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MCM-41-supported Co-Mo catalysts for deep hydrodesulfurization of light cycle oil

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Abstract

Light cycle oil (LCO), a by-product of the fluid catalytic cracking (FCC) process in a petroleum refinery, can be used as a blendstock for the production of diesel and jet fuels. Regulatory and operational issues result in need for new and more active catalysts for the deep hydrodesulfurization (HDS) of diesel feedstocks, such as LCO. This paper reports the activity of a mesoporous molecular sieve MCM-41-supported Co-Mo catalyst in comparison to a commercial γ-alumina (Al_2O_3)-supported Co-Mo catalyst for the desulfurization of a LCO with a sulfur content of 2.19 wt.%. The HDS of dibenzothiophene, 4-methyldibenzothiophene, and 4,6-dimethyldibenzothiophene—polyaromatic sulfur compounds present in LCO—and their relative reactivities in terms of conversion were examined as a function of time on stream in a fixed-bed flow reactor. The MCM-41-supported catalyst demonstrates consistently higher activity for the HDS of the refractory dibenzothiophenic sulfur compounds, particularly 4,6-dimethyldibenzothiophene. The presence of a large concentration of aromatics in LCO appears to inhibit the HDS of the substituted dibenzothiophenes.

Keywords: MCM-41; Catalyst; Desulfurization; Dimethyldibenzothiophene; Fuel; Diesel fuel; Light cycle oil

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1. Introduction

Light cycle oil (LCO) is a by-product of the fluid catalytic cracking process (FCC) in a petroleum refinery. The FCC process enhances gasoline production and the increasing demand for gasoline translates into increased production of LCO. Traditionally, LCO has been used as a blendstock for home heating oil, industrial fuel oil, and diesel fuels. However, the increasing spread of natural gas in recent times for, both, heating homes and producing power has reduced demand for fuel oil and, therefore, LCO [1]. Simultaneously, diesel demand is outpacing that of other transportation fuels [2]. Therefore, refiners are now increasingly using more LCO as a blendstock for the diesel pool.

Even as more of LCO is used to produce diesel, the United States (US) Environmental Protection Agency (EPA) has mandated that automotive diesel fuels have no more than 15 parts per million by weight (wppm) of sulfur by 2006 [3]. LCO has a low cetane index (typically 15–20), sulfur content as high as 3 wt.%, and 50–80 wt.% aromatics [4]. Besides its high sulfur content, the HDS of LCO is further complicated because its sulfur is distributed in the form of highly refractory dibenzothiophenes [5]. Its use in the diesel pool, therefore, requires extensive hydrotreating to meet existing diesel fuel combustion and environmental specifications. Further, the hydrodesulfurization (HDS) of

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LCO will become particularly important in the wake of new processes, such as selective ring opening (SRO) of naphthenes to make premium, high cetane diesel [6]. Current SRO catalysts, such as iridium-based, are highly sensitive to sulfur and the use of LCO as a feedstock for the SRO process will have to be preceded by its deep hydrogenation and desulfurization.

While the increasing stringency of sulfur specifications has motivated intensive HDS research, there have been few studies on real feedstocks, such as LCO. Most studies have relied on mixtures of model compounds to simulate real feedstocks [7–11]. Reports of HDS of real feedstocks have often used hydrotreated or low sulfur LCO [12–18] or feedstock blends with LCO as one of the components [19,20]. The few studies on typical, high-sulfur content LCO had different objectives. For example, Vanrysselberghe and Froment [21] used the HDS of LCO to develop a method to model the kinetics of individual sulfur compounds, while Shih et al. [22] carried out similar experiments to determine reactor temperatures to produce diesel with 500 wppm sulfur. Thus, there is little literature on the HDS of LCO notwithstanding the need for highly active catalysts for the same.

Light cycle oil could also be used to produce advanced thermally stable jet fuel JP-900 on the basis of on-going studies at the Pennsylvania State University. For example, Andrésen et al. [23] have shown that dearomatized, hydrotreated light cycle oil is more thermally stable than a petroleum-derived JP-8 jet fuel at high temperatures above 400 °C. Therefore, should LCO be used for the production of JP-900 jet fuel, it will have to be severely hydrotreated using new, highly active HDS and hydrogenation catalysts. While conventional HDS catalysts demonstrate good hydrogenation activities, noble metals will serve better because of their stronger hydrogenation functionalities. Further, conventional HDS catalysts are active only at high temperatures where hydrogenation becomes thermodynamically limited [24,25]. In contrast, noble metals show good hydrogenation activities at low temperatures. Noble metals, however, are extremely sensitive to sulfur and their use for hydrogenation will require prior removal of sulfur. Thus, even if conventional HDS catalysts are replaced by noble metals to produce JP-900 jet fuel from LCO, good HDS catalysts will be required to desulfurize LCO before being subjected to hydrogenation over noble metal-based catalysts.

MCM-41 is a mesoporous molecular sieve that is characterized by a hexagonal array of uniform mesopores, a narrow pore size distribution, and high surface area, sorption capacity, and thermal stability. It has distinct advantages as a catalytic support [26]. The mesopores of MCM-41 will, perhaps, facilitate easy diffusion of catalyst precursors and polyaromatic sulfur compounds (PASCs) during HDS reactions. Further, MCM-41, with its moderate and tailorable acidity when properly synthesized [27], could isomerize refractory PASCs, such as 4,6-dimethyldibenzothiophene (4,6-DMDBT) to the more reactive variants, such as 2,8- or 3,7-DMDBT without causing cracking as reported in the case of certain zeolite-based HDS catalysts [28]. In a separate paper we have established the efficacy of aluminosilicate MCM-41 supported Co-Mo catalysts for the desulfurization of the model PASC 4,6-DMDBT [29].

2. Experimental

2.1. Catalyst synthesis

The MCM-41 support was synthesized with a SiO_2/Al_2O_3 ratio of 50 using a method based on our previous work [27] and the report by Cheng et al. [30]. The method uses sodium-free reagents because sodium has been found to result in MCM-41 material with poor hydrothermal stability [31]. Aluminum isopropoxide was used as the aluminum source. The dried MCM-41 samples were calcined in air flow of ca. 100 ml/min at 550 °C for 5 h using a temperature-programmable muffle furnace. The heating rate for the furnace was 1–5 °C/min. The acidic form of MCM-41 was obtained by ion-exchange with ammonium nitrate (Aldrich, >98%) solution. The ion-exchanged sample was filtered and washed with copious amounts of deionized water and air dried at 60 °C overnight. The proton (H^+)-form was obtained by calcining the dried, ion-exchanged sample in flowing air at 480 °C for 3 h in a temperature-programmable muffle furnace. The muffle furnace was ramped from room temperature to the final calcination temperature at the rate of 1–5 °C/min. The final catalyst, with 27.0% molybdenum oxide (MoO_3) and 5.8% cobalt oxide (CoO) loadings, were prepared via wet co-impregnation of ammonium heptamolybdate (Aldrich, 99.98%) and cobalt nitrate hexahydrate (Aldrich, >98%). The impregnated samples were dried at 60 °C overnight and calcined in air at 500 °C for 3 h.

The activity of the MCM-41-supported catalyst was evaluated in comparison to a Co-Mo/γ-Al_2O_3 commercial catalyst supplied by Criterion Catalyst Corporation, Houston, TX. This catalyst is referred to in this study by its trade name, C-344. A typical catalyst evaluation experiment used 1 g of the catalyst. All catalysts evaluated in the flow reactor were particles of 0.5–1.0 mm in diameter. The commercial catalyst was supplied as trilobe-shaped extrudates. So the commercial catalyst samples were crushed and sieved using sieves of mesh sizes 18 and 35 (0.5–1.0 mm). In the case of the MCM-41-supported catalysts, the final catalyst was in powder form. Therefore, the MCM-41-supported catalyst was first pressed into pellets which were then crushed and sieved to particles of 0.5–1.0 mm diameter. Five percent by catalyst weight of γ-Al_2O_3 was used as a binder for pellet preparation.

2.2. Catalyst characterization

2.2.1. X-ray diffraction

The aluminosilicate MCM-41 was characterized using powder X-ray diffraction (XRD) on a Philips X'Pert powder diffractometer system with Cu Kα radiation (40 kV, 40 mA). Typically, the diffractograms were obtained from 0.5 to 10° 2θ with a step size of 0.02°. For some samples, the diffractograms were obtained from 4.0 to 80° 2θ with a step size of 0.2°. The count time was 1 s over each step.

2.2.2. Adsorption–desorption isotherms of nitrogen

The physical properties of the calcined and the impregnated MCM-41 samples were evaluated using the adsorption–desorption isotherms of nitrogen. The isotherms were obtained on a volumetric adsorption unit (Autosorb 1, Quantachrome Instruments). Nitrogen adsorption/desorption isotherms were measured at liquid nitrogen temperature of −196 °C after degassing the samples below 1.32×10^{-6} atm at 200 °C for 4 h. The Brunauer–Emmet–Teller (BET) specific surface area was estimated using adsorption data in the relative pressure range of 0.05–0.2. The mesopore size distribution was obtained by analyzing the adsorption data of the nitrogen isotherm using the Kruk–Jaroniec–Sayari (KJS) method [32].

2.3. Catalyst evaluation

All catalysts were evaluated in a laboratory-scale fixed-bed flow reactor. Fig. 1 provides a schematic of the high-pressure and high-temperature continuous flow reactor fabricated and used in this study. The stainless steel 316 reactor tube was custom designed and is about 61 cm (24 in.) in length, has an internal diameter of approximately 0.94 cm (0.37 in.), and has a wall thickness of approximately 0.17 cm (0.065 in.). It is housed in a tubular electric furnace (Applied Test Systems, Series 3210) capable of heating up to 900 °C. An Isco high-pressure syringe pump (Series 500D) was used to measure and pump the liquid feedstock into the reactor against hydrogen pressure. During operation, the pump's liquid storage cylinder was kept at a constant temperature of 60 °C using a heating tape. This led to better control and reliability with the fuel flow rates. A Brooks mass flow controller (5850TR) calibrated for 0–100 ml/min was used to measure and control hydrogen gas flow. A Tescom backpressure regulator was used to maintain the overall system pressure required for deep desulfurization. The reactor pressure was measured using a Coopers Instruments pressure transducer (PTG 135) equipped with an electronic read-out panel. Another independent measurement of the reactor pressure was obtained from the pressure transducer in the Isco liquid pump. An in-house gas–liquid separator was designed and fabricated to separate the reaction products into gas and liquid phases. The gaseous reactor effluents were not analyzed and bubbled through a basic scrubber solution before being vented out. Temperature in the reactor was monitored and maintained using three K-type Omega thermocouples. The first was used to control the temperature of the tubular furnace. The second is a 1/16 in. stainless steel thermocouple connected to the reactor tube such that its tip is always at the center of the catalyst bed. The third is a bare wire thermocouple placed on the outer wall of the reactor tube. All temperature measurements reported in this study refer to the temperature measured by the second thermocouple, i.e. the thermocouple at the center of the catalyst bed.

Silicon carbide of particle diameter 0.177 mm was used to enclose the catalyst bed at both ends in the reactor. While catalyst particles of 0.5–1.0 mm diameter were shown to have minimal mass transfer

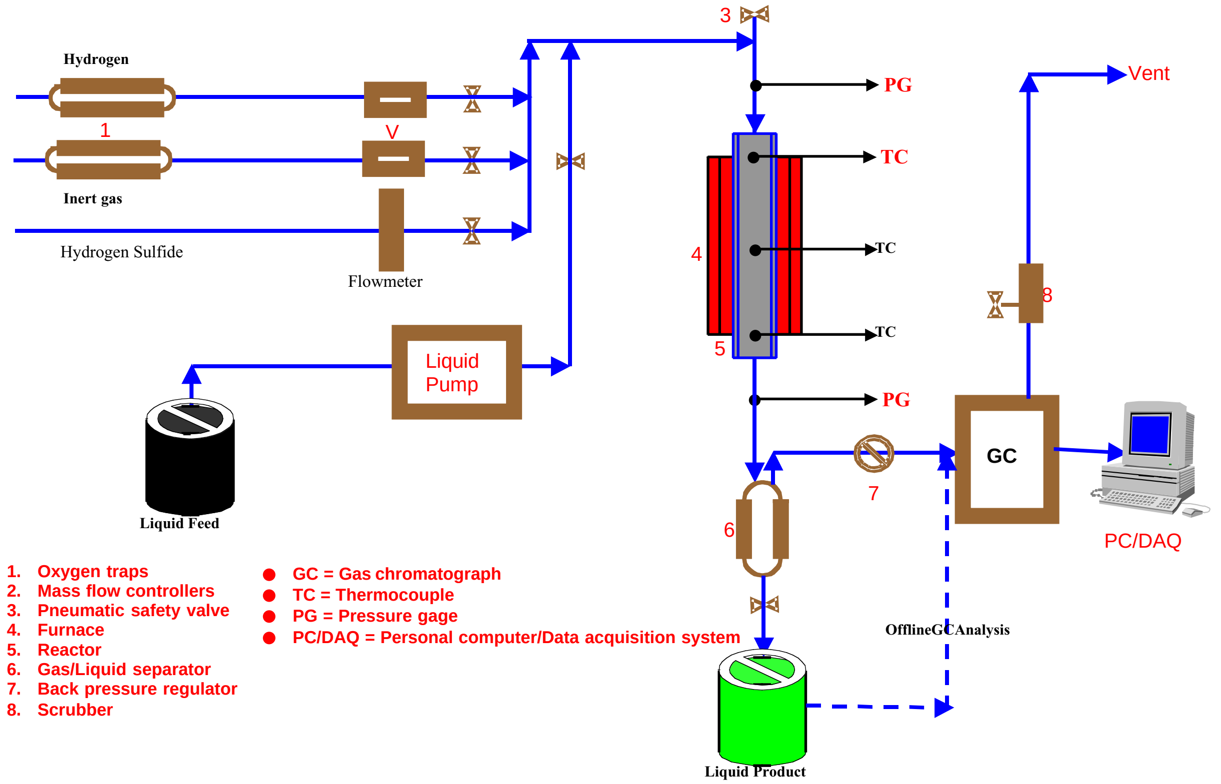

Fig. 1. Schematic of flow reactor used in this study.

limitations, Sie (1996) and Bej et al. (2000) have shown that when catalyst particles are sandwiched between smaller particles of an inert material, it could be assumed that the effective catalyst particle diameter is that of the smaller material. Sie (1996) has explained the importance of the aspect ratio and axial convective diffusion parameters for acceptable evaluation of hydroprocessing catalysts. Table 1 presents the minimum values for these parameters recommended by Sie (1996). The aspect ratio and axial convective diffusion parameters for the catalyst particles used in this study (also featured in Table 1) exceed the minimum recommended values by 3 and 20 times, respectively. It is clear from Table 1 that the present study has used acceptable catalyst evaluation conditions.

The catalyst evaluation conditions used in this work are summarized in Table 2. All catalysts were sulfided

Table 1
Catalyst evaluation parameters

Parameter	Aspect ratio (reactor internal diameter/catalyst particle diameter)	Axial convective diffusion parameter (reactor length/catalyst particle diameter)
Minimum	25.0	50
This study	80.3	1111

Table 2
Flow reactor experimental conditions

Catalyst sulfidation	
Temperature (°C)	350
10% H_2S in H_2 (vol.%) flow rate (ml/min)	200
Time (h)	4
Deep HDS reaction	
Temperature (°C)	300
Pressure (psi)	660
Weight hourly space velocity (h^{-1})	4
Hydrogen/hydrocarbon (ml/ml)	300
Catalyst particle size (mm)	0.5–1.0 (18–35 mesh)
Catalyst weight (g)	1

Table 3
Key properties of LCO sample

Sulfur content (wt.%)	2.19
API	10.2
Cetane index	17.6
ASTM distillation (°C)	
Initial boiling point	217.1
5%	246.6
50%	271.1
95%	325.9
Final boiling point	340.0

in situ at uniform conditions. The catalysts were evaluated for HDS activity over a period of 16–20 h and the reactor effluents were collected at regular intervals. The LCO sample (sample number LCO 2PM), produced in a fluid catalytic cracker, was obtained from United Refining Company, Warren, PA. Table 3 describes the key properties of the LCO sample used in this study.

The liquid reaction products were characterized using Hewlett-Packard 5890 Series II gas chromatograph coupled with a Hewlett-Packard 5971A quadrupole mass spectrometer (MS) detector operating in electron impact (70 eV) mode. A 30 m × 0.25 mm, slightly polar Restek XTI-5 column coated with 5% phenyl–95% methyl polysiloxane was used in the gas chromatograph. The column was heated from 40 to 290 °C at a heating rate of 6 °C/min. The MS was turned off for ∼3 min during elution time to prevent high intensity detection of the dissolution solvent. The sulfur species of interest were identified on the basis of retention times obtained using model compounds. The concentration of various components in the product stream was determined using the following equation:

$$C_s = \frac{1}{\mathrm{RF}_s} C_{\mathrm{std}} \frac{A_s}{A_{\mathrm{std}}}$$

where C_s is the concentration of the PASC, RF_s the response factor for the PASC, C_{std} the concentration of the internal standard, A_s the peak area of the PASC, and A_{std} the peak area of the internal standard.

3. Results and discussion

The catalysts used in this study were characterized for textural properties, such as surface area, pore volume, and pore size distribution using adsorption–desorption isotherms of nitrogen. These and other physicochemical properties are summarized in Table 4. The BET specific surface area (S_{BET}) was estimated using nitrogen adsorption data in the relative pressure range of 0.05–0.2. The total pore volume (V_T) was estimated from the amount adsorbed at a relative pressure of 0.90. The external surface area (S_{EXT}), total surface area (S_T), primary mesopore surface area (S_P), and primary mesopore volume (V_P) were estimated by the α_s-plot method [33]. The properties for the commercial catalyst used in this study were obtained from literature provided by Criterion Catalyst Corporation.

All the MCM-41 samples were characterized using XRD. Fig. 2 presents the X-ray diffractograms of the MCM-41 samples at different stages of catalyst preparation. Fig. 2a shows the XRD pattern characteristic of the hexagonal phase of MCM-41 recorded after normal synthesis and calcination. In addition to the most intense low-angle diffraction peak of (1 0 0) at 2.2° 2θ, higher order reflections, such as (1 1 0) and (2 0 0) are also visible indicating the sample's highly ordered and superior quality. Fig. 2b is a diffractogram of the ion-exchanged and calcined proton-form of MCM-41. While the higher order reflections are weak, the sample continues to be fairly ordered, as indicated by the high relative intensity of the low-angle diffraction peak. The MCM-41 sample upon ion-exchange and

Table 4
Textural properties of catalysts used in this study

Sample	S_{BET} (m^2/g)	S_T (m^2/g)	S_{EXT} (m^2/g)	S_M (m^2/g)	V_T (cm^3/g)	V_P (cm^3/g)	Pore diameter$_{\mathrm{KJS}}$ (Å)
H^+-MCM-41 (50)	812	832	231	601	0.85	0.52	35
CoO-MoO_3/MCM-41 (50)	564	582	175	407	0.56	0.31	32
Spent Co-MoS_2/MCM-41 (50)	440	428	125	303	0.43	0.22	26
Co-MoO_3/γ-Al_2O_3 (C-344)	190				0.56		

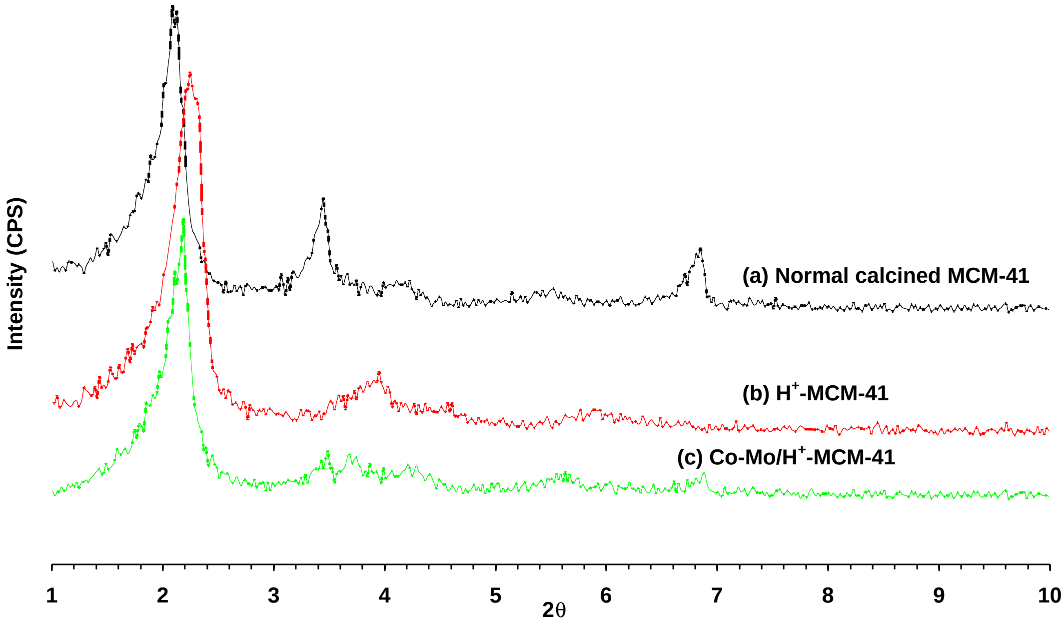

Fig. 2. X-ray diffractograms of MCM-41-samples at different stages of synthesis.

wet co-impregnation of CoO and MoO_3 continues to retain most of its crystallinity, as shown in the X-ray diffractogram presented in Fig. 2c.

Fig. 3 shows the pore size distributions of the MCM-41-supported catalysts before and after use for HDS. The uniform and narrow pore size distributions of the fresh and spent catalysts support the XRD results and provide independent verification of retention of pore structure after both impregnation of the oxidic metal precursors and use as a catalyst. This is

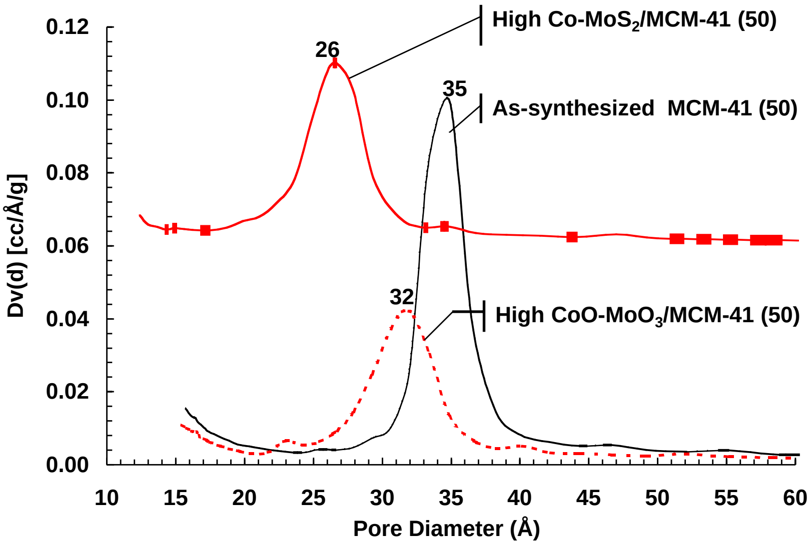

Fig. 3. Pore size distribution of the MCM-41-supported catalysts used in this study.

important for MCM-41-supported catalysts because a few papers have reported pore blockage and collapse following impregnation of the metal oxides. Yue et al. [34] and Cui et al. [35] have, in particular, attributed the low HDS activity of their MCM-41-supported catalysts to pore blockage caused during catalyst preparation. Landau et al. [36], while reporting a new method to synthesize MCM-41-supported HDS catalysts, found it difficult to load more than 5% of MoO_3 without significant pore blockage. The XRD and pore size distribution results presented here suggest that such problems have not been encountered in this study. It should be noted from Fig. 3 that the pore size distribution curves are for three different cases, the first one is for the support MCM-41 with SiO_2/Al_2O_3 molar ratio of 50 possessing a median pore diameter of 35 Å, the second for the support with loaded Co–Mo oxide with a pore diameter of 32 Å, and the third is for the sulfided Co-Mo/MCM-41 that has been used in the HDS. Therefore, the results in Fig. 3 do not represent pore plugging. There appears to be a pore diameter shift to smaller diameter upon sulfidation of Co-Mo/MCCM-41.

The LCO feed sample used in this study was of a particularly poor quality. Table 3 describes the feedstock's key properties. Like a typical LCO sample, the feedstock used in this study has a low cetane index of 17.6, poor density (API gravity of 10.2), and bulk sulfur content of 2.19%. Table 5 presents the feedstock's distribution of sulfur between DBT, 4-MDBT, and 4,6-DMDBT. The other dominant sulfur species, benzothiophenes (BTs) and naphthothiophenes, were not analyzed quantitatively since their desulfurization is relatively easier as compared to that of the dibenzothiophenes.

Table 5
Dibenzothiophenic sulfur distribution

Sulfur species	Parts per million by weight	Total sulfur (%)
Total sulfur in LCO	21900	100.0
Dibenzothiophene	2625	11.9
Methyldibenzothiophenes	3518	16.0
4-Methyldibenzothiophene	1951	9.0
Dimethyldibenzothiophenes	3317	15.1
4,6-Dimethyldibenzothiophene	775	3.5
Total dibenzothiophenic sulfur	9460	43.2

Table 6
Distribution of different sulfur compound classes in LCO (adapted from [5])

No.	Type of sulfur compound[a]	Sulfur (%)
1	C_0-benzothiophene (BT)	1.5
2	C_1-BT	10.2
3	C_2-BT	19.1
4	C_3-BT	16.2
5	C_{4+}-BT	13.1
6	C_0-DBT	3.3
7	C_1-DBT	12.5
8	C_2-DBT	11.8
9	C_{3+}-DBT	12.4

[a] The prefix C_x stands for substituents on the parent sulfur compound with x indicating the number thereof.

The bulk of the sulfur in the LCO sample is distributed amongst benzothiophenes and dibenzothiophenes. The dibenzothiophenic sulfur constitutes 43.2% of the total sulfur. This compares well with the estimate of Depauw and Froment [5] who carried out a detailed molecular analysis of the sulfur components in an LCO sample using GC-AED to conclude that 40% of the feedstock's sulfur was present in the form of highly refractory dibenzothiophenes. The results of Depauw and Froment are summarized in Table 6.

Fig. 4 presents the conversion of various types of dibenzothiophenes in LCO over C-344 and Co-Mo/MCM-41 (50). For the HDS of dibenzothiophenic sulfur in LCO, the activity of MCM-41-supported catalysts is consistently higher than that of the commercial catalyst. More significantly, the MCM-41-supported catalyst continues to be twice more active than the commercial catalyst for the HDS of 4-MDBT and 4,6-DMDBT in LCO. The higher activity of the MCM-41-supported catalyst for the HDS of 4-MDBT and 4,6-DMDBT is remarkable because LCO has a high concentration of mono and diaromatics both of which are strong inhibitors of conventional HDS catalysts [37,38].

Organic sulfur compounds, including polyaromatic sulfur compounds, such as 4-MDBT and 4,6-DMDBT, are known to undergo desulfurization in one of two possible pathways. The first, often referred to as desulfurization or hydrogenolysis, relies on the chemisorption of the sulfur atom in the sulfur-containing molecule on to an exposed Mo ion at a sulfur vacancy through a one-point attachment. This is followed by hydrogen transfer and sulfur elimination

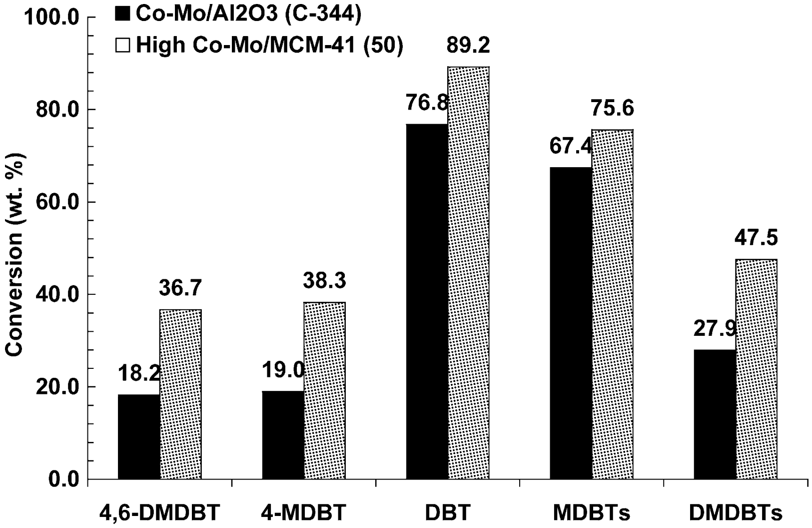

Fig. 4. HDS of various PASCs in LCO over sulfided Co-Mo/MCM-41 (50) and Co-Mo/Al_2O_3 (C-344) catalysts (temperature, 300 °C; hydrogen pressure, 45 atm; WHSV, 4 h^{-1}; hydrogen/hydrocarbon, 300 ml/ml; conversion data obtained after 4 h of time on stream).

to complete desulfurization [39]. Should a molecule of DBT undergo desulfurization through this route, it will typically form a biphenyl molecule. Thus, the presence of biphenyl molecules is often presented as evidence for the hydrogenolysis mechanism of HDS. Hydrogenolysis does not saturate the benzene rings in 4,6-DMDBT. Therefore, HDS catalysts promoting the hydrogen-efficient hydrogenolysis route to HDS are highly desirable.

The second dominant pathway for HDS on MoS_2 catalysts involves hydrogenated intermediates. Molybdenum sulfide has good activity for hydrogenation. It was, in fact, first used in the 1930s for the hydrogenation of coal-derived liquids [40]. In this case, DBT first adsorbs on to the MoS_2 stack through the π-electrons on the aromatic rings. This is followed by hydrogenation of one of the aromatic rings leading to tetrahydro- and hexahydro-dibenzothiophene (k_{HS1}), which is desulfurized to cyclohexylbenzene (k_{D1}). Cyclohexylbenzene is then hydrogenated to form bicyclohexyl (k_{HP2}). Cyclohexylbenzene and bicyclohexyl both provide evidence for the hydrogenation pathway over MoS_2 catalysts. These mechanistic pathways are described in Fig. 5. Conventional γ-Al_2O_3-supported hydrotreating catalysts typically desulfurize PASCs through the hydrogenation route. The HDS of 4,6-DMDBT over commercial catalyst Co-Mo/Al_2O_3 (C-344) used in this study is also speculated to prefer the hydrogenation pathway. In contrast, the MCM-41-supported catalyst with a SiO_2/Al_2O_3 ratio of 50 is proposed to desulfurize PASCs more through the hydrogenolysis route (compared to that with Co-Mo/Al_2O_3). Model compound studies on the C-344 and Co-Mo/MCM-41 catalysts conducted by the authors and reported elsewhere have provided strong support of their predominant reliance on the hydrogenation and hydrogenolysis pathways, respectively, to achieve HDS of PASCs, such as 4,6-DMDBT [29].

It is known that aromatics, diaromatics like naphthalene in particular, inhibit HDS catalysts by strong adsorption on active sites responsible for hydrogenation activity. It is, therefore, highly plausible that the polycyclic aromatics in LCO adsorb on the hydrogenation sites of the commercial catalyst and thereby diminish its activity for the HDS of 4,6-DMDBT. In contrast, aromatics cause little, if any, inhibition of the hydrogenolysis route. Therefore, the high activity of the MCM-41-supported catalyst for the HDS of 4-MDBT and 4,6-DMDBT in LCO is attributed to the different pathway preferences over each catalyst.

While the MCM-41-supported catalyst has distinct advantages for the HDS of the refractory PASCs, such as 4-MDBT and 4,6-DMDBT, it is only slightly

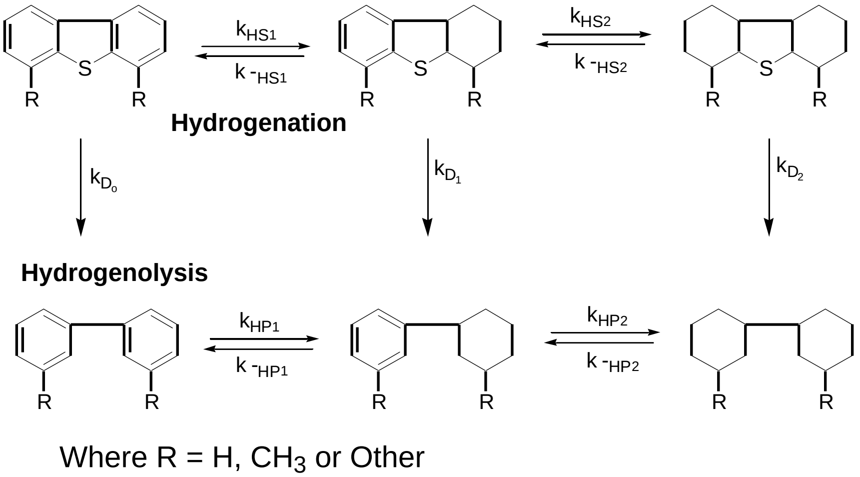

Fig. 5. Mechanistic pathways for desulfurization of PASCs over conventional HDS catalysts (adapted from [46]).

more active than the commercial catalyst for the HDS of the unsubstituted DBT and dibenzothiophenes with substituents at positions other than 4 and 6. This is in accordance with the reactivity patterns of PASCs elucidated by several researchers in literature [41–43].

The results featured in Fig. 4 suggest that a unique feature of the MCM-41-supported catalyst is its superiority over the commercial catalyst for the HDS of the refractory forms of sulfur, e.g. 4-MDBT and 4,6-DMDBT. While acidity does significantly improve hydrogenolysis activity, it alone cannot explain the MCM-41-supported catalyst's specific superiority for the HDS of 4-MDBT and 4,6-DMDBT in the highly aromatic LCO. Instead, it is possible that the MCM-41-supported catalysts result in an active phase that has superior intrinsic activity for HDS as compared to commercial catalysts. This suggestion of a more active phase derives partial support from FTIR spectroscopy of chemisorbed NO, which has shown that the MCM-41-supported catalysts have more surface Co than γ-Al_2O_3-supported catalysts at constant or similar dispersions of MoS_2 [44].

While the MCM-41-supported catalyst has distinct advantages, both catalysts have reduced absolute activities for the HDS of PASCs in LCO in sharp contrast to their respective activities for the HDS of the pure PASCs. This is suggestive of the global inhibition of the catalysts by aromatics and other non-sulfur components in LCO. Light cycle oil, typically, contains 50–80% aromatics with diaromatics content being 30–50% [4]. 4-Methyldibenzothiophene and 4,6-DMDBT undergo desulfurization predominantly through the hydrogenation pathway. Furthermore, hydrogenation active sites are severely inhibited by aromatic compounds, such as naphthalene.

In the literature, there is a well-established reactivity pattern amongst DBT, 4-MDBT, and 4,6-DMDBT [41]. The difficulty of desulfurizing these PASCs increases with the number of methyl substituents at the 4 and 6 positions. While the HDS of PASCs in LCO follows this reactivity pattern for DBT and its substituted derivatives. The conversion of 4-MDBT is slightly higher than that of 4,6-DMDBT, but there is no major difference in the conversion between 4-MDBT and 4,6-DMDBT under the conditions used. This is attributed to the high aromatic content and trace amounts nitrogen compounds of LCO which strongly influence the HDS of PASCs and thus, prevents a clear elucidation of these reactivity differences. Similar lack of clear differences in the reactivity of the substituted dibenzothiophenes has also been observed in the HDS of other real feedstocks, such as light and heavy gas oils [17,18]. It should be mentioned that the observed conversion for 4-MDBT with Co-Mo/MCM-41 catalyst is the net outcome from the conversion of 4-MDBT and the formation of 4-MDBT from related dimethyl DBTs, such as 4,6-DMDBT if

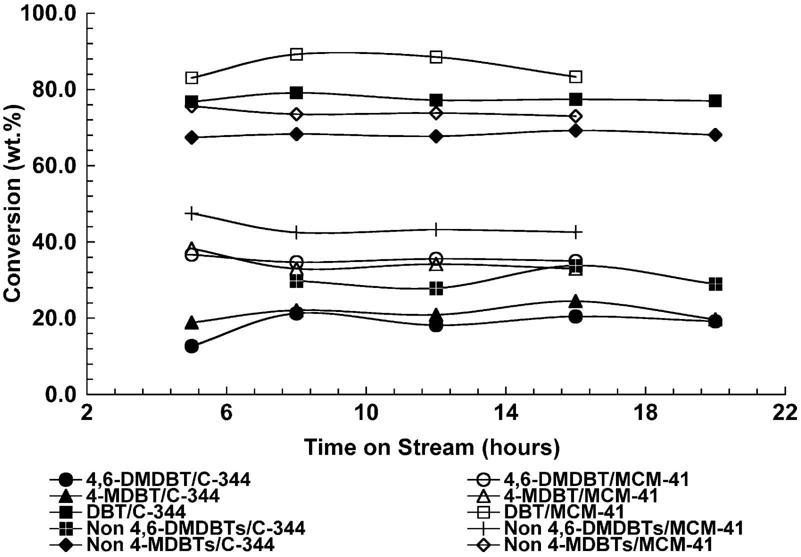

Fig. 6. Time on stream profiles for the HDS of various PASCs in LCO over sulfided Co-Mo/MCM-41 (50) and Co-Mo/Al_2O_3 (C-344) catalysts (temperature, 300 °C; hydrogen pressure, 45 atm; WHSV, 4 h^{-1}; hydrogen/hydrocarbon, 300 ml/ml).

dealkylation is involved, which cannot be completely ruled out.

The time on stream profiles for the HDS of LCO over both catalysts are presented in Fig. 6. Both catalysts attain steady-state activity in about four hours. The MCM-41-supported catalyst demonstrates good steady-state activity for as long as 20 h as shown in Fig. 5. The periods for which time on stream data were obtained during this project are insufficient to evaluate catalyst life and stability. Nevertheless, the time periods are similar to those reported in literature during which substantial changes in the activity of acidic catalysts has been observed. For example, Kostova et al. [45] report that MoS_2 supported on acidic hexagonal mesoporous silica (HMS) deactivates in <2 h for the conversion of thiophene. Finally, it should be mentioned that now there are new HDS catalysts commercialized recently [44] that are more active than the commercial C-344 catalysts used in this work.

4. Conclusions

This study has sought to examine the potential of MCM-41-supported catalysts for the HDS of real feedstocks, such as LCO. MCM-41 represents a new class of inorganic materials with distinct properties, such as high surface area, uniform mesopores, and moderate acidity. It was, therefore, hypothesized to have high relevance and potential for use as a support for more active hydrotreating catalysts whose development is demanded by new environmental regulations. The HDS of LCO was comparatively studied over commercial γ-Al_2O_3- and MCM-41-supported Co-Mo sulfide catalysts. The HDS of DBT, 4-MDBT, and 4,6-DMDBT—PASCs present in LCO—and their relative reactivity in terms of conversion were examined as a function of time on stream. The MCM-41-supported catalyst demonstrates consistently higher activity for the HDS of the refractory dibenzothiophenic sulfur compounds. Through comparative examination, the presence of aromatics in LCO appears to inhibit the HDS of the substituted DBTs. The findings of this work validate this project's hypothesis that mesoporous aluminosilicate molecular sieve MCM-41 with its high surface area, uniform mesopores, and moderate acidity is a promising support for exploring new hydroprocessing catalysts. These results, coupled with the intrinsically desirable structural features of MCM-41, warrant further study of MCM-41 supported hydroprocessing catalysts in the future.

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