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Catalysis Today 43 (1998) 261–272

CATALYSIS TODAY

Mesoporous molecular sieve MCM-41 supported Co–Mo catalyst for hydrodesulfurization of petroleum resids

Kondam Madhusudan Reddy, Boli Wei, Chunshan Song*

Fuel Science Program and Laboratory for Hydrocarbon Process Chemistry, Department of Materials Science and Engineering, The Pennsylvania State University, 209 Academic Projects Building, University Park, PA 16802, USA

Abstract

In this work, we explored the potential of mesoporous zeolite-supported Co–Mo catalyst for hydrodesulfurization of petroleum resids, atmospheric and vacuum resids at 350–450°C under 6.9 MPa of H_2 pressure. A mesoporous molecular sieve of MCM-41 type was synthesized; which has SiO_2/Al_2O_3 ratio of about 41. MCM-41 supported Co–Mo catalyst was prepared by co-impregnation of $Co(NO_3)_2{\cdot}6H_2O$ and $(NH_4)_6Mo_7O_{24}$ followed by calcination and sulfidation. Commercial Al_2O_3 supported Co–Mo (criterion 344TL) and dispersed ammonium tetrathiomolybdate (ATTM) were also tested for comparison purposes. The results indicated that Co–Mo/MCM-41(H) is active for HDS, but is not as good as commercial Co–Mo/Al_2O_3 for desulfurization of petroleum resids. It appears that the pore size of the synthesized MCM-41 (28 Å) is not large enough to convert large-sized molecules such as asphaltene present in the petroleum resids. Removing asphaltene from the resid prior to HDS has been found to improve the catalytic activity of Co–Mo/MCM-41(H). The use of ATTM is not as effective as that of Co–Mo catalysts, but is better for conversions of >540°C fraction as compared to noncatalytic runs at 400–450°C.

Keywords: Hydrodesulfurization; Petroleum resid; Dibenzothiophene; Co–Mo; MCM-41

1. Introduction

With growing worldwide demand for petroleum products, considerable attention has been paid to upgrading heavy and residual oils to middle distillates [1]. It has been a challenge to process petroleum resids because of the large sizes and structural complexity of the resid molecules, their high boiling point range, and their high contents of sulfur, nitrogen and metals. At the same time, it has become clear that crude oils in many existing reserves are heavier and higher in sulfur contents than those already recovered [2]. As a consequence, there is a growing interest in research and development for converting heavy feedstocks (petroleum resids and heavy oils) into lower boiling products of high quality with a low sulfur content. Worldwide, the sulfur contents of light oils were recently limited to 500 ppm in the EEC starting in 1996 and in Japan starting in 1997 [3]. It is expected that further reduction in both the sulfur and aromatics contents of distillate fuels will be required by regulations in the near future [3,4]. Therefore, hydrodesulfurization (HDS) of heavy petroleum feedstocks to produce distillate fuels, particularly diesel fuels and gasoline (either directly or via subsequent fluid catalytic cracking) has become an important research subject.

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*Corresponding author. Tel.: +1 814 8634466; fax: +1 814 8653075; e-mail: csong@psu.edu

PII S0920-5861(98)00155-2

Earlier research has shown that certain sulfur compounds are easier to convert and the reactivities of the 1- to 3-ring sulfur compounds decrease in the order of thiophenes>benzothiophenes>dibenzothiophenes [5,6]. It was also shown that under mild conditions, conventional catalysts are not effective for converting bulky organo-sulfur compounds, particularly 4-methyl and 4,6-dimethyl substituted benzothiophenes [4,6]. Hence, it has become necessary to explore catalysts for converting bulky sulfur compounds in order to produce environmentally friendly transportation fuels.

We are exploring new mesoporous molecular sieve (MCM-41)-supported catalysts for HDS and hydrogenation of liquid fuels [7–9]. Mesoporous molecular sieves of MCM-41 type possessing a hexagonal array of uniform mesopores were recently invented by Mobil scientists [10,11]. We have synthesized mesoporous aluminosilicates with MCM-41 type structure using four different aluminum sources [12–14], and are currently exploring their applications for catalytic fuel processing including HDS [7], hydrogenation [8,15], and hydrocracking [14]. We expect that for HDS of distillate fuels, the uniform pores of MCM-41 type molecular sieve (mesopores, about 30 Å in diameter) can facilitate the diffusion of polycyclic sulfur compounds and the transition metal sulfides serve as HDS and hydrogenating components. The high surface areas of the molecular sieves may lead to high dispersion of active metals and high catalytic activity per unit mass of catalyst.

In this paper we present the preliminary results on upgrading of two petroleum resids over MCM-41 supported Co–Mo catalyst at high metal loading. The catalyst performance is evaluated with regard to the removal of sulfur and the conversion of the resids to materials with boiling points below 540°C. For comparison purposes, upgrading was also carried out over a commercial supported Co–Mo/Al_2O_3 (criterion 344TL) catalyst and dispersed ammonium tetrathiomolybdate (ATTM). ATTM was used as a catalyst precursor, decomposing under reaction conditions to form an unsupported (dispersed) MoS_2 catalyst.

2. Experimental

A mesoporous aluminosilicate molecular sieve with MCM-41 type structure was synthesized by hydrothermal crystallization of a gel with the following molar composition: 50 SiO_2–Al_2O_3-8.64 Na_2O-4.38 $(TAM)_2O$-31.24 CTMABr-6330 H_2O. The gel was prepared from a mixture of silica sources (Cab–O–Sil fumed silica, TMA-silicate solution and sodium silicate), cetyltrimethylammonium bromide, Al isopropoxide and water. Then the gel was transferred to Teflon-lined stainless steel autoclaves (100 ml) and heated statically for crystallization at 100°C in an oven for 24 h. After the crystallization, the solid product was recovered by filtration. The organic template was removed by two step calcination in N_2 and air flow at 550°C. The crystalline solid was converted to proton form by NH_4^+ ion exchange followed by calcination at 450°C in air flow. The detailed synthesis and the treatment procedures are described elsewhere [13,14]. The physico-chemical properties of MCM-41 are given in Table 1.

The metal salts, ammonium heptamolybdate [$(NH_4)_6Mo_7O_{24}$)] and cobalt nitrate [$(Co(NO_3)_2$-

Table 1
Physico-chemical properties of supports and catalysts

Support/catalyst	Metal loading (wt.%)		SiO_2/Al_2O_3 (mole ratio)	Surface area (m^2/g)	Pore diameter (Å)	Pore volume (cc/g)
	MoO_3	CoO				
MCM-41	—	—	40.7	1206	28.02	1.77
Co–Mo/MCM-41 (N)	13.5	2.9	40.7	1096	26.08	0.67
Co–Mo/MCM-41 (H)	27.0	5.8	40.7	492	23.36	0.44
Co–Mo/Al_2O_3 (criterion 344TL)	13.5	2.9	<0.01	211	105	0.54
				190[a]	110[a]	0.56[a]

[a] Values obtained from Mercury infiltration porosimetry whereas all the other values of porosity and surface area from N_2 adsorption.

$\cdot 6H_2O)$], were purchased from Fisher Scientific. Supported Co–Mo catalyst was prepared by co-impregnation of $Co(NO_3)_2 \cdot 6H_2O$ and $(NH_4)_6Mo_7O_{24}$ from their aqueous solution on to MCM-41 support followed by rotary evaporation of water and overnight drying in an oven at 60°C. The dried sample was then transferred to an electric furnace, where calcination was conducted in an air flow at 500°C for 4 h following a programmed heat-up at 5°C/min to 500°C, which ensures complete dehydration of the sample. The calcined oxide catalyst with 27 wt.% MoO_3 and 5.8 wt.% CoO metal loading was sulfided in 80 ml autoclave using 6% CS_2 in *n*-dodecane under hydrogen pressure in a temperature-programmed manner: first at 250°C for 2 h and then at 300°C for 3 h. The amount of catalyst, CS_2 solution and hydrogen were taken such that the atomic ratio of sulfur to metal is 6 and mole ratio of H_2 to CS_2 is 2. Our experience shows that such a procedure is effective for sulfidation in batch reactors [16]. After sulfidation, the catalyst was stored in *n*-tridecane before use. This catalyst is denoted as Co–Mo/MCM-41(H) hereafter with H indicating high metal loading. For comparison, an Al_2O_3-supported commercial Co–Mo catalyst (Criterion 344TL) containing 13.5 wt.% MoO_3 and 2.9 wt.% CoO was ground into fine powder and sulfided under similar conditions. Table 1 shows the properties of the catalysts used in this study; both catalysts were used as powders in the particle size range of 60–270 mesh (0.25–0.05 mm).

HDS of two petroleum resids, AR and VR2 (atmospheric and vacuum resids, from Marathon Oil Company), was carried out at 350–450°C for 1 h in 25 ml horizontal micro autoclaves agitated vertically at 240 cycles/min in a fluidized sand bath. In a typical run, 3 g resid and 0.3 g catalyst were loaded into the reactor. The sealed reactor was flushed with H_2, pressurized to 1000 psig (6.9 MPa), and then plunged into the sand bath preheated to a given temperature. After the reaction, the reactor was quenched in a cold water bath and then allowed to cool to room temperature. After collecting a small part of the reaction products from the reactor for sulfur analysis, the remainder was recovered using CS_2 solvent followed by filtration. The coke yields were estimated from the difference in the weights of CS_2 insoluble solid residue and the catalyst. The sulfur content was analyzed before and after the reaction using a SC-132 sulfur analyzer from LECO Corporation.

After the HDS of petroleum resids, selected spent catalysts were characterized by thermogravimetric analysis (TGA) in order to analyze the coke deposition. Prior to the TGA, the spent catalysts were dried at room temperature then they were heat treated in N_2 flow at a temperature program of 10°C/min from 30°C to 700°C in order to remove all the volatile compounds. Finally TGA was performed in 200 ml/min air flow at similar temperature programming as earlier. The coke deposition was estimated from the weight loss above the 350°C which corresponds to coke burning.

The feedstock and products were analyzed by high temperature simulated distillation (HT-SimDis) GC analysis using Hewlett-Packard 5890 series II plus GC. A high-temperature aluminum clad megabore capillary column (HT5 phase, 6 m length, 0.53 mm i.d., 0.77 mm o.d., and 0.1 μm film thickness; from SGE supplied by Supelco Inc). was used for HT-SimDis GC analysis. Samples were diluted with CS_2 and injected using a cool on-column injector, which was always programmed to have a 3°C higher temperature than the column temperature. The suitable column temperature program and flame ionization detector temperature were established after several tests. The GC conditions used in this work are as follows: oven initial temperature, 40°C; initial time, 1 min; rate, 10°C/min; final temperature, 425°C; final time, 15.5 min; total run time, 55 min; and detector temperature, 435°C. The data were collected with the aid of Hewlett-Packard ChemStation, and HT-SimDis data were processed using SimDis Expert software from Separation System Inc. The boiling point distribution and the undistillable residue (fraction retained in the column) has been estimated using a high temperature lube oil as an external standard. Our HT-SimDis GC analysis provide quantitative distribution of various fractions divided by the atmospheric equivalent boiling points up to 847°C (FBP), which corresponds to a GC column temperature of 425°C. The uneluted fraction on the GC column is quantified, and then classified as the undistillable residue. More details of the method for HT-SimDis GC analysis established in our laboratory are given elsewhere [17].

Table 2
Characteristics of petroleum resids (AR and VR2)

Feedstock	AR	VR2
Elemental analysis (wt.%)		
Carbon	84.64	83.20
Hydrogen	11.14	9.83
Nitrogen	0.23	0.54
Sulfur	3.87	5.01
Oxygen (by difference)	0.12	1.42
BP distribution (wt.%)		
IBP–220°C	0.5	0.3
220–340°C	5.6	0.6
340–450°C	17.7	2.0
450–540°C	19.2	8.5
540–700°C	27.4	43.1
700°C–FBP[a]	13.1	23.9
Residue (>847°C)	16.5	21.6
Solubility (wt.%)		
Hexane-soluble	90.78	85.86
Toluene-soluble but hexane-insoluble	9.22	14.02
Toluene-insoluble	0	0.12

[a] FBP is limited to 847°C under the GC and column temperature conditions.

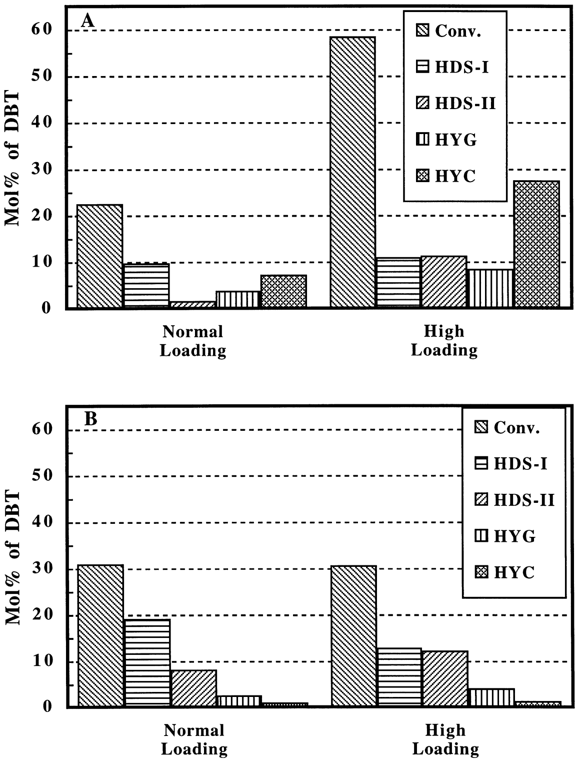

Fig. 1. Effect of loading level of Co–Mo on MCM-41 (A, top) and Al_2O_3 (B, bottom) on dibenzothiophene HDS at 350°C.

3. Results and discussion

The boiling point distribution, the undistillable residue and sulfur contents of feedstocks are given in Table 2. VR2 is very heavy with more high boiling fraction, more residue and with higher sulfur content compared to the AR feedstock. The content of asphaltene was estimated for the two feedstocks, as hexane insoluble fraction, and they are 9.2 and 14.0 wt.% for AR and VR2, respectively. HT-SimDis gas chromatograms of asphaltene (hexane insoluble) suggest that the high temperature peak is due in part to the asphaltene and is more intense in the case of VR2 feedstock. The sulfur contents in AR and VR2 feedstocks are 3.9 and 5.0 wt.%, respectively.

HDS of both AR and VR2 feedstocks was performed using Co–Mo/MCM-41(H), Co–Mo/Al_2O_3 (Criterion 344TL), and ATTM catalysts and without catalyst at different temperatures. Since we used a metal loading on MCM-41 that is higher than that usually used on Al_2O_3, it follows that a brief introduction is warranted of recent work that led to the use of high metal loading [7]. In our recent work on HDS of a model fuel containing 3.5 wt.% sulfur as dibenzothiophene (DBT) in *n*-tridecane at 350°C, we have evaluated the catalytic performance of sulfided Co–Mo catalysts supported on MCM-41 and Al_2O_3 at normal (13.5 wt.% MoO_3; 2.9 wt.% CoO) and high (27 wt.% MoO_3; 5.8 wt.% CoO) metal loadings [7]. Fig. 1 illustrates the effect of level of metal loading on MCM-41 and Al_2O_3 for HDS of DBT [7]. Based on product distribution HDS-I activity represents the yields of the products due to C–S bond hydrogenolysis and HDS-II activity refers to the yields of products from hydrogenation followed by desulfurization. The products resulted from C–C bond hydrogenolysis are used as a measure of hydrocracking activity, and hydrogenation activity is evaluated from the yields of hydrogenated compounds. At normal loading, Co–Mo/MCM-41(N) catalysts showed lower HDS-I and HDS-II activities than Co–Mo/Al_2O_3 catalyst for desulfurization. Since the mesoporous MCM-41 has substantially higher surface area than the γ-Al_2O_3, the normal metal loading level (13.5 wt.% MoO_3; 2.9 wt.% CoO) may lead to higher dispersion but lower degree of stacking of MoS_2-like structure in the catalytically active Co–Mo–S phase on MCM-41 relative to that on Al_2O_3. Hence we attempted to increase the stacking of MoS_2 slab by doubling the metal loading. Fig. 1 shows that doubling the metal loading on MCM-41 more than doubled DBT conversion and increased HDS-II activity. This is accompanied by significant increase in the yields of hydrogenation products such as tetrahydro-dibenzothiophene and hexahydro-dibenzothiophene and a major increase in the yields of hydrocracking products such as benzene and cyclohexane. In contrast, the increased metal loading on Al_2O_3 did not improve DBT conversion. The interesting point is that increasing metal loading on MCM-41 substantially enhanced the catalytic activity although the surface area is lower at higher metal loading (Table 1), whereas doubling the metal loading on alumina has little impact. From the product distribution it is clear that high metal loading on MCM-41 enhances the HDS and hydrocracking. This may be due to the presence of more hydrogenation and hydrocracking sites in the catalytically active phase. Based on the above mentioned results, it is worth to examine the sulfided Co–Mo/MCM-41 catalyst with high metal loading for desulfurization of heavy oils to make use of high hydrocracking activity along with HDS activity.

Figs. 2 and 3 show the typical HT-SimDis gas chromatograms of hydrodesulfurized products of AR and VR2 over Co–Mo/MCM-41(H) catalyst at 425°C and the original feedstocks, respectively. Compared to the AR feedstock, the chromatogram of its product has more lighter components, and the second GC peak (due to heavy fraction of the feedstocks at about 700°C) eluting at higher temperature almost disappeared (Fig. 2). This trend is more remarkable for VR2 (Fig. 3). These results indicate that significant lowering of molecular weight is occurring during HDS. Table 3 shows the boiling point distribution, residue, yields of liquid, coke yields, and sulfur content of hydrodesulfurized resids at 425°C over three types of catalysts and in thermal runs. The sulfur content values in all the cases of AR and VR2 feedstocks at 425°C indicate that Co–Mo/MCM-41(H) and Co–Mo/Al_2O_3 (criterion 344TL) catalysts are active for removal of sulfur as compared with the thermal run where a small amount of sulfur is removed via thermal cracking of some sulfur compounds. The sulfur removal in the presence of ATTM is similar to that of thermal runs of AR and VR2. The sulfur conversion is high with AR feedstock compared to VR2 feedstock. Even though the sulfur content is higher in the case of VR2, the sulfur removal is low; this may be due in part to the bulky nature of sulfur compounds present in the high boiling point fraction of VR2 feedstock, particularly in asphaltene, whose conversion may be limited by diffusional processes. It is also expected that the higher content of asphaltene results in lower level of catalyst performance.

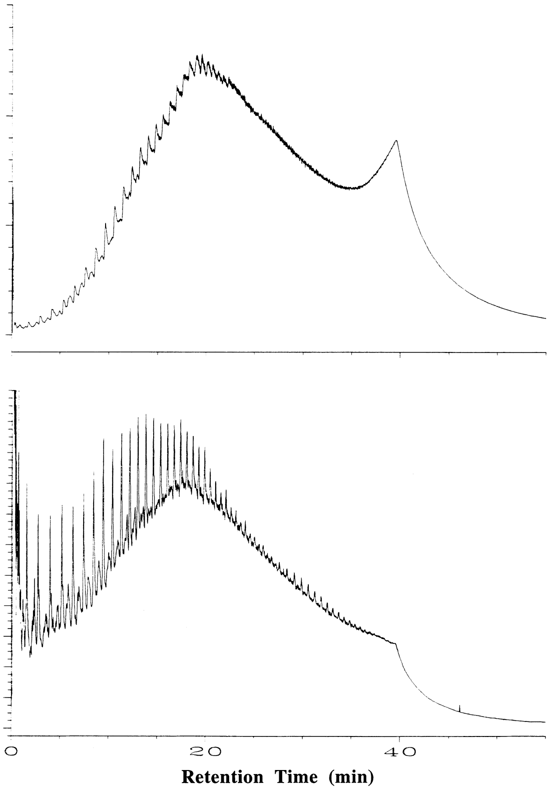

Fig. 2. HT-SimDis gas chromatrograms of AR feed (top) and its product over Co–Mo/MCM-41(H) at 425°C.

Table 4 shows the effect of temperature on boiling point distribution of hydrodesulfurized VR2 in the presence and absence of catalyst. At a higher reaction temperature of 450°C, the low boiling point (below 450°C) fractions increased significantly at the expense of heavy fractions (above 540°C). The sulfur content also decreased significantly at higher reaction temperature. The performance of different catalysts may

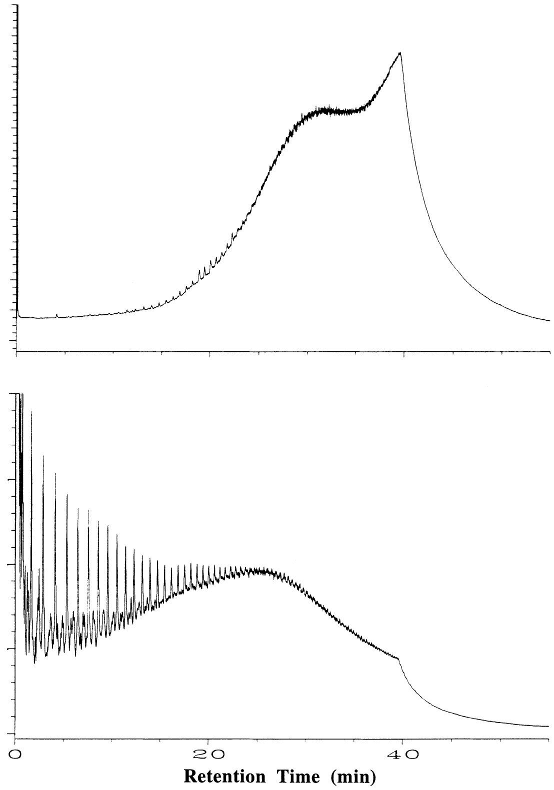

Fig. 3. HT-SimDis gas chromatrograms of VR2 feed (top) and its product over Co–Mo/MCM-41(H) at 425°C.

be compared through the sulfur conversion and resid conversion. The sulfur conversion was determined on basis of sulfur content before and after the reaction and the product liquid yield. The resid conversion was calculated based on the conversion of >540°C boiling fraction. Figs. 4 and 5 show the resid conversion and sulfur conversion, respectively, with varying temperature in the presence and absence of catalyst. Resid conversions are similar among the catalytic and thermal runs at a given temperature but there are significant changes in the liquid and coke yields. At 450°C, the liquid yields of VR2 HDS in the runs without catalyst and with ATTM-derived dispersed catalyst are low (76.2 and 79.0 wt.%, respectively) compared to the runs with Co–Mo/MCM-41(H) and Co–Mo/Al_2O_3 catalysts (89.0 and 86.2 wt.%, respectively). The boiling-point distribution of liquid products with Co–Mo/MCM-41(H) is similar to that with Co–Mo/Al_2O_3. The overall resid conversion increased significantly with increasing temperature. These results indicate that the catalysts did not promote C–C bond cleavage to any significant extent, and the cracking was largely thermally driven during the resid upgrading. However, in the absence of a catalyst, thermal cracking led to large amounts of gases and coke at 450°C (10.2 wt.% of gaseous products and 13.6 wt.% of coke) compared to supported Co–Mo catalysts. The dispersed ATTM

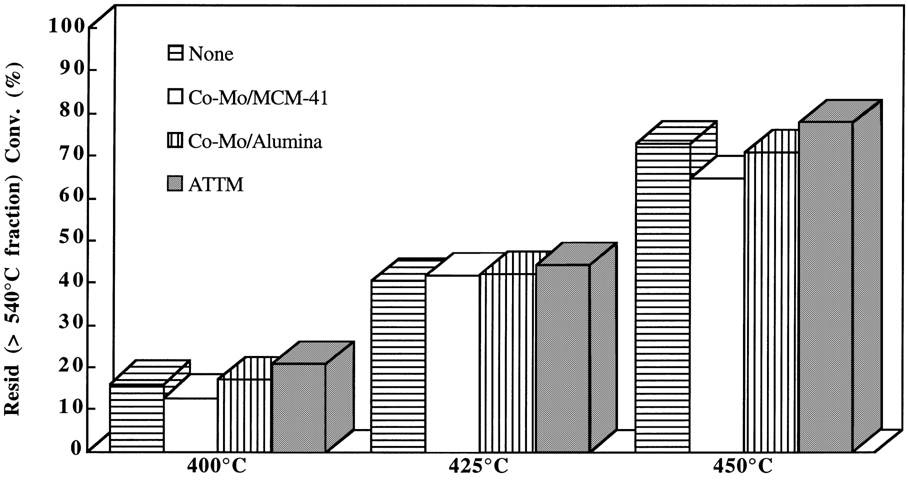

Fig. 4. Effect of temperature on VR2 resid conversion over different catalysts including Co–Mo/MCM-41(H), Co–Mo/Al_2O_3 (criterion 344TL), and ATTM precursor.

Table 3
Effect of catalyst type on resid HDS at 425°C

Expt. ID	Feed	Catalyst	AEBP point distribution of liquid (%)							Liquid yield	Coke yield	Sulfur content
			IBP–220°C	220–340°C	340–450°C	450–540°C	540–700°C	700°C–FBP[a]	Residue[b]	(wt.%)	(wt.%)	(wt.%)[c]
Feed	AR	—	0.5	5.6	17.7	19.2	27.4	13.1	16.5	—	—	3.87
7	AR	None	12.3	19.1	21.1	13.2	13.7	6.1	14.5	97.7	0.4	3.22
29	AR	Co–Mo/MCM-41(H)	4.3	12.6	21.5	18.1	20.3	7.1	16.1	95.5	0.2	2.07
21	AR	Co–Mo/Al_2O_3	5.4	13.7	22.7	18.5	19.9	7.1	12.7	94.8	0.2	1.24
8	AR	ATTM	10.3	19.4	22.5	14.3	14.5	5.1	13.9	97.4	0.3	3.19
Feed	VR2	—	0.3	0.6	2.0	8.5	43.1	23.9	21.6	—	—	5.01
31	VR2	None	6.2	13.0	14.2	13.4	21.3	7.7	24.2	95.2	1.9	4.53
49	VR2	Co–Mo/MCM-41(H)	7.2	12.1	14.7	15.5	23.6	6.9	20.0	97.5	0.5	3.79
33	VR2	Co–Mo/Al_2O_3	5.6	10.7	14.3	17.2	29.1	9.5	13.6	94.6	0.4	3.06
32	VR2	ATTM	7.1	13.1	15.1	14.5	22.2	7.3	20.7	94.1	1.2	4.71

[a] FBP≤847°C for the column under the GC conditions used.

[b] Indicates the >847°C material not eluting out from the column under the GC conditions used.

[c] Sulfur content of the total liquid products.

Table 4
Effect of temperature on HDS of VR2 over different catalysts

Expt. ID	Catalyst	Temperature (°C)	AEBP distribution of liquid (%)							Liquid yield	Coke yield	Sulfur content
			IBP–220°C	220–340°C	340–450°C	450–540°C	540–700°C	700°C–FBP	Residue	(wt.%)	(wt.%)	(wt.%)
Feed	—	—	0.3	0.6	2.0	8.5	43.1	23.9	21.6	—	—	5.01
40	None	400	2.4	4.4	7.1	12.8	39.7	18.9	14.7	97.2	0.3	4.58
48	Co–Mo/MCM-41(H)	400	0.8	3.4	6.3	13.0	42.4	17.7	16.4	96.8	0.2	3.66
42	Co–Mo/Al_2O_3	400	2.6	5.0	7.0	12.9	39.8	18.1	14.6	97.0	0.2	3.66
41	ATTM	400	1.7	6.6	9.0	13.7	37.5	14.7	16.8	97.4	0.2	4.47
37	None	450	8.6	27.2	21.5	12.5	13.3	6.0	10.9	76.2	13.6	2.92
51	Co–Mo/MCM-41(H)	450	10.1	22.7	19.2	14.3	16.8	5.8	11.1	89.0	1.7	2.17
38	Co–Mo/Al_2O_3	450	13.9	22.9	20.6	14.0	15.3	6.1	7.2	86.2	1.5	1.61
39	ATTM	450	14.3	28.2	21.2	12.4	13.5	4.7	5.7	79.0	10.5	2.88

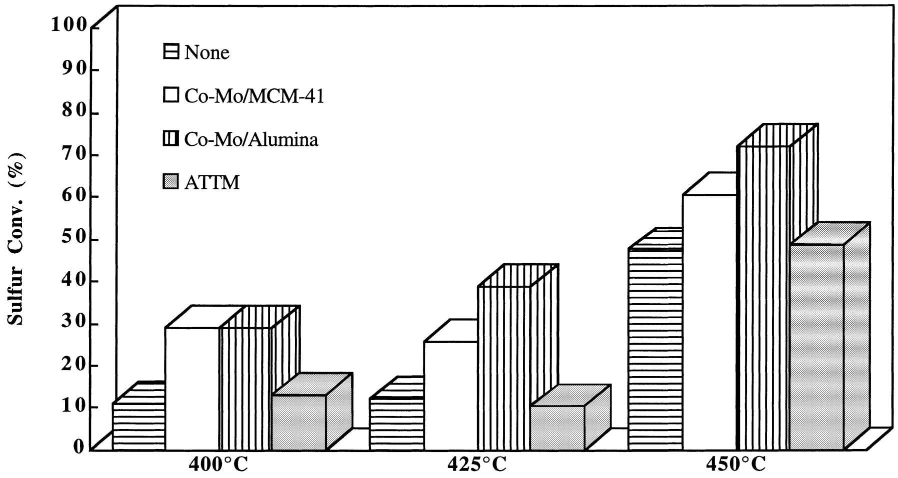

Fig. 5. Effect of temperature on VR2 sulfur conversion over different catalysts including Co–Mo/MCM-41(H), Co–Mo/Al_2O_3 (criterion 344TL), and ATTM precursor.

also gave similar results as the noncatalytic run at 450°C. Nevertheless, the product distribution with ATTM is characterized by relatively large amounts of coke (10.5 wt.%) and gaseous products (5.7 wt.%) as compared to the supported Co–Mo catalysts. These results indicate that under the conditions used for petroleum resid desulfurization, dispersed ATTM precursor does not lead to an effective HDS catalyst.

Fig. 5 shows the effect of temperature on the conversion of sulfur in VR2 feedstock in the presence and absence of catalyst. Both Co–Mo/MCM-41(H) and Co–Mo/Al_2O_3 catalysts promote the removal of sulfur compounds significantly. The Co–Mo/Al_2O_3 catalyst is better than the Co–Mo/MCM-41(H) catalyst at 425 and 450°C. Increasing the temperature from 400°C to 450°C increases the resid upgrading; the conversion of sulfur almost doubled in all the cases. The conversion at high temperature may have partly resulted from thermal cracking, as can be seen from the results of thermal runs. However, it is clear that using either Co–Mo/MCM-41(H) or Co–Mo/Al_2O_3 suppressed the excessive cracking and retrogressive reactions by improving the hydrogen transfer. This added benefit of using a supported Co–Mo catalyst is more apparent for runs at 450°C. In the case of dispersed ATTM precursor the changes of sulfur conversion with temperature is similar to the one with noncatalytic runs, which again confirms that dispersed ATTM is not able to make an effective HDS catalyst. However, the use of ATTM can give better conversions of >540°C fractions than the noncatalytic runs (Fig. 4).

Thermal gravimetric analysis (TGA) of the spent catalysts from the runs with VR2 feedstock at 450°C clearly indicated that they contain coke. Fig. 6 shows

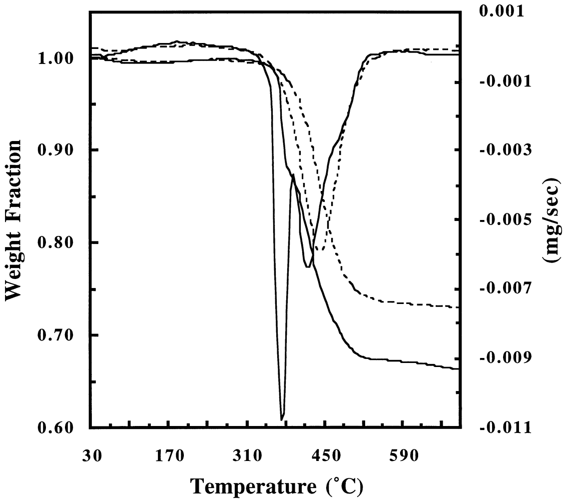

Fig. 6. TGA and DTA profiles from thermogravimetric analysis of spent Co–Mo/MCM-41(H) (solid lines) and Co–Mo/Al_2O_3 (criterion 344TL) (dotted lines) used in VR2 HDS at 450°C.

the TGA of both the Co–Mo/MCM-41(H) and Co–Mo/Al_2O_3 spent catalysts from 450°C runs with VR2 feedstock. The coke deposition on these spent catalysts was estimated and the values are 33.7 and 26.9 wt.% for Co–Mo/MCM-41(H) and Co–Mo/Al_2O_3 catalysts, respectively. Differential thermogravimetric (DTG) curves illustrate that in the case of Co–Mo/MCM-41(H) there are two peaks due to the coke burning (Fig. 6), but only one peak in the case of Co–Mo/Al_2O_3 catalyst. TGA and DTG indicate that in the case of Co–Mo/MCM-41(H) catalyst, coke formation is relatively high and there are two types of coke. One type may be located inside the mesopores of MCM-41 and other type may be on the exterior surface like in the case of Co–Mo/Al_2O_3 catalyst. This may indicate that heavy molecules are not able to diffuse through the mesopores of the MCM-41 support and cause fast deactivation particularly at high temperature due to the coke formation, which leads to the low conversion of resid and sulfur. The acidity of MCM-41 support may not be a major factor for the coke formation, because our acidity measurements on this MCM-41 support has shown that it is weakly acidic compared to microporous aluminosilicates. Moreover acidity of MCM-41 is further lowered upon Co–Mo loading. In our earlier studies in the case of DBT HDS over Co–Mo/MCM-41(H) catalyst, it was observed that high temperature and high metal loading enhanced the desulfurization activity [7]. The pore size of the MCM-41 supported Co–Mo used in our studies is about 23 Å in diameter, which may be large enough for three-ring compounds like dibenzothiophene molecules with or without substituents. However, the 23 Å pore size may not be large enough for conversion of large-sized molecules such as asphaltene present in AR and VR2 feedstock, hence, leading to more coke formation. It has been estimated that the petroleum asphaltene may have peak sizes of larger than 30 Å in diameter [16]. In addition, the coke yields derived from TGA analysis are higher than those estimated from the amount of CS_2-insoluble residue after their actions at 450°C.

To see if we could improve the upgrading efficiency by dilution using a light solvent, we conducted the tests using a 1 : 1 (wt) mixture of VR2: hexane as the feedstock. The catalytic upgrading of the mixture with both Co–Mo/MCM-41(H) and Co–Mo/Al_2O_3 at 425°C displayed similar results to those without the presence of hexane in the feedstock. To examine if the presence of asphaltene has negative impact on HDS reactions, we carried out the runs of deasphalted VR2 (using hexane-soluble fraction as the feedstock) at 425°C. The results given in Table 5 indicate that removing asphaltene significantly improved the HDS activity of Co–Mo/MCM-41(H) catalyst; sulfur conversion increased from 25.9 to 51.8%; and resid conversion increased from 41.7 to 50.5%. The same treatment of the feedstock also improved the HDS over Co–Mo/Al_2O_3 from 57.6 to 65.8% and resid conversion from 41.6 to 54.6%. However, the degree of improvement in sulfur conversion upon removing asphaltene is greater in the case of Co–Mo/MCM-41(H).

The difference in the performance of these catalysts in HDS of petroleum resids may be due to two reasons; one is the differences in surface (metals dispersion, etc.) and other is the difference in pore size. Because MCM-41 and Al_2O_3 are two types of materials different in surface area, pore diameter and acidity, a significant difference in dispersion of the metal species on them is expected. The properties of Co–Mo/MCM-41(H) and Co–Mo/Al_2O_3 (criterion 344TL) in Table 1 show that the pore diameter of the former (23.4 Å) is much smaller compared to the mean pore diameter of the latter (105 Å). Song et al. investigated asphaltene hydroprocessing over Ni–Mo/Al_2O_3 catalysts [16]. It was shown that the pore diameter of Al_2O_3 support has significant effect on hydroprocessing of asphaltene, which indicates that the catalyst pore size is critical in hydroprocessing of petroleum resids. The results in this paper suggest that MCM-41 support with 28 Å pore size and high surface area (1206 m^2/g) led to a supported Co–Mo catalyst that is not effective enough for hydroprocessing of resids containing asphaltene because of the small pore diameter (23.4 Å) of the resulting catalyst, although dispersion of Co–Mo may be better on MCM-41 than on Al_2O_3. Removing asphaltene before the runs can improve the HDS activity of the Co–Mo/MCM-41(H) catalyst, as shown in Table 5. On the other hand, it may be necessary to synthesize MCM-41 with larger mesopores for hydroprocessing of asphaltene in the petroleum resids. It has already been reported that MCM-41 molecular sieves can be synthesized with pore size up to 100 Å [10,11].

Table 5
HDS of hexane soluble fraction of VR2 at 425°C

Expt. ID	Catalyst	Boiling point distribution (%)							Liquid yield (wt.%)	Coke yield (wt.%)	Sulfur content (wt.%)
		IBP–220°C	220–340°C	340–450°C	450–540°C	540–700°C	700°C–FBP	Residue			
Feed[a]	—	0	0.6	1.0	2.3	10.5	51.5	23.4	100.0	—	4.17
71	Co–Mo/MCM-41(H)	7.7	14.1	16.7	18.5	29.2	8.7	6.1	96.3	<0.1	2.09
72	Co–Mo/Al_2O_3	9.9	13.7	16.6	18.3	27.1	6.9	7.5	93.6	<0.1	1.52

[a] Hexane soluble fraction of VR2 resid.

4. Conclusions

Mesoporous molecular sieves of MCM-41 type can be used as effective supports for desulfurization catalysts. However, the results for the upgrading of atmospheric and vacuum resids suggest that sulfided, MCM-41 supported Co–Mo catalysts are not as effective as commercial Co–Mo/Al_2O_3 catalyst (criterion 344TL) for desulfurization of petroleum resids containing asphaltene. This may be because the pore diameter of MCM-41 synthesized (28 Å) is not large enough for converting bulky molecules such as asphaltene in petroleum resids. Consequently, we have shown that removing asphaltene from the resid prior to HDS can improve the catalytic activity of Co–Mo/MCM-41(H).

The results from the present and previous work, though still preliminary, are very useful in directing future research for applying MCM-41 in catalytic fuel processing.

Acknowledgements

We are grateful to Prof. Harold H. Schobert for his encouragement, support, and many helpful discussions, and to Dr. Wei-Chuan Lai for his contribution in setting up the SimDis GC system. We also thank Dr. Mark Plummer of Marathon Oil Company for providing the resid samples.

References

[1] A.D. Bianco, N. Panariti, M. Marichionna, CHEMTECH 25 (1995) 35.
[2] E.J. Swain, Oil & Gas J. 1 March (1993) 62.
[3] B. Ferris, P. Wiederkehr, Chem. Ind. 15 (1995) 573.
[4] C.G. Frye, J.F. Mosby, Chem. Eng. Prog. 63 (1967) 66.
[5] M.J. Girgis, B.C. Gates, Ind. Eng. Chem. Res. 30 (1991) 2021.
[6] M. Houalla, D.H. Broderick, A.V. Sapre, N.K. Nag, V.H.J. De Beer, B.C. Gates, H. Kwart, J. Catal. 61 (1980) 523.
[7] C. Song, K.M. Reddy, Am. Chem. Soc. Div. Petro. Chem. Prepr. 41(3) (1996) 567: The previous results were quoted to facilitate discussion at the request of a peer reviewer of this manuscript.
[8] K.M. Reddy, C. Song, Am. Chem. Soc. Div. Fuel Chem. Prepr. 41(3) (1996) 906.
[9] K.M. Reddy, B. Wei, C. Song, Am. Chem. Soc. Div. Petrol. Chem. Prepr. 42(2) (1997) 396.
[10] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, J.C. Schlenker, J. Am. Chem. Soc. 114 (1992) 10834.
[11] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, Nature 359 (1992) 710.
[12] K.M. Reddy, C. Song, Am. Chem. Soc. Div. Fuel Chem. Prepr. 40(4) (1995) 1003.
[13] K.M. Reddy, C. Song, Catal. Lett. 36 (1996) 103.
[14] K.M. Reddy, C. Song, Mater. Res. Soc. Proc. 454 (1997) 125.
[15] K.M. Reddy, C. Song, Catal. Today 31 (1996) 137.
[16] C. Song, T. Nihonmatsu, M. Nomura, Ind. Eng. Chem. Res. 30 (1991) 1726 and the references cited therein.
[17] K.M. Reddy, B. Wei, C. Song, Catal. Today 43 (1998) 187.