Thiophene hydrodesulfurization over bimetallic and promoted nitride catalysts

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Alumina-supported bimetallic (Co_3Mo_3N/Al_2O_3) and promoted ($Co–Mo_2N/Al_2O_3$) nitride catalysts have been prepared and characterized. Thiophene hydrodesulfurization (HDS) measurements show that the Co_3Mo_3N/Al_2O_3 and $Co–Mo_2N/Al_2O_3$ catalysts are significantly more active than a Mo_2N/Al_2O_3 catalyst with the same Mo loading. Furthermore, the $Co–Mo_2N/Al_2O_3$ catalyst has a substantially higher HDS activity than a sulfided $Co–MoO_3/Al_2O_3$ catalyst with an identical metal loading.

Keywords: thiophene, hydrodesulfurization, nitrides

1. Introduction

In order to meet ambitious goals for reductions in sulfur emissions in the United States, western Europe and Japan [1,2], considerable research is being focused on the development of more active hydrodesulfurization (HDS) catalysts. Early transition metal carbide and nitride catalysts show strong potential for higher HDS activity than the sulfide catalysts currently used in the industrial hydrodesulfurization process [3,4]. The HDS properties of alumina-supported Mo carbide [5–7] and nitride [6–9] catalysts have recently been investigated and these materials have been found to have significantly higher HDS activities than conventional sulfide catalysts.

Studies in our laboratory indicate that a thin layer of sulfided Mo is formed on the surfaces of alumina-supported β-Mo_2C and γ-Mo_2N particles under HDS conditions [6,7]. Based upon chemisorption measurements, we have shown that this Mo carbide (and nitride) supported layer of sulfided Mo adsorbs substantially more CO (and O_2) than sulfided Mo/Al_2O_3 catalysts with the same Mo loading. The higher thiophene HDS activities for Mo_2C/Al_2O_3 and Mo_2N/Al_2O_3 catalysts, when compared to sulfided MoO_3/Al_2O_3 catalysts, can be traced to a higher density of active sites rather than to different, more active sites.

Given that the active sites for thiophene HDS are similar on Mo_2C/Al_2O_3, Mo_2N/Al_2O_3 and sulfided MoO_3/Al_2O_3 catalysts, we are exploring whether the activity of these catalysts can be enhanced by addition of cobalt, as is observed with conventional sulfide-based catalysts. In this letter, we describe the successful preparation of alumina-supported cobalt molybdenum nitride (Co_3Mo_3N/Al_2O_3) and cobalt-promoted molybdenum nitride ($Co–Mo_2N/Al_2O_3$) catalysts, and we compare their thiophene HDS activities to those of conventional sulfide catalysts.

2. Experimental

2.1. Catalyst preparation

Alumina-supported molybdenum trioxide (MoO_3/Al_2O_3) precursors with theoretical loadings of 13.8 and 22.8 wt% MoO_3 were prepared by impregnation of γ-Al_2O_3 (Engelhard AL-3945) with aqueous solutions of ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, J.T. Baker, 99.9%), followed by drying for 24 h at 393 K, and calcination for 3 h at 773 K in air. Alumina-supported cobalt molybdate ($CoMoO_4/Al_2O_3$) precursors were prepared similarly, except that the alumina support was coimpregnated with aqueous solutions of ammonium heptamolybdate and cobalt nitrate ($Co(NO_3)_2\cdot 6H_2O$, J.T. Baker, 99.9%) prior to drying and calcination. $CoMoO_4/Al_2O_3$ precursors with theoretical loadings of 6.7 wt% CoO–12.8 wt% MoO_3 and 10.6 wt% CoO–20.4 wt% MoO_3 were prepared. A cobalt-promoted MoO_3/Al_2O_3 precursor was also prepared in which a sample of MoO_3/Al_2O_3 was impregnated with an aqueous solution of cobalt nitrate followed by vacuum desiccation. Although not calcined following addition of the cobalt nitrate solution, the theoretical loading of this $Co–MoO_3/Al_2O_3$ precursor corresponded to 6.7 wt% CoO–12.8 wt% MoO_3. The γ-Al_2O_3 used to prepare the catalysts in this study had a BET surface area of 255 m^2/g and a pore volume of 0.60 ml/g.

The synthesis procedure for converting the alumina-supported oxide precursors to nitrides has been described in detail elsewhere [6]. The catalyst synthesis apparatus consisted of an atmospheric pressure flow system outfitted with a quartz U-tube type reactor (15 mm OD), stainless steel

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gas manifold, mass flow controllers (MKS Instruments) and a furnace, composed of a ceramic fiber heater (Watlow) and a temperature controller (Watlow). A typical synthesis employed 1.0 g of an alumina-supported oxide precursor on a plug of quartz wool; the oxide precursor was outgassed for 1 h at 673 K in a 30 sccm/min flow of He (Airco, 99.999%) prior to switching to a 60 sccm/min flow of anhydrous ammonia (Airco, 99.99%). Temperature-programmed reduction (TPR) of the oxide precursor was carried out from 673 to 970 K at a heating rate of 30 K/h. The nitrided catalysts were then cooled to room temperature in a 30 sccm/min flow of He and passivated in a 30 sccm/min flow of 1% O_2/He mixture (Airco) at room temperature for 3 h prior to removal of the catalyst from the flow system. The He was purified prior to use by passing through 5A molecular sieve (Alltech) and O_2 purification traps. Sulfided catalysts were synthesized *in situ*. Following outgassing in a 30 sccm/min flow of He at 673 K, oxide precursors or nitride catalysts were sulfided in a 60 sccm/min flow of a 3.03% H_2S/H_2 mixture (Airco) at 623 K for 2 h.

Cobalt-promoted Mo_2N/Al_2O_3 catalysts were prepared in the following manner. After synthesis and passivation of a Mo_2N/Al_2O_3 catalyst as described above, the catalyst was impregnated with an aqueous solution of cobalt nitrate. The catalysts were subsequently dried at room temperature by vacuum desiccation. The theoretical loadings of these catalysts corresponded to 6.7 wt% CoO–12.8 wt% MoO_3 and 10.6 wt% CoO–20.4 wt% MoO_3.

The metal loadings of all catalysts prepared in this study correspond to a cobalt/molybdenum mole ratio equal to one ($Co/Mo = 1$). The Co/Mo ratio is fixed at one by the stoichiometry of cobalt molybdate for catalysts originating from $CoMoO_4/Al_2O_3$ precursors and this same ratio was used for the catalysts derived from other precursors to permit direct comparisons to be made between the HDS properties of all of the catalysts. As described above, catalysts with two different metal loadings were prepared. The lower metal loading (6.7 wt% CoO–12.8 wt% MoO_3) was chosen since it is similar to that employed in commercial HDS catalysts [1], although the Co/Mo ratio is higher than the optimal value of $Co/Mo = 0.3$–0.5. The higher metal loading (10.6 wt% CoO–20.4 wt% MoO_3) was chosen because it yielded catalysts with crystalline Co and/or Mo phases, which could be monitored by X-ray diffraction.

2.2. X-ray diffraction measurements

X-ray diffraction (XRD) patterns were acquired for oxidic precursors as well as nitrided, sulfided and tested catalysts using the packed powder method. Samples of nitrided, sulfided and tested catalysts were passivated, as described in section 2.1, prior to transferring to the X-ray diffractometer. Diffraction patterns were acquired using a Rigaku Geigerflex diffractometer employing Cu Kα radiation ($\lambda = 1.5418$ Å) and are reproduced here without any background or smoothing treatment. The XRD pattern of unsupported Co_3Mo_3N was simulated with POWDER CELL 1.8d [10] using atomic coordinates and lattice parameters determined by zur Loye and coworkers [11,12] for a pure sample of Co_3Mo_3N.

2.3. BET and pulsed chemisorption measurements

BET surface area and pulsed chemisorption (CO and O_2) measurements were carried out using a Micromeritics Pulse Chemisorb 2700 apparatus. For both types of measurements, catalyst samples ($\sim$0.10 g) were placed in a quartz U-tube (15 mm OD), where they were degassed in flowing He (45 sccm/min) at 673 K for 2 h. Nitrided catalysts were then activated by heating to 750 K for 2 h in a 60 sccm/min flow of H_2. Sulfided catalysts were prepared as described above and subsequently reduced at 623 K in a 60 sccm/min flow of H_2 for 1 h. Prior to the BET and chemisorption measurements, catalyst samples were subjected to a final outgassing treatment in which they were heated to 673 K in flowing He (45 sccm/min) for 1 h. The He and H_2 used in the chemisorption system were passed through 5A molecular sieve and O_2 purification traps prior to use.

Single-point BET surface area measurements were carried out using a 28.6% N_2/He mixture (Airco). The instrument was calibrated prior to the BET measurements using pure N_2 gas.

Chemisorption capacities were measured by injecting a calibrated sample loop (0.101 ml) of gas, CO (Airco, 99.99%) or O_2 (Airco, 10.3% in He), at 1 min intervals into an He flow (45 sccm/min for CO, 15 sccm/min for O_2) passing over the catalyst until gas uptake ceased. Prior to injection, the CO was passed through a coil of $1/8''$ stainless steel tubing submerged in a pentane slush to remove metal carbonyl impurities. Carbon monoxide and O_2 chemisorption studies were performed at 273 and 196 K, respectively. Fresh catalyst samples were prepared for each chemisorption measurement.

2.4. Thiophene HDS activity measurements

Thiophene HDS activity measurements were carried out using an atmospheric pressure flow reactor outfitted with a gas chromatograph (HP 5890 Series II) equipped with a flame ionization detector for on-line analysis of thiophene and hydrocarbon products. The major HDS products (butadiene, 1-butene, *cis*-2-butene, *trans*-2-butene, and butane) and unreacted thiophene were separated using a 30 m GS-Alumina column (J & W Scientific). The detector response for the C_4 hydrocarbon products was calibrated with analytical gas standards (Scott) in order to facilitate conversion calculations.

The flow reactor system has been described in detail elsewhere [6]. Catalyst samples ($\sim$0.10 g) were supported on a quartz wool plug in a quartz U-tube reactor (15 mm OD) in a 50 sccm/min flow of a 1.8 mol% thiophene/H_2 mixture prepared by means of a two-stage thiophene bubbler apparatus. The thiophene used in this study (Aldrich Chemical Co., 99+%) was purified according to the procedure of Spies and Angelici [13] prior to use in order to remove thiol impurities. The reaction temperature was maintained using a ceramic-fiber furnace (Watlow) outfitted with a programmable temperature controller (Omega). Nitrided catalyst samples were degassed in a 30 sccm/min flow of He at 673 K for 1 h, activated in a 60 sccm/min flow of H_2 at 750 K for 2 h, and then cooled to the desired reaction temperature prior to switching to the thiophene/H_2 flow. Sulfided catalysts were prepared as described above, outgassed in flowing He (30 sccm/min) at the desired reaction temperature for 30 min and the flow then switched to the thiophene/H_2 mixture. Thiophene HDS conversion data were collected at 1 h intervals over 24 h at a reaction temperature of 693 K. Steady-state conversion was achieved after $\sim$12–16 h; catalyst activities reported here are the values after 24 h on stream.

3. Results and discussion

3.1. Catalyst synthesis and characterization

A number of studies have recently appeared in the literature which report the successful synthesis of unsupported Co_3Mo_3N [11,12,14,15] as well as a bimetallic oxynitride phase with the composition $Co_{1.0}Mo_{1.0}O_{1.6}N_{0.79}$ [16]. In addition, two other studies have reported synthesis of an unsupported $Co_2Mo_3N_x$ phase [17] and a nitrided Co–Mo/Al_2O_3 catalyst prepared from a 3 wt% CoO–12 wt% MoO_3/Al_2O_3 precursor [18]. No XRD features, other than those of the γ-Al_2O_3 support, were observed by Park et al. [18] for their nitrided Co–Mo/Al_2O_3 catalyst.

The synthesis procedure employed to prepare our nitrided Co–Mo/Al_2O_3 catalysts is similar to those described by others for preparation of unsupported Co_3Mo_3N, in that it uses a cobalt molybdenum oxide precursor. Shown in figure 1 are XRD patterns for the γ-Al_2O_3 support and the oxidic precursor; the theoretical loading of the latter corresponds to 10.6 wt% CoO–20.4 wt% MoO_3. The XRD pattern for the alumina-supported oxidic precursor (labeled β-$CoMoO_4$/Al_2O_3) shows numerous peaks in addition to those of the alumina support. Comparison of this XRD pattern with those taken from the JCPDS powder diffraction file reveals that the additional peaks match very well in both position and intensity with those of β-$CoMoO_4$ (card no. 21-868) [19]. Nitridation of the alumina-supported cobalt molybdate produced a supported Co–Mo–N phase with a well-defined XRD pattern (labeled Co_3Mo_3N/Al_2O_3). In addition to peaks associated with the γ-Al_2O_3 support, XRD features are apparent at 23.0, 32.9, 35.7, 40.2, 42.8, 44.5, 46.6, 49.8, 65.04 and 72.8°. All of the peaks, except the one at 44.5°, are in good agreement with those for unsupported Co_3Mo_3N [11,12,14,15]. For comparison purposes, a simulated XRD pattern of Co_3Mo_3N is shown at the top of figure 1. The simulated XRD pattern was prepared using crystallographic data provided by zur Loye and coworkers [12] which were obtained from a Rietveld refinement of the XRD pattern of a pure sample of Co_3Mo_3N. The peak at 44.5° in the XRD pattern of our nitrided catalyst indicates that the alumina-supported Co_3Mo_3N is not pure. A search of the JCPDS powder diffraction file [19] suggests that the impurity is most likely a Co–N phase; the most intense peaks in the XRD patterns of $Co_{5.47}N$ (card no. 41-0943) and $Co_2N_{0.67}$ (card no. 06-0691) are at 43.716 and 44.370°, respectively. Milad et al. [20] have reported an XRD pattern for a Co–N phase they identify as Co_4N which has its most intense peak at 43.64°. Another possibility for the impurity in our alumina-supported Co_3Mo_3N is cobalt metal (card no. 15-0806); the most intense peak in its XRD pattern is located at 44.2°. Because no additional impurity-related peaks are apparent in the XRD pattern acquired for the Co_3Mo_3N/Al_2O_3 catalyst prepared in this study, we cannot distinguish between the different possible impurities. No XRD peaks other than those of the alumina support were observed for the lower loading Co_3Mo_3N/Al_2O_3 catalyst. For the cobalt-impregnated Mo_2N/Al_2O_3 catalysts, only XRD features associated with the alumina support were observed.

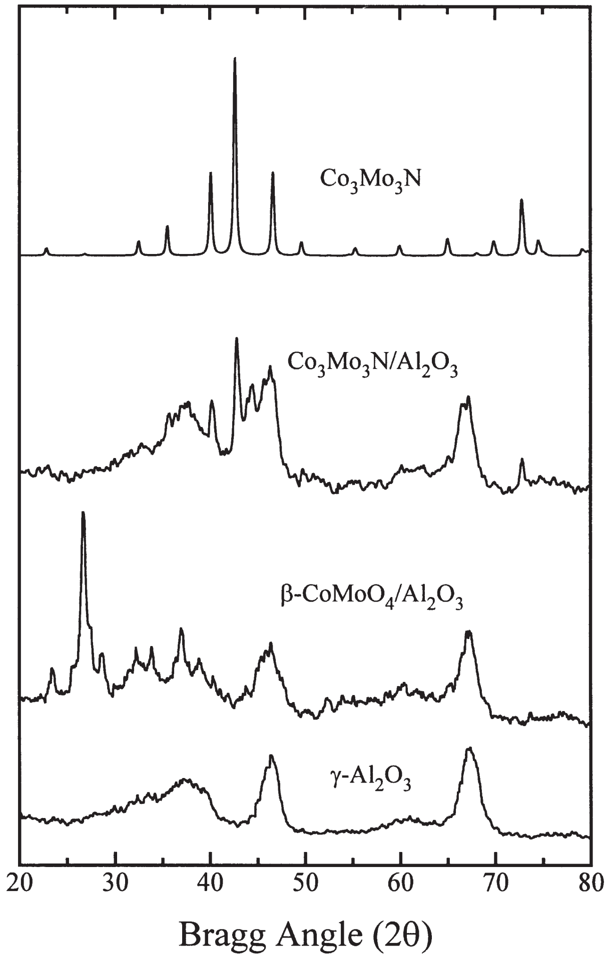

Figure 1. X-ray diffraction patterns for an alumina-supported oxidic precursor and a nitrided catalyst (10.6 wt% CoO–20.4 wt% MoO_3). An XRD pattern for the γ-Al_2O_3 support and a simulated XRD pattern for unsupported Co_3Mo_3N are included for comparison purposes.

Listed in table 1 are the surface areas as well as the CO and O_2 chemisorption capacities for the different cat-

Table 1
Surface area and chemisorption data.

Catalyst	Surface area (m^2/g)	CO chem. capacity (273 K)		O_2 chem. capacity (196 K)	
		Reduced (μmol/g)	Sulfided (μmol/g)	Reduced (μmol/g)	Sulfided (μmol/g)
MoO_3/Al_2O_3	178	–	37.0	–	50.0
Mo_2N/Al_2O_3	188	78.0	49.0	115	59.0
$CoMoO_4/Al_2O_3$	190	–	35.9	–	32.8
Co_3Mo_3N/Al_2O_3	175	42.0	20.1	42.3	18.4
Co–MoO_3/Al_2O_3	178	–	53.0	–	56.2
Co–Mo_2N/Al_2O_3	178	92.7	65.8	157	69.0

Table 2
Thiophene HDS activities.

Catalyst	HDS activity[a] (nmol Th/g s^{-1})	Relative HDS activity
Sulf. MoO_3/Al_2O_3	587	1.00
Red. Mo_2N/Al_2O_3	668	1.14
Sulf. $CoMoO_4/Al_2O_3$	2195	1.00
Red. Co_3Mo_3N/Al_2O_3	1139	0.52
Sulf. Co_3Mo_3N/Al_2O_3	1911	0.87
Sulf. Co–MoO_3/Al_2O_3	3029	1.00
Red. Co–Mo_2N/Al_2O_3	2533	0.84
Sulf. Co–Mo_2N/Al_2O_3	4028	1.33

[a] Measured after 24 h at 693 K.

alysts prepared in this study. The molybdenum loading is similar for the catalysts; the monometallic catalysts have a theoretical loading of 13.8 wt% MoO_3, while the bimetallic and promoted catalysts have a loading of 6.7 wt% CoO–12.8 wt% MoO_3. Nitridation of the oxidic precursors has no measurable effect on the surface area of the Co–Mo catalysts as indicated by a comparison of the surface areas of the different catalysts. Chemisorption capacities were measured for both freshly reduced and sulfided catalysts, except in the case of the oxidic catalysts for which only the sulfidation pretreatment was used. The method by which cobalt is incorporated into the nitrided catalysts substantially affected their chemisorption capacities. The Co–Mo_2N/Al_2O_3 catalyst, prepared via impregnation of a Mo_2N/Al_2O_3 catalyst with an aqueous solution of cobalt nitrate followed by vacuum drying, has higher CO and O_2 chemisorption capacities than its parent molybdenum nitride catalyst. This is also true when the Co–Mo_2N/Al_2O_3 and Mo_2N/Al_2O_3 catalysts are sulfided prior to the chemisorption measurements. The Co_3Mo_3N/Al_2O_3 catalyst, on the other hand, has low CO and O_2 chemisorption capacities. When sulfided, the chemisorption capacities of the Co_3Mo_3N/Al_2O_3 catalyst are only about 55% of those of the $CoMoO_4/Al_2O_3$ catalyst from which it was prepared by nitridation. These results indicate that cobalt addition by impregnation of Mo_2N/Al_2O_3 has little effect on the dispersion of the nitride phase, while cobalt incorporation by formation of a bimetallic nitride phase causes a significant decrease in the dispersion of the active phase. Efforts are under way to optimize the synthesis procedure of the Co_3Mo_3N/Al_2O_3 catalysts with respect to the dispersion of the nitride phase.

3.2. Catalyst activity and stability

Thiophene HDS activity measurements were carried out for the different catalysts prepared in this study and the results are summarized in table 2. We have previously shown that Mo_2N/Al_2O_3 catalysts with a range of Mo loadings are 1.22 ± 0.20 times more active for thiophene HDS than sulfided MoO_3/Al_2O_3 catalysts with the same Mo loading [7]. The activities reported here for Mo_2N/Al_2O_3 and sulfided MoO_3/Al_2O_3 catalysts prepared from an oxidic precursor with a 13.8 wt% MoO_3 loading are consistent with this result. As is well documented in the literature [1], addition of cobalt to sulfided Mo catalysts significantly enhances their HDS activity. Sulfided Co–Mo/Al_2O_3 catalysts prepared in this study from β-$CoMoO_4/Al_2O_3$ and Co–MoO_3/Al_2O_3 oxidic precursors (6.7 wt% CoO–12.8 wt% MoO_3) are 3.7 and 5.2 times more active, respectively, than a sulfided MoO_3/Al_2O_3 catalyst with a similar Mo loading. The difference in HDS activity observed for the sulfided Co–Mo catalysts prepared from the different precursors is not surprising. While a recent study indicates that unsupported β-$CoMoO_4$ is a precursor of an active thiophene HDS catalyst when sulfided [21], most researchers agree that alumina-supported $CoMoO_4$ is not a desired precursor of sulfided Co–Mo/Al_2O_3 catalysts [22]. On the other hand, impregnation of Mo/Al_2O_3 catalysts with cobalt nitrate without subsequent calcination has been shown by others to yield sulfided Co–Mo/Al_2O_3 catalysts with high HDS activities [23]. In this article, we use the naming scheme "sulfided $CoMoO_4/Al_2O_3$" and "sulfided Co–MoO_3/Al_2O_3" to distinguish between the two types of sulfided Co–Mo/Al_2O_3 catalysts investigated.

The thiophene HDS activities measured in this study for Co–Mo–N/Al_2O_3 catalysts are strongly dependent on the method in which cobalt is incorporated into the catalysts as well as the pretreatment of the catalysts. Focusing initially on catalysts which are reduced in hydrogen prior to the HDS activity measurement, neither the Co_3Mo_3N/Al_2O_3 nor the Co–Mo_2N/Al_2O_3 catalyst is as active for thiophene HDS as its comparable sulfided Co–Mo/Al_2O_3 catalyst (see table 2). However, when the Co_3Mo_3N/Al_2O_3 and Co–Mo_2N/Al_2O_3 catalysts are sulfided prior to measuring their HDS activities, these catalysts are nearly as active and considerably more active, respectively, than their comparable sulfided Co–Mo/Al_2O_3 catalysts (see table 2). In all cases, incorporation of cobalt into the nitride catalysts increases their thiophene HDS activity by a factor of nearly two or more compared to a Mo_2N/Al_2O_3catalyst with a similar Mo loading. For the catalysts which were subjected to a sulfidation pretreatment, the Co_3Mo_3N/Al_2O_3 and Co–Mo_2N/Al_2O_3 catalysts are 2.9 and 6.0 times more active than the Mo_2N/Al_2O_3 catalyst, indicating that Co is an excellent promoter of the thiophene HDS activity of molybdenum nitride-based catalysts. The promotional effect of cobalt measured in our study is consistent with the results of others. Kim et al. [14] and Ihm et al. [15] found unsupported Co_3Mo_3N to be approximately four times more active (per unit surface of catalyst) than unsupported γ-Mo_2N for thiophene HDS. For pyridine hydrodenitrogenation (HDN), Li et al. [17] observed unsupported Co_3Mo_3N to be about two times more active (per gram of catalyst) than unsupported γ-Mo_2N while Oyama and coworkers [24] found an unsupported Co–Mo–O–N phase to be 35% more active than unsupported γ-Mo_2N. Park et al. [18] found a nitrided Co–Mo/Al_2O_3 catalyst to be about 25% less active (per gram of catalyst) than a Mo_2N/Al_2O_3 catalyst for dibenzothiophene HDS. It is important to note that the cobalt-to-molybdenum ratio was not one in the nitrided Co–Mo/Al_2O_3 catalyst (Co/Mo = 0.48) prepared by Park et al. [18] and no XRD peaks associated with the nitrided Co–Mo phase were observed, so it is unclear whether a well-defined Co–Mo–N phase was present in this catalyst. Except for the Co–Mo–O–N catalyst which was reduced at 723 K for 3 h, the catalysts in the studies described above were reduced for 2 h in flowing hydrogen at 673 K prior to the catalytic activity measurements.

Consistent with the results of Ihm et al. [15] for unsupported Co_3Mo_3N catalysts, we have observed that sulfidation of Co_3Mo_3N/Al_2O_3 (and Co–Mo_2N/Al_2O_3) catalysts significantly improves their HDS activity. Ihm et al. [15] reported that sulfidation of unsupported Co_3Mo_3N at 773 K resulted in a two-fold increase in the thiophene HDS activity (per unit surface of catalyst) of unsupported Co_3Mo_3N, which is similar in magnitude to the increase in activity (per gram of catalyst) observed here for Co_3Mo_3N/Al_2O_3 catalysts (see table 2). It should be noted that studies in our laboratory indicate that sulfidation of Mo_2N/Al_2O_3 catalysts at 623 K has little effect on their HDS activity [25], in contrast to what we observe for the bimetallic and promoted nitride catalysts. Ihm et al. [15] have reported similar results for unsupported γ-Mo_2N which was either reduced in H_2 or sulfided in an H_2S/H_2 mixture at 673 K. In an effort to understand the beneficial effects of sulfidation for Co_3Mo_3N catalysts, we have used XRD to characterize Co_3Mo_3N/Al_2O_3 catalysts subjected to different pretreatments, and also catalysts which have been tested on stream in our flow reactor for 24 h. Shown in figure 2, these XRD patterns are for Co_3Mo_3N/Al_2O_3 catalysts with a loading of 10.6 wt% CoO–20.4 wt% MoO_3. Focusing initially on the two bottommost XRD patterns, the first is for a freshly synthesized and passivated Co_3Mo_3N/Al_2O_3 catalyst, while the second is for a sample of this same catalyst which has been reduced (as described in section 2), tested for 24 h in our thiophene HDS flow reactor, and then passivated in 1% O_2/He flow for 3 h at room temperature. Comparison of the two XRD patterns reveals that all peaks associated with the supported Co_3Mo_3N phase remain after the catalyst has been subjected to the sulfiding conditions of our HDS reactor for 24 h. However, a number of differences are apparent in the XRD patterns, the most noticeable being the disappearance of the peak at 44.5° and the appearance of new peaks at 29.9, 31.3, 33.0, 34.0, 38.2, 52.4, ~60.0 and 75.0°. As discussed earlier, the peak at 44.5° is due to an impurity, thought to be either a Co–N phase or Co metal. The disappearance of this peak and the appearance of new peaks at 29.9 and 52.4°, which are most likely associated with the presence of Co_9S_8 (card no. 19-0364 [19]), suggests that the impurity is readily converted to Co_9S_8 under HDS reaction conditions. The other new peaks, located at 31.3, 33.0, 34.0, 38.2 and ~60.0 and 75.0°, are consistent with the XRD pattern of MoS_2 (card no. 17-0744 [19]) and suggest that some of the supported Co_3Mo_3N is converted to MoS_2 (and presumably Co_9S_8) under the sulfiding conditions present in our HDS reactor. Oyama et al. [24] acquired XRD patterns for an unsupported Co–Mo–O–N catalyst before and after performing simultaneous HDS/HDN activity measurements at 643 K. Following 60 h on stream, the XRD pattern for the tested Co–Mo–O–N catalyst showed no XRD features associated with the fresh catalyst, but instead displayed sharp features assigned to Co_4S_3.

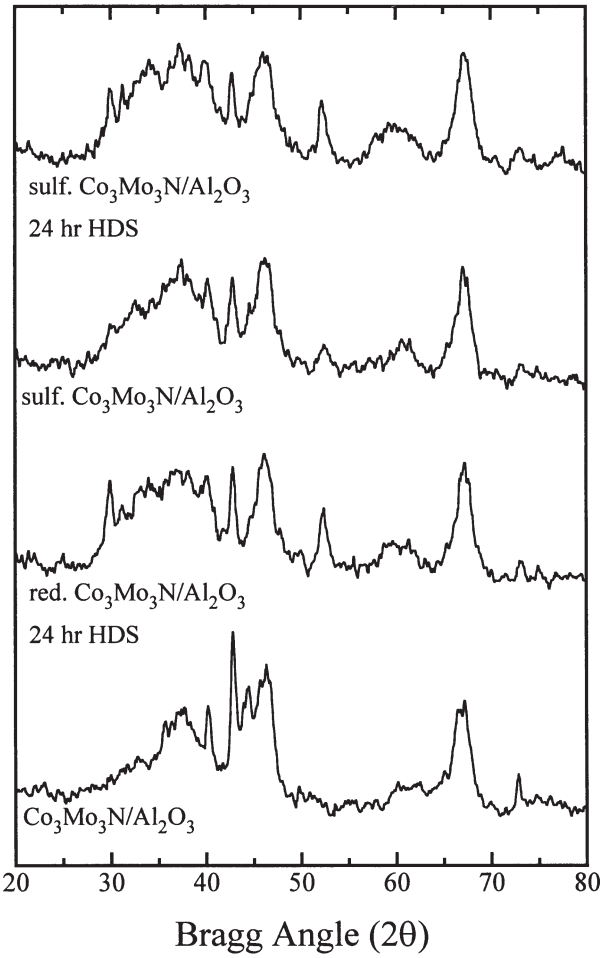

Figure 2. X-ray diffraction patterns for fresh and tested Co_3Mo_3N/Al_2O_3 catalysts (10.6 wt% CoO–20.4 wt% MoO_3) subjected to different pretreatments.

Returning to the current study, changes are also observed in the XRD pattern of a Co_3Mo_3N/Al_2O_3 catalyst which is sulfided as described in section 2. The two uppermost XRD patterns shown in figure 2 are for a freshly sulfided Co_3Mo_3N/Al_2O_3 catalyst and a sulfided sample of this same catalyst which has been tested in our thiophene HDS reactor. While peaks associated with Co_3Mo_3N are still readily visible, sulfidation of a Co_3Mo_3N/Al_2O_3 catalyst results in the disappearance of the peak at 44.5°, and the appearance of new peaks at 30.3, 34.4, 37.5, 38.2, 52.4 and ~60.5 and 75.0°. These changes indicate the formation of Co_9S_8 and MoS_2 at the catalyst surface at the expense of the cobalt-containing impurity and some of the supported Co_3Mo_3N phase. These observations are consistent with XRD studies carried out by Ihm et al. [15] in which sulfidation of unsupported Co_3Mo_3N at increasing temperatures was examined. The XRD pattern of unsupported Co_3Mo_3N sulfided at 673 K shows peaks associated with Co_9S_8, while the XRD pattern following sulfidation of Co_3Mo_3N at 773 K reveals XRD peaks associated with both Co_9S_8 and MoS_2. The fact that we observe XRD peaks attributable to Co_9S_8 and MoS_2 for a Co_3Mo_3N/Al_2O_3 catalyst sulfided at 623 K indicates that alumina-supported Co_3Mo_3N is more susceptible to sulfidation than the bulk compound.

Following testing for 24 h in our thiophene HDS reactor, the peaks associated with Co_9S_8 and MoS_2 in the XRD pattern of the sulfided Co_3Mo_3N/Al_2O_3 catalyst are more intense than in the freshly sulfided catalyst, and the XRD pattern is quite similar to that of a reduced Co_3Mo_3N/Al_2O_3 catalyst tested for 24 h under the same reactor conditions. Based upon the XRD analysis, we are not able to determine why sulfidation strongly enhances the thiophene HDS activity of our Co_3Mo_3N/Al_2O_3 catalysts. One possibility is that presulfidation of the bimetallic nitride catalyst promotes formation of a surface Co–Mo nitridosulfide phase, which in turn has a high thiophene HDS activity. Dhandapani et al. [26] have suggested that the high HDS activity of an unsupported molybdenum carbide catalyst may be due to the formation of a surface carbosulfide phase. It is important to note that the sulfidation pretreatment increases the HDS activity of $Co–Mo_2N/Al_2O_3$ catalysts as well, and an explanation of this observation is also lacking. At this time, we can only speculate that the sulfidation pretreatment increases the amount of cobalt available for promotion when the outermost layers of the $Co–Mo_2N/Al_2O_3$ catalysts become sulfided. Ratnasamy et al. [27] investigated the reducibility of a Co/Al_2O_3 catalyst which was prepared by impregnation of γ-Al_2O_3 with cobalt nitrate, followed by drying but without a subsequent calcination step. A significant fraction of the cobalt in this catalyst could not be reduced in hydrogen at 823 K and was presumed to have migrated into Al^{3+} vacancies of the support. It may be the case that a reduction pretreatment of our $Co–Mo_2N/Al_2O_3$ catalysts results in a significant amount of the cobalt becoming associated with the alumina support and, therefore, being unavailable to promote the Mo-containing phases.

Given that sulfidation enhances the activity of Co_3Mo_3N/Al_2O_3 and $Co–Mo_2N/Al_2O_3$ catalysts and that XRD indicates that the supported nitride phases remain sulfided under HDS conditions, we have used the CO or O_2 chemisorption capacities of the freshly sulfided catalysts to calculate normalized thiophene HDS activities (see table 3). Whether normalized using CO and O_2 chemisorption capacities, all of the catalysts containing cobalt are at least four times more active than a sulfided MoO_3/Al_2O_3 catalyst. Interestingly, the normalized HDS activities of the sulfided Co_3Mo_3N/Al_2O_3 catalyst are 55% higher than those of the sulfided $CoMoO_4/Al_2O_3$ catalyst with the identical Co and Mo loadings. The higher normalized HDS activity of the sulfided Co_3Mo_3N/Al_2O_3 catalyst is consistent with the idea that a Co–Mo nitridosulfide phase is formed on the surface of the supported Co_3Mo_3N which has a higher intrinsic activity than the Co–Mo–S phase formed in conventional sulfide catalysts. These results also suggest that if the dispersion of the Co_3Mo_3N/Al_2O_3 catalysts can be substantially improved, then Co_3Mo_3N/Al_2O_3 catalysts have the potential to be very active catalysts for the HDS process.

Table 3
Normalized thiophene HDS activities.

Catalyst	Normalized HDS activities[a]	
	(mmol Th/mol CO s^{-1})[b]	(μmol Th/mol O_2 s^{-1})[c]
Sulf. MoO_3/Al_2O_3	15.9	11.7
Sulf. $CoMoO_4/Al_2O_3$	61.1	66.9
Sulf. Co_3Mo_3N/Al_2O_3	95.1	104
Sulf. $Co–MoO_3/Al_2O_3$	57.2	53.9
Sulf. $Co–Mo_2N/Al_2O_3$	61.2	58.4

[a] Measured after 24 h at 693 K.
[b] CO chemisorption capacity measured at 273 K.
[c] O_2 chemisorption capacity measured at 196 K.

In contrast to the bimetallic nitride catalyst, the normalized HDS activities of the $Co–Mo_2N/Al_2O_3$ catalysts are less than 10% higher than those of the sulfided $Co–MoO_3/Al_2O_3$ catalyst with the same Co and Mo loadings. The high HDS activity (per gram of catalyst) of the $Co–Mo_2N/Al_2O_3$ catalyst investigated here can likely be traced to the high dispersion of the active catalytic phase in this catalyst. This conclusion is consistent with the results of our studies of Mo_2C/Al_2O_3 and Mo_2N/Al_2O_3 catalysts [6,7], in which we attribute the higher HDS activity of these catalysts (compared with a sulfided MoO_3/Al_2O_3 catalyst) to the high density of sites present in a layer of highly dispersed, or strained sulfided Mo formed on their surfaces under HDS reaction conditions.

Efforts focused on optimizing the synthesis of Co_3Mo_3N/Al_2O_3 catalysts to increase the dispersion of the nitride phase, and on understanding the role of sulfidation in increasing the HDS activity of Co_3Mo_3N/Al_2O_3 and $Co–Mo_2N/Al_2O_3$ catalysts are continuing in our laboratory. The synthesis parameters we are currently examining include the time and ultimate nitridation temperature of the TPR program as well as the NH_3 flow rate. Infrared spectroscopy of adsorbed CO is being used to probe the distribution of adsorption sites on the surfaces of Co_3Mo_3N/Al_2O_3 and $Co–Mo_2N/Al_2O_3$ catalysts as a function of the pretreatment procedure.

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