

ACTIVITY AND SELECTIVITY OF MOLYBDENUM
CATALYSTS IN COAL LIQUEFACTION REACTIONS

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During coal liquefaction, coal fragments forming a liquid product with reduced heteroatom content. Coal can be considered to be a large network of polynuclear aromatic species connected by heteroatoms and alkyl bridging structures. Predominant heteroatoms contained in coal are sulfur, oxygen, and nitrogen. Predominant alkyl bridges are methylene and ethylene structures. The purpose of this work is to evaluate how effectively three different molybdenum catalysts promote reactions involving heteroatom removal and cleavage of alkyl bridge structures. The reactions studied include: hydrogenation (HYD), hydrodeoxygenation (HDO), hydrodesulfurization (HDS), hydrodenitrogenation (HDN) and hydrocracking (HYC).

Both model and coal liquefaction reactions were performed to test the activity and selectivity of three different molybdenum catalysts. The three catalysts used were molybdenum naphthenate, molybdenum supported on gamma alumina ($\text{Mo}/\text{Al}_2\text{O}_3$) and precipitated, poorly crystalline molybdenum disulfide (MoS_2). The model compounds, chosen to mimic coal structure, on which the effectiveness of the catalysts for the model reactions was tested were: 1-methylnaphthalene, representing aromatic hydrocarbons, for hydrogenation; 1-naphthol, representing oxygen containing compounds, for deoxygenation; benzothiophene, representing sulfur containing compounds, for desulfurization; indole, representing nitrogen containing compounds, for denitrogenation; and bibenzyl, representing alkyl bridging structures, for hydrocracking. Catalytic reactions of combinations of reactants were performed to simulate a complex coal matrix. Thermal and catalytic coal liquefaction reactions were performed using Illinois No. 6 coal with anthracene as a solvent. The efficacy of the catalysts was determined by comparing the product and compound class fractions obtained from the liquefaction reactions.

Molybdenum Catalysts. All the catalysts used in this study have the element Mo (molybdenum) as the active metal component complexed with sulfur in a MoS_x form. Mo naphthenate is a thermally decomposable, hydrocarbon-soluble organometallic compound which was dispersed directly in the reaction mixtures. The catalytic species was generated *in situ*. Bearden et al. (1) postulates that at elevated temperatures and pressures inherent to coal liquefaction the metal naphthenate is converted to the active form by thermal decomposition. The active form is postulated to be MoS_2 (2,3) which is formed during pretreatment with H_2S or sulfur present in the feedstock. The Mo naphthenate used in this study was obtained from Shepherd Chemical consisting of ~6% Mo. The active form of the catalyst was generated *in situ* by introduction of excess sulfur to the reaction mixtures.

The $\text{Mo}/\text{Al}_2\text{O}_3$ used in this study was Amocat 1B obtained from Amoco. The active form was generated by presulfiding. The surface area of this material was 212 m^2/g .

Precipitated MoS_2 was prepared by the method of Chianelli and Dines (4) by precipitating MoS_2 from an ethyl acetate solution of MoCl_4 and Li_2S followed by annealing in H_2S . Precipitated MoS_2 exhibits a poorly crystalline "rag" structure (5), consisting of several stacked and highly disordered S-Mo-S layers. The layers have unusual flexibility in terms of number of dimension of the stacks and increased ability to intercalate organic species (5-7). Despite its poorly crystalline structure, precipitated MoS_2 exhibits an X-ray diffraction pattern similar to that of highly crystalline hexagonal MoS_2 (7). The synthesis of precipitated MoS_2 was confirmed by X-ray diffraction in this work. The surface area of precipitated MoS_2 was 42 m^2/g .

Experimental

Model Reactions. Model reactions were performed in horizontally mounted stainless steel tubing bomb reactors of ~20 ml volume. The model compounds and solvent, hexadecane, were obtained from Aldrich. All compounds of less than 99% purity were recrystallized before use. Model compound reactions were performed at 380°C with 1250 psig H₂ (cold) for 25 minutes and were agitated at rates greater than 800 cpm. For the individual reactions, the reactants were charged at 2 wt% in n-hexadecane; for the reactions with combined reactants, each component was introduced at 1 wt% giving 5 wt% reactant solutions. The reaction products were analyzed using a Varian 3700 FID chromatograph with a DB-5 fused silica capillary column. Para-xylene was used as internal standard. Catalyst, if used, was added in the individual reactant experiments at 1500 ppm Mo/g of reactor charge and in the combined reactions at 3500 ppm Mo/g of reactor charge. Elemental sulfur was added only to those reactions involving Mo naphthenate at a ratio of 2.5 to 1 sulfur to Mo by weight. Thermal reactions with excess sulfur were also performed to determine the independent effects of sulfur on reactant activity. Sulfur was added in the thermal reactions at a sulfur to Mo ratio of 2.5 to 1, calculated by assuming Mo would have been present at a loading of 1500 ppm/g reactor charge for the individual reactions.

Coal Liquefaction Reactions. Coal liquefaction reactions were performed thermally and catalytically with all three molybdenum catalysts in ~50 ml stainless steel horizontal reactors. The reactor charge was 0.5g coal with 0.5g anthracene as solvent and 1250 psig H₂ (cold). Reactions were performed at 425°C for 30 minutes at an agitation rate of 850 rpm. The catalyst loading was 3500 ppm Mo/reactor charge; 0.01g of sulfur was used for the Mo naphthenate reactions.

The liquid and solid products were separated by sequential washing with methylene chloride-methanol (9:1 v/v) solution (MCM) and tetrahydrofuran (THF). The separation produced three fractions: MCM solubles (MCMS), MCM insolubles-THF solubles (THFS) and THF insolubles or ash-free insoluble organic matter (IOM). The MCMS fraction was further fractionated by the chromatographic method of Boduszynski (8) into compound class fractions: hydrocarbons (HC), nitrogen heterocycles (NH), hydroxyl aromatics (HA) and polyfunctional compounds (PC). The HC fraction was further analyzed for anthracene and its hydrogenation products using the same GC analysis procedure as the model systems.

Results and Discussion

A sequence of reactions was performed with each model which included thermal reactions, thermal reactions with excess sulfur, and catalytic reactions using Mo naphthenate, Mo/Al₂O₃, and precipitated MoS₂. The product distributions achieved from the model reactions were summarized using several defined terms. The terms are: (1) percent hydrogenation which is the number of moles of hydrogen required to achieve the obtained product distribution as a percentage of the moles of hydrogen required for the most hydrogenated product; (2) percent hydrogenolysis which is the summation of the mole percent of components resulting from carbon-carbon and carbon-heteroatom bond cleavage; (3) percent desulfurization which is the summation of the mole percents of components not containing sulfur; (4) percent hydrodeoxygenation which is the summation of the mole percents of components not containing oxygen; (5) percent hydrodenitrogenation which is the summation of the mole percents of components from which nitrogen has been removed; and (6) percent hydrocracking which is the summation of the mole percents of components resulting from the breakage of an alkyl bridge structure.

Hydrogenation of 1-Methylnaphthalene. Hydrogenation of 1-methylnaphthalene proceeds through two pathways, both culminating in the production of decalin. 1-methylnaphthalene can either be hydrogenated to methyltetralins (tetrahydromethylnaphthalenes) followed by demethylation to naphthalene and

further hydrogenation, or demethylated initially forming naphthalene and its hydrogenation products, tetralin and decalin (9-11).

Under thermal and thermal with sulfur conditions, essentially no hydrogenation of 1-methylnaphthalene occurred as presented in Table 1. Under catalytic conditions, Mo naphthenate produced the highest conversion of 1-methylnaphthalene among the three Mo catalysts, yielding major products of 5-methyltetralin and 1-methyltetralin. Conversion to hydrogenated naphthalenes was not observed with any of the Mo catalysts, although small quantities of naphthalene were produced. Very little hydrogenolysis of the methyl group was observed, indicating that these Mo catalysts were not selective for cleavage of the carbon-carbon bond.

Table 1
Activity and Selectivity of Mo Catalysts in Model Compound Systems

	Thermal	Thermal with Sulfur	Mo Naphthenate	Mo/Al ₂ O ₃	P-MoS ₂ *
<u>1-Methyl-Naphthalene</u>					
Hydrogenation, %	0.7±0.3	0.8±0.6	31.3±0.8	13.5±0.6	7.6±0.5
Hydrogenolysis, %	0.4±0.1	0.5±0.1	1.6±0.4	0	0
<u>1-Naphthol</u>					
Hydrogenation, %	28.5±4.0	10.6±2.7	53.1±0.6	41.0±0.3	46.1±0.6
Deoxygenation, %	38.5±1.7	17.4±3.3	100.0	100.0	100.0
<u>Benzothiophene</u>					
Hydrogenation, %	1.3±0	1.1±0.1	51.9±0.5	51.0±0.2	51.1±0.1
Hydrodesulfurization,0	1.4±0.1	1.2±0.1	100.0	100.0	100.0
<u>Indole</u>					
Hydrogenation, %	1.6±0.5	1.1±0.2	35.6±4.3	22.6±0.1	8.2±1.6
Hydrodenitrogenation, %	0	0	18.6±4.7	11.9±0.1	2.0±0.8
Hydrogenolysis, %	1.7±1.0	0.5±0.2	69.6±5.4	38.2±0.5	10.4±5.0
<u>Bibenzyl</u>					
Hydrogenation, %	2.7±0.1	1.7±0.1	2.3±0.2	1.9±0.3	1.8±0.01
Hydrocracking, %	4.8±0.3	2.7±0.1	3.8±0.3	3.2±0.1	3.2±0.1

*P-MoS₂ = precipitated MoS₂

Hydrodeoxygenation of 1-Naphthol. Two reaction pathways for the hydrodeoxygenation of 1-naphthol are available, one in which 1-naphthol is hydrodeoxygenated and then hydrogenated to tetralin and decalin and one in which 1-naphthol is hydrogenated without removal of oxygen forming 5,6,7,8-tetrahydro-1-naphthol and 1-tetralone (12).

Significant thermal hydrogenation of 1-naphthol which followed both reaction pathways was observed. When sulfur was added, a marked inhibition of naphthol hydrogenation activity was obtained (Table 1), although the reaction still proceeded through both reaction pathways. In the catalytic reactions (Table 1), considerably more hydrogenation of 1-naphthol was observed. However, the catalytic hydrogenation proceeded through only one reaction pathway, the one involving immediate removal of the hydroxyl group with the major product being tetralin. All three Mo catalysts completely deoxygenated 1-naphthol; however, differences were observed in their ability to hydrogenate the deoxygenated 1-naphthol. Mo naphthenate was most active for hydrogenating 1-naphthol, followed

by precipitated MoS_2 and then $\text{Mo/Al}_2\text{O}_3$.

Hydrodesulfurization of Benzothiophene. The reaction pathway for benzothiophene involves first hydrogenation to the dihydro form, then ring cleavage at the carbon-sulfur bond and finally hydrodesulfurization releasing H_2S (10,11,13,14).

Sulfur had no effect on thermal reactions of benzothiophene which was only slightly reactive without a catalyst present (Table 1). The thermal reactions formed the products, dihydrobenzothiophene and ethylbenzene, in small quantities. In the catalytic reactions, complete desulfurization was achieved with all of the Mo catalysts, producing primarily ethylbenzene and a minor product of ethylcyclohexane in all cases. Similar results have been observed over $\text{CoMo/Al}_2\text{O}_3$ catalysts (13). The hydrogenation activity of all of the catalysts was also nearly equivalent (Table 1).

Hydrodenitrogenation of Indole. The reaction pathway for indole hydrodenitrogenation proceeds by hydrogenation of the five-membered ring, followed by ring cleavage, removal of NH_3 and then hydrogenation to a six-membered ring alkane (15).

Thermal reactions of indole showed nearly 6% conversion primarily to dihydroindole. The addition of sulfur to thermal indole reaction had little or no effect on indole reactivity. The catalytic reactions yielded substantially more hydrogenation and hydrodenitrogenation of indole (Table 1). Mo naphthenate proved the most selective for denitrogenation of indole, with the major products being o-ethylaniline and ethylcyclohexane, with minor products of dihydroindole and ethylbenzene. Neither complete denitrogenation nor hydrogenation was achieved with any of the catalysts. The ranking for denitrogenation selectivity among the three catalysts was Mo naphthenate > $\text{Mo/Al}_2\text{O}_3$ > P-MoS_2 .

Hydrocracking of Bibenzyl. The reaction pathway for the hydrocracking of the ethylene bridge in bibenzyl can either proceed by cleaving the carbon-carbon bond of the bridge structure forming toluene or by cleaving the bond between the aromatic ring carbon and the ethylene bridge, forming ethylbenzene and benzene. Under proper conditions, these hydrocracked products can be further hydrogenated (16).

Hydrocracking of bibenzyl only occurred to a small degree both thermally and catalytically. For all cases, percent hydrocracking was ~3% (Table 1). Products observed in most cases were minor amounts of ethylbenzene, ethylcyclohexane, toluene and benzene.

Combined Reactant Reactions. Reactions were performed thermally and catalytically with solutions composed of 1 wt% of all five model compounds in order to simulate the interaction among the different functionalities in a coal liquefaction system. Combined thermal reactions resulted in an increase of indole conversion to indoline and a decrease in the reactivity of 1-naphthol compared to the individual reactions.

Catalytic reactions performed with Mo naphthenate revealed the same trend as the thermal reactions but to a much greater degree. Complete conversion of indole was observed as well as complete deoxygenation of 1-naphthol; however, significant inhibition of the hydrogenation products of 1-naphthol was observed. Also, a decrease in hydrogenation of 1-methylnaphthalene and in bibenzyl hydrocracking was observed compared to the individual reactions. Since increased catalyst loading was used for the combined reactions, individual reactions with indole were performed with increased Mo loading of 3500 ppm Mo per g of reactor charge to ascertain the effect of increased catalyst loading compared to additional reactants. The same trends were observed as stated above, with small increases in inhibitive effects.

Reactions performed on combined solutions with $\text{Mo/Al}_2\text{O}_3$ exhibited different trends. The inhibitive effects noted with Mo naphthenate were reversed with $\text{Mo/Al}_2\text{O}_3$. Increases were achieved in the hydrogenation products of 1-methylnaphthalene and 1-naphthol, with the same corresponding conversion of indole

as observed with the Mo naphthenate reactions.

Reactions performed with precipitated MoS₂ on the combined solutions yielded results similar to that of Mo naphthenate, but to a lesser degree. Hydrogenation of 1-methylnaphthalene and 1-naphthol products was inhibited as was hydrocracking of bibenzyl. An amplification of indole conversion was also observed.

Coal Liquefaction Reactions. A series of coal liquefaction reactions was performed to assess the activity and selectivity of the three Mo catalysts for the conversion of Illinois No. 6 coal to soluble products. Final assessments of selectivity and activity were based upon the production of the different solubility fractions and compound classes described in the Experimental section. Hydrogenated products of the solvent, anthracene, were also analyzed to assess the percentage of hydrogenation achieved during the reaction.

Thermal reactions of Illinois No. 6 coal yielded a coal conversion of 62%. The product distributions of gas, MCMS, THFS, and IOM, given in Table 2, indicate low thermal gas production and appreciable IOM after reaction. Much higher coal conversion was produced during the catalytic reactions as shown in Table 2. Mo naphthenate achieved 92% coal conversion; Mo/Al₂O₃ yielded 90%, and precipitated MoS₂ converted much less at 79%.

Production of THFS ranged from 22% thermally to 31% with Mo/Al₂O₃. The production of THFS was generally related to an increase or decrease in the amount of the MCMS fraction. The lowest production of THFS was generated by Mo naphthenate at 17% which was accompanied by the highest production of MCMS, 48%. The largest production of THFS was obtained with Mo/Al₂O₃, which also exhibited a relatively high MCMS fraction, 40%. Mo/Al₂O₃ was not as effective as Mo naphthenate in converting THFS to MCMS. Precipitated MoS₂ produced low THFS at 21% and a MCMS of 37% which was comparable to Mo/Al₂O₃ but was not as effective for overall coal conversion.

Table 2
Product Distribution from Coal Liquefaction Reaction

Product Fraction	Weight Percent			
	Thermal	Mo Naphthenate	Mo/Al ₂ O ₃	P-MoS ₂
Gas	8.7±3.3	28.2±4.3	19.6±1.7	20.2±0.9
MCMS				
HC	11.5±1.8	24.0±1.0	16.6±0.1	15.0±0.7
NH	3.9±1.2	4.6±1.4	6.1±0.1	5.0±0.1
HA	8.1±2.0	8.8±0.2	9.7±0.5	10.8±2.3
PC	8.4±0.5	9.5±0.6	7.5±0.4	6.3±1.4
THFS	21.6±5.2	16.5±0.9	30.9±0.3	21.4±2.8
IOM	37.8±3.8	8.4±3.8	9.6±1.9	21.3±0.3
Coal Conversion, %	62.2±3.8	91.6±3.8	90.4±1.9	78.7±0.3

Comparisons of the compound class separations given in Table 2 indicate that Mo naphthenate produced the largest percentage of hydrocarbons (HC) at 24%. The other catalysts yielded less, 17% with Mo/Al₂O₃ and 15% with precipitated MoS₂. The nitrogen heterocycles (NH) were 4% thermally and in the presence of a catalyst

increased only slightly to 6%. The same trend was observed with hydroxyl aromatics (HA) with thermal production at 8% and increasing to 11% with the precipitated MoS₂ catalyst. The increase in the NH and HA fractions in the catalytic reactions was due to increased coal conversion and MCMS production, yielding more nitrogen heterocycles and hydroxyl aromatics soluble and analyzable.

The relative differences in the NH and HA fractions of the catalytic reaction can be seen more easily by examining the average results on a MCMS basis as given in Table 3. A general trend could be seen for Mo naphthenate and Mo/Al₂O₃, where the catalysts produced the NH and HA fractions on a proportionate basis, although the former produced less overall of the two fractions. P-MoS₂ produced a different distribution with the HA fraction produced being disproportionately higher than that of the other catalysts and the NH fraction being lower than Mo/Al₂O₃ but not as low as Mo naphthenate. These compound class distributions indicated that precipitated MoS₂ was more selective for denitrogenation than for deoxygenation.

Table 3
Compound Class Fractions from Coal Liquefaction
Reactions on a MCMS Basis

Compound Classes, Wt% on MCMS Basis	Mo			
	Thermal	Naphthenate	Mo/Al ₂ O ₃	P-MoS ₂
HC	36.1±4.0	51.3±1.7	41.7±0.2	40.4±0.2
NH	12.2±2.6	9.8±3.2	15.1±0.1	13.5±0.4
HA	25.3±3.5	18.7±0.3	24.3±1.3	29.1±4.9
PC	26.4±3.0	20.2±1.1	18.9±0.5	17.0±4.6

Polyfunctional compound (PC) decreased smoothly from thermal conditions at 26% to catalytic with precipitated MoS₂ at 17% on a MCMS basis. These results are best interpreted in terms of the HC fraction. The increase of HC to 51% for Mo naphthenate was a result of the reduction of all the other classes, NH, HA and PC. Mo/Al₂O₃ followed the same patterns but only produced ~42% HC. Precipitated MoS₂ yielded 40% HC which was produced more from denitrogenation than from deoxygenation.

In terms of the greatest selectivity for hydrocarbon production, hydrodeoxygenation and coal conversion to soluble products, the catalysts can be ranked as Mo naphthenate > Mo/Al₂O₃ > P-MoS₂. However, for hydrodenitrogenation selectivity of greatest impact was Mo naphthenate > P-MoS₂ > Mo/Al₂O₃.

Anthracene Hydrogenation. Anthracene hydrogenation during coal liquefaction ranged from 33% under thermal conditions up to 41% for Mo naphthenate reactions (Table 4). Reaction products resulting from anthracene hydrogenation included dihydroanthracene (DHA), hexahydroanthracene (HHA) and octahydroanthracene (OHA). Some cracking of anthracene was observed, from 4 to 6 mole percent, with the cracked products being in the boiling point range for naphthalene and its derivatives. Reactions with Mo/Al₂O₃ produced the highest level of cracking. The percent hydrogenation of the solvent remained within a deviation of 3 mole percent for all catalysts with only slight variations in product distributions.

Table 4
Anthracene Hydrogenation in Thermal and Catalytic
Coal Liquefaction Reactions

<u>Reaction</u>	<u>Hydrogenation, %</u>
Thermal	33.0±0.7
Mo Naphthenate	41.1±2.7
Mo/Al ₂ O ₃	36.1±2.3
P-MoS ₂	40.1±1.2

Summary

The oil-soluble Mo naphthenate was the most effective catalyst for reactions involving hydrogenation, deoxygenation and denitrogenation. Effective hydrocracking was not achieved with any of the catalysts involved. Roughly equal activity for desulfurization was observed for each Mo catalyst. Reactions containing model compounds representative of the five reactions studied, experienced interactive effects which included hydrogenation and hydrocracking inhibition and increased reactivity of nitrogen compounds in the presence of Mo naphthenate and precipitated MoS₂. These inhibitive effects were reversed to promotional effects in the presence of Mo/Al₂O₃.

Mo naphthenate was also the most effective catalyst for overall coal conversion and the production of MCMS fraction and hydrocarbons. This catalyst also proved most effective for denitrogenation and deoxygenation. Mo/Al₂O₃, while exhibiting comparable coal conversion as Mo naphthenate, produced less MCMS and hydrocarbons. Precipitated MoS₂ showed the least propensity for coal conversion, but did exhibit somewhat better selectivity for denitrogenation than did Mo/Al₂O₃. The anthracene hydrogenated thermally and catalytically forming hydroaromatic species. Hydrocracking of anthracene was observed in all reactions, with those using Mo/Al₂O₃ producing the most.

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