	96	0.30
	+7.1	141	0.18

2. Indene

<u>Sulfur Amount</u>	<u>% Loss Drying*</u>	<u>Surface Area, M<sup>2</sup>/g</u>	<u>Pore Volume CC/g</u>
3	15.4	198	0.39
12	—	—	—

3. Benzothiophene

<u>Sulfur Amount</u>	<u>% Loss Drying*</u>	<u>Surface Area, M<sup>2</sup>/g</u>	<u>Pore Volume CC/g</u>
3	13.8	214	0.30
12	—	—	—

4. Indole

<u>Surface Amount</u>	<u>% Loss Drying*</u>	<u>Surface Area, M<sup>2</sup>/g</u>	<u>Pore Volume CC/g</u>
3	8.7	35	0.31
	+5.3	103	0.22
12	9.8	161	0.39

5. Benzofuran

<u>Surface Amount</u>	<u>% Loss Drying*</u>	<u>Surface Area, M<sup>2</sup>/g</u>	<u>Pore Volume CC/g</u>
3	16.6	179	0.30
12	—	—	—

\*Drying conditions were 250°C, 16 hours, 20 torr.

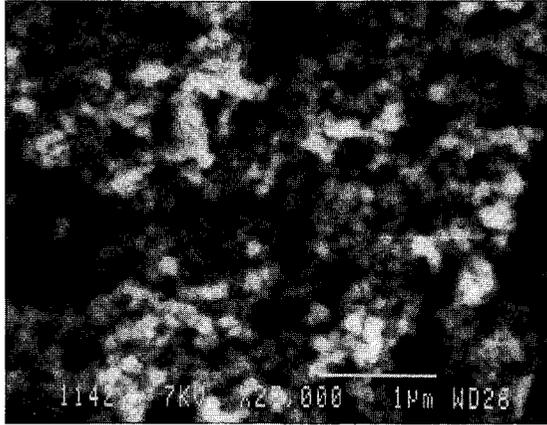


Figure 1 - SEM Photomicrograph of Sample 4B (x 25,000)

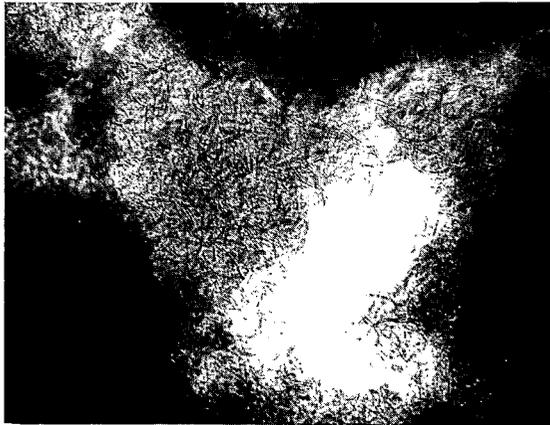


Figure 2 - TEM Photomicrograph of Sample 5A (x 800,000)