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ABSTRACT

The conversion of coal into high-quality, clean-burning transportation fuels is a key part of the U.S. energy strategy. Coal liquefaction and coal-oil co-processing are among the most promising technologies for coal conversion. The formulations used in most commercial hydrotreatment catalysts were developed and optimized for petroleum refining, but coal-derived liquids differ from petroleum crude oils. Thus, there is a need to develop new catalytic materials specifically for hydrotreating coal-derived liquids. Research described in this report was aimed at synthesizing and evaluating supported Mo oxynitrides and oxycarbides for the selective removal of nitrogen, sulfur and oxygen from model and authentic coal-derived liquids. These materials are related to Mo nitrides and carbides, catalysts that have demonstrated high activities for hydrotreating crude oils and coal-derived liquids. The Al_2O_3-supported oxynitrides and oxycarbides were synthesized via the temperature programmed reaction of supported molybdenum oxides or hydrogen bronzes with NH_3 or an equimolar mixture of CH_4 and H_2. Phase constituents and composition were determined by x-ray diffraction, CHN analysis, and neutron activation analysis. Oxygen chemisorption was used to probe the surface structure of the catalysts. The reaction rate data was collected using specially designed micro-batch reactors.

The Mo oxynitrides and oxycarbides were x-ray amorphous and therefore their structures could not be determined from x-ray diffraction; however, compositional analysis revealed that significant amounts of nitrogen and carbon were incorporated into the materials. In comparison to corresponding Mo nitride and carbide catalysts, the oxygen chemisorption capacity was suppressed for the oxynitride and carbide catalysts. This observation was most likely a consequence of the presence of oxygen in the oxynitride and oxycarbide lattices.

The Al_2O_3-supported Mo oxynitrides and oxycarbides were competitively active for quinoline hydrodenitrogenation (HDN), benzothiophene hydrodesulfurization (HDS) and benzofuran hydrodeoxygenation (HDO). In fact, the HDN and HDO specific reaction rates for several of the oxynitrides and oxycarbides were higher than those of a commercial Ni-Mo/Al_2O_3 hydrotreatment catalyst (Crosfield 504). Furthermore, the product distributions indicated that the oxynitrides and oxycarbides were more hydrogen efficient than the sulfide catalysts. Among the synthesis parameters that were varied, the Mo loading had the most significant influence on the activity. For HDN and HDS the catalytic activity was a strong inverse function of the Mo loading. In contrast, the benzofuran hydrodeoxygenation (HDO) activities did not appear to be affected by the Mo loading but were affected by the heating rate employed during nitridation or carburization. This observation suggested that HDN and HDS occurred on the same active sites while HDO was catalyzed by a different type of site. The oxynitrides and oxycarbides were generally more active and selective than their corresponding nitrides and carbides suggesting that the introduction of oxygen into the lattice enhanced the catalytic performance.

Selected materials were also evaluated for the hydrotreatment of 9-methylcarbazole, dibenzothiophene and dibenzofuran. The oxycarbides were typically more active than the Ni-Mo/Al_2O_3 sulfide catalyst but less active than the Co-Mo/Al_2O_3 catalyst (Crosfield 477). For dibenzothiophene HDS one of the carbide catalysts was more active than both the Co-Mo/Al_2O_3 and Ni-Mo/Al_2O_3 sulfide catalysts.

INTRODUCTION

Coal liquefaction and coal-oil co-processing are perhaps the most promising technologies for the conversion of coal into high-quality, clean-burning transportation fuels. An important step in the conversion process involves upgrading (e.g., heteroatom removal and hydrogenation) the coal-derived liquids. These liquids tend to be richer in heteroatoms, more aromatic and higher molecular weight than typical crude oils, and conventional petroleum hydrotreatment catalysts are not very effective for upgrading coal-derived liquids (Xu et al., *1991*). Current coal liquefaction research and development efforts have taken one of two approaches to solving this problem (Derbyshire, *1989*). The first is to develop improved coal dissolution catalysts that will lead to liquid products with characteristics more closely resembling that of petroleum crude oil. This approach, if successful, would facilitate the implementation of existing crude oil refining technology for the downstream processing of coal-derived liquids. The second approach, which is adopted in this research, recognizes that coal-derived liquids differ from petroleum crude oils and aims to develop new catalysts specifically for the upgrading process. If effective, these catalysts could be integrated into existing coal liquefaction and co-processing technologies and significantly improve the economic feasibility of developing commercial processes for the conversion of coal into transportation fuels.

In this project we synthesized and characterized supported molybdenum oxynitride and oxycarbide catalysts, and evaluated their activity and selectivity patterns for the hydrodenitrogenation (HDN), hydrodesulfurization (HDS), and hydrodeoxygenation (HDO) of model compounds. These catalysts are related to molybdenum nitrides and carbides, materials have been reported to be comparable or superior to sulfide catalysts, such as Ni-Mo/Al_2O_3 and Co-Mo/Al_2O_3, for the hydrotreatment of model compounds. We expected the introduction of oxygen into the nitride and carbide lattices would improve the selectivity and stability of these catalysts (see proposal for additional details concerning the materials design strategy).

PROJECT OBJECTIVES

The principal objective of this research was to evaluate the hydrotreatment properties of Al_2O_3 supported Mo oxynitride and oxycarbide catalysts. This information will be used to assess the potential of these materials for use as commercial catalysts for hydrotreating coal-derived liquids. The specific research objectives included the:

1. Preparation of series of γ-Al_2O_3 supported Mo oxynitride and oxycarbide catalysts. Novel synthesis strategies have been devised for this purpose. Molybdenum oxynitrides and oxycarbides will also be prepared for comparison with the oxynitrides and oxycarbides.
2. Evaluation of their catalytic properties for the HDN, HDS and HDO of model reactants and *authentic* coal-derived liquids. This will include determining their activities, selectivities and reaction pathways.
3. Characterization of the sorption and bulk structural properties of the catalysts at various stages during their genesis and following the reaction studies. This will provide useful information for the development of structure-function relationships.

All of the research objectives were accomplished except for evaluation of the oxynitrides and oxycarbides in authentic coal-derived liquids. We intend to complete this objective in the near future using a well-characterized coal-derived liquid from Consol.

EXPERIMENTAL

Catalyst Synthesis

The catalysts was prepared by nitriding or carburizing γ-Al_2O_3 supported molybdenum oxides or hydrogen bronzes. The oxides were prepared using the incipient wetness technique. An aqueous solution of ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}\bullet 4H_2O$) was added dropwise to γ-Al_2O_3 (190 m^2/gr) which had been previously calcined at 500 °C for 5 hours in dry air. The solution was stirred into the support until the point of incipient wetness was reached, at which time the mixture was calcined again for 5 hours at 500 °C. The initial concentration of the ammonium heptamolybdate solution was adjusted in an attempt to achieve loadings of 4, 8, and 14 wt % molybdenum. Only one impregnation was needed for the 4 and 8 wt % molybdenum materials; however, because of the solubility limits of ammonium heptamolybdate in water, the 14 wt % materials required two impregnations. The materials were calcined following each impregnation. It has been reported that the method of preparation does not significantly affect the character of the resulting molybdenum oxide (Deo and Wachs, 1991).

We used thermal gravimetric analysis and *in situ* x-ray diffraction to determine the character of solid-state reactions between MoO_3 or H_xMoO_3 and NH_3. Thermal gravimetric analysis (TGA) was performed using a TAI Instruments TGA/DTA/DSC. The bronze, H_xMoO_3 ($x \leq 0.3$), was prepared by the reduction of MoO_3 with HCl and Zn metal powder as originally described by Glemser and Lutz (*1951*). The reaction temperature was increased from room temperature to 600 °C at 40 or 100 °C/hr. The oxynitride isomorph of γ-Mo_2N, γ-$Mo_2O_yN_{1-y}$, was identified as an intermediate during the nitridation of both MoO_3 and H_xMoO_3. The oxynitride had a diffraction pattern very similar to that of γ-Mo_2N. The reaction of MoO_3 at temperatures lower than 500 °C produced mixtures of H_xMoO_3, MoO_2 and γ-$Mo_2O_yN_{1-y}$. The slower heating rate enhanced the selectivity to H_xMoO_3 and γ-$Mo_2O_yN_{1-y}$. The reaction of H_xMoO_3 to γ-$Mo_2O_yN_{1-y}$ was favored by use of faster heating rates. The selectivity to γ-$Mo_2O_yN_{1-y}$ was highest when H_xMoO_3 was used as the precursor.

The oxynitrides were therefore synthesized by reacting γ-Al_2O_3 supported bronzes with NH_3. The supported bronze was prepared by mixing ≈4 gr of the supported molybdenum oxide with ≈6 gr of Zn metal in 200 ml of 5.0 N HCl. This Zn:MoO_3 ratio (1:1) was found to be optimum for the preparation of bulk H_xMoO_3 from MoO_3. The mixture was sealed and stirred overnight then the solids were filtered off. The resulting materials were washed thoroughly with distilled water then dried in a desiccator over phosphorous pentoxide. Approximately 2.5 g of the supported bronze were placed in a quartz reaction tube. Details of the reactor are given elsewhere (Colling and Thompson, 1994). The material was supported on a plug of glass wool which was held up by a fritted disk. The NH_3 flowrate was adjusted to result in a molar hourly space velocity of 17 hr^{-1}. Previously we observed that the space velocity does not significantly affect the catalytic properties of supported Mo nitrides (Colling and Thompson, 1994). The precursor was heated from room temperature to 350 °C in 30 minutes then 350 to 450 °C at 50 or 100 °C/hr in NH_3 flowing at 150 cc/min. The materials were coded as follows: XXyy where XX represents the catalyst formulation, and yy indicates the intended Mo loading. This is followed by a - or + sign which indicates the level of the heating rate. For example, MON08+ represents the supported Molybdenum OxyNitride with a target loading of 8 wt% Mo prepared using a heating rate of 100 °C/hr.

The oxycarbides were prepared by partially oxidizing supported Mo carbides. The supported Mo carbides were synthesized via TPR of the γ-Al_2O_3 supported oxides with 49.0% CH_4 in H_2. The supported oxide was placed in the quartz reaction tube and the gas flowrate was adjusted to produce a space velocity of 10 hr^{-1} (usually 150 cc/min). The material was heated from room temperature to 550 °C in 0.5 hr and then to 820 °C at 60 °C/hr or 120 °C/hr where it was held for one hour. The carburized material was reduced in flowing hydrogen (120 cc/min) at 820 °C for one hour and then cooled to room temperature in hydrogen over one hour. The catalyst was purged with helium for 10 minutes to remove any remaining methane or hydrogen and was finally passivated for two hours in a flowing stream of 0.98% O_2/He at 20 cc/min. The oxycarbide was then prepared by reacting the supported carbide with a mixture of 25% CO in H_2 at 400 °C for 14.5 hrs. The CO/H_2 flowrate was 75 cc/min.

The supported nitrides were prepared using methods previously developed and described (Colling and Thompson, 1994). Briefly, the nitrides were prepared by reacting supported molybdenum oxides with an NH_3 while heating the materials from room temperature to 350 °C in 0.5 hr and from 350 to 450 °C at 40 °C/hr or 100 °C/hr. The material was then heated to 700 °C at 200 °C/hr and held at 700 °C for one hour. The NH_3 space velocity was 17 hr^{-1}. After being quickly cooled, the material was passivated for two hours in a flowing stream of 0.98% O_2/He at 20 cc/min. Passivation was performed to prevent bulk oxidation of the catalyst. The catalyst code denotes the level of the first heating rate.

Catalyst Characterization

X-ray diffraction (XRD) was used to determine the phase constituents of the materials. Diffraction patterns were collected using a Rigaku DMAX-B diffractometer and CuKα radiation (λ = 1.542 Å). Data acquisition, peak identification, and plotting were performed using a Gateway 2000 486/33C computer which was interfaced to the diffractometer.

Neutron activation analysis (NAA) was used to measure the bulk aluminum and molybdenum in the materials. The catalysts were bombarded with neutrons and the resulting radiation was measured as the radioisotopes decayed. Aluminum produced an isotope with radiation of about 1779 keV, and molybdenum produced an isotope with radiation of 140.5 keV. We used NIST-SRM-1633b as a standard for aluminum and NIST-330 for molybdenum.

The amounts of carbon, hydrogen, and nitrogen in the catalysts were determined using a Perkin Elmer 2400 CHN Elemental Analyzer equipped with a thermal conductivity detector. Approximately 0.5 mg of catalyst was loaded into a tin capsule and placed in the analyzer. The catalyst was then combusted at 925 °C and some of the gaseous products were reduced at 640 °C. The amounts of CO_2, H_2O, and N_2 were measured and recorded.

Oxygen chemisorption was measured using a Quantasorb Sorption Analyzer (Model QS-17). Approximately 100 mg of material was placed in a quartz U-tube and reduced in hydrogen at 20 cc/min. for 3 hours. The oxynitrides and nitrides were reduced at 400 °C, and the oxycarbides and carbides were reduced at 480 °C. Following reduction, the catalyst was purged with helium at the reduction temperature. The material was then cooled to room temperature in helium flowing at 20 cc/min and finally placed in a dry ice/acetone bath at -78 °C. Pulses of a gas mixture containing 10.1% O_2 in helium were injected into a flowing stream of helium and passed over the catalyst. The amount of oxygen that did not adsorb on the catalyst was measured by a thermal conductivity detector (TCD) and recorded. When several consecutive injections produced a relatively constant TCD signal, the catalyst was assumed to be saturated. Oxygen uptake was then calculated based on the TCD signal and the number of injections. The sulfides were reduced at 400 °C for 3 hours prior to chemisorbing oxygen.

Catalytic Activity

Reaction rate measurements were made using a batch micro-reactor system. This system is similar to that employed by several groups in the past (Stohl and Malhotra, 1988; Miller et al., 1988; Rhee et al., 1988; Shin et al., 1988; Kim and Curtis, 1990). The reaction volume was 2 ml. The stainless steel micro-reactors were made of Swagelok components including two caps (3/8") and a port connector (3/8"). The reactor was connected to a Whitey Union Bonnet needle valve and a Swagelok quick connect via a 4 inch length of 1/4 inch tubing. The reactor was loaded with approximately 10 mg of catalyst and 100 mg of reactant. The reactants were quinoline, benzothiophene, benzofuran, 9-methyl-carbazole, dibenzothiophene or dibenzofuran. Two glass beads (d = 4 mm) were added to the reactor to enhance mixing. The reactor was then sealed and pressurized with hydrogen to 1000 psig at room temperature (expected pressure at reaction temperatures of ≈2000 psi). The reactor portion was immersed in a heated fluidized sand bath so that only the valve remained above the surface of the bath. The bath temperature was maintained at 390 °C for all reactions except benzothiophene HDS, which was run at 320 °C. These conditions were chosen so as to achieve no more than 10% conversion. The reactor was agitated manually every 10 minutes. When the reaction time had expired, the reactor was removed from the bath and immediately cooled to room temperature. The pressure in the reactor was measured then the gases were vented. The liquid products were extracted with hexadecane, and the reactor was cleaned with acetone and baked overnight for subsequent use.

Liquid product identification was performed using a Hewlett Packard 5890 gas chromatograph (GC) equipped with a Hewlett Packard 5970 mass spectrometer (MS). All subsequent quantitative measurements were carried out on a separate HP 5890 GC equipped with a flame ionization detector (FID). Both systems were equipped with HP-1 crosslinked methyl silicone gum columns (12 m × 0.2 mm × 0.33 µm film thickness).

Catalytic properties of the molybdenum oxynitrides and oxycarbides were compared to those of analogously prepared nitrides and carbides, and commercial Ni-Mo/Al_2O_3 (Crosfield 504) and Co-Mo/Al_2O_3 (Crosfield 477) hydrotreatment catalysts. The commercial catalysts were sulfided in a mixture of 2% hydrogen sulfide in hydrogen at 400 °C for 4 hours. They were then cooled to room temperature in the hydrogen sulfide mixture and purged with helium.

RESULTS AND DISCUSSION

Catalyst Characterization

No peaks other than those associated with the support were observed in diffraction patterns for the nitrided and carburized materials indicating that the oxynitride and oxycarbide domains were small and/or lacked long range order. The Al_2O_3 support produced broad peaks that may have masked peaks which were due to other crystalline species. Diffraction patterns for the high loaded supported molybdenum oxide indicated the presence of crystalline MoO_3 (Figure 1). The absence of oxide peaks in the oxynitride and oxycarbide patterns suggested that the oxide was completely consumed during nitridation and carburization. Similar conclusions about the degree of nitridation and carburization can be drawn for the supported nitride and carbide catalysts. The expected oxynitride and oxycarbide phases have structures that are similar to those of γ-Mo_2N and β-Mo_2C, respectively. The results implied that nitridation and carburization caused a redispersion of the molybdenum.

Table 1 shows the compositions of the oxynitrides and oxycarbides as determined by NAA and CHN analysis. The molybdenum loadings were lower than those expected based on the precursor solution concentrations. Note that the Mo loading required to form a monolayer of the oxynitride or oxycarbide on the Al_2O_3 surface is >10%. Together with the x-ray diffraction results, the submonolayer Mo loadings suggested the presence of raft-like oxynitride and oxycarbide particles. This is consistent with our previous findings for Al_2O_3 supported Mo nitrides (Colling and Thompson, 1994). The measured loadings were appropriate for the experimental design. That is, materials with a range of loadings each separated by approximately a factor of two were produced. There was no evidence of Zn in the oxynitrides. Nitridation incorporated a significant amount of nitrogen suggesting that oxynitrides were formed even for the low loaded catalysts (no nitrogen or carbon was incorporated into the alumina during nitridation or carburization, respectively). The N/Mo ratios were intermediate to those of the β-$Mo_{16}N_7$ and δ-MoN phases, and were of a similar magnitude to those reported by Colling and Thompson (1994) for 'as-prepared' nitrides. A small amount of the ammonia appeared to have adsorbed on the catalyst as indicated by the hydrogen detected in the nitrided materials. The C/Mo ratios for the oxycarbides were less informative. The C/Mo ratios are considerably higher than the expected stoichiometric ratio. This excess carbon was likely graphitic. Unsupported carbides prepared under similar conditions had an average C/Mo ratio of 0.77, which is close to that expected for Mo_2C. Apparently, the presence of the Al_2O_3 support facilitated the deposition of excess carbon.

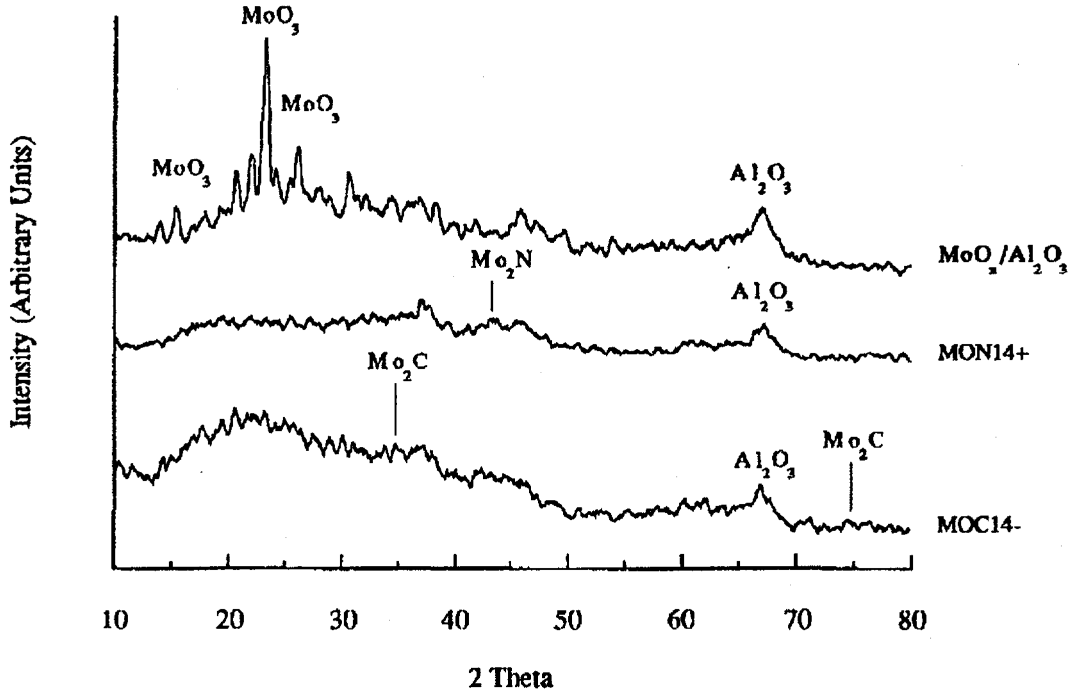

Figure 1. X-ray diffraction patterns for the γ-Al_2O_3 supported Mo oxide, oxynitride and oxycarbide with the highest Mo loadings.

Table 1. Compositions and Oxygen Uptakes of Oxynitrides and Oxycarbides

Catalyst Code	Mo Loading (wt %)	X/Mo*	O_2 Uptake (μmol O_2/g_{cat})	O/Mo
MON04-	1.1	0.74	<0.01	<0.0002
MON04+	1.1	0.81	<0.01	<0.0002
MON08-	2.2	0.42	0.52	0.005
MON08+	2.2	0.48	0.04	0.0003
MON14-	5.1	0.34	3.82	0.01
MON14+	4.5	0.34	6.04	0.03
MOC04-	2.9	22	6.38	0.04
MOC04+	3.2	16	4.58	0.03
MOC08-	5.3	16	0.16	0.001
MOC08+	5.4	10	0.11	0.0004
MOC14-	9.1	11	<0.01	<0.00002
MOC14+	9.4	7.1	<0.01	<0.00002

* For oxynitrides X=N. For oxycarbides X=C.

For unsupported molybdenum nitrides and carbides, the oxygen uptake scaled linearly with the surface area (Markel and Miyao, 1990; Lee et al., 1987). The average O/Mo stoichiometries were 0.21 ± 0.05 for the nitrides and 0.13 ± 0.03 for the carbides. Given this observation, we expected that oxygen chemisorption could be used to quantify the dispersion of the oxynitride and oxycarbide catalysts. Oxygen uptakes for the supported oxynitrides and oxycarbides are given in Table 1. Oxygen did not adsorb onto γ-Al_2O_3 under the chemisorption conditions employed. For the oxynitrides, the amount of adsorbed oxygen increased as the molybdenum loading increased. Uptakes for the low and high loaded materials differed by as much as two orders of magnitude. The oxycarbides, however, exhibited the opposite trend. The oxygen uptake decreased as the loading increased. The difference between the low and high loaded materials was again approximately two orders of magnitude. Oxygen in or on molybdenum nitrides and carbides is known to suppress the oxygen uptake, therefore we were not able to unambiguously determine dispersions for the oxynitrides and oxycarbides.

Table 2 lists the compositions of the supported nitrides and carbides. Molybdenum loadings for the nitrides were higher than those of the corresponding oxynitrides. Because the precursors were essentially the same, the results indicated that conditions used to synthesize the oxynitrides caused a loss of Mo compared to the nitride. We believe that conversion of the oxide to the bronze, an intermediate during formation of the oxynitrides, caused a significant loss of Mo. The N/Mo ratios for the nitrides were greater than those for the oxynitrides. This result is consistent with the oxynitrides being partially oxidized relative to the nitrides perhaps retaining oxygen from the precursor. Molybdenum loadings for the carbides were nearly identical to those of the oxycarbides. However, the C/Mo ratios for the carbides were higher than those for the oxycarbides indicating that partial oxidation removed carbon from the carbide. Because the C/Mo ratios were in excess of the stoichiometric values, much of the carbon that was removed was probably graphitic carbon at the surface.

Table 2. Compositions and Oxygen Uptakes of Nitrides and Carbides

Catalyst Code	Mo Loading (wt %)	X/Mo*	O_2 Uptake (μmol O_2/g_{cat})	O/Mo
MN04-	3.6	1.02	5.54	0.03
MN04+	3.8	1.01	4.66	0.02
MN08-	6.5	1.26	13.9	0.04
MN08+	6.5	0.75	8.37	0.02
MN14-	10.9	0.96	26.9	0.05
MN14+	11.2	0.79	33.2	0.06
MC04-	3.0	29	7.94	0.05
MC04+	2.9	23	8.5	0.06
MC08-	4.8	26	1.71	0.01
MC08+	4.9	24	2.46	0.01
MC14-	8.2	14	14.0	0.03
MC14+	8.6	14	14.1	0.03
Ni-Mo/Al_2O_3	13	---	94.2	0.14
Co-Mo/Al_2O_3	9	---	93.9	0.20

* For nitrides X=N. For carbides X=C.

The oxygen uptakes for the nitrides and carbides were substantially higher than those for the oxynitrides and oxycarbides. This result is consistent with the presence of oxygen causing a decrease in the O_2 uptake. The O/Mo ratios for the nitrides and carbides were relatively constant with loading indicating that the dispersions were not significantly influenced. Using O/Mo ratios for the unsupported materials as a basis, we estimated that the dispersions for the supported nitrides were ≈17% while those for the carbides were ≈24%.

Oxygen chemisorption is also useful for measuring the dispersion of supported and unsupported molybdenum sulfides (Concha and Bartholomew, 1983; Muralidhar et al., 1984). The Ni-Mo/Al_2O_3 and Co-Mo/Al_2O_3 sulfide catalysts adsorbed significantly more oxygen than the oxynitrides and oxycarbides. Based on O/Mo ratios reported in the literature for molybdenum sulfide catalysts (Concha and Bartholomew, 1983; Muralidhar et al., 1984; Brenner, 1994), it appeared that the promoted sulfides used in our study were more highly dispersed than the oxynitrides and oxycarbides.

Catalytic Activity and Selectivity

The supported molybdenum oxynitrides and oxycarbides were highly active for quinoline HDN, benzothiophene HDS, and benzofuran HDO. Their activities were reproducible to within approximately ±10%. Activities of the oxynitrides and oxycarbides were generally comparable or superior to that of the sulfided Ni-Mo/Al_2O_3 catalyst but lower than that of the Co-Mo/Al_2O_3 catalyst. Considering that the sulfides have been optimized for hydrotreatment, the performance of the oxynitrides and oxycarbide is encouraging. The following sections provide additional information concerning the activities of the oxynitrides and oxycarbides as well as comparisons between their properties and those of corresponding nitrides and carbides. Differences greater than the experimental error (typically 10%) were considered significant. In general, variations in the heating rates had little effect on the hydrotreatment activities of the oxynitrides and oxycarbides; however, changing the Mo loading resulted in very significant changes in the activity. Unless otherwise stated, comparisons are made between catalysts with similar loadings.

Quinoline HDN

The HDN reaction rates and activities of the supported oxynitrides and oxycarbides are compared in Table 3. For similar loadings the oxycarbides were more active than the oxynitrides. For both classes of catalyst the activity on an Mo basis decreased with increasing Mo loading (Figure 2). The decrease was dramatic and suggested either a decrease in site density or a change in the character of the active sites.

Product distributions for the oxynitrides and oxycarbides were not significantly affected by their Mo loadings or heating rates. Products for quinoline HDN included substituted benzenes, cyclohexenes, and cyclohexanes (Figure 3), as well as 1,2,3,4-tetrahydroquinoline, propylaniline, and aniline. These products are typical for quinoline HDN over molybdenum nitrides and carbides (Ramanathan et al., 1994; Lee et al., 1993). Unsaturated products (benzenes and cyclohexenes) are more desirable than the saturated products (cyclohexanes). In this respect the oxynitrides were more selective than the oxycarbides..

The oxynitrides had similar activities to their corresponding nitrides; however, the oxycarbides were more active than the carbides. This latter observation may be due to the exposure of additional active sites that were blocked by surface carbon. Catalytic properties of the nitrides and carbides are given in table 4. Like the oxynitrides and oxycarbides, activities of the nitrides and carbides decreased with increasing loading. All of the materials were less active than the supported Co-Mo/Al_2O_3 sulfide catalyst but several of the oxynitride and oxycarbide catalysts were more active than the Ni-Mo/Al_2O_3 catalyst. Our observation that the supported Ni-Mo/Al_2O_3 sulfide catalyst was less active than the Co-Mo catalyst for HDN was unexpected (Choi et al., 1992; Satterfield, 1991; Katzer and Sivasubramanian, 1979). Typically Ni-Mo/Al_2O_3 catalysts are preferred over Co-Mo/Al_2O_3 catalysts for HDN reactions (Shabtai et al., 1987). This discrepancy may be partially due to the absence of a pretreatment step (other than presulfidation) prior to the reaction. Furthermore, it is likely that the two commercial catalysts were optimized for different reactant feed streams.

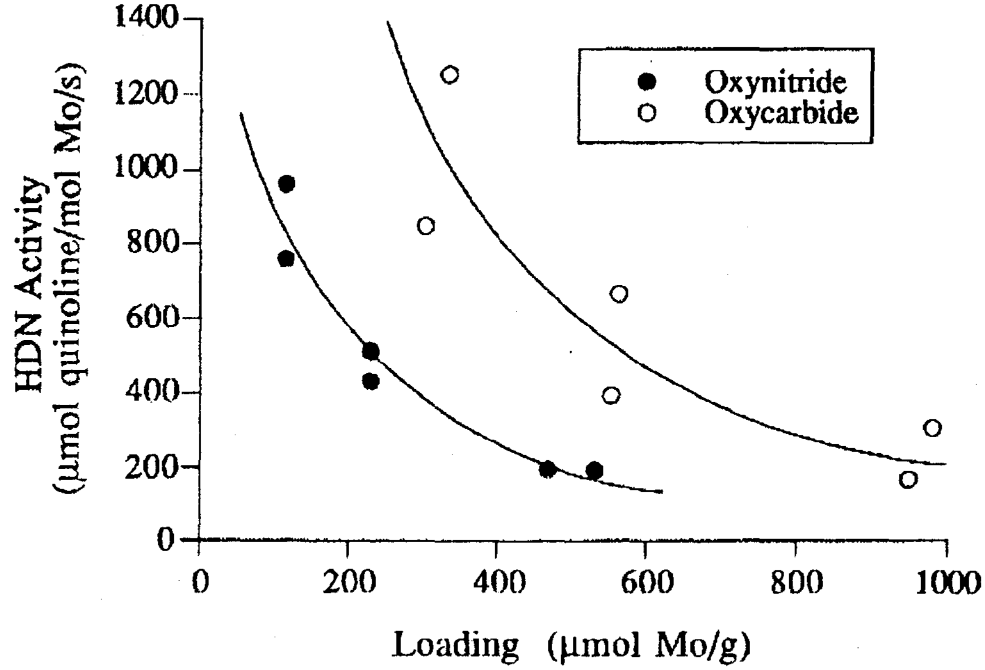

Figure 2. Effect of the Mo loading on the quinoline HDN activities.

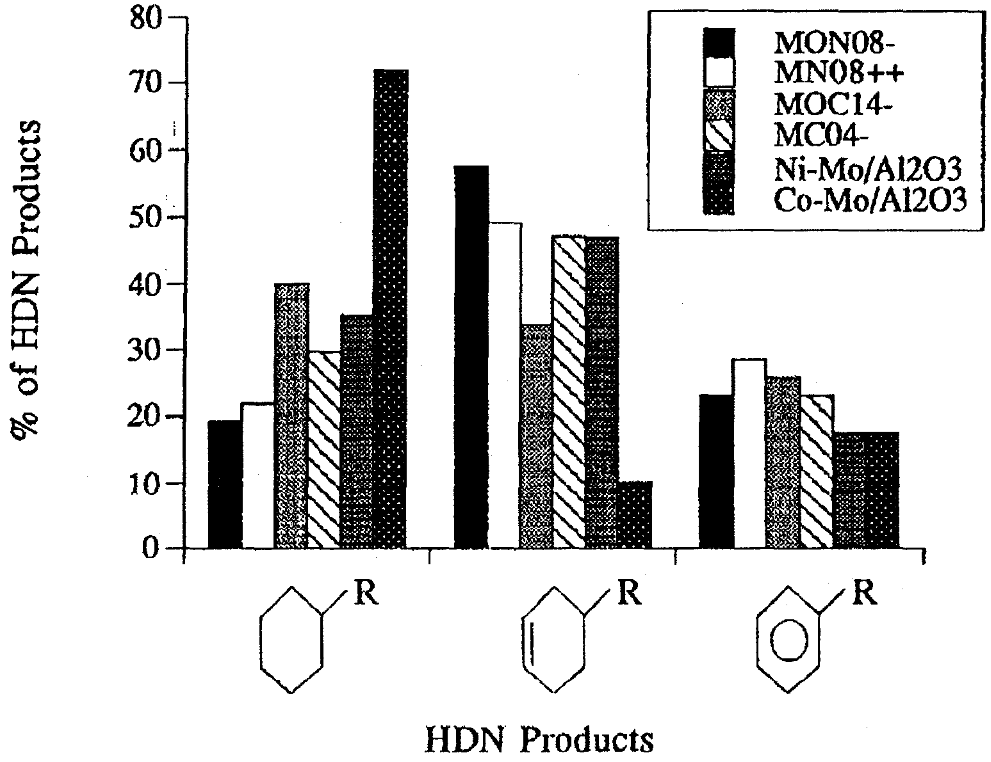

Figure 3. Comparison of the product distributions for quinoline HDN.

Table 3. Quinoline Hydrodenitrogenation Over Oxynitrides and Oxycarbides

Catalyst Code	Loading (wt% Mo)	Reaction Rate ($nmol/g_{cat}/s$)	Activity ($\mu mol/mol_{Mo}/s$)
MON04-	1.1	110	959
MON04+	1.1	87	755
MON08-	2.2	116	510
MON08+	2.2	96	429
MON14-	5.1	89	191
MON14+	4.5	104	194
MOC04-	2.9	251	845
MOC04+	3.2	425	1,253
MOC08-	5.3	217	392
MOC08+	5.4	374	663
MOC14-	9.1	161	170
MOC14+	9.4	301	306

The HDN activities decreased in the following order: Co-Mo≈MOC04>MON04>MOC08>MC04>MN04≈MOC14>Ni-Mo. For materials with similar loadings the ranking was as follows: Co-Mo>Ni-Mo-S≈MOC14>MC14>MN14. Quinoline HDN selectivities of the catalysts were similar, accept for the Co-Mo/Al_2O_3 catalyst which had a high selectivity to cyclohexanes, a less desirable product. Differences in the product distributions were not a consequence of differing conversion levels and suggested an intrinsic selectivity advantage for the oxynitrides and oxycarbides over the sulfides. The differences in the product distributions also suggested differences in reaction pathways. Reaction pathways for the oxynitrides and oxycarbides appeared to be more selective towards C-N hydrogenolysis than those of the sulfide catalysts.

Table 4. Quinoline Hydrodenitrogenation Over Nitrides and Carbides

Catalyst Code	Loading (wt% Mo)	Reaction Rate ($nmol/g_{cat}/s$)	Activity ($\mu mol/mol_{Mo}/s$)
MN04-	3.6	84	223
MN04+	3.8	124	310
MN08-	6.5	100	148
MN08+	6.5	121	177
MN14-	10.9	140	123
MN14+	11.2	110	94
MC04-	3.0	135	435
MC04+	2.9	141	464
MC08-	4.8	49	97
MC08+	4.9	58	113
MC14-	8.2	107	126
MC14+	8.6	104	116
Ni-Mo/Al_2O_3	13	332	252
Co-Mo/Al_2O_3	9	1,260	1,300

Benzothiophene HDS

The HDS reaction rates and activities of the supported oxynitrides and oxycarbides are compared in Table 5. In general, these materials were more active for benzothiophene HDS than quinoline HDN. For similar loadings the oxynitrides were more active than the oxycarbides. The HDS activities for both classes of material decreased with increasing loading while the heating rates had little affect on the catalyst performance. The primary reaction product for all the catalysts tested was ethylbenzene. Very small amounts of cyclohexanes were produced and only trace amounts of cyclohexenes were observed.

Table 5. Benzothiophene Hydrodesulfurization Over Oxynitrides and Oxycarbides

Catalyst Code	Loading (wt% Mo)	Reaction Rate (nmol/g_{cat}/s)	Activity (μmol/mol_{Mo}/s)
MON04-	1.1	571	4,982
MON04+	1.1	599	5,220
MON08-	2.2	1,060	4,659
MON08+	2.2	717	3,201
MON14-	5.1	1,210	2,591
MON14+	4.5	1,260	2,347
MOC04-	2.9	937	3,154
MOC04+	3.2	1,071	3,161
MOC08-	5.3	799	1,444
MOC08+	5.4	932	1,650
MOC14-	9.1	1,018	1,074
MOC14+	9.4	1,334	1358

As we found for quinoline HDN, the benzothiophene HDS activities of the oxynitride and nitride catalysts were similar and those of the oxycarbides were superior to those of the carbides (see Table 6). The oxynitride, oxycarbide, nitride and carbide catalysts were less active than the Co-Mo/Al_2O_3 and Ni-Mo/Al_2O_3 sulfide catalysts. The activities on an Mo loading basis decreased in the following order: Co-Mo>Ni-Mo>MON04>MON08>MOC04>MN04. The oxynitrides and oxycarbides with the highest loadings were as much as an order of magnitude less active than the commercial sulfided catalysts on an Mo loading basis. Product distributions for the oxynitride and oxycarbide catalysts were insignificantly different from those of the commercial sulfide and the nitride and carbide catalysts.

Table 6. Benzothiophene Hydrodesulfurization Over Nitrides and Carbides

Catalyst Code	Loading (wt% Mo)	Reaction Rate ($nmol/g_{cat}/s$)	Activity ($\mu mol/mol_{Mo}/s$)
MN04-	3.6	1,060	2,820
MN04+	3.8	1,180	2,970
MN08-	6.5	1,620	2,390
MN08+	6.5	1,670	2,450
MN14-	10.9	2,080	1,830
MN14+	11.2	2,080	1,790
MC04-	3.0	570	1,830
MC04+	2.9	1,010	3,320
MC08-	4.8	429	850
MC08+	4.9	681	1,340
MC14-	8.2	892	1,050
MC14+	8.6	759	844
Ni-Mo/Al_2O_3	13	8,960	6,790
Co-Mo/Al_2O_3	9	10,130	10,420

Benzofuran HDO

The activity and selectivity patterns exhibited during benzofuran HDO were different from those observed during quinoline HDN and benzothiophene HDS. The HDO reaction rates and activities of the supported oxynitrides and oxycarbides are compared in Table 7. Activities for benzofuran HDO were less than those for quinoline HDN or benzothiophene HDS. The oxycarbides were more active than the oxynitrides. Unlike their performance in HDN and HDS, the Mo loading only had a small affect on the HDO activity while the heating rates had marked effects on the catalytic performance, in particular for the oxycarbides. Oxycarbides prepared using the lower heating rate were less active than those prepared using the higher heating rate. The difference in activity widened somewhat as the loading was increased. These observations suggest that the active sites for quinoline HDN and benzothiophene HDS are different from those for benzofuran HDO.

Product distributions for the oxynitrides and oxycarbides were very different; however, they were not significantly affected by Mo loading or heating rate (figure 4). The oxynitrides produced mostly substituted benzenes while the oxycarbides produced almost equal amounts of cyclohexanes, cyclohexenes and benzenes. These differences were not due to differences in their overall conversions and indicated a subtle difference between reaction pathways for the oxynitrides and oxycarbides.

The oxynitrides were less active than the nitrides while the oxycarbides were more active than the carbides. Again this general trend is different from that observed for quinoline HDN and benzothiophene HDS over these catalysts. All of the materials were less active than the supported Co-Mo sulfide catalyst but several of the oxycarbide catalysts were more active than the Ni-Mo/Al_2O_3 catalyst (Table 8). The activities decreased in the following order: Co-Mo>MOC08+>MOC04->MOC14+>Ni-Mo.

Product distributions for the oxynitrides were similar to those for the nitride and Co-Mo sulfide catalyst. Distributions for the oxycarbides were similar to those for the carbide and Ni-Mo catalyst accept for the production of cyclohexanes.

Table 7. Benzofuran Hydrodeoxygenation Over Oxynitrides and Oxycarbides

Catalyst Code	Loading (wt% Mo)	Reaction Rate (nmol/g_{cat}/s)	Activity (µmol/mol_{Mo}/s)
MON04-	1.1	7.6	66.0
MON04+	1.1	7.5	65.8
MON08-	2.2	25	110
MON08+	2.2	16.6	74.0
MON14-	5.1	81.9	153
MON14+	4.5	29.6	63.5
MOC04-	2.9	320	1,076
MOC04+	3.2	606	1,789
MOC08-	5.3	476	860
MOC08+	5.4	1,093	1,935
MOC14-	9.1	249	263
MOC14+	9.4	1,713	1,745

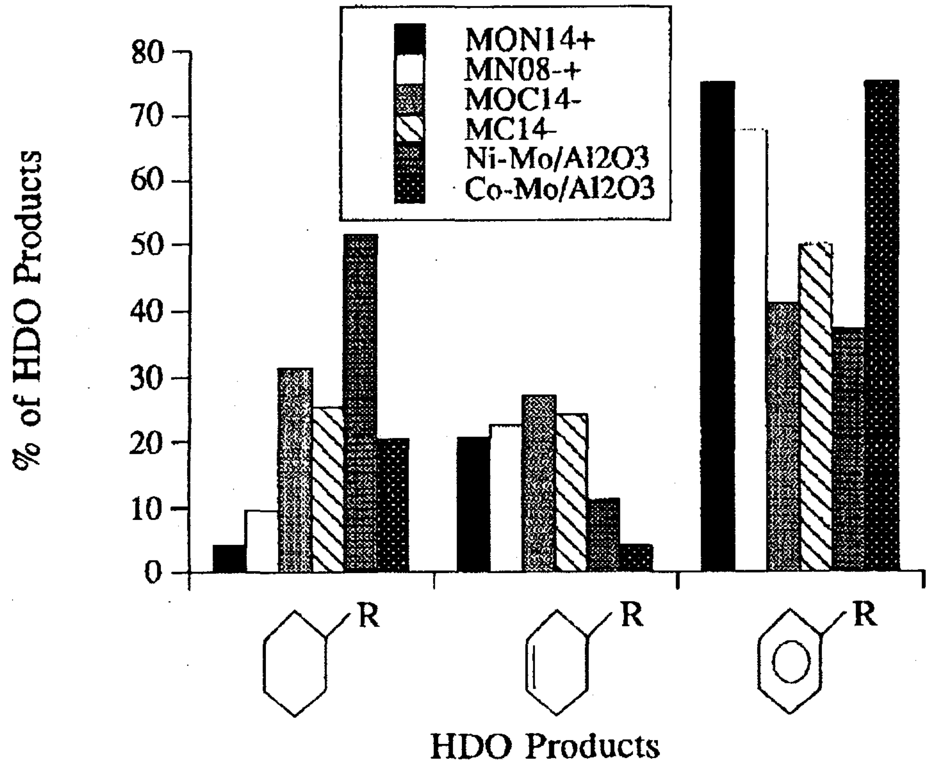

Figure 4. Comparison of the product distributions for benzofuran HDO.

Table 8. Benzofuran Hydrodeoxygenation Over Nitrides and Carbides

Catalyst Code	Loading (wt% Mo)	Reaction Rate (nmol/g_{cat}/s)	Activity (μmol/mol_{Mo}/s)
MN04-	3.6	80	214
MN04+	3.8	68	170
MN08-	6.5	206	304
MN08+	6.5	160	234
MN14-	10.9	260	229
MN14+	11.2	398	342
MC04-	3.0	91	293
MC04+	2.9	152	498
MC08-	4.8	49	97
MC08+	4.9	44	87
MC14-	8.2	349	409
MC14+	8.6	507	564
Ni-Mo/Al_2O_3	13	2,270	1,720
Co-Mo/Al_2O_3	9	5,130	5,280

Methylcarbazole HDN, Diobenzothiophene HDS and Dibenzofuran HDO

The oxycarbides were generally more active than the oxynitrides. Three of the oxycarbide catalysts were tested for 9-methyl carbazole HDN, dibenzothiophene HDS, and dibenzofuran HDO. These molecules are among the most difficult to hydrotreat (Girgis and Gates, 1991). Reaction rates for the oxycarbides are compared to those of nitride, carbide and sulfide catalysts in Table 9. These initial experiments demonstrate that the oxycarbides were quite active for hydrotreating multiple-ring heteroatom compounds. In some cases, the oxycarbides were considerably more active than the commercial sulfide catalysts.

Table 9. Hydrotreatment Reaction Rates of Selected Catalysts

Catalyst Code	Methyl Carbazole HDN (μmol/mol_{Mo}/s)	Dibenzothiophene HDS (μmol/mol_{Mo}/s)	Dibenzofuran HDO (μmol/mol_{Mo}/s)
MOC04-	474	4,362	45
MOC04+	362	2,812	866
MOC08+	403	2,795	1,766
MN04+	30	4,649	116
MC04+	170	4,783	758
Ni-Mo/Al_2O_3	356	3,372	1,300
Co-Mo/Al_2O_3	679	4,710	3,950

Measured at 390 °C and ~2000 psi.

Figure 5 shows the product distributions for 9-methylcarbazole HDN. The oxynitrides and oxycarbides were competitive with and in some cases superior to the sulfide catalysts in terms of hydrogen efficiency. All of the catalysts formed significant amounts of bicyclic compounds, indicating a low selectivity towards C-C bond cleavage. The product distributions for dibenzothiophene HDS are shown in Figure 6. The oxycarbides, which were highly active, also appeared to be the most hydrogen efficient. Almost all of the HDS products were bicyclic compounds and benzenes over this catalyst. The sulfide catalysts exhibited higher selectivities towards hydrogenation and C-C hydrogenolysis than the oxycarbides, indicating that the oxycarbides were more hydrogen efficient than the sulfide catalysts. Figure 7 shows the dibenzofuran HDO product distributions. For this reaction, all of the catalysts had high C-C hydrogenolysis activities, but the sulfide catalysts also exhibited high hydrogenation selectivities. The oxycarbide formed less cyclohexanes, and more benzenes and cyclohexenes, indicating a more efficient use of hydrogen.

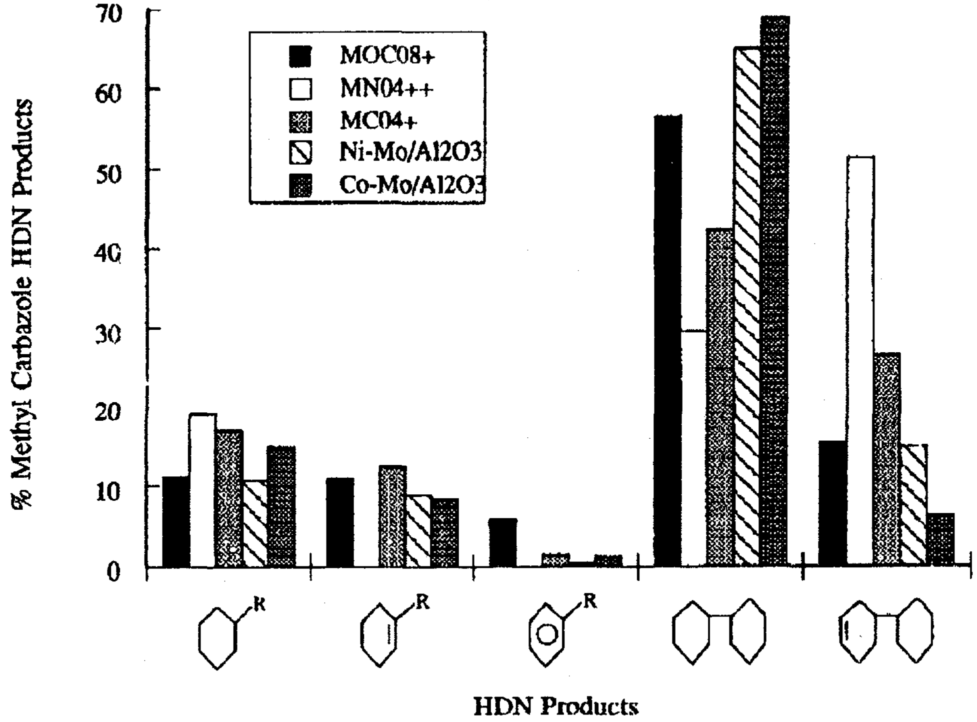

Figure 5. Comparison of the product distributions for 9-methylcarbazole HDN.

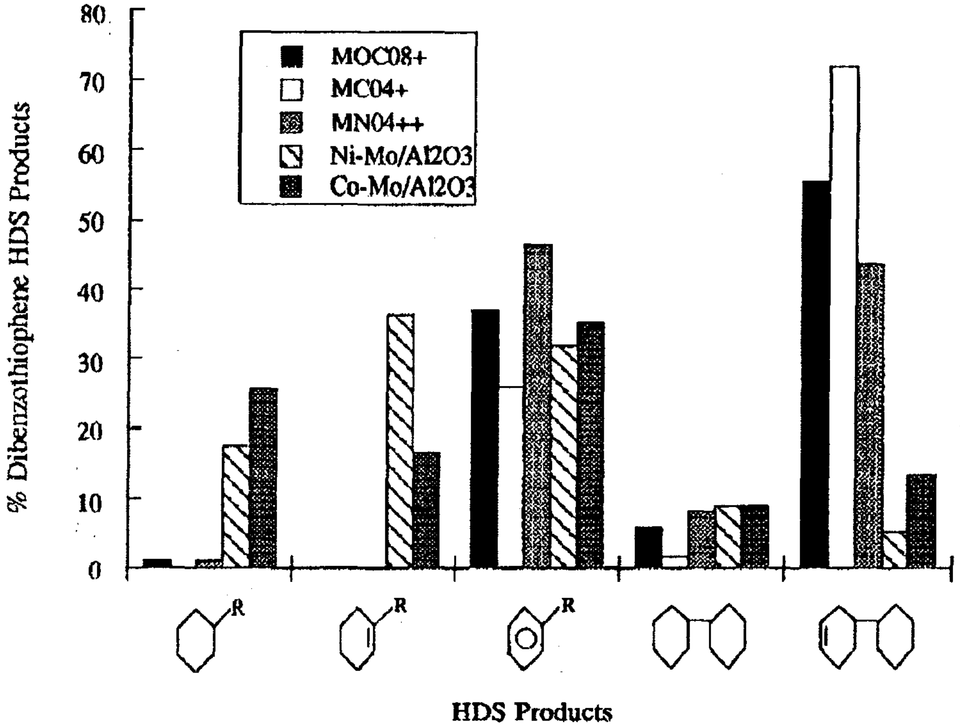

Figure 6. Comparison of the product distributions for dibenzothiophene HDS.

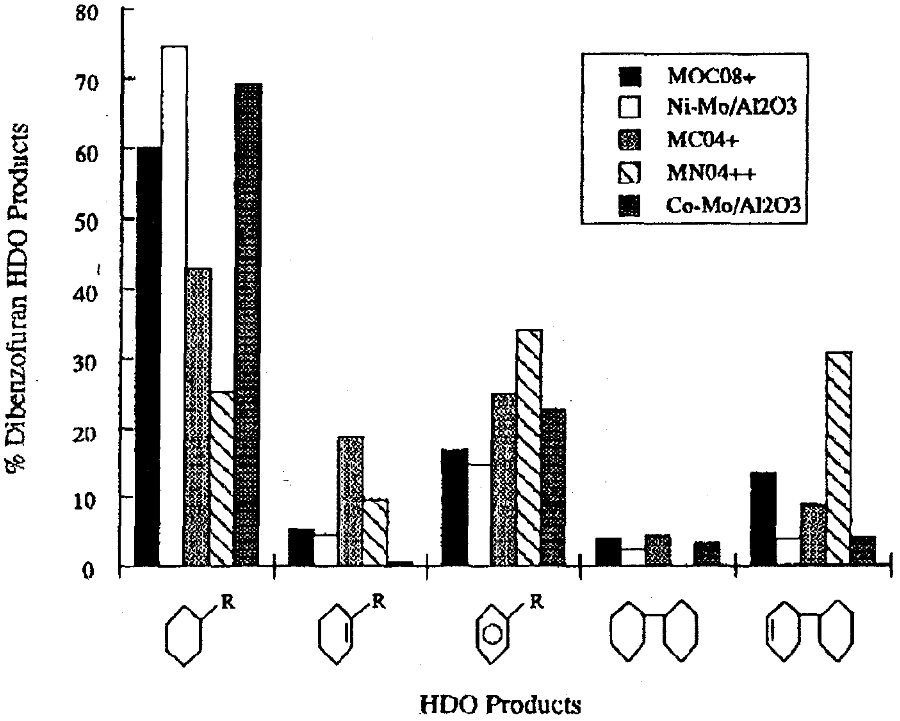

Figure 7. Comparison of the product distributions for dibenzofuran HDO.

SUMMARY

Series of γ-Al$_2$O$_3$-supported molybdenum oxynitrides and oxycarbides were synthesized via the temperature programmed reaction of supported molybdenum oxides or hydrogen bronzes. The nitridation or carburization heating rates were varied in an attempt to vary properties of the oxynitrides and oxycarbides. The molybdenum loadings ranged from 1-10 wt%. These were somewhat lower than those expected based on the solution concentrations used during the incipient wetness preparations, in particular for the Mo oxynitrides. The relatively low loadings for the oxynitrides have been attributed to a loss of molybdenum during conversion of the supported oxide to the bronze. Like nitrogen and carbon, oxygen is small enough to fit into the octahedral interstitial sites in the molybdenum nitride and carbide lattice. Therefore we expected structures for the Mo oxynitrides and carbides to be similar to those of γ-Mo$_2$N and β-Mo$_2$C, respectively. Unfortunately, the oxynitrides and oxycarbides were x-ray amorphous and no conclusions can be drawn with respect to their microstructures. Nitridation and carburization incorporated a significant amount of nitrogen and carbon into the materials. The amounts were consistent with the formation of oxynitrides and oxycarbides. A substantial amount of excess carbon was present in the oxycarbide, probably due to the deposition of graphitic carbon at the surface. In all cases the N/Mo and C/Mo ratios for the oxynitrides and oxycarbides were lower than those for their corresponding nitrides and carbides. This result is consistent with the oxynitrides and oxycarbides being partially oxidized compared to their parent materials. The suppressed oxygen chemisorption capacities for the oxynitrides and oxycarbides compared to their corresponding nitrides and carbides can also be accounted for if we conclude that oxygen was present in the lattice.

The quinoline HDN, benzothiophene HDS, and benzofuran HDO activities and selectivities of the supported oxynitrides and oxycarbides were compared to those of supported nitrides and carbides and commercial Ni-Mo/Al$_2$O$_3$ and Co-Mo/Al$_2$O$_3$ sulfide catalysts. The HDN and HDS activities for the oxynitrides and oxycarbides decreased with increasing loading but were not significantly affected by varying the heating rate. In contrast, the HDO activities were relatively constant with Mo loading but varied with heating rate. This suggests that the active sites for HDN and HDS were similar but different from those for HDO. In general, the oxycarbides were more active than the oxynitrides. The activities on a Mo basis decreased as follows:

HDN	Co-Mo≈MOC04>MON04>MOC08>MC04>MN04≈MOC14>Ni-Mo/Al$_2$O$_3$
HDS	Co-Mo>Ni-Mo>MON04>MON08>MOC04>MN04
HDO	Co-Mo>MOC08+>MOC04->MOC14+>Ni-Mo

Note that for quinoline HDN and benzofuran HDO, several of the oxynitride and oxycarbide catalysts were more active than the commercial Ni-Mo/Al$_2$O$_3$ sulfide catalyst. Product distributions for the Mo oxynitride and oxycarbide catalysts were typically better than those for the sulfide catalysts. That is, the oxynitrides and oxycarbides were more selective for C-X (X=N, S or O) hydrogenolysis, the desired reaction, than C=C hydrogenation and C-C hydrogenolysis.

Several of the oxycarbides were tested for the hydrotreatment of 9-methyl carbazole, dibenzothiophene and dibenzofuran. These materials were competitively active and in most cases were superior to the Ni-Mo/Al$_2$O$_3$ catalyst. The activities on a Mo basis decreased as follows:

HDN	Co-Mo>MOC04-≈MOC08+>MOC04+≈Ni-Mo
HDS	MC04+≈Co-Mo≈MOC04+>MOC04->Ni-Mo
HDO	Co-Mo>MOC08+>Ni-Mo

Again selectivities for the oxycarbides, carbides and nitrides were better than those for the sulfides suggesting that these materials will make more efficient use of process hydrogen than presently available Co-Mo/Al_2O_3 and Ni-Mo/Al_2O_3 sulfide catalysts.

Considering that we made no attempt to optimize the oxynitride and oxycarbide catalysts, results described in this report are encouraging and suggest that with further development their performance will substantially exceed those of presently available hydrotreatment catalysts. Possible approaches to enhancing the properties of Mo oxynitrides and oxycarbides include adding promoters and/or varying the support type. One might not only anticipate a highly active catalyst but also a very selective catalyst. As hydrogen economy is an important issue in petroleum refining, the superior selectivities associated with the oxynitrides and oxycarbides compared to sulfides represent a significant competitive advantage.

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Hazardous Waste Report

Approximately 10 grams of each of the following chemicals were used throughout the course of the project:

Quinoline
Benzothiophene
Benzofuran
9-Methyl Carbazole
Dibenzofuran
Dibenzothiophene

In addition, approximately 1.2 L of hexadecane was used as a solvent. Only about 10% of each chemical was collected as hazardous waste. The remainder was retained for experimental purposes.

Also, material preparation and synthesis resulted in minute amounts of solid waste in the form of:

Alumina
Molybdenum Trioxide/Al_2O_3
Molybdenum Nitride/Al_2O_3
Molybdenum Carbide/Al_2O_3

The small amount of solid waste was collected and retained for proper disposal.

All of the chemical listed above were used in bench-scale laboratory experiments. The work was performed in the H.H. Dow Building at the University of Michigan. Details of the University's waste management procedures are on record. Further information can be found at:

Occupational Safety and Environmental Health
1101 North University Building
The University of Michigan
Ann Arbor, MI 48109-1057
313-764-8310

The waste was collected, labeled, and disposed of according to OSEH rules and regulations. The waste was picked up by OSEH and disposed of via an outside licensed contractor.