Conclusions

During the coprocessing of subbituminous coal and vacuum bottoms, a marked improvement in process operability and increased distillate yield were observed at low coal concentrations. In the range of 10–30 wt % maf coal concentration, the distillate yield was constant and similar to that for the no coal case; that is, the distillate yield was not adversely affected when oil was replaced by coal. For the conditions of this study, the overall distillate yield started to drop beyond 30 wt % maf coal concentration. A minimum naphtha yield associated with a maximum in light gas oil yield was observed at about 25 wt % maf coal concentration. This could prove advantageous for the selective production of a given end-use fuel. The yield of the heaviest gas oil fraction continued to decrease as the coal concentration was increased, showing the beneficial effect that the addition of coal has on minimizing the production of heavy distillate product.

The gross distillate quality measured by H/C atomic ratio, specific gravity, and aromaticity changed only marginally over the range of coal concentrations studied. Hydrogen addition became more efficient as oil was replaced by coal. The oxygen content of the distillate increased slightly with increasing coal concentration although the oxygen removal increased. The sulfur removal remained relatively constant as the coal concentration was increased, but the sulfur content of the distillate decreased due to less sulfur in the feedstock.

The extent of anisotropic solids formation was markedly decreased by adding coal to the feedstock compared with that for the no coal case. The extent of vanadium and nickel removal also improved with increasing coal concentration. The coal conversion reached a minimum at about 10 wt % maf coal concentration, suggesting that the liquefaction step occurs via two different mechanisms depending on the availability of primary coal-derived products in the reaction mixture.

Registry No. Fe, 7439-89-6; Ni, 7440-02-0; V, 7440-62-2; H_2S, 7783-06-4; C, 7440-44-0; iron sulfate, 10124-49-9.

Activity and Selectivity of Three Molybdenum Catalysts for Coal Liquefaction Reactions[†]

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The activity and selectivity of three different molybdenum catalysts for reactions occurring in coal liquefaction, specifically for hydrogenation (HYD), hydrodeoxygenation (HDO), hydrodenitrogenation (HDN), hydrodesulfurization (HDS), and hydrocracking (HYC), have been examined. The three molybdenum catalysts used were molybdenum naphthenate, molybdenum on γ-alumina, and a precipitated, disordered MoS_2. Molybdenum naphthenate was most selective for HYD and HDN. All three catalysts exhibited approximately equal activity for HDS and HDO and little selectivity for HYC of alkyl bridge structures. The activity and selectivity of the three molybdenum catalysts for producing hydrocarbons and removing heteroatoms from coal during liquefaction were determined and compared. Molybdenum naphthenate was the most active catalyst for hydrocarbon production and removal of nitrogen- and oxygen-containing species during coal liquefaction.

Introduction

The purpose of coal liquefaction processes is to fragment coal and obtain a liquid product with an increased hydrogen content and a reduction in heteroatoms. Coal can be considered to be a large network of polynuclear aromatic species connected by heteroatom and alkyl bridge structures. Predominant heteroatoms contained in coal are sulfur, oxygen, and nitrogen. Predominant alkyl bridges are methylene and ethylene structures. These heteroatoms and bridging atoms cleave when a coal is liquefied. Different molybdenum catalysts have been shown to be effective in liquefying coal. Among them, molybdenum naphthenate has been shown to be highly effective.[1,2] In addition, a new molybdenum sulfide catalyst has been developed by using low temperature precipitation[3] and has the potential for being an effective catalyst for coal liquefaction. However, the efficacy of a particular catalyst for removal of specific heteroatoms can be obscured by the complex combination of species involved in coal. Thus, the use of model species and model reactions in conjunction with actual liquefaction studies provides a better understanding of the activity and selectivity of different catalysts for reactions common in coal liquefaction. The reactions important in liquefaction include hydrogenation (HYD), hydrodeoxygenation (HDO), hydrodesulfurization (HDS), hydrodenitrogenation (HDN), and hydrocracking (HYC).

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(1) Hawk, C.; Hiteshue, R. W. *U.S. Bur. Mines Rep.* **1965**, *No. 622*, 24.
(2) Kottenstette, R. J. Sandia Report No. SAND-82-2495; *Energy Abstr.* **1983**, 22936.
(3) Chianelli, R. R.; Dines, M. B. *Inorg. Chem.* **1978** *17*, 2758.

0887-0624/89/2503-0160$01.50/0

This study investigated the activity and selectivity of three molybdenum-containing catalysts for reactions occurring in coal liquefaction as well as for producing products from coal. The catalysts chosen included an oil-soluble molybdenum naphthenate (MoNaph), molybdenum supported on γ-alumina (Mo/Al_2O_3), and a precipitated poorly crystalline molybdenum disulfide (MoS_2). For the model reactions, model compounds were chosen as representative coal structures: 1-methylnaphthalene for aromatic hydrocarbons; 1-naphthol for oxygen-containing compounds; benzothiophene for sulfur-containing compounds; indole for nitrogen-containing species; bibenzyl for alkyl bridge structures. Experiments were performed to determine the activity and selectivity of the catalysts for HYD, HDO, HDS, HDN, and HYC reactions. A limited investigation was made to characterize the state of the catalysts recovered from model compound reactions in terms of activity and composition. To observe the activity of the catalysts based on conversion of coal to soluble products, coal liquefaction experiments were also performed.

Molybdenum Catalysts. The catalysts used in this study have in common the element molybdenum as the active metal component complexed with sulfur in a MoS_x form. This MoS_x species is the component that is thought to account for hydrotreating activity. The mechanism by which this active form is obtained is quite different for the three catalysts, and therefore, the differences in activity and selectivity of these catalysts in liquefaction reactions were examined.

Molybdenum Naphthenate. The organic constituent of MoNaph is naphthenic acid, the most common of which is pentamethylenemonocarboxylic acid.[4] MoNaph is a thermally decomposable organometallic compound which is hydrocarbon soluble and is often introduced into coprocessing or coal liquefaction systems by impregnation of the coal[1] or dispersion of the catalyst in situ.[5,6] The catalytic species is generated in situ by thermal decomposition[7] at the conditions inherent to coal liquefaction. The active form is postulated to be MoS_2,[2,8] which is formed during pretreatment with H_2S or formed from sulfur present in the feedstock.

Molybdenum on Alumina. The catalyst used in this study was Mo/Al_2O_3 (Amocat 1B), which was presulfided to form the active species. The crystalline structure of the MoS_2 species typically formed on the alumina support is hexagonal and highly crystalline.[9] The active species has been described as a distribution of very small two-dimensional hexagonal patches.[10]

Precipitated Molybdenum Disulfide. In 1978, Chianelli and Dines[3] developed a novel MoS_2 catalyst that is prepared by precipitation from nonaqueous solvents at room temperature producing a material having unusual crystalline properties. Precipitated MoS_2 exhibits a poorly crystalline form, termed the "rag" structure,[11] consisting of several stacked and highly disordered S–Mo–S layers. These layers are reported to have unusual flexibility in terms of number and dimension of the stacks.

Table I. Analysis (wt %) of Illinois No. 6 Coal[a]

Ultimate Analysis	
C	68.4
H	4.7
O	8.9
N	1.4
S	3.2
Cl	0.1
Proximate Analysis	
moisture	2.5
ash	10.5
volatile matter	37.6
fixed carbon	49.4
Distribution of Sulfur	
pyritic	1.1
sulfate	0.00
organic	2.1
total	3.2

[a] Refer to ref 15.

The unique physical properties of this catalyst due to its disordered crystalline structure have been examined in some detail.[11-13] Because of its structure the precipitated MoS_2 has an increased ability to intercalate organic substances. This unique form also has a varying surface area from one preparation mixture to the next, dependent on the dimensions of the stacked layers. Surface areas of this catalyst have been reported as ranging from 18 to 115 m^2/g, with the median at 50 m^2/g.[12]

Experimental Section

Equipment. Model compound reactions were performed in horizontally mounted stainless-steel tubing bomb reactors with ~20 mL volume. Coal liquefaction reactions were performed in similarly constructed reactors with volumes of ~50 mL. These reactors were equipped with a Nupro fine metering valve for introducing hydrogen.

Materials. Model compounds were commercially obtained from Aldrich Chemical Co. and included 1-methylnaphthalene (99%), 1-naphthol (99%), benzothiophene (97%), indole (99%), bibenzyl (99%), and hexadecane (99%), which was used as a solvent in all model reactions. All compounds of less than 99% purity were recrystallized.

Catalysts employed included MoNaph (Shepherd Chemical Co.), Mo/Al_2O_3 (Amocat 1B, Amoco), Shell 324 $NiMo/Al_2O_3$ (Shell Chemical Co.), and a precipitated molybdenum disulfide (MoS_{2+x}) prepared in the laboratory. Li_2S and $MoCl_4$ used in the preparation of the precipitated MoS_2 were obtained from Alfa and used as received. Precipitated MoS_2 was prepared by dissolving $MoCl_4$ in ethyl acetate; the resulting solution was then added to a slurry of Li_2S, precipitating the MoS_2. The product was annealed with pure H_2S at 400 °C, washed with 12% acetic acid, and then sulfided with 10% H_2S/H_2 at 400 °C for 1 h. The composition of the precipitated MoS_2 was confirmed by X-ray diffraction. Elemental sulfur (Fisher) was used for in situ sulfiding of the MoNaph. The commercially prepared Mo/Al_2O_3 and $NiMo/Al_2O_3$ were presulfided and then ground to less than 150 mesh prior to use in reactions.

For coal liquefaction reactions, a bituminous Illinois No. 6 coal, whose elemental analysis is given in Table I, was obtained from Air Products and Chemicals, Inc. The coal was powdered, dried in a vacuum oven overnight at 60 °C, and stored in a desiccator. Anthracene (99%) obtained from Aldrich was used as received as solvent in all liquefaction experiments. Hydrogen gas of 99.9% purity and having a moisture content of less than 3 ppm was used in all experiments.

Solvents used in the liquid separation of coal were obtained from Fisher and included methylene chloride, methanol, hexane, toluene, chloroform, and tetrahydrofuran. Column packings included Fluoropak 80, 40/60 mesh (Alltech Associates), and ac-

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(4) Petrov, A. D.; Ivanov, I. Z. *J. Am. Chem. Soc.* **1932**, *54*, 239.

(5) Aldridge, C. L.; Bearden, R., Jr. U.S. Patent 4,111,787, 1978.

(6) Aldridge, C. L.; Bearden, R., Jr. U.S. Patent 4,298,454, 1981.

(7) Bearden, R., Jr.; Aldridge, C. L. U.S. Patent 4,134,825, 1979.

(8) Bockrath, B. C. Quarterly Report for the Period Ending June 30, 1981; Pittsburgh Energy Technology Center: Pittsburgh PA, Nov 1981.

(9) Wildervanck, A.; Jellinek, Z. *Z. Anorg. Allg. Chem.* **1964**, *328*, 309.

(10) Kasztelan, S.; Toulhoat, H.; Grimblot, J.; Bonnell, J. P. *Appl. Catal.* **1984**, *13*, 127.

(11) Chianelli, R. R.; Prestridge, E. B.; Pecoraro, T. A.; DeNeufville, J. P. *Science* **1979**, *203*, 1105.

(12) Chianelli, R. R. *Catal. Rev.—Sci. Eng.* **1984**, *26*, 3 and 4, 361.

(13) Chianelli, R. R. *J. Cryst. Growth* **1976**, *34*, 239.

tivated basic alumina, grade AG-10 100/200 mesh (Bio Rad Laboratories). Compounds used to determine elution patterns for liquid chromatography separations included anthracene (99%), acridine (99%), carbazole (99%), and 1-naphthol (99%) (Aldrich). Light solvent refined coal (L-SRC) samples were obtained from Catalytic, Inc., Wilsonville, AL.

Model Compound Reactions. Model compound reactions were performed at 380 °C, with 1250 psig of H$_2$ (charged at ambient temperature) for 25 min with an agitation rate of 850 cpm for vertical agitation and 500 cpm for horizontal agitation. Reactants were charged at 2 wt % in *n*-hexadecane. Catalyst, if used, was added at a loading of 1500 ppm of Mo/g of charge to reactor. Elemental sulfur was added only to those catalytic reactions involving MoNaph at a ratio of 2.5:1 sulfur:Mo by weight. Thermal reactions were also performed with sulfur present, with sulfur introduced at the same level as the catalytic MoNaph reaction. The products were recovered from the reactor and analyzed by gas chromatography using a 60-m DB-5 column and *p*-xylene (Aldrich, 99%) as an internal standard.

Coal Liquefaction Reactions. Coal liquefaction reactions were performed thermally and with all three molybdenum catalysts. The charge to the reactor was 0.5 g of coal with 0.5 g of anthracene as solvent and 1250 psig of H$_2$ (cold). Reactions were performed at 425 °C for 30 min at an agitation rate of 850 rpm. The catalyst loading when used was 3500 ppm Mo/total charge. For the MoNaph reactions, 0.01 g of sulfur was used. Recovery of the product from the reactor was based upon the weights of the solid, liquid, and gas fractions. In calculating the product distributions, all losses were equally distributed among the solid and liquid fractions. The product distributions are reported on a maf coal basis. Hydrogen consumption was determined by using a molecular sieve column with TCD detection in conjunction with standard *PVT* methods.

The liquid and solid products were separated by sequential washing with a methylene chloride–methanol (9:1 v/v) solution (MCM) and tetrahydrofuran (THF). This 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[14] into compound-class fractions: hydrocarbons (HC), nitrogen heterocycles (NH), hydroxyl aromatics (HA), and polyfunctional compounds (PC). Model compounds such as anthracene, acridine, carbazole, and 2-naphthol were chromatographed and verified the procedure. L-SRC, a heavy coal liquid, was used to verity the reproducibility of the analysis. The hydrocarbon fraction separated from the MCMS fraction was further analyzed for anthracene hydrogenation products by using a 60-m DB-5 capillary column. The sample, dissolved in toluene with phenanthrene (Aldrich) as the internal standard, was analyzed isothermally at 180 °C. Anthracene (ANTH) and three major hydrogenation products were observed: 9,10-dihydroanthracene (DHA), hexahydroanthracene (HHA), and 1,2,3,4,5,6,7,8-octahydroanthracene (OHA). The isomer of HHA produced was not determined. Some lighter hydrocracked products were also observed and are designated as naphthalene derivatives (NDRV).

Instrumental Analysis. X-ray diffraction patterns were obtained by the powder diffraction method on a Phillips Norelco XRG 3100 instrument equipped with a copper Kα source. GC–mass spectrometry was performed on a Varian 3700 Model gas chromatograph in conjunction with a VG Analytical 70-E mass spectrometer. Surface area analysis was performed on a Quantachrome Monosorb single-point nitrogen BET surface analyzer. Fourier transform infrared analysis (FTIR) was performed with a Nicolet Model 5SXC spectrometer with CsI$_2$ optics.

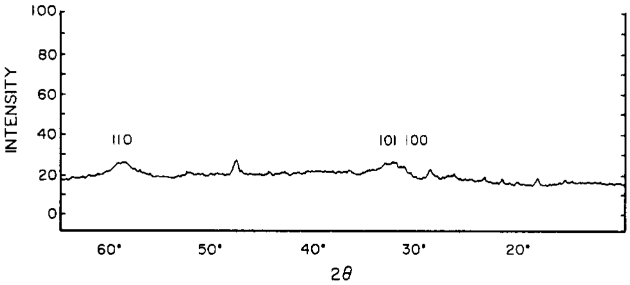

Figure 1. X-ray diffraction of recovered catalytic solids from molybdenum naphthenate reaction.

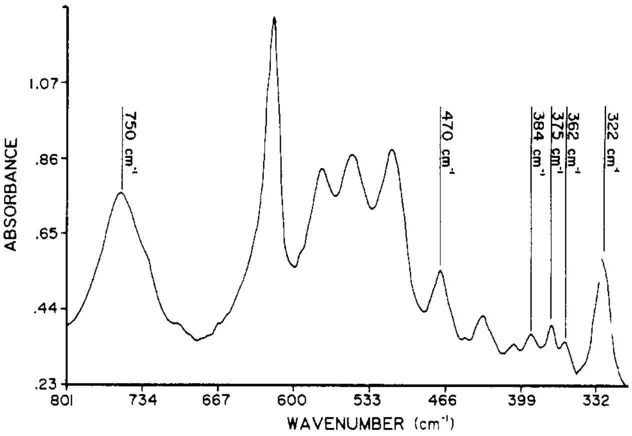

Figure 2. FTIR spectrum of recovered catalytic solids from molybdenum naphthenate reactions.

Table II. Comparison of X-ray Diffraction Patterns of Recovered Mo Catalyst with Standards[a]

standard molybdenite		recovered catalyst from reactions with			
		MoNaph		MoS$_2$	
d spacing	I/I_1	*d* spacing	I/I_1	*d* spacing	I/I_1
6.15	100	no peak		6.20	100
2.74	16	2.70	16	2.72	12
2.28	45	no peak		2.28	46
1.58	11	1.56	12	not scanned	

[a] Note: *d* spacing is the distance between each set of planes of the crystal lattice, in Å; I/I_1 is the peak intensity measured as a percent of the largest peak.

The elemental state of the catalyst formed from MoNaph was characterized through X-ray diffraction, FTIR spectral analysis, and elemental analysis of Mo and S. The results showed roughly 55% Mo and 45% S (on a carbon-hydrogen-free basis), which compares approximately with theoretical values for MoS$_2$ of 60% Mo and 40% S. The X-ray diffraction pattern shown in Figure 1 was compared with the *d* spacings and relative intensities found for crystalline MoS$_2$ standards,[15] as shown in Table II. The absence of peaks at *d* spacings of 6.15 and 2.28 indicates no reflections from the 002 and 103 planes. Values at *d* spacings of 2.70 and 1.56 are indicative of reflections from the 100 and 110 planes of crystalline MoS$_2$. None of the peaks found exhibited strong maxima as shown in Figure 1. The diffraction pattern was characterized by very broad, irregular peaks, similar to those of amorphous MoS$_2$ as produced by using the same precipitation method[3] as well as by other methods.[9]

FTIR analysis of the recovered solid catalyst revealed a strong peak in the region characteristic of the strongest band for crystalline MoS$_2$ at 470 cm^{-1}[16] as shown in Figure 2. The weak band of crystalline MoS$_2$ also appeared at 384 cm^{-1}, and evidence of peak shifts in the region of 375 and 362 cm^{-1} was also observed. This shift may be evidence of amorphous MoS$_2$.[3] Peaks appearing at 322 and 750 cm^{-1} may be caused by the bending and stretching modes, which are known to absorb at 320 cm^{-1} (bend) and 740–850 cm^{-1} (stretch).[17] The appearance of these bands invites speculation as to whether complete decomposition of the naphthenate

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(14) Boduszynski, M. M.; Hurtubise, R. J. *Anal. Chem.* **1982**, *54*, 372.

(15) *Ninth Set of the X-Ray Powder Data File*; Special Technical Publication No. 48-H; American Society for Testing Materials: Philadelphia, PA, 1959.

(16) Farmer, V. C., Ed. *The Infrared Spectra of Minerals*; Mineralogical Society: London, England, 1974.

(17) Zdrazil, M. *J. Catal.* **1979**, *58*, 436.

occurred, or whether the catalytic solid was a mixed Mo–O–S compound.

FTIR patterns for spent Mo/Al_2O_3 showed formation of a broad, strong peak in the characteristic regions for crystalline MoS_2. The peak appeared as a shoulder on the absorbance pattern of the alumina support, confirming the presence of a crystalline MoS_2 species.

The composition of the precipitated MoS_2 prepared for this study was analyzed by X-ray diffraction. Comparisons were made by comparing the *d* spacings with a standard reference for crystalline MoS_2.[16] Relative intensities were also compared on the same basis. The results shown in Table II verify the presence of some MoS_2 hexagonal structures. The peaks found, however, were broad, indicating a poorly crystalline structure. A well-defined maximum was found at a *d* spacing of 6.20 in the low-angle region which was similar to those reported for the 002 reflection of highly crystalline MoS_2.[9] A very broad peak envelope was observed in the high-angle region containing well-defined maxima at *d* spacings of 2.72, 2.70, and 2.28, which are indicative of the 100, 101, and 103 reflections also found in ordered MoS_2.

FTIR absorbance patterns of precipitated MoS_2 showed a strong peak in the region characteristic of the strongest band for crystalline MoS_2, 470 cm^{-1}.[17] Strong peaks were also observed at 382 and at 415 cm^{-1}. The peak at 382 cm^{-1} is characteristic of the weaker band due to crystalline MoS_2 while the source of the shifted peak at 415 cm^{-1} is not clearly understood. Similar shifts in peaks have been obtained with poorly crystalline TiS_2 prepared in the same manner[3] and may be caused by random stacking of the crystal layers. Broad, unidentified absorbance patterns in the 600–650-cm^{-1} region were also observed by others with MoS_2 prepared in this manner and may be the result of the sulfiding procedure or oxygen contamination.

Results and Discussion

Model Reactions. In this study, representative model compounds were chosen to simulate the reactions of the functional groups commonly found in coal. A sequence of reactions was performed with each model that included thermal, thermal with sulfur, and catalytic reactions using MoNaph, presulfided Mo/Al_2O_3, or precipitated MoS_2. Limited reactions were performed with $NiMo/Al_2O_3$ and recovered catalysts.

The product distributions achieved from the model reactions are given in terms of mole percents of products achieved. To summarize the data several terms have been defined. They are (1) percent hydrogenation (HYD), which is the number of moles of H_2 added to achieve the final product distribution as a percentage of the number of moles of H_2 required to achieve the most hydrogenated product; (2) percent hydrogenolysis (HYG), which is the summation of the mole percents of components resulting from carbon–carbon or carbon–heteroatom bond cleavage; (3) percent hydrodenitrogenation (HDN), which is the summation of the mole percents of components from which nitrogen has been removed; and (4) percent hydrodeoxygenation (HDO), which is the summation of the mole percents of components not containing oxygen.

Hydrogenation of 1-Methylnaphthalene. The reaction pathway for the hydrogenation of 1-methylnaphthalene (MN) is shown in Figure 3. Hydrogenation can be seen to proceed by two pathways, both culminating in the production of decalin (DEC).[18-20] Hydrogenation reactions were performed both thermally and thermally with sulfur to determine the effect of sulfur without the presence of catalyst. As shown in Table III, the addition of sulfur to the thermal reaction had no appreciable effect on the reactivity of MN, which showed minimal thermal conversion.

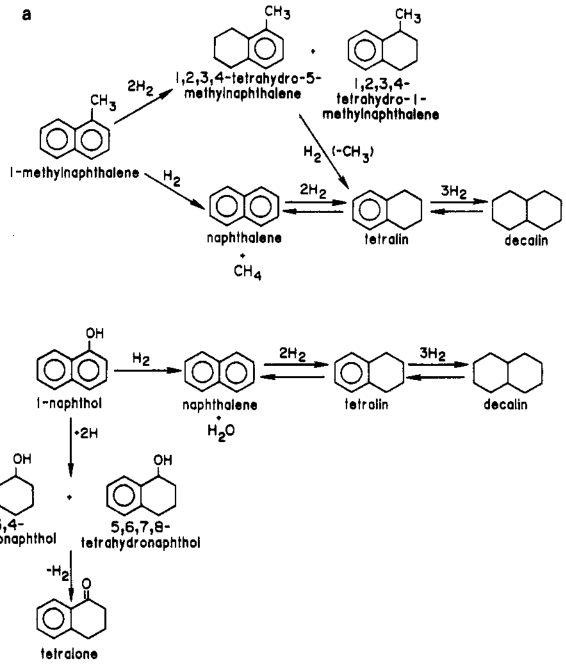

Figure 3. (a) Reaction pathway for the hydrogenation of 1-methylnaphthalene. (b) Reaction pathway for the hydrodeoxygenation of 1-naphthol.

MoNaph produced the highest conversion of MN among the three Mo catalysts, yielding major products of 5-methyltetralin (T5MN) and 1-methyltetralin (T1MN). Conversion to hydrogenated naphthalenes was not observed with any of the Mo catalysts used, although small quantities of naphthalene (NAPH) were produced. Very little hydrogenolysis of the methyl group was observed, an indication that these Mo-containing catalysts are not very selective for cleavage of the C–C bond. Between the two methyltetralins produced, the species T5MN was favored where hydrogenation of the nonsubstituted aromatic ring selectively occurred. This selectivity may be due to increased stability and delocalization of the aromatic ring containing the methyl group or due to steric hinderance caused by the methyl group.

Reactions were performed with a typical commercial hydrotreating catalyst, Shell 324 $NiMo/Al_2O_3$, for comparison of hydrogenation and hydrogenolysis. At the same catalyst loading, this catalyst produced a percent HYD of only 4% more than that noted for MoNaph (Table III). The selectivity was quite different, however, with the major hydrogenation product being T1MN, with intermediate conversion to T5MN and small amounts of naphthalene derivatives such as dihydronaphthalene (DNAP) and tetralin (TET). Hydrogenolysis with this catalyst increased to 16% compared to 1.6% for MoNaph, which was possibly due to the promotional effects of Ni.

Final ranking for the three Mo-containing catalysts for hydrogenation activity of MN was MoNaph > Mo/Al_2O_3 > P-MoS_2.

Hydrodeoxygenation of 1-Naphthol. The reaction pathway for the hydrodeoxygenation of 1-naphthol (NPOH) is shown in Figure 3.[21] Two pathways are available, one in which NPOH is hydrodeoxygenated and then hy-

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[18] Vamos, E.; Siklos, P.; Pozsgai, T. *Period. Polytech., Chem. Eng.* **1972**, *16*, 1, 253.

[19] Sonada, R.; Ohmae, T. German Patent, German Offen. 2,229,844, 1973; *Chem. Abstr.* **1973**, *78*, 97381.

[20] Patzer, J. R., II; Farrauto, R. J.; Montagna, A. A. *Ind. Eng. Chem. Process Des. Dev.* **1979**, *18*, 625.

[21] Vogelzang, C. L.; Li, G. C.; Schuit, A.; Gates, B. C.; Petrakis, L. *J. Catal.* **1983**, *84*, 170.

Table III. Hydrogenation Reactions of 1-Methylnaphthalene at 380 °C

	reaction category					
	thermal	thermal with sulfur	MoNaph catalyst	Mo/Al_2O_3 catalyst	MoS_2 catalyst	NiMo/Al_2O_3 catalyst
product distribn,[a] mol %						
MN	97.7 ± 1.0	97.0 ± 2.4	12.8 ± 2.0	59.6 ± 1.8	79.2 ± 1.5	1.2 ± 0.4
T1MN	0.4 ± 0.2	0.8 ± 0.8	39.2 ± 1.3	15.5 ± 0.1	7.8 ± 0.3	58.2 ± 6.4
T5MN	1.5 ± 0.7	1.7 ± 1.1	46.4 ± 1.2	24.9 ± 1.9	13.0 ± 1.2	25.0 ± 4.1
NAPH	0.4 ± 0.1	0.5 ± 0.1	1.6 ± 0.4	0	0	1.7 ± 1.1
DNAP	0	0	0	0	0	5.2 ± 3.6
TET	0	0	0	0	0	8.7 ± 6.1
DEC	0	0	0	0	0	0
HYD,[b] %	0.7 ± 0.3	0.8 ± 0.6	31.3 ± 0.8	13.5 ± 0.6	7.6 ± 0.5	35.3 ± 0.3
HYG, %	0.4 ± 0.2	0.5 ± 0.1	1.6 ± 0.4	0	0	15.6 ± 10.8
recovery, %	99.4 ± 1.4	97.0 ± 1.4	96.7 ± 0.7	94.2 ± 0.1	95.1 ± 0.4	93.6 ± 3.3

[a] On a HX-free basis. [b] Percent HYD was based on conversion of 1-MN to DEC.

Table IV. Hydrodeoxygenation Reactions of Naphthol at 380 °C

	reaction category					
	thermal	2.5:1 S:Mo thermal with sulfur	2.5:1 S:Mo MoNaph catalyst	8:1 S:Mo MoNaph catalyst	Mo/Al_2O_3 catalyst	MoS_2 catalyst
product distribn,[a] mol %						
NPOH	46.8 ± 2.3	76.9 ± 5.35	0	0	0	0
NAPH	4.7 ± 1.3	4.3 ± 2.21	15.2 ± 5.8	2.6 ± 2.2	31.6 ± 1.4	18.5 ± 2.1
TET	33.8 ± 0.7	13.1 ± 1.12	80.5 ± 5.5	89.1 ± 1.3	65.4 ± 1.4	77.0 ± 2.3
DEC	0	0	4.3 ± 0.7	8.3 ± 1.4	3.0 ± 0.1	4.5 ± 0.2
TTON	7.7 ± 2.0	4.7 ± 0.62	0	0	0	0
THN	7.0 ± 5.2	1.0 ± 1.41	0	0	0	0
isomer distribn, mol %						
cis-DEC	0	0	44.1 ± 1.8	43.6 ± 2.6	49.3 ± 0.4	46.4 ± 2.5
trans-DEC	0	0	55.9 ± 1.8	56.4 ± 2.6	50.7 ± 0.4	53.6 ± 2.5
HYD,[b] %	28.5 ± 4.0	10.6 ± 2.7	47.1 ± 2.1	53.1 ± 0.6	41.0 ± 0.3	46.1 ± 0.6
HDO, %	38.5 ± 1.7	17.4 ± 3.3	100.0	100.0	100.0	100.0
recovery, %	100.2 ± 6.2	87.0 ± 5.1	93.6 ± 7.7	94.6 ± 1.3	100.0 ± 4.0	81.9 ± 0.6

[a] HX-free basis. [b] % HYD was based on conversion of NPOH to DEC.

Table V. Hydrodenitrogenation Reactions of Indole at 380 °C

	reaction category				
	thermal	thermal with sulfur	MoNaph catalyst	Mo/Al_2O_3 catalyst	MoS_2 catalyst
product distribn,[a] mol %					
IND	92.5 ± 1.7	94.0 ± 1.1	23.3 ± 3.5	43.7 ± 0.2	64.8 ± 3.5
DHIN	5.8 ± 0.7	5.5 ± 0.9	7.2 ± 1.9	18.2 ± 0.6	24.8 ± 1.5
ETAN	1.7 ± 1.0	0.5 ± 0.2	51.0 ± 1.0	26.2 ± 0.4	8.4 ± 4.2
EBZ	0	0	2.3 ± 0.6	2.2 ± 0.01	1.4 ± 0.7
ECH	0	0	16.2 ± 4.1	9.7 ± 0.04	0.6 ± 0.1
HYD,[b] %	1.6 ± 0.5	1.1 ± 0.2	35.6 ± 4.3	22.6 ± 0.1	8.2 ± 1.6
HDN, %	0	0	18.5 ± 4.7	12.1 ± 0.1	2.0 ± 0.8
HYG,[c] %	1.7 ± 1.0	0.5 ± 0.2	69.5 ± 5.4	38.3 ± 0.5	10.4 ± 5.0
recovery, %	88.8 ± 4.1	87.5 ± 0.7	54.9 ± 2.2	55.2 ± 5.5	78.8 ± 0.8

[a] HX-free basis. [b] % HYD is based on conversion of IND to ECH. [c] % Hydrogenolysis is based on conversion of IND to products in which ring cleavage and nitrogen carbon bond breakage has occurred (IND to ETAN, EBZ, and ECH).

drogenated to DEC and one in which NPOH is hydrogenated without removal of the oxygen.

Reactions performed thermally and thermally with sulfur indicated a marked inhibition of NPOH activity by sulfur. The effects of sulfur inhibition on phenolic aromatics have been studied by Odebunmi and Ollis[22] and found to profoundly affect the amount of hydrodeoxygenation that occurs. To examine this effect, both low and high sulfur levels were added to catalytic MoNaph reactions. At high sulfur levels a higher percent HYD was obtained than at the lower sulfur levels. This difference due to sulfur would indicate the possibility of synergism between water produced from deoxygenation of NPOH and H_2S formed from the addition of elemental sulfur.

Major products formed from the catalytic reactions were NAPH, TET, and DEC with TET being the major product. Thermal reactions produced small quantities of 1-tetralone (TTON) and 5,6,7,8-tetrahydro-1-naphthol (THN), which were not observed catalytically. These results agree with earlier works.[22,23] These workers also observed the products 1-TTON and THN over CoMo/Al_2O_3 at lower temperatures than used in this study.

As shown in Table IV, MoNaph was the most effective catalyst for hydrogenating NPOH. Complete deoxygenation was achieved with all the catalysts; therefore, they were ranked according to percent hydrogenation: MoNaph > P-MoS_2 > Mo/Al_2O_3.

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(22) Odebunmi, E. O.; Ollis, D. F. *J. Catal.* **1983**, *80*, 65.

(23) Schlosberg, R. H.; Kurs, A. *J. Org. Chem.* **1984**, *49*, 3032.

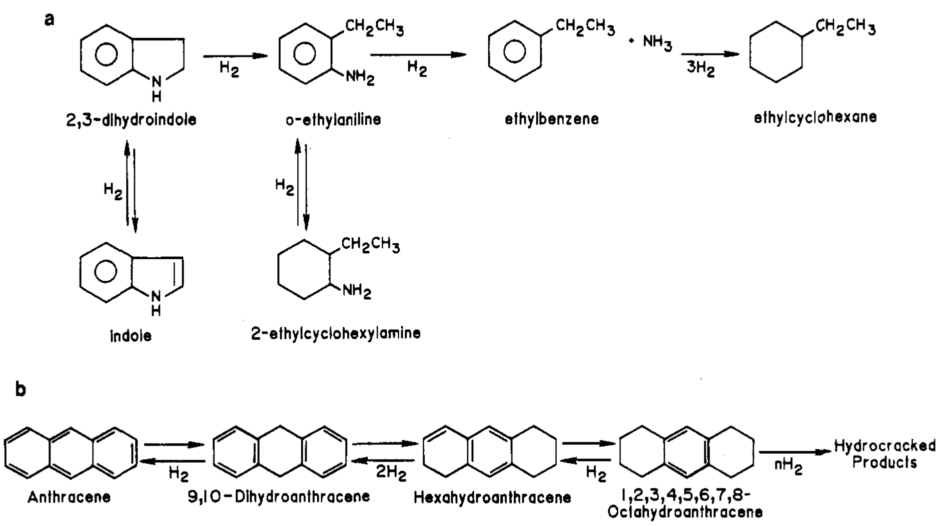

Figure 4. (a) Reaction pathway for the hydrodenitrogenation of indole. (b) Reaction pathway for the hydrogenation of anthracene.

Table VI. Comparison of Surface Areas and C-H-N Analysis of Various Catalysts

catalyst and conditions	anal., wt % carbon	hydrogen	nitrogen
MoNaph, IND reaction	26.3	3.1	1.7
	26.4	3.2	1.6
Mo/Al_2O_3, IND reaction,	45.3	15.4	1.4
support-free basis	46.4	15.0	1.7
Mo/Al_2O_3, IND reaction,	5.0	1.7	0.2
support included	5.3	1.7	0.2

catalyst and conditions	surface area, m^2/g
MoNaph, IND reaction	3
MoNaph, MN reaction	25
Mo/Al_2O_3, fresh catalyst	212
precipitated MoS_2, fresh catalyst	42

Table VII. Comparison of Recovered Catalytic Solids with Fresh Catalyst

	MoNaph		Mo/Al_2O_3		MoS_2	
	fresh	recovered	fresh	recovered	fresh	recovered
product distribn, mol %						
MN	12.8	44.8	59.6	61.5	79.2	82.9
T1MN	39.2	23.5	15.5	12.9	7.8	6.6
T5MN	46.4	30.7	24.9	25.9	13.0	10.5
NAPH	1.6	1.0	0	0	0	0
DNAP	0	0	0	0	0	0
TET	0	0	0	0	0	0
DEC	0	0	0	0	0	0
HYD,[a] %	31.3	19.8	13.5	14.0	7.6	6.2

[a] % HYD is based on conversion of 1-MN to DEC.

Hydrodenitrogenation of Indole. The reaction pathway for hydrodenitrogenation of indole (IND) is shown in Figure 4.[24] This pathway proceeds by hydrogenation of the five-membered ring, ring cleavage, removal of NH_3, and hydrogenation of the remaining aromatic to a cyclic alkane. Thermal reactions of IND showed nearly 8% conversion primarily to dihydroindole (DHIN). The addition of sulfur to thermal IND reactions had little effect on the reactivity of IND.

The results of catalytic reactions are summarized in Table V. MoNaph proved the most selective for denitrogenation of IND, with the major products being *o*-ethylaniline (ETAN) and ethylcyclohexane (ECH), with minor products of DHIN and ethylbenzene (EBZ). Complete conversion of IND was not obtained with any of the catalysts. HDN of IND was not achieved to a large degree, producing only a 19% maximum with MoNaph. The selectivity observed toward the aniline product was consistent with results obtained by Aboul-Gheit over a $CoMo/Al_2O_3$ catalyst.[25]

Ranking for the denitrogenation activity among the three catalysts was MoNaph > Mo/Al_2O_3 > P-MoS_2.

Poor recoveries were noted for reactions with MoNaph and Mo/Al_2O_3. As nitrogen compounds, amines and anilines are known to adsorb strongly on catalyst surfaces; hence, nitrogen poisoning was suspected.[26,27] Surface area analysis of catalyst solids generated from MoNaph and recovered from MN reactions yielded an average of 25 m^2/g while those from IND reactions averaged 3 m^2/g (Table VI). Several possible explanations exist for this datum including decreased dispersion of the particles or possible poisoning of the catalyst surface. The organic composition of the recovered catalyst solids of MoNaph and Mo/Al_2O_3 from IND reactions was determined by elemental analysis. The results presented in Table VI show considerable deposition of carbon, hydrogen, and nitrogen on the catalyst. The disproportionate amounts of carbon and hydrogen indicate the possibility of polymeric indoles forming, which has been noted by other researchers.[28]

Hydrodesulfurization and Hydrocracking. All three Mo catalysts completely desulfurized benzothiophene (BZT) and yielded the same selectivity for the hydrogenation products. The major product was EBZ with minor amounts of ECH being produced. At 380 °C, all of the Mo catalysts as well as the thermal reaction yielded the same amount of hydrocracking, ~3%, of bibenzyl (BB). Products observed in minor amounts were EBZ, ECH, toluene (TOL), and benzene (BZ).

Catalytic Activity of Recovered Catalysts. Experiments were performed with catalyst solids recovered from reactions with MoNaph, Mo/Al_2O_2, and precipitated MoS_2. Calculations for Mo loading were made based on a stoichiometry of MoS_3 (50 wt % Mo), assuming that some

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[24] Stern, E. W. *J. Catal.* **1979**, *57*. 390.

[25] Aboul-Gheit, A. K. *Prepr.—Am. Chem. Soc., Div. Pet. Chem.* **1987**, *32*, 278.

[26] Odebunmi, E. O.; Ollis, D. F. *J. Catal.* **1983**, *80*, 76.

[27] Mills, G. A.; Boedecker, E. R.; Oblad, A. G. *J. Am. Chem. Soc.* **1950**, *72*, 1554.

[28] Weisser, O.; Landa, S. *Sulphide Catalysts, their Properties and Applications*; Pergamon Press: Oxford, U.K., New York, 1973.

Table VIII. Product Distributions from Coal Liquefaction Reactions

	thermal	MoNaph	Mo/Al_2O_3	MoS_2
compound class distribn,[a] wt %				
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 ± 5.0
PC	26.4 ± 3.0	20.2 ± 1.1	18.9 ± 0.5	17.0 ± 4.6
MCMS recovery, %	107.9 ± 3.1	108.0 ± 4.7	90.4 ± 0.6	103.1 ± 6.8
tot. product distribn,[b] wt %				
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 ± 1.0	6.1 ± 0.05	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 conversn, %	62.2 ± 3.8	91.6 ± 3.8	90.4 ± 1.9	78.7 ± 0.3
H_2 consumptn, %	4.3 ± 1.2	13.5 ± 1.9	9.0 ± 2.7	7.1 ± 1.5
overall recovery, %	85.7 ± 2.4	83.2 ± 0.7	90.4 ± 1.5	93.0 ± 0.3
anthracene production distribn,[c] mol %				
ANTH	25.9 ± 1.7	8.4 ± 1.6	13.5 ± 6.7	18.6 ± 2.7
DHA	38.8 ± 0.4	50.1 ± 0.3	48.7 ± 7.0	35.2 ± 3.9
HHA	31.1 ± 1.0	35.8 ± 2.8	31.4 ± 0.04	40.0 ± 0.8
OHA	0	1.7 ± 0.6	0.4 ± 0.6	1.3 ± 0.4
NDRV[d]	4.2 ± 1.1	4.0 ± 1.5	6.0 ± 0.8	4.9 ± 1.7
HYD,[e] %	33.0 ± 0.7	41.1 ± 2.7	36.1 ± 2.3	40.1 ± 1.2
recovery, %	92.1 + 4.6	70.9 + 1.3	52.9 + 5.3	87.1 + 4.1

[a] MCMS basis. [b] Maf coal basis. [c] Coal-free basis. [d] Naphthalene derivatives resulting from hydrocracking are combined in this category. [e] Percent HYD is based on conversion of ANTH to OHA.

nonstoichiometric excess sulfur was adhered to the catalyst surface. This assumption was made because the composition of the recovered solids was being analyzed simultaneously and the stoichiometry of the solids was not then definitely known. The results shown in Table VII indicate that recovered Mo/Al_2O_3 and precipitated MoS_2 appeared to retain nearly the same level of activity as fresh catalysts. MoNaph experienced a drop in activity but remained most selective for hydrogenation.

Coal Liquefaction Studies. A series of coal liquefactioin experiments was performed in order to assess the activity and selectivity of the three Mo catalysts for conversion of Illinois No. 6 coal to soluble products. Final assessments of selectivity and activity were based on the production of MCMS, THFS, and IOM products. The MCMS products were further analyzed by means of a liquid chromatography separation to compare production of specific compound class fractions such as HC, NH, HA, and PC. The products of the solvent, anthracene, were also analyzed to assess the degree of hydrogenation. The hydrogenation reaction pathway for anthracene is given in Figure 4.

Thermal Coal Experiments. Reactions performed under thermal conditions gave an average coal conversion of 62%. The product distributions shown in Table VIII indicate low production of gases and appreciable IOM after reaction. Overall recovery was low due to the difficulty in removing adhered, intractable thermal residue from the reactor. Thermal coal reactions were also the least reproducible of all reactions performed due to difficulties in recovering IOM and THFS fractions.

Catalytic Coal Experiments. The summary of product distributions from the catalytic reactions given in Table VIII indicates that the amount of IOM decreased from 38% thermally to 8% with MoNaph, 10% for Mo/Al_2O_3, and 21% for MoS_2. Coal conversion was found to be correspondingly highest with MoNaph and Mo/Al_2O_3 producing almost the same percentage, 92% and 90%, respectively. Coal conversion obtained by MoS_2 ranked much lower at 79% conversion.

Production of THFS ranged from 22% thermally to 31% with Mo/Al_2O_3. The production of THFS was generally related to the amount of MCMS produced. The lowest production of THFS solubles was generated by MoNaph at 17% and was accompanied by the highest production of MCMS, 47%. The largest production of THFS solubles was obtained with Mo/Al_2O_3, which also exhibited a relatively high MCMS fraction, 40%. Mo/Al_2O_3, while converting 90% of the coal to soluble products, was not as effective as MoNaph in converting THFS to MCMS. MoNaph generated both high overall conversion and greater activity for conversion of THFS to MCMS, which was more desirable. MoS_2 yielded low coal conversions and produced a low THFS of 21% and a MCMS of 37%, which was comparable to those for Mo/Al_2O_3.

Hydrogen consumption with MoNaph was the highest reported for all coal experiments, as was the production of gas during the reaction. Any increase in product gas due to the addition of excess sulfur was accounted for by subtracting the amount of excess H_2S produced. This calculation subtracted the amount of stoichiometric sulfur required for MoS_2 formation from the amount of sulfur added. The balance was assumed to have formed excess H_2S. The nature of the increase in gas production and hydrogen consumption is not definitively understood. However, in a study by Kottensette[2] of MoNaph impregnated on Illinois No. 6 coal at similar catalyst loadings, this same trend was also observed. Molybdenum and nickel naphthenates were found to have H_2 consumption as high as 3 times that for other naphthenate catalysts and about 20% higher than that observed for a CoMo supported catalyst.

The results of compound class separations indicated that MoNaph produced the largest percentage of HC at 24% on a moisture- and ash-free (maf) coal basis. The other catalysts were less yielding 17% with Mo/Al_2O_3 and 15%

with MoS_2. On a MCMS basis, MoNaph produced 51% HC, Mo/Al_2O_3 yielded ~42%, and MoS_2 achieved 40%. On a maf coal basis, the NH values were 4% for the thermal reaction and increased only slightly to 6% in the presence of a catalyst. The same trend was observed with HA, with thermal production at 8% increasing to 11% with catalyst. The relative differences in the HC, NH, and HA can be examined more closely by comparing the average results on an MCMS basis as given in Table VIII. Both MoNaph and Mo/Al_2O_3 produced the NH and HA fractions on a proportionate basis, although the former produced less overall of both NH and HA. MoS_2 produced a different distribution, with the HA fraction produced being disportionately higher than that of the other catalysts and the NH fraction being lower than Mo/Al_2O_3 but not as low as MoNaph. These compound class distributions would indicate that, although coal conversion with MoS_2 was low, MoS_2 yielded a greater reactivity for HDN than for HDO.

PC decreased from 26% under thermal conditions to 17% for the catalytic reaction with MoS_2 (MCMS basis). These results are best interpreted in terms of the HC fraction. The increase of HC to 51% for MoNaph was a result of reduction of all the other compound classes, NH, HA, and PC. Mo/Al_2O_3 followed the same pattern but only produced 42% HC and, thus, was not as effective for HYD, HDN, or HDO. The MoS_2 yield of HC was 40% and was produced more from HDN than from HDO, as reflected in a low NH fraction.

In terms of the greatest selectivity for HC production, the catalysts can be ranked as MoNaph > Mo/Al_2O_3 > MoS_2; for HDN selectivity, as MoNaph > MoS_2 > Mo/Al_2O_3; for HDO selectivity, as MoNaph > Mo/Al_2O_3 > MoS_2; and for overall coal conversion to soluble products, as MoNaph > Mo/Al_2O_3 > MoS_2.

The amount of HYD of the ANTH solvent during coal liquefaction reactions is shown in Table VIII. For clarity, ANTH products are reported on a coal-free basis only. Solvent reduction to hydroaromatic species was measured by percent HYD, which reached 33% under thermal conditions and ranged up to 41% for MoNaph reactions. Hence, ANTH was thermally reactive under these conditions. Products found as a result of ANTH hydrogenation included DHA, HHA, and OHA. Some cracking of ANTH was observed, from 4 to 6 mol %. Cracked products were found in the boiling point range for NAPH and its derivatives but were not positively identified. Reaction with Mo/Al_2O_3 produced the highest cracking, probably due to the acidity of the support. Similar results have been reported by others.[29-31] The product THA, reported in some works, was not observed.

As shown in the average results shown in Table VIII, the values for HHA produced increased in going from thermal to catalytic reactions, with a maximum value found in the presence of MoS_2. The DHA produced was less for MoS_2 as a direct result and was higher for all other catalysts. The percent HYD of the solvent remained within a deviation of 3 mol % for all catalysts with only slight variations in product distribution.

Summary and Conclusions

The oil-soluble catalysts, MoNaph, was shown to be an effective catalyst for model reactions involving HYD and HDN. Evaluation of the activity and selectivity of the catalyst for these reactions was determined by comparison with other Mo-containing catalysts in experiments performed on representative coal model compounds. Effective HYC was not achieved with any of the catalysts employed, while roughly equal activity for HDS was observed for each. Although all three Mo catalysts showed the same activity for deoxygenating phenol, MoNaph was more effective than the other two catalysts for hydrogenating the deoxygenated products.

Of the recovered catalyst solids tested, MoNaph experienced the largest decrease in activity when compared to fresh catalyst, but still remained the most selective for HYD. Spent MoNaph catalyst was tentatively identified as being composed of crystalline MoS_2, but the degree of crystallinity could not be ascertained. The presence of a mixed amorphous and crystalline state could not be excluded.

MoNaph was also shown to be the most effective catalyst for overall coal conversion and production of MCMS and HC product fractions. This catalyst also proved most effective for HDN and HDO. Mo/Al_2O_3, while exhibiting comparable coal conversion, produced less MCMS and hydrocarbons. MoS_2 showed the least propensity for coal conversion but did exhibit a somewhat better selectivity for HDN than did Mo/Al_2O_3.

The solvent used in coal experiments, ANTH, was found to hydrogenate to form hydroaromatic species of DHA, HHA and OHA. The product OHA was found only in small quantities in all coal experiments. This observation is consistent with theories proposed[31] that the source of cracked products from ANTH hydrogenation is OHA, which rapidly hydrocracks once hydrogenated. This hydrocracking to lighter, unidentified products was also the source of the low ANTH recovery listed for Mo/Al_2O_3 reactions (53%). The HYC of ANTH, although observed to some degree in all experiments, was not prohibitive, except in the case of reactions involving Mo/Al_2O_3.

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Nomenclature

ANTH	anthracene
BB	bibenzyl
BZ	benzene
BZT	benzothiophene
$CoMo/Al_2O_3$	cobalt and molybdenum on alumina
DEC	decalin
DHA	dihydroanthracene
DHIN	dihydroindole
DNAP	dihydronaphthalene
DYBT	dihydrobenzothiophene
EBZ	ethylbenzene
ECH	ethylcyclohexane
ETAN	ethylaniline
FTIR	Fourier transform infrared spectroscopy
H_2S	hydrogen sulfide
HA	hydroxyl aromatics
HC	hydrocarbons
HDN	hydrodenitrogenation
HDO	hydrodeoxygenation
HDS	hydrodesulfurization

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(29) Curtis, C. W.; Cahela, D. *Energy Fuels*, following paper in this issue.

(30) Salim, S. S.; Bell, A. T. *Fuel* **1984**, *63*, 469.

(31) Wiser, W. H.; Singh, S.; Qader, A. A.; Hill, G. R. *Ind. Eng. Chem. Process Des. Dev.* **1970**, *9*, 350.

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HHA	hexahydroanthracene
HX	hexadecane
HYC	hydrocracking
HYD	hydrogenation
HYG	hydrogenolysis
IND	indole
IOM	insoluble organic matter
Li_2S	lithium sulfide
MAF	moisture and ash free
MCMS	methylene chloride/methanol solubles
MN	1-methylnaphthalene
Mo	molybdenum
Mo/Al_2O_3	molybdenum on γ-alumina
$MoCl_4$	molybdenum chloride
Mo-Naph	molybdenum naphthenate
NAPH	naphthalene
NDRV	naphthalene derivatives
NH	nitrogen heterocycles
NH_3	ammonia
NiMo/Al_2O_3	nickel and molybdenum on γ-alumina
NPOH	1-naphthol
OHA	octahydroanthracene
P-MoS_2	precipitated molybdenum sulfide
PC	polyfunctional compounds
T1MN	1,2,3,4-tetrahydro-1-methylnaphthalene
T5MN	1,2,3,4-tetrahydro-5-methylnaphthalene
TET	tetralin
THFS	tetrahydrofuran solubles
THN	tetrahydronaphthol
TOL	toluene
TTON	tetralone

Registry No. Mo, 7439-98-7; MoS_2, 1317-33-5; 1-methylnaphthalene, 90-12-0; 1-naphthol, 90-15-3; benzothiophene, 11095-43-5; indole, 120-72-9; bibenzyl, 103-29-7.

Hydrodenitrogenation of Quinoline and Coal Using Precipitated Transition-Metal Sulfides

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The hydrodenitrogenation (HDN) of quinoline was investigated by using precipitated transition-metal sulfides from group VIB and VIII metals. The precipitated transition-metal sulfides have a disordered rag structure and a higher surface area than their commercial mineralogical analogues. The selectivity for quinoline HDN of the precipitated and commercial WS_2, Cr_2S_3, and FeS_2 was very similar; however, the higher surface area precipitated MoS_2 showed a higher HDN than did its commercial analogue. Precipitated MoS_2 and RuS_2 were comparable to CoMo/Al_2O_3 and NiMo/Al_2O_3, respectively, in their hydrogenation activity for quinoline. Pt/SiO_2 showed higher hydrogenation activity at lower temperatures than the transition-metal sulfide or the commercial hydrotreating catalysts but was not as effective for HDN. The activity and selectivity of MoS_2, RuS_2, and NiMo/Al_2O_3 for producing hydrocarbons and nitrogen removal in coal liquefaction reactions were also examined. Both MoS_2 and RuS_2 produced more hydrocarbons than the thermal reaction, with RuS_2 being the more active of the two; however, neither was as effective as NiMo/Al_2O_3 for hydrocarbon production and HDN of coal liquefaction products.

Introduction

The effectiveness of unsupported, precipitated transition-metal sulfides as hydrogenation and hydrodenitrogenation catalysts for quinoline and coal under liquefaction conditions is investigated. Precipitated transition-metal sulfides of moderate surface areas were produced by a method developed by Chianelli and Dines[1] in the late 1970s. The unique physical properties of the precipitated transition-metal sulfides due to their disordered structure have been examined.[2,3] These materials crystallize in weakly interacting layers that allow for ready intercalation of appropriate species. The precipitated transition-metal sulfides have varying surface areas dependent on the dimensions of the stacked layers and, hence, on the details of the preparation method. Although these precipitated metal sulfides are poorly crystalline, they exhibit X-ray diffraction pattens similar to those of their commercially available crystalline metal sulfide counterparts.

A number of different precipitated transition-metal sulfides have been tested for hydrodesulfurization activity by using dibenzothiophene[4] and are good candidates for hydrodenitrogenation studies. Development of catalysts for nitrogen removal from coal is needed since liquids derived from coal have naturally high nitrogen contents due to the nitrogen present in the feedstock. These nitrogen-containing compounds are detrimental because of their poisoning and deactivating effect on catalysts used in further refining,[5] their forming NO_x upon combustion,

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(1) Chianelli, R. R.; Dines, M. B. *Inorg. Chem.* **1978**, *17*, 2758.
(2) Chianelli, R. R. *Catal. Rev.—Sci. Eng.* **1986**, *26*, 361.
(3) Chianelli, R. R. *J. Cryst. Growth* **1976**, *34*, 239.
(4) Pecoraro, T. A.; Chianelli, R. R. *J Catal.* **1981**, *67*, 430–445.
(5) Stohl, F. V.; Stephens, H. P. *Prepr. Pap.—Am. Chem. Soc., Div. Fuel Chem.* **1986**, *31*(4), 251.

0887-0624/89/2503-0168$01.50/0