Stability of MCM-41-supported CoMo hydrotreating catalysts

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The performance of sulfided CoMo hydrotreating catalysts supported on MCM-41 has been evaluated using hydrodesulfurization of 4-ethyl, 6-methyl- dibenzothiophene (4E,6M-DBT) model compound in *n*-hexadecane and of 4-methyl, 6-methyl-dibenzothiophene (4,6-DMDBT) in a commercial feed as a test reaction. Although the performance of CoMoS/MCM-41 is high for the model feed reaction as compared to commercial CoMoS/alumina, for the commercial feed reaction the performance of the commercial catalyst is much better. Model feed reaction with the addition of carbazole shows that, although this nitrogen-containing compound has a strong inhibiting effect, the lower catalytic performance of CoMoS/MCM-41 in the commercial feed test is probably not solely due to the presence of nitrogen.

TEM investigations show that the decrease in activity of the CoMoS/MCM-41 in the nitrogen-containing and commercial feed reactions is not due to sintering of the sulfidic phase. However, it appears that the MCM-41 collapses during the catalytic reactions, and this effect is most pronounced for the commercial feed test. The degradation of the MCM-41 support material does not affect the dispersion of the CoMoS, but induces increased coking.

KEY WORDS: MCM-41; hydrodesulfurization; 4-ethyl, 6-methyl-dibenzothiophene.

1. Introduction

With the ever more stringent limitations to sulfur contents of transportation fuels, the quest for better-performing hydrodesulfurization (HDS) catalysts continues. Most commercially available catalysts mainly consist of Co–Mo sulfide on an alumina support material. In view of the surface area of the alumina support material (about 300 m^2/g), the Co+Mo loading is limited to about 15 wt% of metal. As the mesoporous material MCM-41 has a much higher total surface area (up to about 1000 m^2/g) than the aluminas that are conventionally used to support CoMoS, higher loading per gram of the catalyst can be achieved [1]. For the hydrodesulfurization of dibenzothiophene (DBT) model compound in *n*-tridecane, it was found that at "normal" loading (i.e., similar to what is used for commercial alumina-supported catalysts) the performance of CoMoS/alumina is better than that of CoMoS/MCM-41. However, doubling the loading of CoMoS resulted in a tremendous increase (more than doubling) of DBT conversion for CoMoS/MCM-41, whereas no difference in DBT conversion was found for the alumina-supported system upon doubling of the loading. The high-loading CoMoS/MCM-41 is therefore much more active than CoMoS/alumina, regardless of the loading of the latter. Similar results have been reported recently for NiWS/SBA-15 mesoporous material [2]. For the conversion of real petroleum resid feeds, however, the performance of high-loading CoMoS/MCM-41 always seems to be lower than that of commercial (normal-loading) CoMoS/alumina, at least under the microbatch conditions tested [3]. This was attributed to the smaller pore diameter (and thus decreased accessibility of the active phase) of the CoMoS/MCM-41 (2.34 nm) compared to the mean pore diameter of the CoMoS/alumina (10.5 nm). No other publications are known to us that compare the catalytic performance of this kind of catalysts under more realistic conditions than model feed reactions.

In real feeds, however, an important factor influencing the rate of HDS is inhibition by nitrogen-containing compounds due to competitive adsorption on the active sites [4,5]. Also, the decrease in catalytic activity for real feed conversion could be due to coke formation. Therefore, the current paper compares the hydrotreating performance of CoMoS/MCM-41, CoMoS/ASA and CoMoS/alumina in the conversion of 4E,6M-DBT without and with the addition of carbazole as a nitrogen-containing model compound, and in the conversion of 4,6-dimethyl-dibenzothiophene (4,6-DMDBT) in a commercial feed. Transmission electron microscopy (TEM) is used to study the dispersion of the

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CoMoS after the catalytic reactions and the stability of the MCM-41 support material. Additional information on the stability of the MCM-41 and the accessibility of the active phase after the catalytic test reactions is obtained using powder X-ray diffraction (XRD), nitrogen adsorption and thiophene HDS.

2. Experimental

Mesoporous MCM-41 type material was synthesized as described in [6]. It was loaded with Co and Mo by coimpregnation using cobalt nitrate and ammonium heptamolybdate, followed by drying at 333 K and calcination in an airflow at 773 K for 4 h (heating rate 300 $\mathrm{K h^{-1}}$). The Co/Mo ratio was the same for all MCM-41-supported catalysts, but two different loadings were prepared on two batches of MCM-41 (having a silica/alumina ratio of 25 and 50). Catalysts are denoted by "CoMo/MCM-41 *Xyy*", where *X* is *N* for normal loading (i.e., equivalent to commercial catalysts) or *H* for high loading (i.e., double amounts of Co and Mo), and *yy* indicates the silica/alumina ratio.

Co and Mo were loaded onto amorphous silica–alumina (ASA) using co-impregnation of an ammoniacal solution. The impregnated ASA was dried at 355 K under inert atmosphere and calcined in air at 725 K. A commercial CoMo/alumina catalyst, C444, was obtained from Shell. Basic properties of the catalysts studied in this work are presented in table 1.

Liquid-phase model feed reactions were carried out in a stirred batch reactor with an internal volume of 250 mL. The catalysts were crushed and sieved, and typically 200 mg with a particle size fraction of between 100 and 250 μm was used. The samples were presulfided in a separate pretreatment reactor, which was an add-on to the liquid-phase reactor, in a flow of 6 $\mathrm{mmol\,s^{-1}}$ H_2S and 60 mmol/s H_2 at 0.1 MPa. The pretreatment reactor was heated at a rate of 600 $\mathrm{K\,h^{-1}}$ and kept isothermal at 673 K for 1 h. After cooling to room temperature, the catalyst was dropped into the reaction mixture in the batch autoclave at room temperature without exposure to air. Heating was started and when the reactor contents reached the reaction temperature, the stirrer was switched on at 2000 rpm to avoid mass transfer limitations. A model reaction with 4E,6M-DBT was carried out at 633 K at a total pressure of 6.0 MPa. The feed consisted of a solution of 150 mg 4E,6M-DBT in 100 g *n*-hexadecane; 100 mg octadecane was added as internal reference for quantitative GC analysis of the reaction mixture. To assess the possible role of the presence of nitrogen-containing compounds, additional measurements were carried out at the same reaction conditions in the presence of 27.5 mg carbazole.

Test reactions using a commercial feed (prehydrotreated straight-run gas oil, Shell Pernis) and one model feed MCM-41 stability test were performed under similar conditions but at 673 K. Owing to inhibition by nitrogen- and sulfur-containing components in the commercial feed, activity at 633 K was very low for all catalysts tested. The data presented for the commercial feed reactions are based on the conversion of one of its main components, 4,6-DMDBT. This latter compound shows a reactivity that is very similar to that of the 4E,6M-DBT used in the model reactions, allowing direct comparison of the catalytic performance in model and commercial feed reactions. The composition of the commercial feed is given in the sulfur-specific gas chromatogram in figure 1. Total sulfur content is 760 ppm, total nitrogen content is 60 ppm and total aromatic content is 1104 mmol/kg (88% monoaromatics).

The first-order reaction rate constant, k_1, was evaluated in mole of reactant converted per hour and per gram of the catalyst from fitted first-order plots of $\ln(c_t/c_0)$ versus tw/F, where c_t refers to the time dependent concentration of the reactant, w to the catalyst weight in grams and F to the amount of

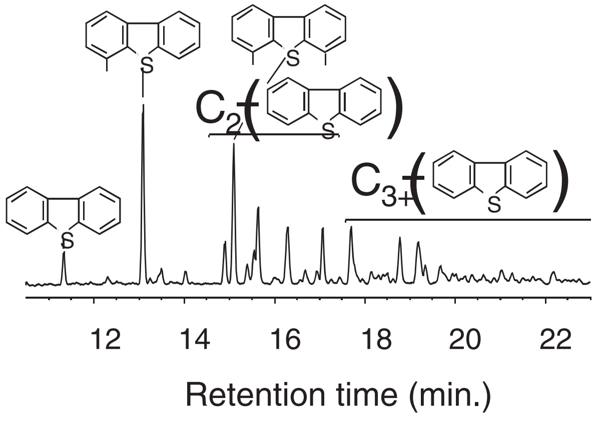

Figure 1. Sulfur-specific gas chromatogram of the commercial feed.

Table 1
Basic properties of the catalysts tested

Catalyst	Si/Al ratio	Co loading (wt%)	Mo loading (wt%)
CoMo/MCM41 (N50)	100	2.9	13.5
CoMo/MCM41 (H50)	100	5.8	27
CoMo/MCM41 (H25)	50	5.8	27
CoMo/ASA	0.7	3.6	10.8
CoMo/Al_2O_3 (Shell C444)	–	3.2	9.6

reactant in mole. Relative reaction rate constants normalized to Mo loading were also evaluated. Used catalysts from the batch reactor were rinsed with hexadecane and transported to the glove box (for later preparation for TEM measurements) under hexadecane.

In order to evaluate the accessibility of the active phase after apparent deactivation in the liquid-phase DBT HDS reactions described above, selected spent catalysts were tested for their performance in gas-phase thiophene HDS. They were pretreated in 16.67 vol% H_2S in hydrogen at 350 °C and atmospheric pressure for 2 h before thiophene HDS performance was tested with 6 vol% thiophene in hydrogen at 350 °C and atmospheric pressure [7].

Nitrogen adsorption/desorption isotherms were recorded for selected spent catalysts (after evacuation at 333 K) to evaluate the mesopore volume still available after apparent deactivation in substituted DBT HDS.

High-resolution TEM was performed using a Philips CM30T transmission electron microscope equipped with a lanthanum boride filament operated at 300 kV. Samples were mounted on a microgrid carbon polymer supported on a Cu 400 mesh grid under exclusion of air in a protective atmosphere glove box (Ar, maximum partial pressures for oxygen and water of 1 ppm) by dripping a few drops of a suspension of the ground catalyst in *n*-hexane onto the grid followed by drying at ambient temperature. Samples were transferred to the microscope in a special vacuum-transfer sample holder under exclusion of air [8].

Slab length distribution and degree of stacking distribution were determined by manually measuring at least 250 slabs per sample from the TEM images. Average slab length and average degree of stacking were calculated from their respective distributions.

The stability of the MCM-41 support material was monitored using powder X-ray diffraction (XRD).

3. Results and discussion

Table 2 lists the results of the catalytic tests. For the model HDS reactions with only the sulfur-containing compound, all CoMoS/MCM-41 catalysts tested here show much better performance than the commercial CoMoS/alumina catalyst. In agreement with results published by Klimova *et al.* [9], the catalytic activity for the catalyst supported on MCM-41 with an Si/Al ratio of 50 (sample H25) is much better than that supported on MCM-41 with an Si/Al ratio of 100 (sample H50). Our Si/Al ratio of 50 is close to the optimal value of 60 reported by Klimova *et al.* [9]. The catalytic performance of the CoMoS/ASA catalyst is in between that of the CoMoS/MCM-41 catalysts and that of the CoMoS/alumina catalyst. This holds for the catalytic performance per gram catalyst as well as per equivalent molybdenum loading ("relative"). In general, acidic supports show a higher sensitivity to HDS inhibition by nitrogen-containing compounds than non-acidic supports. Indeed, the proportional decrease in activity upon addition of carbazole to the model feed is much higher for CoMoS/MCM-41 and CoMoS/ASA than for CoMoS/alumina, even though both CoMoS/MCM-41 and CoMoS/ASA still show much better performance than CoMoS/alumina. The acidity of MCM-41 is roughly equivalent to that of ASA and much higher than that of alumina. The CoMoS/ASA shows a lower relative decrease in activity than CoMoS/MCM-41 upon addition of carbazole to the model feed, indicating that inhibition of HDS by nitrogen-containing compounds is not the only factor influencing the catalytic performance here.

However, for the commercial feed reaction, the commercial CoMoS/alumina catalyst performs much better than either CoMoS/MCM-41 or CoMoS/ASA. Next to inhibition of HDS by nitrogen-containing compounds, inhibition of HDS by aromatic compounds could be an issue for the commercial feed catalytic test reaction. As CoMoS/alumina was found to be much less sensitive to the inhibition of HDS by aromatic compounds than NiMoS/alumina and MoS_2/alumina [10], we surmise that other factors influencing the catalytic performance must play a role for our catalysts.

A decrease of the dispersion of the active CoMoS can be the cause of severe deactivation. Average slab lengths

Table 2
First-order reaction rate constants ($h^{-1}\ g_{cat}{}^{-1}$) and relative rate constants normalized to Mo loading for the HDS of 4E,6M-DBT at 633 K and 6 MPa in the absence and presence of carbazole (275 ppm) and for 4,6DMDBT the commercial feed

Catalyst	4E,6M-DBT		4E,6M-DBT + carbazole		4,6DMDBT in commercial feed	
	$g^{-1}{}_{cat}$	Relative	$g^{-1}{}_{cat}$	Relative	$g^{-1}{}_{cat}$	Relative
CoMo/MCM41 (N50)	6.01	35.6	0.29	1.7	nd[a]	nd[a]
CoMo/MCM41 (H50)	2.03	6.0	1.05	3.1	0.09	0.3
CoMo/MCM41 (H25)	6.97	20.6	0.69	2.0	nd[a]	nd[a]
CoMo/ASA	1.80	13.3	0.42	3.1	0.09	0.7
CoMo/Al_2O_3 (Shell C444)	0.34	2.8	0.16	1.3	0.12	1

[a] nd = not determined.

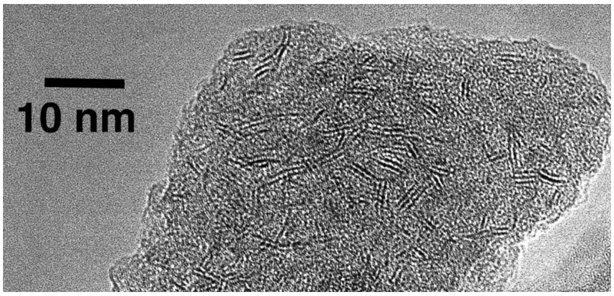

Figure 2. HRTEM image of the H50 catalyst after use in the commercial feed catalytic test reaction.

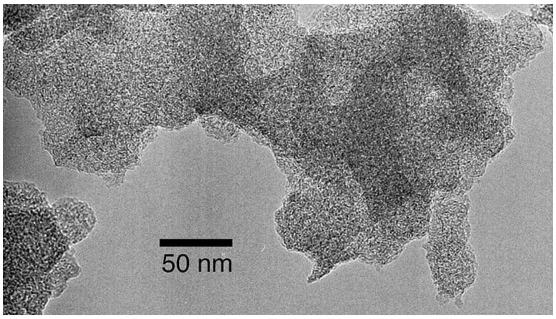

Figure 4. TEM image of the H50 catalyst after use in the commercial feed catalytic test reaction.

and degrees of stacking have been determined from TEM for many of our catalysts. A typical example of the slabs as visible in HRTEM is shown in figure 2. For the MCM-41-supported catalysts after various catalytic tests, the average slab length lies between 2.5 and 2.6 nm. The degree of stacking for these samples lies between 1.6 and 1.8 layers. These very small differences between the different MCM-41-supported catalysts after catalytic tests with very different catalytic activities indicate that sintering is not the cause of deactivation. For comparison, the average slab length for the commercial CoMoS/alumina after sulfidation is 3.1 nm with an average degree of stacking of 1.2 layers. For the CoMoS/ASA catalyst tested here, the values are 3.3 for the average slab length and 1.8 for the average degree of stacking.

TEM data show an unexpected feature for the MCM-41-supported catalysts after the various catalytic test reactions: the porous structure of the MCM-41 is lost. Figure 3 shows that the H50 oxidic precursor consists of well formed but mainly disordered MCM-41-type material. Large clusters of Co- or Mo-oxide were not observed. After model reaction of H25 with only the sulfur compound at 633 K, the quality of the MCM-41 has decreased somewhat but the support material is still clearly recognizable as disordered MCM-41. The quality of the MCM-41 has decreased even more for H25 after the catalytic reaction with model feed containing carbazole at 633 K. However, after reaction with the commercial feed and after model reaction with only the sulfur compound at 673 K, the MCM-41 of H50 has disintegrated completely, as is illustrated in figure 4. Apparently, the stability of the MCM-41 used as support material is not very high under hydrotreating test conditions! Powder XRD measurements confirm that the MCM-41 of the oxidic precursor does not contain any higher-order reflections and thus no substantial amounts of hexagonally ordered mesoporous material. The intensity of the one low-angle reflection seems to decrease when degeneration of the MCM-41 is observed in the TEM.

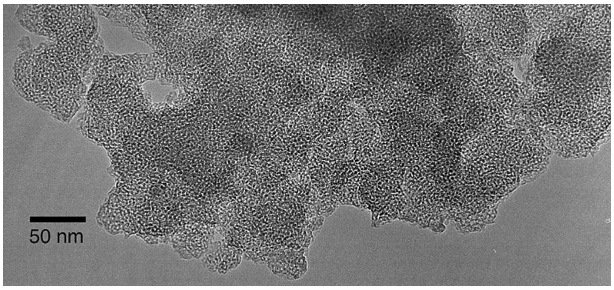

Figure 3. TEM image of the H50 oxidic precursor, clearly showing the high quality disordered MCM-41 mesoporous material.

The main cause for the extreme decrease in HDS performance could, therefore, be the instability of the MCM-41 support material. One reason could be reduced accessibility of the active phase after destruction of the channel system of the MCM-41. Loss of accessibility of the active phase has been tested using thiophene HDS of our used catalysts. Another reason could be increased coke formation, which has been investigated using nitrogen adsorption/desorption experiments on the used catalysts. Spent catalysts H25 after model feed reaction at 633 K with only the sulfur compound and H50 after commercial feed reaction at 673 K have been tested for pore volume and surface area using nitrogen adsorption/desorption, and for remaining catalytic activity using gas-phase thiophene HDS. Prior to nitrogen adsorption/desorption, the samples have been degassed at 333 K. This means that any coke formed during the catalytic tests has not been removed. Prior to thiophene HDS, these samples were resulfided in H_2/H_2S at 623 K. This means that most of the soft coke eventually formed during the test reaction could have been removed 7. For the H25 catalyst after model feed reaction at 633 K with only the sulfur compound, 2.5-nm mesopores are found to contribute about 25% to the total BET surface area (which amounts to only 87 m^2/g). Catalyst H50 after commercial feed test clearly has an even further decreased BET surface area (33 m^2/g) and a completely reversible isotherm, indicating that all mesopore volume has been lost. For comparison, the BET surface area of a CoMoS/ASA catalyst before and after use in a commercial full-range gas oil HDS test has been determined. It changes from

280 to 130 m^2/g, i.e., the decrease is only about 50%, compared to 80–90% for the MCM-41-supported catalysts. The difference in performance in thiophene HDS (after resulfidation) between the two spent samples is small, both showing a conversion of about 50% and a selectivity to C4 products of about 95%. These catalytic data are very similar to those of fresh commercial catalysts, indicating that the decrease in BET surface and mesopore volume for the H50 after commercial feed test is mainly due to coke formation, and that for both used MCM-41-supported samples, the active phase is still largely accessible to small sulfur-containing molecules. Apparently, although the smaller pores of the MCM-41 support material already give rise to higher coke formation than the alumina, the sensitivity to coking increases even more upon destruction of the MCM-41. The higher coke formation may be due to reduced diffusivity in the smaller pores. It will be very interesting to test the catalytic performance of similar catalysts supported on more stable (ordered) MCM-41. This is the subject of a continuing research project.

4. Conclusions

The MCM-41 used as support material is not stable under typical HDS reaction conditions (prehydrotreated gas oil at 673 K and a total pressure of 6 MPa). Already, for the model reaction with only the sulfur compound at 633 K, the quality of the MCM-41 decreases, but it really disintegrates after reaction at 673 K. The degradation of the MCM-41 support material does not affect the dispersion of the CoMoS, but induces increased coking.

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