

ACTIVATION OF HYDROUS TITANIUM OXIDE-SUPPORTED
CATALYSTS FOR HYD, HDS, and HDO REACTIONS*

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INTRODUCTION

The objective of our current work is to develop catalysts, based on hydrous titanium oxide (HTO) ion exchangers [1], for use in direct coal liquefaction processing. The ultimate goal of the program is an improved coal liquefaction catalyst produced in quantities that allow testing in a large-scale process development unit such as the Advanced Coal Liquefaction R & D Facility at Wilsonville, Alabama. This paper will give an overview of Sandia's catalyst development program and present results of studies of HTO catalyst preparation and pretreatment procedures.

Catalysts currently employed in process development units for coal liquefaction are hydroprocessing catalysts developed for petroleum refining [2]. They are composed of combinations of the metals Mo or W along with Co, Ni and other promoters dispersed on alumina or silica-alumina supports. When used in liquefaction, these catalysts deactivate rapidly [3], causing decreases in product yield and quality and problems with process operability. Thus the existing generation of supported catalysts cannot adequately meet the demanding requirements for use in coal liquefaction processes.

Past efforts for development of coal liquefaction catalysts have focused on alumina-supported systems and, except for exploratory studies, little attention has been given to systematic development of novel formulations. A particularly promising approach to the development of new catalysts specifically designed for coal liquefaction processes lies in the formulation of multicomponent systems that, in comparison to work on single or bimetallic systems, are essentially unexplored. Use of multimetallic systems offers the possibility of multifunctional catalysts that are needed to perform the many different reactions encountered in coal processing. Because of its versatility for the preparation of multimetallic catalysts, the HTO system is an excellent candidate for further development.

Hydrous titanium oxide ion exchange compounds exhibit a number of properties that make them desirable as substrates for active

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metals: (1) ions of any active metal or mixture of metals can be atomically dispersed over a wide range of concentrations by an easily controlled process; (2) the ion exchange capacity of the materials is large, permitting high loadings of active metals; (3) solution chemistry can be used to provide control of the oxidation state of the active metal; (4) catalyst acidity can be modified by ion exchange; (5) the materials have high surface areas; (6) the ion exchanger substrates are stable in oxidizing and reducing atmospheres, and over a wide pH range in aqueous solution; and 7) the ion exchangers can be prepared as thin films on a wide variety of supports. The latter property offers the potential for tailor-made catalysts for chosen chemical, physical, and mechanical characteristics.

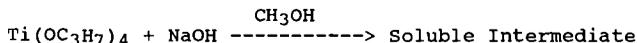
HTO catalysts have been evaluated in several fossil fuel applications including direct coal liquefaction and hydrolysis. Initial batch microreactor tests [4] using equal weights of Shell 324M (a NiMo/Al₂O₃ catalyst that is commonly used in direct coal liquefaction), Ni HTO, Mo HTO, and Pd HTO catalysts with Illinois #6 coal and SRC-II heavy distillate showed that the HTO catalysts, even at low active metals loadings of 1 wt%, are equally effective for conversion of coal to low molecular weight products as Shell 324M, which contains 15 wt% active metals. In addition, for the same oil yield, the HTO catalysts used less hydrogen than the commercial catalyst. HTO catalysts have also been evaluated at the Pittsburgh Energy Technology Center in bench-scale tests with a 1:1 distillate solvent/residuum feed from the Wilsonville Advanced Coal Liquefaction R & D Facility. Results [5] showed that a CoNiMo HTO catalyst gave conversions to cyclohexane solubles, H/C product ratios, and hydrodesulfurization activities that were similar to those obtained with Shell 324M. The CoNiMo HTO catalyst had not been optimized for hydrotreating coal-derived liquids. Studies [6] of hydrolysis using a coal coated with a Pd HTO catalyst (0.7 wt% Pd on daf coal basis) showed a 50% increase in tar yield compared to a reaction performed with the addition of ground NiMo/Al₂O₃ catalyst (3.6 wt% active metals on daf coal basis). These results all indicate that HTO catalysts have potential in coal liquefaction processes.

EXPERIMENTAL

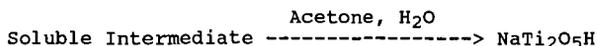
HTO Catalyst Preparation

Hydrous titanium oxide ion exchangers are amorphous inorganic compounds synthesized in the form of salts of weak acids represented by the empirical formula C(Ti_xO_yH_z)_n, where C is an exchangeable cation. HTO catalysts can be prepared by a technique that consists of synthesis of sodium hydrous titanate ion exchange material followed by exchanging active metal ions for the sodium. The synthesis involves three steps:

(1) Reaction of tetraisopropyl titanate with an alkali or alkaline earth metal hydroxide in alcohol solution to form a soluble intermediate:



(2) Hydrolysis of the soluble intermediate in acetone/water mixtures to form the HTO exchange material:



(3) Ion exchange of the alkali or alkaline earth metal for active metal ions in aqueous solution to form the catalyst:



Co, Mo, Pd, and NiMo HTO catalysts are prepared by similar procedures. HTO-Si support materials were made by adding tetraethyl orthosilicate to the tetraisopropyl titanate prior to addition of NaOH.

Activity Testing

All catalysts were tested as powders and were sulfided in an atmospheric pressure flow reactor prior to activity testing. Sulfiding was carried out at 425°C for 2 h using a 10 mol% H₂S/H₂ mixture. Some of the catalysts were calcined in air by heating at 5°C/min to 450°C followed by a 10°C/min increase to 500°C with 2 h at this temperature. All activity results are reported on a weight of active metals basis and results are compared to those of Shell 324M.

Hydrogenation (HYD) activities were determined by measuring the rate of hydrogenation of pyrene to dihydropyrene. Experiments were performed at 300°C in 26 cm³ batch microreactors that were loaded with 100 mg pyrene, 1 g of hexadecane as the solvent, and 500 psig H₂ cold charge pressure. Reaction times were 20 min and catalyst loadings, which were varied depending on the activity of the catalyst, ranged from 10 to 25 mg. The concentrations of pyrene and dihydropyrene in the products were determined using gas chromatography (GC).

Hydrodeoxygenation (HDO) activities were evaluated using the rate of disappearance of dibenzofuran (DBF). Experiments were performed at 300°C in 26 cm³ batch microreactors that were loaded with 100 mg DBF, 25 mg catalyst, 1 g hexadecane, and 1200 psig H₂ cold charge pressure. Reaction times were 15 min and products were analyzed by GC.

Hydrodesulfurization (HDS) activities were measured in a flow reactor system using thiophene as the model compound. Reaction rates for the HDS of thiophene to butene were determined at 325°C and atmospheric pressure.

RESULTS and DISCUSSION

Because the HTOs are new catalytic materials with properties that are significantly different from well-known catalysts such as those supported on alumina, a thorough and systematic approach to their development must be taken. The elements included in this approach are (1) process definition and catalyst requirements; (2) catalyst preparation, pretreatment and characterization; (3) catalyst testing; and (4) catalyst scaleup and processing evaluation. The relationship among the program elements is shown in

Figure 1. The aspects of this program that will be discussed in this paper involve studies of the catalyst preparation and pretreatment procedures that are aimed at enhancing catalyst activity for coal liquefaction.

Seven NiMo HTO catalysts were prepared at an acidification pH of 4. They were evaluated for HYD and HDO activities and the results compared to Shell 324M (Table 1). This series of catalysts was analyzed to determine the effects on catalyst activity of the 500°C calcination procedure, Si addition to the HTO support, and removal of Na from the catalyst. The results show that there is a direct correlation (correlation coefficient = 0.98) between HYD and HDO activities for all the catalysts (HTOs and Shell 324M).

Analysis of the activities of the first three pairs of catalysts (runs 1-6) shows that the calcined catalyst in each pair has significantly greater activity than the noncalcined. The NiMo HTO catalysts without Si gave the lowest activities and the sulfided, calcined catalyst with a Ti:Si ratio of 5 (run 6) gave the highest HYD and HDO activities. These results show that Si addition is beneficial, but that too much Si (Ti:Si=3) causes a decrease in activity. The first six catalysts in Table 1 contained small amounts of Na (0.6 to 1.1 wt %), whereas the catalyst used in run 7 had <0.1 wt%. Comparison of activity results from runs 6 and 7 shows that removal of the Na gives a catalyst with the highest HYD activity; this catalyst has 90% of the HYD activity of Shell 324M. These results are in agreement with studies that show Na can poison catalyst sites. Parameters that are currently being studied to improve the performance of NiMo HTO catalysts include optimizing the Si content, evaluating the effects of the pH used in the acidification step, determining the impacts of different calcining conditions, and analyzing the effects of varying the active metal loadings.

Studies have been performed to determine why Si addition in the support increases catalyst activity. This work was performed with Pd HTO catalysts, which also show an increase in activity with Si addition to the support. Figure 2a shows the effects of the Ti:Si ratio in the support and the acidification pH on the surface areas of Pd HTO catalysts that have been calcined at 300°C in air. The presence of a 6:1 Ti:Si mole ratio results in a 2- to 3-fold increase in surface area with respect to Pd HTO. When the Ti:Si ratio is increased to 2, any discernible enhancement in surface area is limited to materials with the lower pHs. The effect of pH on the surface areas of catalysts prepared on the same supports is more difficult to discern. There appears to be a general trend whereby the surface areas of samples acidified at pH 4 and 5 are slightly enhanced with respect to materials that were not acidified (pH>6) or were treated at pH 2. Increasing the calcination temperature to 500°C (Figure 2b) shows similar trends to those observed at 300°C. As would be expected, the higher temperature resulted in an overall decrease in surface area for all materials. The results of this study on Pd HTO catalysts suggest that it may be possible to increase the activity of the NiMo HTO catalysts by decreasing the calcination temperature, decreasing the Ti:Si ratio to lower values than those shown in Table 1, and using a somewhat higher pH during acidification.

Optimization of the calcination process for these materials is

aimed at maintaining the dispersion of the active metals in the as prepared material while giving a catalyst that is stable under reaction conditions. The usual procedure for preparing alumina supported catalysts involves calcining after the metals have been impregnated onto the support. This procedure has been used in all previous studies of HTO catalysts. However, a different method, calcination of the support prior to ion exchange, may be possible with these materials. The potential benefit of this procedure, which will subsequently be referred to as precalcining, is that the metal is not present during calcination so that it will not sinter, while the possible disadvantage is that the ion exchange capacity of the calcined material may be too low to enable preparation of a good catalyst. The impact of precalcining temperature on the ion exchange capacities of HTOs are shown in Figure 3. The results obtained on two sets of catalysts, one exchanged with Co and the other with Mo, show that the exchange capacity decreases with increasing precalcination temperature. For Co, about 2/3 of the HTO's noncalcined exchange capacity is maintained between 400°C and 700°C. In contrast, Mo exchange shows a sharp decrease due to precalcining at 200°C and a more gradual decrease with increasing precalcination temperature. After a 500°C precalcination, only about 1/4 of the initial Mo exchange occurs. These results suggest that formation of a CoMo HTO catalyst may require two separate exchange steps: the Mo could be exchanged at room temperature followed by calcination and subsequent exchange with Co. Studies are currently underway to compare activities of catalysts prepared using precalcination and calcination after ion exchange.

Studies of HTO calcination after ion exchange are also being performed. Recent work (Figure 4) has shown the effect of calcination temperature on the thiophene HDS activities of two NiMo HTO catalysts. With calcination above 400°C, both catalysts show a significant increase in HDS activity. Differential thermal analyses of these catalysts showed that a thermal event occurred at this temperature. The NiMo HTO catalyst with the lower total metals loading maintains this higher activity up to a calcination temperature of at least 600°C. The NiMo HTO with the higher metals loading shows additional activity enhancement up to a calcination temperature of 500°C and then an activity decrease. The reasons for these phenomena are not yet known. Differential scanning calorimetry and thermal gravimetric analysis techniques are currently being performed in conjunction with activity testing to learn more about calcination and activation procedures for these materials.

CONCLUSIONS

Hydrous titanium metal oxide catalysts are extremely versatile materials that have promise as coal liquefaction catalysts. Previous studies have shown that they perform well in both batch and bench-scale coal liquefaction tests. Efforts to improve preparation and activation procedures for these catalysts have identified several promising research areas that either have or may lead to enhancements in catalyst activity. For, example, addition of Si to the support of NiMo HTO catalysts has yielded 2- to 3-fold increases in surface areas and has resulted in a 33% increase in HYD activity

and a doubling of HDO activity compared to an HTO catalyst without Si. In addition, it may be possible to maintain the high atomic dispersion of the metals at reaction conditions by calcining prior to ion exchange of the metal onto the support or reducing the calcination temperature. Current research is addressing these areas.

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Table 1. HYD and HDO testing of NiMo HTO catalysts.

Run	Ti:Si ^b	Pretreatment	Wt % Metals		Activity Testing ^a	
			Ni	Mo	HYD	HDO
1	No Si	Sulfide	3.23	12.40	0.134	0.004
2	No Si	Sulfide+calcine	3.23	12.40	0.480	0.037
3	3	Sulfide	3.03	9.69	0.236	0.017
4	3	Sulfide+calcine	3.03	9.69	0.613	0.069
5	5	Sulfide	2.69	9.62	0.227	NA ^c
6	5	Sulfide+calcine	2.69	9.62	0.812	0.080
7	5(No Na)	Sulfide+calcine	4.08	9.75	0.904	NA
	Shell 324M	Sulfide	2.80	12.40	1.026	0.112

a k(g⁻¹(active metal) sec⁻¹)

b Mole ratio

c Not analyzed.

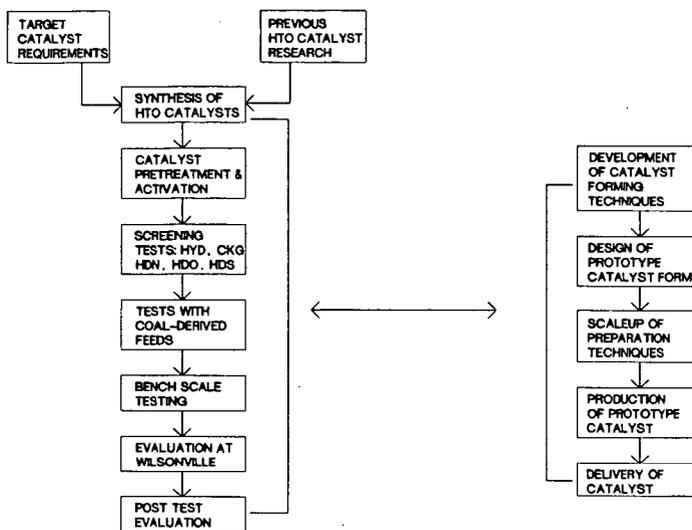


Figure 1. Overview of Sandia's catalyst development program.

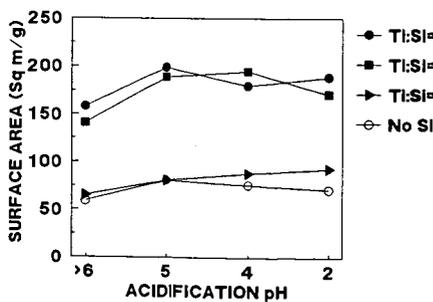


Figure 2a. Calcination at 300 C

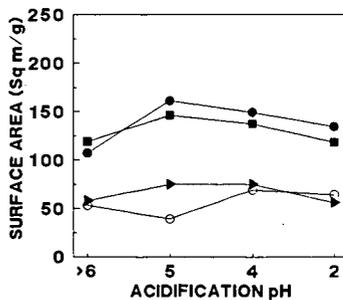


Figure 2b. Calcination at 500 C.

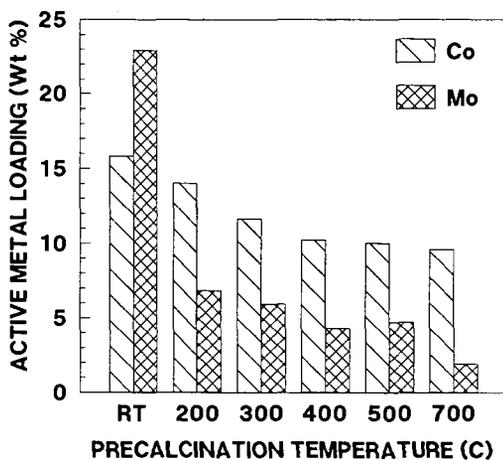


Figure 3. Effects of HTO precalcination temperature on ion exchange capacity.

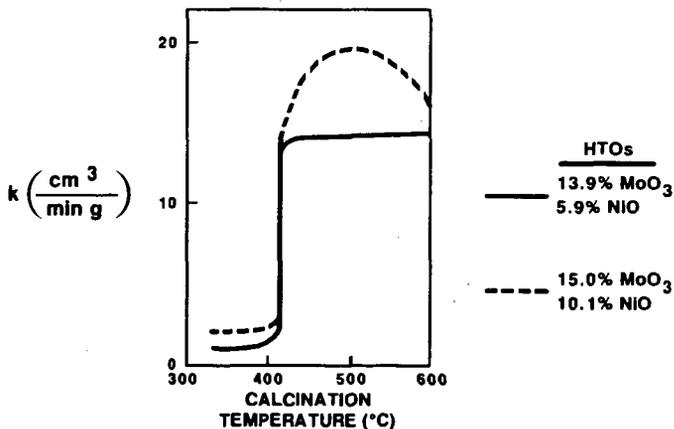


Figure 4. Effects of calcination temperature on thiophene HDS activity for two NiMo HTO catalysts.

DISPERSED-PHASE CATALYSIS IN COAL LIQUEFACTION

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ABSTRACT

The specific reaction ("preactivation") conditions for the conversion of catalyst precursors to unsupported catalysts have a direct effect on the catalytic activity and dispersion. The importance of reaction intermediates in decomposition of ammonium heptamolybdate and ammonium tetrathiomolybdate, and the sensitivity of these intermediates to reaction conditions, were studied in coal liquefaction systems. Recent results indicate that optimization of preactivation conditions facilitates the formation of a highly dispersed and active form of molybdenum disulfide for coal liquefaction. The use of the catalyst precursors ammonium heptamolybdate, ammonium tetrathiomolybdate, and molybdenum trisulfide for the conversion of coal to soluble products will be discussed.

INTRODUCTION

The use of an unsupported dispersed-phase catalyst for direct coal liquefaction is not a novel concept and has been employed with varying success. Dispersed-phase catalysts have been introduced via impregnation techniques (1-4), as water-soluble (5-8) and oil-soluble (9-12) salts, and as finely divided powders (1,2). While some methods of catalyst introduction result in greater dispersion of the catalyst and greater activity for the liquefaction of coal, all of the techniques allow the formation of a finely dispersed inorganic phase. The use of dispersed-phase catalysts in direct coal liquefaction offers several advantages. Since they could be considered "once-through" catalysts, deactivation problems are reduced when compared to supported catalysts, and catalytic activity remains high. Diffusion limitations are minimized because of the high surface area of small catalyst particles. Maximum interaction of coal, vehicle, and gaseous hydrogen can occur on the catalyst surface with a highly dispersed catalyst.

One of the more popular techniques for producing dispersed-phase catalysts involves the use of water- or oil-soluble catalyst precursors. Small amounts of the water-soluble catalyst precursor are added to the coal-vehicle feed and are subsequently converted to a highly dispersed insoluble catalytic phase. The reaction conditions that convert the soluble catalyst precursor to a highly active and dispersed-phase catalyst are critical. The objective of this paper is to identify techniques that will convert a molybdenum catalyst precursor to a highly dispersed MoS₂ phase that has greater activity for coal liquefaction than previously identified dispersed-phase MoS₂ catalysts.

EXPERIMENTAL

Catalyst screening tests were conducted in 40-mL microautoclave reactors. The liquefaction conditions were the following: temperature, 425°C; reaction pressure, 1000 psig H₂ (pressure at room temperature); residence time, 1 hour; and solvent/coal, 2/1. The coal used was Illinois No. 6, Burning Star Mine (ultimate analysis: C, 71.02 wt%; H, 4.95 wt%; O(diff.), 9.26 wt%; N, 1.41 wt%; S, 3.23 wt%; and ash, 10.12 wt%, on a moisture-free basis), and the vehicle used was tetrahydronaphthalene (tetralin). Rapid heat-up rates were obtained by immersing the microautoclave in a preheated fluidized sand bath at 425°C. The microautoclave reached reaction temperature in 1-2 minutes. Slow heat-up rates were obtained by immersing the microautoclave in the fluidized sand bath at room temperature and gradually heating the sand bath to reaction temperature in 3/4 hour to 1 hour. Catalyst loadings were 1000 ppm, based on the weight of coal. Coal conversion was measured by the solubility of coal-derived products in methylene chloride and heptane using a pressure filtration technique(13).

Molybdenum trisulfide (MoS₃) was prepared by acidifying a solution of ammonium tetrathiomolybdate with 24 wt% formic acid (14). All other reagents were ACS grade.

X-ray diffraction studies were conducted with a Rigaku computer-controlled diffractometer equipped with a long fine-focus Cu X-ray tube, a receiving graphite monochromator to provide monochromatic Cu-K_α radiation, and a scintillation detector.

RESULTS AND DISCUSSION

Conversion of an aqueous solution of ammonium heptamolybdate [(NH₄)₆Mo₇O₂₄·4H₂O] to an active and high-surface-area catalyst is dependent on a number of factors. Gaseous hydrogen sulfide (H₂S) is required to convert ammonium heptamolybdate (AHM), which is essentially an oxide salt, to a series of oxysulfide salts (15) and ultimately to molybdenum disulfide (MoS₂), as shown in Figure 1. The ratio of ammonium ion to molybdenum may also be important, since studies have shown that increased NH₄/Mo ratios result in higher hydrogen consumption for the conversion of petroleum to upgraded products when AHM is used as a dispersed-phase catalyst (7,15). Petroleum upgrading studies demonstrated that the heat-up rate for the conversion of AHM to MoS₂ is extremely important (15). Slower heat-up rates resulted in a gradual transition of AHM to MoS₂ and significantly higher conversions of petroleum to distillate products.

Information on the dispersion of MoS₂ was obtained from X-ray diffraction measurements, which are sensitive to the degree of stacking and dispersion of the MoS₂ layers (Figure 2). The diffraction pattern of single layers of MoS₂ shows the (100) and (110) bands, but no (002) band, as in the middle curve of Figure 2. These crystallites are considered two-dimensional, since there is no growth in the third dimension. When only a very small number of MoS₂ layers are in multilayer stacks, a weak (002) band is present, as in the top curve with the catalyst precursor, MoS₃. When many multilayer stacks of MoS₂ are present, a strong (002) band can be seen, as in the lower curve. The pattern is that obtained for three-dimensional crystallites. The widths-at-half-maximum can be

used to estimate the size of the MoS_2 crystallites. The MoS_2 crystallites formed during a gradual heat-up of AHM, in the absence of coal, are three-dimensional, as shown in the bottom curve of Figure 2. Coal added to AHM under the same reaction conditions prevents the MoS_2 layers from growing in the third dimension. Since the crystallite size in the plane of the MoS_2 layers is about the same in both cases (150-200 angstroms), the addition of the coal produces a more highly dispersed, minimally stacked MoS_2 . All of these results suggest that many factors can affect the extent of dispersion of MoS_2 . The factors that have been identified include heat-up rate of the catalyst precursor during the conversion to MoS_2 ; the NH_3/Mo ratio; the H_2S pressure; and other reagents, such as coal, that might affect the transition of AHM to MoS_2 .

Previous studies by Lopez et al. (16) show that small amounts of ammonium tetrathiomolybdate [$(\text{NH}_4)_2\text{MoS}_4$] are produced during the decomposition of AHM, which represents an intermediate of a minor decomposition pathway. One advantage of using ammonium tetrathiomolybdate (ATTM) as a dispersed-phase catalyst in coal liquefaction is that an external source of H_2S is not required because the catalyst precursor already exists as a water-soluble sulfide salt. It is known that ATTM thermally decomposes to MoS_3 and subsequently to MoS_2 (17). Eggertsen et al. (14) examined the reaction conditions for the thermal decomposition of MoS_3 to MoS_2 and determined that rapid heat-up (direct introduction of MoS_3 into a stream of hydrogen at 450°C) gave MoS_2 having a surface area of 85-158 m^2/gm , while gradual heat-up (25 min to 450°C) resulted in MoS_2 surface areas of less than $5\text{m}^2/\text{gm}$. Naumann and coworkers (17) applied the results of Eggertsen to the catalyst precursor ATTM, since MoS_3 was considered to be an intermediate in the decomposition of ATTM (Figure 3). The results show that high-surface area MoS_2 is formed (88 m^2/gm) if the thermal transition of ATTM to MoS_2 is rapid, and the surface area is low if the thermal transition is gradual.

Studies at PETC examined the conversion of coal to methylene chloride- and heptane-soluble products using ATTM as a catalyst precursor. Experiments were performed using both rapid and gradual heat-up rates for the preparation of the dispersed-phase catalyst and were compared with results using AHM as a catalyst (Figure 4). The results demonstrate that rapid heat-up of ATTM resulted in coal conversions to methylene chloride- and heptane-soluble material that were higher than conversions from experiments done at a slower heat-up, consistent with expectations for surface area studies of pure compounds. Experiments were also performed with MoS_3 , wherein MoS_3 was suspended in the same amount of water used for the water-soluble precursor, ATTM. Results show that conversion of coal to methylene chloride- and heptane-soluble products is greater for rapid heat-up experiments and is comparable to those using AHM (Figure 4). Experiments that verify the microautoclave studies were also performed in a 1-liter stirred autoclave, using both batch and continuous modes of operation.

Experiments were also performed with moisture-free solid MoS_3 . Elimination of water has several advantages. The addition of water causes a decrease in hydrogen partial pressure within the reactor and is more energy intensive because water is being heated. Experimental results presented in Figure 4 demonstrate that the addition of the dry catalyst precursor, MoS_3 , produced coal conversions comparable to those

obtained with the water-soluble catalyst precursors. Therefore, MoS₂ may represent an ideal choice in the preparation of dispersed-phase catalysts. The X-ray diffraction pattern of MoS₂, from MoS₃, showed a very small (002) band, indicating minimal stacking. Minimal stacking infers a well-dispersed, high-surface-area material that provides comparable conversions to the water-soluble catalyst precursors. Scanning electron microscopy (SEM) was not able to detect the presence of MoS₂, suggesting that the particle size was less than 1000 angstroms. These results support the existence of highly dispersed MoS₂, which has resulted in the high conversion to solvent-soluble products.

CONCLUSIONS

Two catalyst precursors have been identified that result in high conversions of coal to solvent-soluble products when heated rapidly to reaction temperature. The use of MoS₃ and ATTM as catalyst precursors, rather than AHM as a catalyst precursor, offers a number of advantages. Both catalyst precursors are in a sulfided form, and therefore additional H₂S is not required, while AHM requires the addition of H₂S in order to form the oxysulfide intermediates and the final product, MoS₂. Both of the sulfided precursors are activated and highly dispersed when heated rapidly to reaction temperature, while AHM requires a gradual heat-up, and therefore activation of AHM is much more energy intensive. The ultimate goal is to identify a dry, highly dispersed, catalyst precursor or catalyst that can be added to a coal-vehicle feed without the addition of water and that results in yields of coal-derived products comparable to those produced using water- or oil-soluble catalyst precursors. Possibly MoS₃ is the catalyst precursor that satisfies those requirements.

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DISCLAIMER

Reference in this report to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

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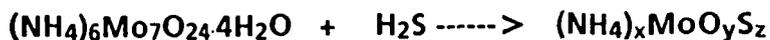


Figure 1. Conversion of Ammonium Heptamolybdate to Molybdenum Disulfide.

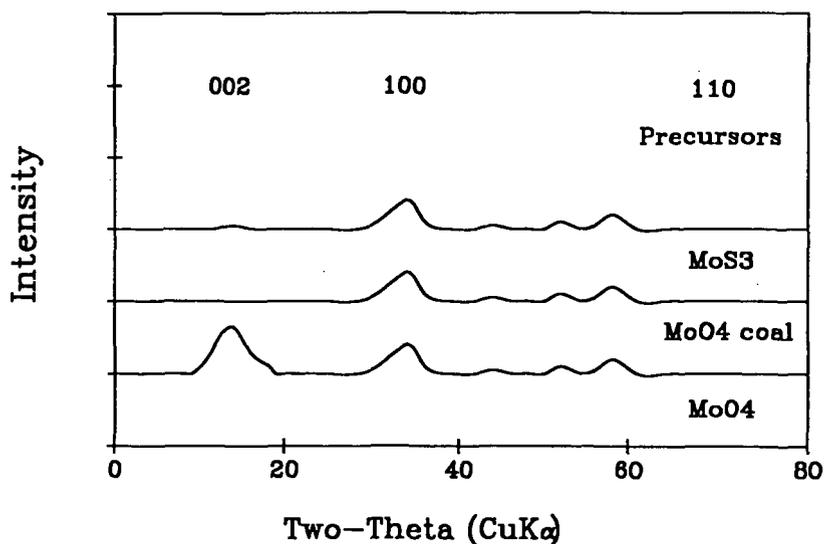


Figure 2. X-Ray Diffraction Patterns for Molybdenum Disulfide (h,k,l) Generated from Mo(VI) Precursors Reacted at Coal Liquefaction Conditions.

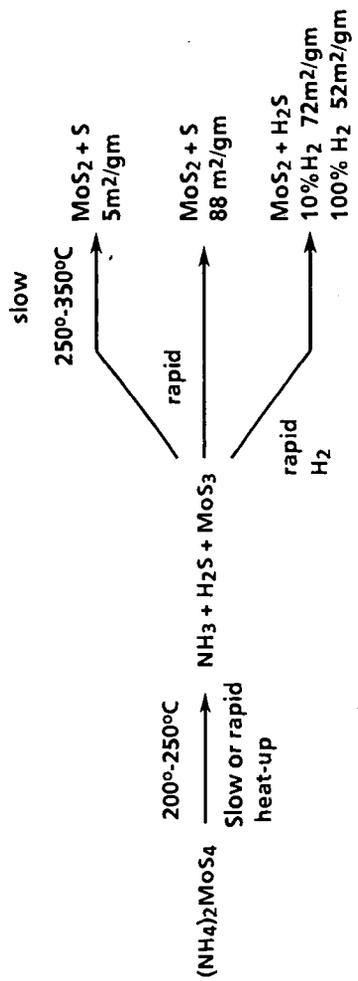


Figure 3. Decomposition of Ammonium Tetrathiomolybdate.

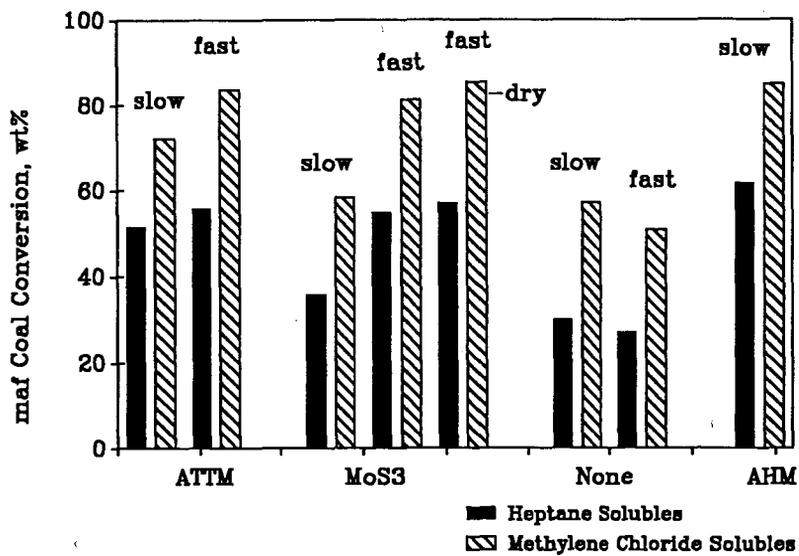


Figure 4. Effect of heat-up rate on coal conversion using presulfided catalyst precursors.

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 m²/g by reacting MoCl₄ with Li₂S in a tetrahydrofuran solvent. The precipitated sulfide was then treated with acetic acid to remove residual Li₂S. It was then treated with H₂S/H₂ 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 MoS₂ 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 cm³. 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 MoS₂. Reactions were conducted at 380°C for 30 minutes with H₂ 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 N₂), 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 m²/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 MoS₂ 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 MoS₂. 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 MoS₂. 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 m²/g, than previously reported.

Acknowledgments

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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 MoS₂

** 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, M²/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, M²/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, M²/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, M²/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, M²/g</u>	<u>Pore Volume CC/g</u>
3	16.6	179	0.30
12	—	—	—

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

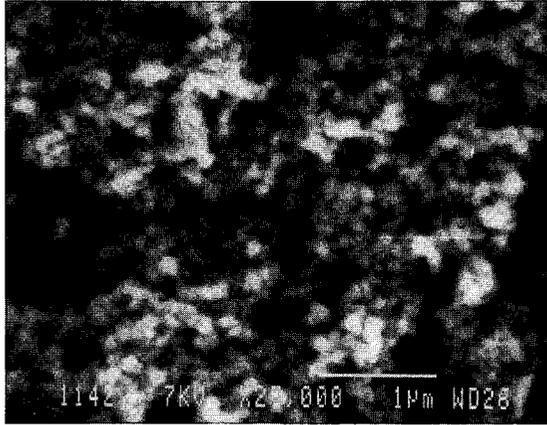


Figure 1 - SEM Photomicrograph of Sample 4B (x 25,000)

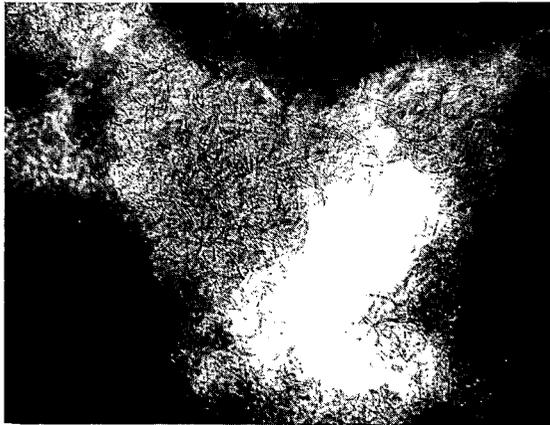


Figure 2 - TEM Photomicrograph of Sample 5A (x 800,000)

Colloidal Coal Hydroliquefaction Catalyst Preparation

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Introduction

Typical hydrotreating catalysts, consisting of Mo and W or Ni on aluminoxide, are pelletized and added to and withdrawn from the reactor in batches. The effects of diffusivity on the global reaction rate as well as on dispersion of the active metals are poorly understood.

Current research efforts aimed at cost reduction include dispersion of "disposable" unsupported metals in the feed streams (ref. 1) and impregnation of high surface aerogel supports (ref 2). In the standard incipient wetness impregnation a strongly bridging solvent such as water is used to dissolve the metal salt precursor. On drying, the support is compacted and pore structure of the final product may bear little resemblance to the original starting material. This study involves utilization of commercial colloiddally sized aluminum supports to prepare a homologous series of catalysts to study the effects of solvent and solvent removal on structure of the support and on dispersion of the active phase.

Experimental

Four impregnation techniques utilizing Degussa Aluminoxide-C (fumed process, 150-200 Å discrete spherical particles) and ammonium molybdate from Fisher Scientific Co. (83% MoO₃) are described below.

Incipient Wetness, (IW)

The Mo salt is dissolved in distilled water and added dropwise to the support. This continues until the support is at "incipient wetness", i.e. the point where unbound moisture is about to become available. The catalyst is dried at ca. 120°C for 12 to 24 hours,

ground with a mortar and pestle and calcined at 500°C for 4 to 6 hours.

Ethanol Slurry, Vacuum Dried, (EtOH-V)

The salt is dissolved in excess ethanol and a slurry is made by adding the support material. The mixture is stirred for several hours and then placed in a vacuum oven at ca. 100°C for 36 to 48 hours. This is followed by grinding as described above.

Ethanol Slurry, Rotary Evaporated, (EtOH-R)

Identical to EtOH-V except that solvent removal is achieved in a rotary evaporating apparatus over a period of 4 to 6 hours.

Critical Point Solvent Evaporation, (CPSE)

A slurry of is made of metal salt, solvent and support material as described for EtOH-V. The slurry is maintained under an inert gas pressure which is higher than the vapor pressure of the solvent at a temperature slightly lower than the critical temperature; the slurry is then heated above the critical point. A very rapid evaporation of the solvent occurs at the critical point (on the order of minutes or less). The catalyst is then removed and calcined as above.

Scanning Electron Microscopy was performed on the samples to observe gross differences in physical structure. The instrument used was an ETEC Omniscan SEM equipped with a PGT-1000 data acquisition and analysis system. Pore structure and surface area measurements were calculated from nitrogen adsorption/desorption isotherms made on a Digisorb 2500 instrument and from combining Hg penetration scans made at three pressure ranges on a Quantachrome Autoscan Porosimeter.

Catalyst Structure

Physical characteristics for five catalysts prepared by the methods described above, for fresh Al₂O₃, and for Al₂O₃ which has been wetted and dried as described for the IW sample are summarized in Table 1. The data show that the tap density (determined by measuring the volume of a known weight of material which had been gently tapped in a graduated cylinder) increases significantly in all treatments of the support material except for the case of the CPSE preparation. SEM micrographs indicate that the IW, EtOH-V, and EtOH-R processes yield irregularly shaped particles with a wide distribution of sizes as is typical for a grinding process. In contrast, the sample prepared using the CPSE process is composed of secondary particles which are much more uniform in size and shape.

The BET surface area of Al₂O₃ increases when wetted and dried. This is due primarily to the large numbers of interparticle contacts formed during drying; condensation around

an interparticle contact zone essentially adds a contribution to the isotherm volume. Figure 1 shows the comparison of pore volumes calculated from the nitrogen adsorption isotherms for these catalyst samples with fresh Degussa aluminoxide-C. The CPSE most closely resembles the fresh support material (shown by the dotted line), the wetted alumina and the IW sample show the greatest increase, and the EtOH-V and EtOH-R samples are intermediate in calculated volume increase from fresh Al_2O_3 . The mercury porosimetry data for total pore volume indicates that decreasing the severity of compaction during catalyst preparation, either by lowering the bridging strength of the solvent or by increasing the rate of solvent removal, results in an increase in pore volume.

Active Phase Dispersion

It is known that the selectivity for octenes in the catalytic dehydration of octanol is a function of the acid/base properties of the catalyst used (ref. 3). This reaction has been used in measuring the dispersion of MoO_3 on alumina (ref. 4). The selectivity, at constant conversion, for our series of catalysts, for pure MoO_3 and for pure $\gamma\text{-Al}_2\text{O}_3$ is shown in figure 2; the line represents selectivity for a series of IW catalysts with increasing MoO_3 loadings. These data indicate that dispersion of the active phase decreases in the order:

IW > EtOH-V > EtOH-R > CPSE.

X-Ray diffraction scans suggest that both the IW and CPSE contain little or no crystalline MoO_3 .

Hydrogenolysis Performance

Hydrogenolysis of 1,3,5-trimethylbenzene (tmb) in a plug-flow reactor was used to compare activity for the series of catalysts (ref 5). The catalysts were diluted with an inert $\alpha\text{-Al}_2\text{O}_3$ (Fisher Scientific, $0.96\text{m}^2/\text{g}$) to minimize the effects of physical differences in the test catalysts by making the reactor beds similar in density, volume and particle size. The catalyst was first reduced in flowing H_2 overnight at 450°C ; the reaction mixture was a 10:1 molar mixture of H_2 and 1,3,5-trimethylbenzene.

For the IW catalyst, hydrogenolysis of 1,3,5-tmb to m-xylene was the dominant reaction; equilibrium between the two had been reached at residence times of 15 minutes. Small amounts of o- and p-xylene as well as 1,2,3- and 1,2,4-tmb were also detected. The EtOH-V and CPSE showed the same product selectivity, although concentrations are shifted downward and the equilibrium between m-xylene and 1,3,5-tmb was not reached until residence times of approximately 1 hour.

The greatest tendency toward hydrogenolysis was seen for the 17% MoO_3 catalyst. The equilibrium between 1,3,5-tmb and m-

xylene is already established at residence times of 15 minutes, but at longer times the m-xylene production declines and a corresponding increase in benzene and methane is observed. TEM micrographs revealed large MoO_3 crystallites on the 17% MoO_3 sample not seen in any of the 12% loading samples. XPS analyses on the two EtOH-V catalysts show the presence of a peak for a more reduced species of Mo in the 17% loading not present in the 12% catalyst reduced under the same conditions. These data suggest that the Mo in excess of one monolayer is apparently more reduced than the supported Mo.

Conclusions

Choice of solvent and method of solvent removal are critical factors in determining the final structure of a supported catalyst. The use of a less polar solvent and subsequent rapid removal is shown to minimize compaction of the colloidal alumina particles. However, greater metal dispersion and higher hydrogenolysis activity is indicated for catalysts prepared using water. Further investigation is needed to determine the effects of subsequent impregnation, and coimpregnation, of promoters, as well as the removal of water at it's critical point.

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Table 1.
Physical Properties

	Tap Density (g/cc)	BET Surface Area (m ² /g) Corrected for Mo	Total Pore Volume (cc/g) Mercury Penetration
Fresh Aluminoxide	0.07	98.32	3.88
Wetted Aluminoxide	0.70	117.39	0.89
IW 12% MoO ₃	0.56	111.01	1.33
EtOH-V 12% MoO ₃	0.34	110.73	2.60
EtOH-V 17% MoO ₃	-	126.01	-
EtOH-R 12% MoO ₃	0.29	108.03	2.17
CPSE 11% MoO ₃	0.05	102.88	7.33

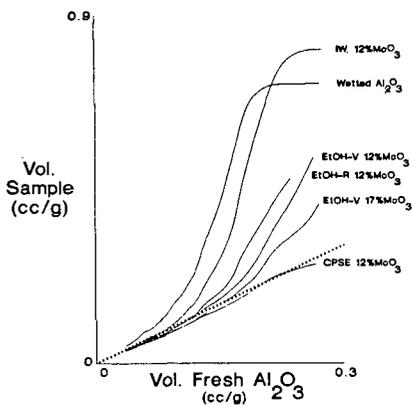


Figure 1. Comparison of pore volumes calculated from nitrogen adsorption isotherms for this catalyst series with fresh Degussa Aluminoxide-C.

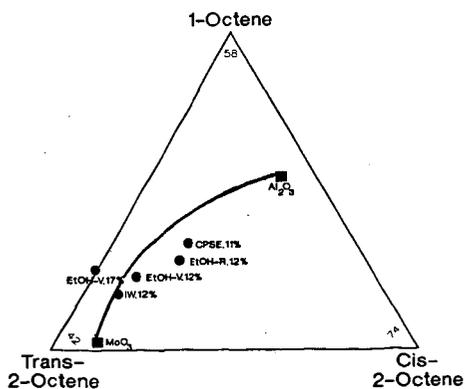


Figure 2. Product selectivity of the dehydration of octanol for pure Al_2O_3 and MoO_3 , a series of $\text{MoO}_3/\text{Al}_2\text{O}_3$ catalysts prepared by incipient wetness (-), and the series of $\text{MoO}_3/\text{Al}_2\text{O}_3$ prepared for this study (●).

EVALUATION OF THE ACTIVITY OF NICKEL IN COPROCESSING USING MODEL SYSTEMS

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The coprocessing of coal with petroleum residuum offers an alternate technology to direct liquefaction by simultaneously upgrading coal, coal liquids and residuum into higher quality products (1-3). Residuum as the solvent contains indigenously the metals, nickel and vanadium, which may be present at a level of a few to several thousand ppm. The objective of this study is to evaluate the catalytic activity of the indigenous Ni in coprocessing by reacting model systems with Ni generated in situ from Ni complexes under coprocessing conditions.

Experimental

Model Reactants and Nickel Precursors. The model reactants used were naphthalene, indan, indene, benzothiophene, o-cresol, benzofuran, quinoline and indole. All of which were obtained from Aldrich. The nickel sources used were oil-soluble metal salts of organic acids, nickel naphthenate (NiNaph), and nickel octoate (NiOct), and solid complexes, nickel acetylacetonate (NiAcAc) and nickel citrate (NiCit), which were obtained from Air Products, Shepherd Chemical, Strem Chemical and Aldrich.

Reactions and Analyses. Hydrogenation reactions were conducted in 20 cm³ stainless steel microtubing bomb reactors. For each reaction, 4 grams of 2 weight percent naphthalene and/or 1 weight percent of each of the other reactants in hexadecane were charged. The nickel precursor was introduced at 2850 to 2950 ppm Ni; the Ni to reactant ratio was held constant. The reactions were conducted at 380°C for 30 minutes with 1250 psig H₂ (ambient) while being agitated at 550 cpm.

The liquid products were analyzed by gas chromatography using a 30m fused silica DB-5 column from J & W Scientific with FID detection and p-xylene as the internal standard. Some of the reaction products were identified by GC/MS using a VG 70EHF mass spectrometer and a Varian 3700 gas chromatograph.

Results and Discussion

The catalytic activity of Ni generated in situ from different nickel precursors were evaluated in the hydrogenation of hydrocarbons and heteroatomic species. The degree to which hydrogenation and heteroatom removal occurred in each reaction is reported in the defined terms of: (1) percent hydrogenation (% HYD) which is the number of moles of hydrogen required to achieve the final product distribution as a percentage of the moles of hydrogen required to achieve the most hydrogenated product; (2) percent hydrogenolysis (% HYG) which is the summation of the mole percents of products resulting from carbon-carbon or carbon-heteroatom bond cleavage; and (3) percent hydrodesulfurization (% HDS), percent hydrodeoxygenation (% HDO) and percent hydrodenitrogenation (% HDN) which are the summation of the mole percents of products not containing sulfur, oxygen, and nitrogen, respectively.

Catalytic Activities of Nickel from Different Precursors. The catalytic activity of in situ generated Ni catalysts produced from several different catalyst precursors were compared using a naphthalene-indan system at 380 and 400°C as shown in Table 1. Three of the Ni precursors, NiOct, NiCit, and NiAcAc, showed

activity for saturating the aromatic rings in both naphthalene and indan while NiNaph did not.

Effect of Sulfur. Since both residuum and coal contain substantial amounts of sulfur, the most likely form of Ni during coprocessing reaction is that of a sulfide. Sulfur was added to the naphthalene reactions to evaluate the catalytic activity of Ni sulfide during coprocessing. As shown in Table 2, elemental sulfur was added from zero to seven times the stoichiometric amount required to form Ni₃S₂, and organic sulfur as benzothiophene was added at a level of 0.1 to 1.0 weight percent. A small amount of sulfur completely inhibited the catalytic activity of Ni giving a % HYD of naphthalene similar to that observed with thermal reactions.

The inhibiting effect of sulfur on the catalytic activity of Ni from NiAcAc and NiCit was examined in naphthalene-indan combined reaction systems. When elemental sulfur was introduced at 0.01g level (2.3 times the amount of sulfur required to form Ni₃S₂) the naphthalene conversion was reduced from ~98% to 10% and 7%, respectively. No conversion of indan was observed.

Catalytic Activity of Ni for Saturating Aromatic Hydrocarbons. The activity of three different catalysts, NiOct, presulfided powdered NiMo/Al₂O₃ and *in situ* generated MoS₂ from molybdenum naphthenate, for saturating aromatic hydrocarbons are compared in Table 3. The model systems tested were reaction products observed from the model systems used in this study. Each reaction was reacted with the same amount of total metal, ~ 3000 ppm from each catalyst. Both NiOct and NiMo/Al₂O₃ showed high activity for saturating aromatic rings while MoS₂ did not. NiOct showed a higher activity for hydrogenating alkylaromatics to alkylalicyclics while presulfided NiMo/Al₂O₃ showed a higher activity for saturating aromatics to alicyclics and for slightly hydrogenolyzing aromatic and hydroaromatic species.

Catalytic Activity and Selectivity of Ni for Hydrogenation of Model Hydrocarbon and Heteroatomic Compounds. The catalytic activity and selectivity of Ni for hydrogenation, hydrogenolysis, and heteroatom removal were evaluated by performing reactions using partially saturated hydrocarbons, aromatics and heteroatom containing species.

Indan and Indene. The Ni catalysts produced from NiOct and NiAcAc showed high activity for saturating the aromatic ring of both indan and indene. The only products observed were saturated species of indan primarily hexahydroindan. No hydrogenolysis was observed.

Benzothiophene. Benzothiophene was not completely desulfurized with either NiOct or NiAcAc, producing ethylbenzene as the major product and dihydrobenzothiophene as the secondary product. Benzothiophene produced 25% HYD and 44% HDS with NiOct in the individual reaction and 26% HYD and 46% HDS in a combined system with naphthalene. The combined system with NiAcAc yielded 31% HYD and 54% HDS. Although NiAcAc yielded slightly higher desulfurization and conversion of benzothiophene, the presence of organic sulfur in benzothiophene appeared to severely poison both of these catalysts. The Ni catalysts did not show the activity previously observed for saturating aromatics in the presence of organic sulfur.

O-Cresol. O-cresol was highly reactive in the presence of NiOct where 98% was converted to methylcyclohexane and fully hydrogenated oxygen-containing hydrocarbons such as trans- and cis-methylcyclohexanol as the major product and methylcyclohexanone as the secondary product. In combined systems with either

naphthalene or indole, the products produced from o-cresol were very similar to those in the individual system. However, when elemental sulfur or benzothiophene was added to the system, the catalytic activity of Ni was completely eliminated. No o-cresol was converted.

Benzofuran. Nearly 100% of benzofuran was converted to alicyclic compounds but less than 17% of the oxygen was removed with NiOct. The major products were trans- and cis-ethylcyclohexanol and ethylcyclohexanone. All of the products produced were saturated yielding - 67% HYD. The hydrogenation of benzofuran remained the same when combined with naphthalene while HDO decreased to 7%. The addition of elemental sulfur or benzothiophene at 0.1 weight percent decreased the catalytic activity of Ni for benzofuran and yielded a product distribution similar to that of thermal reactions.

Indole. Indole was totally converted with NiOct or NiAcAc. Neither dihydroindole (indoline) nor o-ethylaniline was observed in the product distribution while small amounts of methylcyclohexane and ethylcyclohexane were observed. Several groupings of unknown chromatographic peaks with broad tailing that is usually characteristic of nitrogen containing compounds were observed. These peaks are postulated to be perhydroindole or o-ethylcyclohexylamine. The addition of sulfur to the reaction system completely eliminated any catalytic activity of NiOct and NiAcAc.

Quinoline. Hydrogenation of quinoline with NiOct or NiAcAc resulted in total conversion of quinoline; however, the reaction products typically seen from quinoline such as 1,2,3,4-tetrahydroquinoline, o-propylaniline, n-propylbenzene and n-propylcyclohexane were not present in the chromatograms (5). A small amount of 5,6,7,8-tetrahydroquinoline as well as a peak representing a substantial amount of decahydroquinoline was observed. Sulfur addition resulted in the elimination of the catalytic activity of the Ni catalyst and yielded a product slate similar to that of a thermal reaction.

Catalytic Reaction of Combined Systems. The effect of other hydrocarbon and heteroatomic compounds on the naphthalene hydrogenation in the presence of NiOct was evaluated. Table 4 shows the effects of these compounds on the hydrogenation of naphthalene. When reacted individually naphthalene yielded 36% tetralin and 64% decalin although the reproducibility was very poor. With the introduction of the other compounds, the reproducibility of naphthalene hydrogenation was improved substantially. None of the additional compounds except for benzothiophene had a significant effect on the naphthalene hydrogenation within the error bounds of the experiments.

Combining naphthalene or a mixture of naphthalene and other compounds with 0.1 weight percent and 1 weight percent benzothiophene severely inhibited the catalytic activity of NiOct. Under these conditions, naphthalene was hydrogenated only to the extent of that observed in thermal reactions.

Summary

The catalytic activity of the different Ni precursors for hydrogenating aromatics and partially hydrogenated aromatics ranked in the order of NiAcAc > NiCit > NiOct while NiNaph showed no activity. The reaction pathways observed with oxygen compounds such as o-cresol and benzofuran with NiOct produced methyl and ethyl cyclohexanols and methyl and ethyl cyclohexanones as the major products, respectively. The Ni catalyst from NiOct was highly active for hydrogenating both indole and quinoline but was not effective for removing nitrogen from the rings. Combinations of hydrocarbon and heteroatomic compounds

except for benzothiophene did not affect the hydrogenation of naphthalene in the presence of the Ni catalyst. However, even a small amount of elemental sulfur or benzothiophene completely inhibited the catalytic activity of Ni.

In actual coprocessing systems, a large portion of the nonporphyrinic complexes of Ni are contained in derivatives of naphthenic acid (6) which may be catalytically inactive based on the observed activity of NiNaph in this study. The sulfur content of both coal and residuum can be quite high (7,8). The release of this indigenous sulfur in the coprocessing system would readily poison any nickel released to the coprocessing system and render it inactive.

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Table 1. Catalytic Activity of Ni for Hydrogenation of Naphthalene and Indan Combined Using Different Precursors

	Ni Precursor			
	NiNaph	NiOct	NiCit	NiAcAc
<u>Reactions at 380°C</u>				
% HYD of Naphthalene*	2.4	71.3	97.0	98.8
% HYD of Indan*	0	84.0	100.0	100.0
<u>Reactions at 400°C</u>				
% HYD of Naphthalene	2.4	74.4	98.2	98.8
% HYD of Indan	0	85.0	100.0	99.0

Decalin and hexahydroindan were the most hydrogenated products from naphthalene and indan, respectively.

Table 2. Catalytic Activity of Ni for the Hydrogenation of Naphthalene in the Presence of Sulfur

<u>Amount of Elemental Sulfur^a</u>	<u>% HYD of Naphthalene</u>	<u>Amount of Benzothiophene^b</u>	<u>% HYD of Naphthalene</u>
0.0	78 ± 8	0.0	78 ± 8
0.2	0.1	0.1	1.6
0.6	0.2	0.2	0.8
3.5	1.0	0.5	0.8
7.0	0.8	1.0	0.8

^a Multiples of the stoichiometric amount of sulfur in Ni₃S₂ (0.0043g).

^b Weight percent of benzothiophene in hexadecane.

Table 3. Hydrogenation of Aromatic Compounds with Ni Octoate, Presulfided Powder NiMo/Al₂O₃ and Mo Naphthenate with Excess Sulfur

Reactants Products (mole %)	Catalyst		
	Ni Octoate	Presulfided NiMo/Al ₂ O ₃	Mo Naphthenate with Excess Sulfur
- Toluene			
Toluene	5	20	98
Methylcyclohexane	95	79	2
Ethylcyclopentane	0	1	Trace
- Ethylbenzene			
Ethylbenzene	8	18	97
Ethylcyclohexane	91	82	2
Toluene	0	0	1
Methylcyclohexane	1	Trace	Trace
- Propylbenzene			
Propylbenzene	16	20	100
Propylcyclohexane	83	78	0
Butylcyclopentane	0	2	0
Methylcyclohexane	1	Trace	0
- Butylbenzene			
Butylbenzene	11	23	98
Butylcyclohexane	89	75	2
Pentylcyclopentane	0	2	0
Ethylbenzene	0	0	Trace
- Tetralin			
Tetralin	27	13	95
Decalin	73	83	5
n-Butylbenzene	0	2	Trace
others ^a	0	2	0
t-D/c-D ^b	0.45	2.85	1.62
- Naphthalene			
Naphthalene	0	0	2
Tetralin	36	9	92
Decalin	64	87	6
n-Butylbenzene	0	2	Trace
others ^a	0	2	0
t-D/c-D ^b	0.43	2.93	1.39

(a) Unknown products of molecular weight = 138

(b) Approximate weight ratio of trans-decalin to cis-decalin

Table 4. Effect of Other Compounds on Catalytic Hydrogenation of Naphthalene Using Ni Octoate Without Additional Sulfur

(A)						
Additional Compound ^a	Indan	Indene	o-Cresol	Benzofuran	Quinoline	Indole
Products (mole %)						
Naphthalene	Trace	0	0	0	0	Trace
Tetralin	48	48	50	53	52	58
Decalin	52	52	50	47	48	42
t-D/C-p ^b	0.43	0.40	0.42	0.42	0.40	0.40
% Hydrogenation	71.3	71.0	70.1	68.0	69.1	64.5
(B)						
Additional Compound ^a	EZT (1 wt%)	EZT ^c (0.1 wt%)	Indene EZT ^c	o-Cresol EZT ^c	Benzofuran EZT ^c	Indole EZT ^c
Products (mole %)						
Naphthalene	95	88	95	93	90	96
Tetralin	5	12	5	7	10	4
Decalin	0	0	0	0	0	0
% Hydrogenation	1.8	5.0	2.1	3.0	3.8	1.5

(a) Amount of additional compound: 1 weight percent of each in the reactant solution.

(b) Approximate weight ratio of trans-decalin to cis-decalin.

(c) EZT (benzothioephene): 0.1 weight percent of EZT unless noted otherwise.