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Effect of EDTA on hydrotreating activity of CoMo/γ-Al_2O_3 catalyst

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γ-Al_2O_3 supported Co (0–4.5 wt%) Mo (9.0 wt%) sulfide catalysts were prepared in the presence and the absence of ethylenediaminetetraacetic acid (EDTA). The hydrodenitrogenation (HDN) activity of these catalysts was studied in the model reaction of 2,6-dimethylaniline (DMA) at 300 °C under 4 MPa. The CoMo/Al_2O_3 catalysts prepared with the EDTA showed higher HDN of DMA than those prepared without EDTA. The maximum of 36% increase in rate constant of HDN of DMA was observed over the catalyst with 3% Co prepared using EDTA. The FT-IR spectroscopy of adsorbed CO on CoMo catalysts showed that EDTA addition promoted the formation of catalytically active "CoMoS" phase as evidenced from increases in intensity of band at 2070 cm^{-1}, which is maximum for 3% Co loaded catalysts. The HDN and hydrodesulfurization (HDS) activity of 3% Co loaded catalyst prepared using EDTA was tested and compared with those catalyst prepared without EDTA in a trickle bed reactor using heavy gas oil derived from Athabasca bitumen in the temperature range 370–400 °C and 8.8 MPa. Improved HDN and HDS conversion of heavy gas oil was obtained for the catalyst prepared with EDTA.

KEY WORDS: CoMo catalysts; ethylenediaminetetraacetic acid; CO adsorption; 2,6-dimethylaniline; hydrodesulfurization; hydrodenitrogenation; heavy gas oil.

1. Introduction

Research on the cleaning of fuels, including hydrodesulfurization (HDS), hydrodenitrogenation (HDN) and dearomatization has become an important subject of environmental catalysis studies worldwide. Because the requirements as to the legally permitted sulfur and nitrogen contents in fuels are becoming ever stricter, there is a continuous need for hydrotreating catalysts with improved activity. Development of highly active hydrotreatment catalysts is one of the most urgent subjects in the petroleum industry not only to protect the environment but also to efficiently utilize limited natural resources. Supported nickel or cobalt molybdenum catalysts are used extensively in the hydrotreatment of petroleum feedstocks. The catalytically active phase of nickel or cobalt molybdenum catalysts consists of small MoS_2 slabs with the promotor ions dispersed over the edges, the so-called "Co(Ni)MoS" phase [1–4]. There are two types of "CoMoS" phases with distinctly different activities, CoMoS type I and type II, the latter exhibiting about two times higher activity than the former [5]. It is, accordingly, expected that highly active cobalt molybdenum catalysts are composed of a highly dispersed CoMoS type II phase. van Veen *et al.* [6] have reported a ways to increase the CoMoS type II phase in cobalt molybdenum catalysts, based on the generally accepted model of the CoMoS phase. A key element in effective preparation routes toward CoMoS type II phases is that the transition of oxidic Co to their sulfidic state should occur after MoS_2 phases are formed [7–11]. Chelating agents such as nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA), and derivatives of these molecules stabilize Ni and Co with respect to sulfide formation to temperatures where all or most of the Mo have converted to sulfides. These procedures enable one to prepare highly active CoMoS, NiMoS catalysts irrespective of the support [6,7,12–16]. The first use of a chelating agent (*viz.* NTA) in the design of silica-supported nickel- and cobalt-promoted molybdenum based hydrotreating catalysts was patented by Thompson [17]. There upon it was reported by van Veen *et al.* [18] that catalyst preparation with a chelated cobalt–NTA precursor complex yielded catalysts containing exclusively the catalytically active CoMoS phase, whereas catalyst preparation without NTA resulted in a mixture of catalytically less active phases. Cattaneo *et al.* [12] showed that this advantageous effect was not restricted to NTA, but that a wide range of chelating agents was able to direct the formation of the highly active CoMoS phase. Works in the laboratories of Prins [7,12,13], and Niemantsverdriet group [8,10,11,14] have identified retardation of Ni and Co sulfide formation as the key step in enabling the formation of the active NiMoS and CoMoS phases. A number of studies have been aimed at the elucidation of the processes by which chelating agents influence the generation of the active phase [7–11,13,14,19–22]. The techniques used for this

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purpose were mainly X-ray photoelectron spectra (XPS) [8–11,14,19–21] and (Quick) extended X-ray absorption fine structure (EXAFS) [7,13,22].

All studies of the catalytic activity of silica-supported Co–Mo and Ni–Mo catalysts have shown that chelating ligands improve the hydrotreating activity [7,8,10,11,13]. The effect of chelating ligands on the hydrotreating properties of alumina-supported catalysts has been studied in few cases only. van Veen *et al.* [23] reported that CoMo/Al_2O_3 and NiMo/Al_2O_3 catalysts prepared in the presence of NTA are about 20% less active in the HDS of dibenzothiophene as the corresponding catalysts prepared without NTA. A positive result was obtained for the HDS of thiophene, while NTA hardly influenced the HDN of quinoline [23]. Cattaneo *et al.* [22] reported that NTA strongly enhanced the activity of NiMo/Al_2O_3 catalyst for the HDN of *o*-toluidine but hardly improved its activity in the HDS of thiophene. Shimizu *et al.* [15,16] observed that chelating agents, NTA, EDTA and *trans*-1,2- cyclohexanediamine-*N*,*N*,*N′*,*N′*-tetraacetic acid improve the activity in HDS of benzothiophene and in hydrogenation of *o*-xylene over NiW/Al_2O_3 catalysts.

Most of the work reported on CoMo sulphide catalysts prepared with chelating agents deals with the study of hydrotreating activity using model compounds. There is no detailed study available in open literature using gas oils. The purpose of this work is to prepare a highly active CoMo/γ-Al_2O_3 sulfide catalyst using EDTA and investigation of hydrotreating activity using heavy gas oil derived from Athabasca bitumen. In this paper, first CoMo sulfide catalysts containing different Co content were synthesized with and without EDTA addition, followed by characterisation of surface sites by CO adsorption and screening in the model reaction of 2,6-dimethylaniline (DMA) hydrodenitrogenation. 2,6 dimethylaniline was chosen as model compound, because its reaction network contains the most important reactions that take place in HDN: dearomatization of DMA followed by either hydrogenation–elimination to dimethylcyclohexenes and dimethylcyclohexanes, or NH_3 elimination to *m*-xylene, and disproportionation of DMA to 2-methylaniline and 2,4,6-trimethylaniline. Moreover, an aniline model molecule is representative of the *o*-propylaniline intermediate in the quinoline reaction network. Second, the hydrotreating of heavy gas oil derived from Athabasca sand oil was performed using a best active catalyst, identified from HDN of 2,6-dimethylaniline.

2. Experimental

2.1. Catalyst preparation

All the catalysts were prepared on γ-Al_2O_3 support ($258\ m^2/g$, $0.66\ cm^3/g$) by a sequential pore filling impregnation procedure. The γ-Al_2O_3 support was calcined at 500 °C for 3 h prior to impregnation. The Mo/Al_2O_3 catalyst (8.7 wt% Mo) was prepared by impregnation of a γ-alumina support with $(NH_4)_6Mo_7O_{24}\ 4H_2O$ (Aldrich) solution. The sample was dried at 120 °C for 5 h and calcined at 500 °C for 3 h to get MoO_3/Al_2O_3. This was used to prepare CoO–MoO_3/Al_2O_3 catalysts having various Co (0–4.5 wt%) contents with and without using chelating agent.

A series of CoMo/Al_2O_3 catalysts without chelating agent was prepared by impregnation of the MoO_3/Al_2O_3 with a cobalt nitrate (Aldrich) solution, drying, and finally calcining at 500 °C for 3 h with a heating rate of 3 °C/min. Another series of CoMo/Al_2O_3 catalysts with chelating agent addition was prepared by impregnating of the MoO_3/Al_2O_3 with cobalt nitrate dissolved in an aqueous solution of ammonia (25%) together with the chelating agent, ethylenediaminetetraacetic acid (EDTA) (Alrich). The molar ratio of a chelating agent to Co was 1.0. The impregnated powder was dried overnight at 120 °C for 5 h. Calcination was not carried out in order to avoid the decomposition of the complexes in the catalyst precursors. Mo/Al_2O_3-EDTA catalyst was prepared in the same way as CoMo–EDTA (4.5), without Co.

2.2. FT-IR spectroscopy of adsorbed CO

IR spectra of adsorbed CO were recorded with a Nicolet Magna 550 IR spectrometer equipped with a MCT detector using 256 scans and a resolution of $4\ cm^{-1}$. The catalyst powder was pressed into a self-supported wafer ($\sim$10 mg, $1.6\ cm^2$) and placed into the IR cell, equipped with CaF_2 windows and double walls with a space for cooling agent. The catalyst was sulfided with 10% H_2S/H_2 (30 mL/min) at a rate of 3 °C /min up to 350 °C. After 2 h of sulfiding, the catalyst was flushed with N_2 for 30 mins and the temperature was decreased to 25 °C. The sulfided catalyst was rapidly evacuated at 300 °C (10 °C/min) at a residual pressure of 10^{-5} Torr and finally cooled to -173 °C under vacuum for CO adsorption. The catalyst was contacted with 133 Pa CO at equilibrium. A first spectrum of the wafer was recorded as reference. The spectra were normalized to an equivalent sample mass of 10 mg. The spectra of adsorbed CO reported in this study are in fact substracted spectra, i.e., the spectra of adsorbed CO minus the reference spectrum of the sample before CO adsorption.

2.3. HDN of 2,6-dimethylaniline

The reactor (stainless steel reactor system from Sotelem, $L = 300$ mm, i.d. = 9 mm) was loaded with 0.3 g of catalyst grains (0.5–0.8 mm) and pressurized at 4 MPa. The catalysts were sulfided for 2 h at 350 °C (heating rate, 3 °C/min) with 10% H_2S/H_2 (30 mL/min) that flowed through the reactor from the beginning of the heating process. Thereafter, the catalyst was cooled under H_2S/H_2 to the reaction temperature of 300 °C, and the H_2S content was adjusted at 56 kPa ($H_2/H_2S = 70$). The liquid feed (10 vol.% 2, 6-dimethylaniline, reactant; 80% heptane, solvent; and 10% decane as internal standard) was introduced by an HPLC pump and vaporized in the H_2S/H_2 stream. The reaction products were condensed at the reactor exit and the liquid was analyzed on a gas chromatograph equipped with a CPSIL-5CB capillary column and a FID detector. The partial pressure of 2,6-dimethylaniline (DMA) was kept constant at 13 kPa for all experiments. Reaction conditions at steady state were varied by changing the contact time (67–140 h.g/mol) at a fixed H_2S partial pressure. Conversions of DMA were kept below 20%.

2.4. *Hydrodenitrogenation and hydrodesulfurization of heavy gas oil derived from Athabasca bitumen*

All the experiments were performed in a micro-scale trickle bed reactor under typical industrial conditions. The total pressure, liquid hourly space velocity, and H_2/feed ratio were maintained at 8.8 MPa, 1 h^{-1} and 600 mL/mL, respectively. The high pressure reaction set up used in this study simulates the process that takes place in industrial hydrotreater. The system consisted of liquid and gas feeding sections, a high-pressure reactor, a heater with temperature controller for precisely controlling the temperature of the catalyst bed, a scrubber for removing the ammonium sulfide from the reaction products, and a high pressure gas–liquid separator. The length and internal diameter of the reactor were 240 and 14 mm, respectively. The catalyst bed inside the reactor was diluted with 90 mesh of silicon carbide. Before loading, the catalyst was dried for 3 h at 120 °C. For loading the catalyst, the reactor was packed from bottom to top in nine parts. The bottom 2.2 cm was first loaded with 3 mm size glass beads followed by 2.5 cm with 16 mesh, 1.0 cm with 46 mesh and 1.0 cm with 80 mesh silicon carbide. The catalyst bed, approximately 10.5 cm long, was packed with 5 mL of catalyst (3.8 g) and 12 mL of 90 mesh silicon carbide. Small quantities of catalyst and silicon carbide were alternately loaded in the reactor with spatula and mildly vibrating the reactor intermittently. Then the top part of the catalyst bed was loaded with 80 mesh (0.8 cm), 46 mesh (0.8 cm), 16 mesh (0.8 cm) silicon carbide and 3.5 mm glass beads (2.0 cm). Then the reactor was placed in the unit.

Pressure of the reactor was raised to 8.8 MPa using helium, which was then fed at the controlled rate of 50 mL/min, and the temperature of the reactor was then raised to 100 °C. Then, the sulfidation of the catalyst was started using sulfidation solution containing 2.9 vol.% of butanethiol in straight run atmospheric gas oil. Initially, the flow rate of the sulfiding solution was kept high at 0.5 mL/min to wet the catalyst bed. After passing sulfiding solution for 2 h at this rate, the flow rate was reduced and adjusted to maintain a LHSV of 1 h^{-1}. Helium flow rate was then stopped. Hydrogen flow rate was then started corresponding to H_2/sulfiding solution ratio of 600 mL/mL. The temperature of the reactor was then slowly increased from 100 to 193 °C and was maintained at this temperature for 24 h. The temperature of the reactor was again increased slowly to 350 °C and was then maintained at 350 °C for another 24 h. After sulfidation was over, the catalyst was precoked by passing heavy gas oil at the rate of 5 mL/h for 5 days at 375 °C. After precoking, the operating parameters were set at the desired level and experiments were performed at steady state and at different temperatures using heavy gas oil. The product samples were collected after 24 h interval for 3 days at each temperature. The products were stripped with nitrogen for removing the dissolved ammonia and hydrogen sulfide. The total nitrogen content of the liquid product was measured by combustion/chemiluminence technique following ASTM D4629 method and the sulfur content was measured using combustion/fluorescence technique following ASTM 5463 procedure. Both sulfur and nitrogen were analyzed in an Antek 9000 NS analyzer. Gas chromatography simulated distillation was used to determine the boiling point range distribution of gas oil.

3. Result and discussions

Conventional CoMo sulfide catalysts with cobalt loading of 0, 1.5, 3.0 and 4.5 wt% were prepared and denoted as CoMo(x), where x is the cobalt weight percentage. Similarly, EDTA added CoMo sulfide catalysts with cobalt loading of 0, 1.5, 3.0 and 4.5 wt% were prepared and denoted as CoMo–EDTA(x), where x is the cobalt weight percentage.

3.1. *Infrared spectroscopy of adsorbed CO*

The surface sites on the sulfided CoMo catalysts were characterized by infrared spectroscopy of adsorbed CO. The adsorption was done at −173 °C in order to increase the coverage of the probe molecule on weak sites such as those present on the unpromoted Mo phase. Under these conditions, the IR spectra show the interaction of the probe with the alumina carrier and with the sulfide phase [24,25]. Results obtained on the series of sulfided CoMo catalysts are presented in figure 1. For all samples, CO adsorbs on the coordinated unsaturated (CUS) Al^{3+} sites (band at around 2190 cm^{-1}) and interacts with the hydroxyl groups of the alumina carrier (band at 2154 cm^{-1}). The sulfide phase is characterized by a band at 2110 cm^{-1} assigned to the CUS located on molybdenum and by a signal at 2070 cm^{-1} for the promoted sites (CoMoS phase) [26,27]. The variation of the band intensities with cobalt content confirms such an assignment, since the number of promoted sites increases at the expense of unpromoted Mo sites. For CoMo–EDTA catalysts, the intensity of signal at 2070 cm^{-1} for the

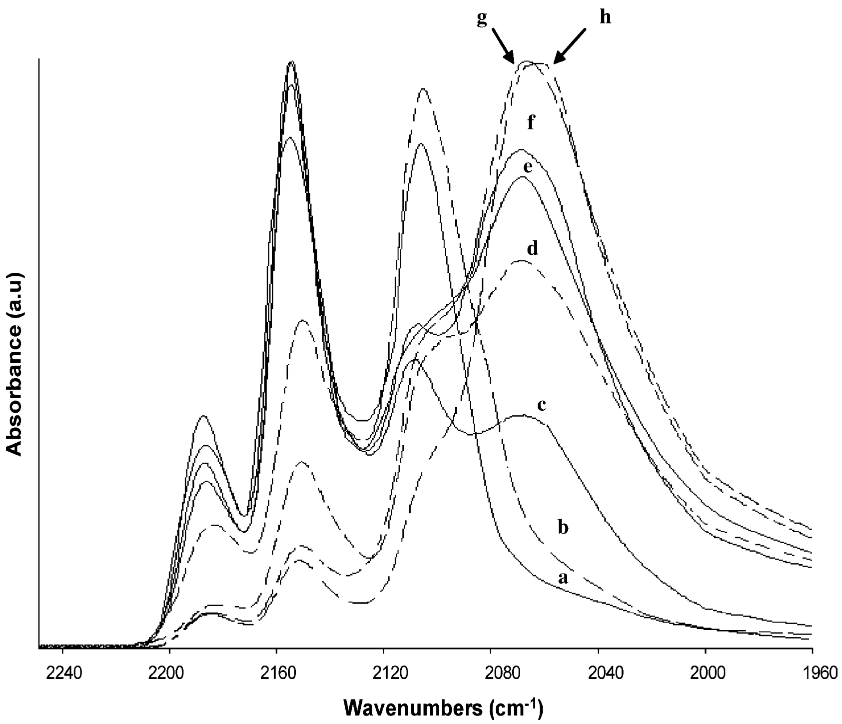

Figure 1. FT-IR spectra of CO adsorbed on sulfided Mo and CoMo catalysts at −173 °C. CoMo series (solid line), CoMo–EDTA series (dashed line), (a) Mo, (b) Mo–EDTA, (c) CoMo(1.5), (d) CoMo–EDTA(1.5), (e) CoMo(3.0), (f) CoMo(4.5), (g) CoMo–EDTA(3.0), (h) CoMo–EDTA(4.5).

promoted site is higher than that of corresponding CoMo catalysts. Shimizu *et al.* [15] have reported similar increase in promoted sites of CoMo catalyst prepared with the chelating agents by NO adsorption. The CO adsorption studies suggested that Co is highly dispersed over the edges of the MoS_2 slabs, and much amount of Co-site to which CO can be adsorbed are generated over the surface, when the catalysts were prepared using the EDTA. The added EDTA not only disperses the Co but also disperses the MoS_2 as evidenced from increase in unpromoted sites of Mo–Al_2O_3 catalyst on EDTA addition (spectrum a & b).

3.2. *Hydrodenitrogenation of 2,6-dimethylaniline (DMA)*

Products analysis shows that dimethylcyclohexenes and dimethylcyclohexanes are the major denitrogenation products. The other denitrogenation product is *m*-xylene, formed in small quantity. Finally, large quantities of 2-methylaniline and 2,4,6-trimethylaniline is observed, in approximately equal amounts. These products result from the disproportionation of DMA. A plot of the product yield versus contact time shows that all three groups of products appear to be primary products. Figure 2 shows the product yield obtained on the typical CoMo–EDTA(3.0) catalyst at various contact times. The reaction orders for the formation of dimethylcyclohexenes + dimethylcyclohexanes (k_1), *m*-xylene (k_2), and 2-methylaniline + 2, 4, 6-trimethylaniline (k_3') as 0, 0, and 0.4, respectively. This is in agreement with the previous results [27]. The reaction network for DMA is depicted in figure 3. HDN of 2,6-dimethylaniline shows three parallel routes: dearomatization of DMA followed by either hydrogenation–elimination to dimethylcyclohexenes and dimethylcyclohexanes, or NH_3 elimination to

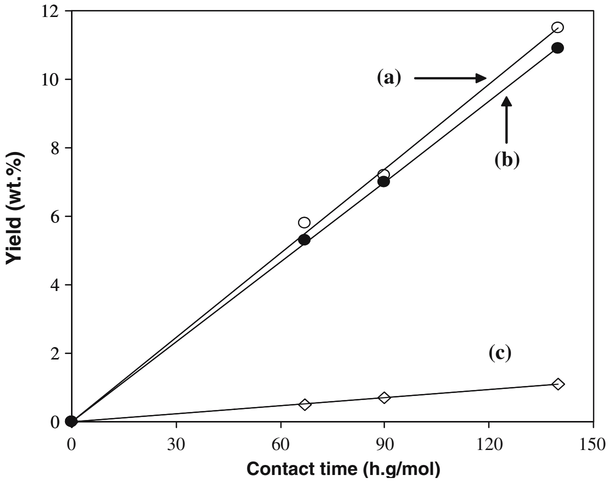

Figure 2. Product yield for the reaction of 2,6-dimethylaniline on the CoMo–EDTA(3.0) catalyst at various contact time. (a) dimethylcyclohexenes + dimethylcyclohexanes; (b) 2-methylaniline + 2,4,6-trimethylaniline; (c) *m*-xylene, Temperature = 300 °C, Pressure = 4 MPa and H_2S = 56 kPa.

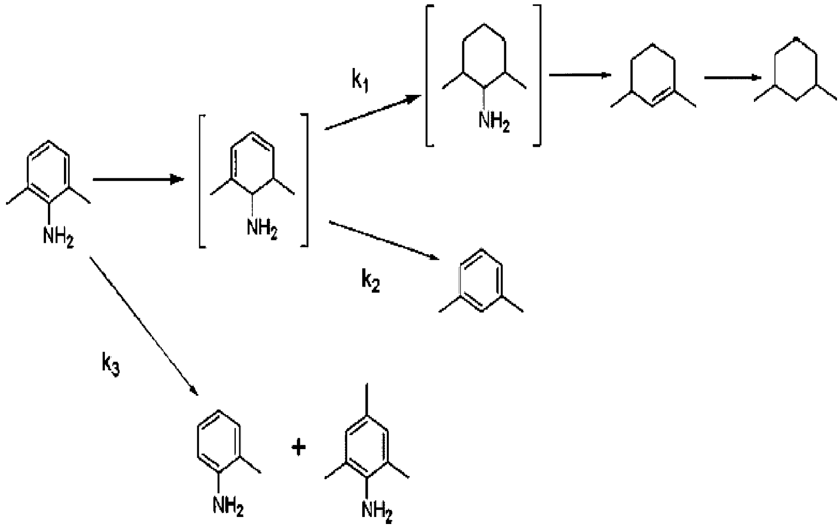

Figure 3. Reaction network of 2,6-dimethylaniline.

m-xylene, and disproportionation of DMA to 2-methylaniline and 2,4,6-trimethylaniline.

The reactivity of DMA over both the series of Co (0–4.5%) Mo/Al_2O_3 samples were studied and activities are expressed by the rate constants. For the sake of uniformity of units, the activity for disproportionation is given by $k_3 = k'_3 \cdot (P^{o}_{DMA})^{0.4}$ mol h kg^{-1}. Figure 4 shows the influence of the cobalt content on the rate constants. All three routes are promoted by cobalt. As the concentration of Co promoter increases, the catalytic activity increases to an optimum for 3% Co. The activity levels off for Co contents above 3 wt% for both series of catalysts. Thus, the maximum of promotion is obtained for a Co/Mo ratio of 0.33, as expected for mixed sulfide catalysts. This is in agreement with our Co adsorption studies (figure 1), which also reveals maximum promotion for a Co/Mo ratio of 0.33. At very low cobalt loadings (≤3%), all the cobalt atoms can be positioned around the MoS_2 edges and the catalytic activity initially increases with increasing Co/Mo ratio. If all the edge positions are occupied (≥3% Co loading), then additional cobalt atoms present separately as cobalt sulfide (Co_9S_8) clusters [28], which do not contribute significantly to the catalytic activity.

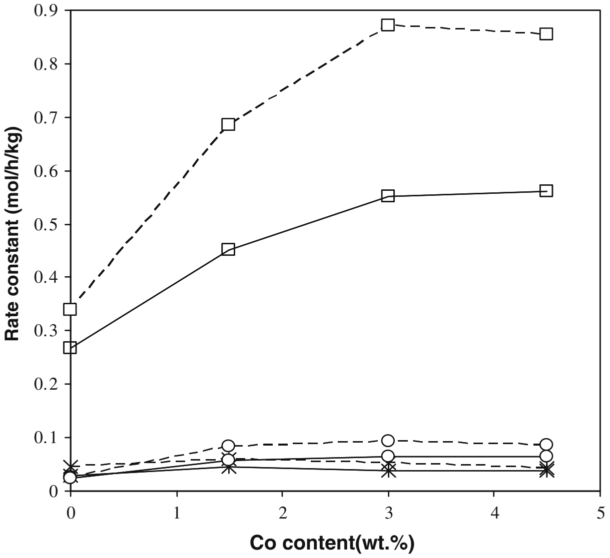

Figure 4. The effect of EDTA addition on the rate constants for dimethylcyclohexenes + dimethylcyclohexanes (k_1), *m*-xylene (k_2) and 2-methylaniline + 2,4,6-trimethylaniline (k_3). CoMo–EDTA catalysts (dashed line), CoMo catalysts (solid line), (□) – k_1; (×) – k_2; (○) – k_3.

As seen in figure 4, CoMo–EDTA catalysts have higher rate constants k_1 and k_2 than the CoMo catalysts. The maximum of 36% increase in rate constant of hydrodenitrogenation of DMA was observed over the catalyst with 3% Co prepared using EDTA. To distinguish whether this promotion in activity of CoMo–EDTA catalysts in hydrodenitrogenation of DMA is due to the EDTA addition or the pre-treatment conditions (that is CoMo–EDTA catalysts are not calcined before sulfidation whereas CoMo catalysts are calcined before sulfidation), the HDN of DMA was also studied on uncalcined CoMo(1.5) and CoMo(3.0) sulfide catalysts. The k_1 of 4.52 and 4.18 mol/h/kg and k_2 of 0.716 and 0.678 mol/h/kg were obtained for HDN of DMA over calcined and uncalcined CoMo(1.5) respectively. Over CoMo(3.0) calcined and uncalcined catalysts, the k_1 of 5.52 and 5.28 mol/h/kg and k_2 of 0.615 and 0.589 mol/h/kg were obtained respectively for HDN of DMA. The k_1 and k_2 values showed that both calcined and uncalcined catalysts without EDTA possess almost similar activity on HDN of DMA. Whereas the k_1 and k_2 values for CoMo(1.5) and CoMo(3.0) catalysts showed a substantial increase when EDTA was added. ZThis indicates that improvement in activity of

CoMo–EDTA catalyst is due to EDTA addition during the catalyst preparation and not due to pre-treatment conditions. The added EDTA forms a complex with Co^{2+} and delay the sulfidation of Co, which occurs at a temperature at which all the Mo is fully sulfided to MoS_2 [8,14,19]. Once the Co atoms are released by the chelating agent at elevated temperatures, they can move to the edges of the already formed MoS_2 and create the highly active CoMoS phase. Whereas, CoMo catalysts prepared without EDTA, cobalt starts to sulfide before the end of MoS_2 formation. As a result, cobalt sulfides into bulk Co_9S_8, which is not able to redisperse over the MoS_2 slabs at higher temperatures. As a consequence, the CoMoS phase is formed to a small extent only. The HDN of DMA over Mo–Al_2O_3 catalyst was increased slightly with addition of EDTA. This is in line with FT-IR CO adsorption, which shows an increase in dispersion of MoS_2 sites due to addition of EDTA.

3.3. *The hydrodenitrogenation (HDN) and hydrodesulfurization (HDS) of heavy gas oil*

The characteristics of heavy gas oil derived from Athabasca bitumen are given in table 1. Hydrodenitrogenation of 2,6-dimethylaniline over CoMo–EDTA catalysts shows that CoMo–EDTA(3.0) catalyst has maximum HDN activity. This catalyst was used to study hydrodenitrogenation and hydrodesulfurization of heavy gas oil along with the CoMo(3.0). To achieve steady state activity, precoking was done for 5 days at the temperature, pressure, LHSV and H_2/feed ratio of 375 °C, 8.8 MPa, 1 h^{-1} and 600 mL/mL. The stabilization curves for the typical CoMo–EDTA catalyst is shown in figure 5. The figure shows that the catalyst activity decreases with time for first 2 days because of the deposition of coke on the catalyst surface and then the activity remained constant for the rest of run time. Similar trend was observed with CoMo(3.0) catalyst also (figure not shown). This indicates that 5-day period is sufficient to stabilize both the catalysts prior to the activity studies. The performance test of CoMo–EDTA (3.0) and CoMo (3.0) catalysts was carried out at 370, 380, 390 and 400 °C using heavy gas oil. The HDN and HDS activities are given in table 2. These data are the average of those obtained after 48 and 72 h of TOS. Table shows that CoMo–EDTA catalyst shows considerably higher nitrogen conversion compared to that of CoMo catalyst at all temperatures. An increase of 16.2, 11.7, 9.3 and 7.2% in HDN conversion respectively at 370, 380, 390 and 400 °C was observed on EDTA addition. Similarly, the CoMo–EDTA catalyst exhibited better hydrodesulfurization than CoMo catalyst (96.8 versus 93.5% at 370 °C). It should be mentioned that HDS data were obtained at most severe operating conditions, and because of this, the difference between CoMo and CoMo–EDTA catalysts in sulfur removal is not clearly observed in the temperatures 380–400 °C.

Table 1
Characteristics of heavy gas oil derived from Athabasca bitumen

Nitrogen (ppm)	3072
Sulfur (ppm)	40132
Density (g/mL)	0.98
Simulated distillation (°C)	
IBP	206
FBP	636
Boling range (°C)	wt%
IBP–300	10.6
301–350	10.4
351–400	17.0
401–450	21.8
451–500	19.3
501–600	17.9
601–FBP	3.0

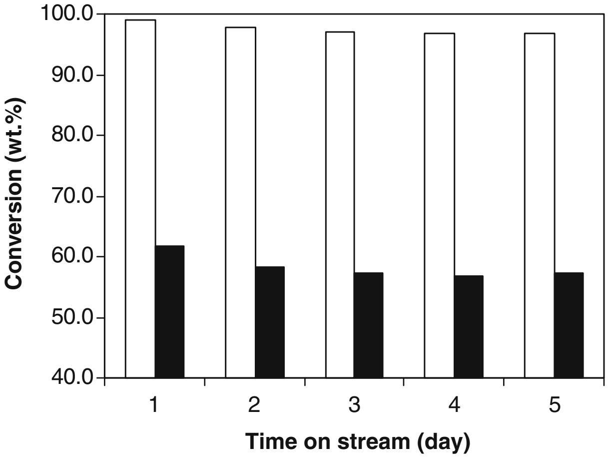

Figure 5. Effect of time on stream on the stability of the CoMo–EDTA(3.0) catalyst during hydroprocessing of heavy gas oil. $T = 375$ °C, $P = 8.8$ MPa, LHSV = 1 h^{-1}, and hydrogen/oil ratio = 600 mL/mL. (□) Sulfur, (■) Nitrogen.

The hydrocarbons distribution was derived from GC simulated distillation for the feed and the products of hydrotreating at different temperatures are given in table 3. The results show that species with $> C_{30}$ were converted into lighter species, C_{10}–C_{20} and C_{20}–C_{30}, and the conversion increased with increase of temperature. The lighter species are formed due to hydrogenation and subsequent heteroatom (sulfur and nitrogen) removal. Hydrotreatment of HGO over CoMo and CoMo–EDTA follows similar trend in conversion of heavy fraction into lighter fraction with increase of temperature but slight increase of C_{10}–C_{20} and C_{20}–C_{30} fraction was obtained over later catalyst at the studied temperatures.

3.4. *Kinetics of HDN and HDS of heavy gas oil*

The HDN and HDS reaction path can represented as shown below

$$\text{Nitrogen compound} \xrightarrow{k_N} \text{Hydrocarbon products} + NH_3 \quad (1)$$

Table 2
Effect of EDTA addition on hydrodenitrogenation and hydrodesulfurization of heavy gas oil

Temperature (°C)	N conversion (wt%)		S conversion (wt%)	
	CoMo(3.0)	CoMo–EDTA(3.0)	CoMo(3.0)	CoMo–EDTA(3.0)
370	46.1	53.6	93.5	96.8
380	55.5	62.0	95.9	97.2
390	62.9	68.8	97.6	97.5
400	71.5	76.7	98.0	98.4

$$\text{Sulfur compound} \xrightarrow{k_S} \text{Hydrocarbon products} + H_2S \tag{2}$$

Applying the power law model

$$-r_n = dN/dt = k_N\ N^n$$

$$-r_s = dS/dt = k_S\ S^n$$

where r_n and r_s are the rate of the HDN and HDS respectively, k_N and k_S are the apparent reaction rate constants for HDN and HDS, N and S are the respective concentration of N and S in wt% and n is order.

Based on previous studies [29], it is assumed that HDS follows 1.5th order kinetics and that HDN follow first-order kinetics.

Then the following rate equations can be used for calculating apparent rate constants

$$k_N = \frac{N_p}{N_f} e^{(-k/\text{LHSV})} \quad \text{for} \quad n = 1$$

$$k_S = \frac{\text{LHSV}}{(n-1)}(1/S_p^{1-n} - 1/S_f^{1-n} \quad \text{for} \quad n = 1.5$$

where N_f is nitrogen concentration of the feed, S_f is sulfur concentration of the feed, N_p is nitrogen concentration of the product, S_p is sulfur concentration of the product and LHSV is liquid hourly space velocity.

The apparent rate constants k_N and k_S at different temperatures are given in Table 4. It can be seen that CoMo–EDTA catalyst gives higher k_N and k_S values than that of CoMo catalyst, which confirms the better HDN and HDS activity exhibited by former catalyst. The maximum of 24.2% increase in the apparent rate constant for HDN of heavy gas oil was obtained at 400 °C over CoMo–EDTA(3.0) catalyst, whereas 36% increase in apparent rate constant for HDN of DMA was observed over CoMo–EDTA(3.0) catalyst. The CoMo–EDTA catalyst has high HDN activity for model compound (DMA) compared with heavy gas oil. The heavy gas oil contains 3072 ppm of nitrogen inform of heterocyclic and non-heterocyclic and they are more complex in structure and more difficult to denitrogenate. The heavy gas oil contains fractions with boiling range from 206 to 636 °C. As the boiling point of the feed increases, not only the nitrogen contents increase much faster, but also the size of molecules of these nitrogen-containing compounds increases, which reduces their accessibility to the catalyst surface. Hence less HDN activity was obtained for heavy gas oil compared with model compound (DMA).

Table 3
Hydrocarbons distribution (wt%) of hydrotreated heavy gas oil over (a) CoMo(3.0) and (b) CoMo–EDTA(3.0) catalysts at various temperatures, $P = 8.8$ MPa, LHSV $= 1\ h^{-1}$ hydrogen to oil ratio = 600 mL/mL

Temperature (°C)	C_{10}–C_{20}	C_{20}–C_{30}	C_{30}–C_{40}	C_{40}–C_{50}	C_{50}–C_{60}
CoMo(3.0)					
Feed	18.6	39.4	27.7	8.0	6.3
370	29.3	43.8	20.7	5.2	1.0
380	31.6	44.3	19.4	3.7	1.0
390	35.2	41.4	17.8	4.8	0.8
400	41.0	40.2	15.2	3.6	0
CoMo–EDTA(3.0)					
370	31.8	44.5	18.4	4.3	1
380	34.4	43.6	17.0	4.0	1
390	38.7	41.5	16.8	3.0	0
400	42.5	41.0	13.5	3.0	0

Apparent activation energy with both catalysts was calculated by plotting the inverse of absolute temperatures against the logarithm of apparent kinetic constant according to the Arrhenius equation (figure 6). Apparent activation energy of 83.4 and 75.6 kJ/mol for HDN and 88.5 and 55.6 kJ/mol for HDS were obtained over CoMo (3.0) and CoMo–EDTA (3.0) catalysts, respectively. This shows that EDTA addition lowers the activation energy by 7.8 and 32.9 kJ/mol, respectively for HDN and HDS reactions. The FT-IR spectra of CO adsorption (figure 1) on Mo and Mo–EDTA catalysts showed that EDTA addition not only promotes the CoMoS sites, but also increases the number of CUS located on molybdenum. It is evident from the increase of intensity of band at 2110 cm^{-1}. Further HDN of DMA over Mo and Mo–EDTA catalysts showed that increase of denitrogenation $(k_1 + k_2)$ activity on Mo catalyst by EDTA without Co. These studies suggest that EDTA prepared catalysts have different active sites than that of non EDTA catalysts. The difference in active sites of EDTA added catalysts lead to reduction in activation energies of HDN and HDS of heavy gas oil.

4. Conclusions

CoMo-sulfide catalysts supported on alumina are prepared in the absence and in the presence of the chelating ligand,EDTA. FT-IR of adsorbed CO indicated that the catalysts prepared using EDTA have much more dispersive and exposed Co sites than the conventional one. On EDTA addition to CoMo(3.0) catalyst, the apparent rate constant for HDN of heavy gas oil derived from Athabasca bitumen at 400 °C increased by

Table 4

Apparent kinetic parameters for hydrodenitrogenation and hydrodesulfurization of heavy gas oil at 8.8 Mpa, LHSV of 1 h^{-1} and hydrogen to oil ratio of 600 mL/mL

Temperature (°C)	k_N (h^{-1})		k_S (h^{-1} wt% $^{-0.5}$)	
	CoMo (3.0)	CoMo–EDTA(3.0)	CoMo (3.0)	CoMo–EDTA(3.0)
370	0.62	0.77	2.91	4.36
380	0.81	0.97	3.95	4.91
390	0.99	1.16	5.05	5.87
400	1.25	1.46	6.07	6.88

24.2%, and 36% for DMA at 300 °C. HDN of 2,6-dimethylaniline and HDN and HDS of heavy gas oil showed that EDTA addition have beneficial effect on the catalytic activity of CoMo catalyst supported on Al_2O_3.

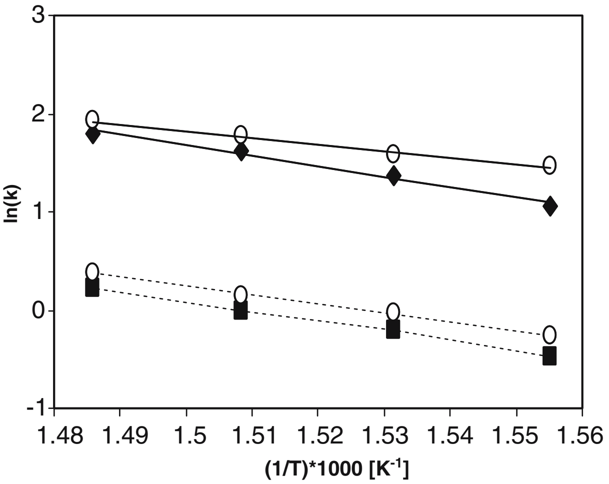

Figure 6. Arrhenius plots of rate data for the HDN and HDS of heavy gas oil. $P = 8.8$ MPa, LHSV $= 1$ h^{-1} and hydrogen to oil ratio $= 600$ mL/mL, HDS (solid lines), HDN (dashed lines), (■) – CoMo(3.0) and (○) – CoMo–EDTA (3.0).

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