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Catalytic hydrodesulfurization of gas oil and model sulfur compounds over commercial and laboratory-made CoMo and NiMo catalysts: Activity and reaction scheme

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Abstract

Hydrodesulfurization (HDS) of gas oil (GO), light cycle oil (LCO) and a model sulfur compound 4,6-dimethyldibenzothiophene (4,6-DMDBT) was compared over a series of six commercial and laboratory-made catalysts. The difference between the HDS activities of the catalysts for the model compound and the real feed stocks indicates their sensitivity to the intrinsic inhibitors (aromatics and H_2S) present under industrial conditions. A severe inhibition of H_2S on NiMo catalysts should be noted. Detailed analysis of the HDS products from the model feed provided information on the reaction pathways involved over the present catalysts and how they are modified in presence of inhibitors. Complementary standard tests with other model compounds were examined to determine the Brønsted acidity and hydrogenation activity of each catalyst. Such activities and their relationship explain the differences in performance of the catalysts and the relative importance of the respective reaction pathways in the HDS. Isomerization and dealkylation of 4,6-DMDBT took place prior to the desulfurization over the CoMo on the acidic support enhancing the desulfurization. Moreover, such a pathway was inhibited strongly by the aromatic partners and lost stationary activity by coke formation. © 1997 Elsevier Science B.V.

Keywords: Hydrodesulfurization; CoMo catalysts; NiMo catalysts

1. Introduction

Since gas oil requires deep desulfurization for the protection of the atmospheric environment, desulfurization catalysts of better performance are continuously looked for to achieve the objective sulfur level under milder conditions, including the desulfurization of refractory molecules such as 4,6-dimethyldibenzothiophene [1,2]. Since cobalt and nickel molybdenum sulfides are basically established as the active species for the commercial catalyst, the better supports are the targets for research, although γ-alumina supports are widely used because of their structural as well as mechanical performances.

In the present study, six commercial and laboratory made alumina hydrodesulfurization (HDS) catalysts including zeolite and silica–alumina are examined for HDS of gas oil (GO), light cycle oil (LCO), and 4,6-DMDBT in decane, transalkylation of isopropylbenzene and hydrogenation of naphthalene. We want to clarify the factors of the support for the high HDS activity and HDS mechanisms through their comparisons. Since the acidic support appears to enhance the

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HDS activity, their contents in the support and deactivation after the long run of GO HDS were also studied to find their influences on HDS activity and mechanism.

2. Experimental

2.1. Apparatus

The catalytic HDS tests were performed in a 100 cm^3 batch autoclave equipped with a mechanically driven turbine (1000 rpm) with two inclined blades.

2.2. Materials

4,6-DMDBT of 99.7 wt% purity was synthesized according to an improved method by Gerdil and Lucken [3]. This model compound was dissolved in *n*-decane, an inert non-inhibiting solvent.

A straight run GO (1.19 wt% S, ASTM D86 5–50–95 wt%: 242–295–373°C, 31 wt% Arom. (SM)) obtained from Iranian heavy crude oil in a European refinery was used as a real feed stock for HDS tests. Also an LCO cut from a Japanese fluid catalytic cracking (FCC) unit (0.18 wt% S, ASTM D86 5–50–95 wt%: 195–258–311°C, 73 wt% Arom. (HPLC)) was used as a high aromatic content real feed stock.

Six commercial catalysts were supplied by different manufacturers. The available properties of these catalysts are summarized in Table 1. A series of laboratory-made modified C and D catalysts were prepared, changing the acidic additive content. A spent C catalyst, used for two years in a GO HDS unit, was also tested.

Some laboratory made Ni,Co–Mo catalysts were prepared according to the following procedure: Al_2O_3→Mo impregnation→130°C drying→Ni, Co impregnation→130°C drying→500°C calcination.

The catalyst was presulfided for 2 h at 360°C under an atmospheric pressure of $H_2 : H_2S$ (molar ratio 95 : 5). After cooling down to room temterature under the same atmosphere, the catalyst was immediately weighed and charged to the reactor for the HDS reactions.

2.3. Analysis

Sulfur species in the real feed stocks were analyzed by GC–FPD. HDS products of 4,6-DMDBT in solvent were analyzed qualitatively by GC–MS and quantitatively by GC–FID equipped with a silicone capillary column (OV101; 0.25 mm×50 m).

2.4. HDS reaction conditions

HDS of 4,6-DMDBT (0.01 g) in decane (10 g) was conducted for 0–60 min at 270–360°C under 2.4–5 MPa (initial hydrogen pressure at room temperature) over 1.0 g of presulfided catalyst. HDS with GO or LCO (10 g) was performed for 0–60 min at 340°C under 2.4 MPa (initial hydrogen pressure) over 1.0 g of presulfided catalyst. After reaction, the HDS products were separated from the catalyst by extracting for 40 min with THF in case of GO or LCO and with acetone in case of 4,6-DMDBT in decane.

2.5. Kinetics calculations

Individual sulfur compounds were assumed to be desulfurized in first order. The decrease of the total

Table 1
Properties of commercial catalysts

Catalyst name	A	B	C	D	E	F
General properties	Usual CoMo	Usual NiMo	Deep HDS CoMo	Deep HDS CoMo	Low Content NiMo	Deep HDS CoMo
Support	Al_2O_3	Al_2O_3	Al_2O_3+zeolite	Amorphous SiO_2–Al_2O_3	Al_2O_3	Al_2O_3
Surface area (m^2/g)	268	273	220	215	140	220
Pore volume (ml/g)	0.53	0.52	0.44	0.45	0.60	0.45
CoO (NiO) (wt%)	4.2	3.1	4.0	3.8	2.0	4.1
MoO3 (wt%)	15.0	15.0	16.0	16.5	6.0	20.5

sulfur content in the GO and LCO was assumed in pseudo-1.65 order based on [4].

3. Results

3.1. Catalytic activities: Cracking and hydrogenation activities of the catalysts

3.1.1. Cracking activity of the catalysts

The cracking activity (related to the Brønsted acidity) of the catalysts A–F was estimated from their activity for transalkylation of neat isopropylbenzene as a standard test (pure, 250°C, 2.4 MPa hydrogen, 30 min). Products were mainly benzene and diisopropylbenzene. Fig. 1 shows that the zeolite in catalyst C provided a very high activity compared to the others. Catalyst D, which was supported on amorphous silica–alumina, exhibited a higher acidity than alumina supported catalysts. More acidic additive in C and D series increased the acidity as shown in Table 2. Spent C catalyst lost its acidity entirely, being less active than virgin alumina supported catalysts. The highest activity of F was noted among the alumina supported catalysts even if its higher loading of metals was taken into account.

3.1.2. Hydrogenation activity of the catalysts

The hydrogenation activity was determined with naphthalene (1 g in 20 g octane, 250°C, 3 MPa hydrogen, 30 min). Tetralin was the main product; some decalin was also obtained. Based on the yield of hydrogenated products, catalyst B of the highest Ni content showed a very high hydrogenation activity (Fig. 2), being higher than that of Co promoted catalysts. Low nickel–molybdenum catalyst E exhibited a very low activity. Among the cobalt catalysts, the activity ranking C≈D>F>A was observed.

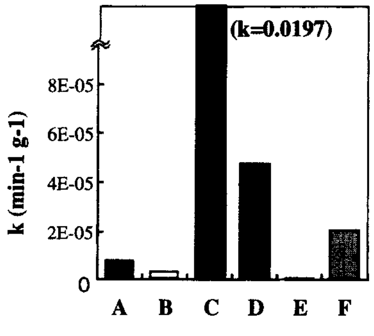

Fig. 1. Rate constant of cumene transalkylation over commercial catalysts.

Table 2
Cracking (Brønsted acidity) and hydrogenation activities for catalysts

Catalyst	k (cracking) ($\mathrm{min}^{-1}\,\mathrm{g}^{-1}$)	k (hydrogenation) ($\mathrm{min}^{-1}\,\mathrm{g}^{-1}$)
C	1.97E−02	4.98E−03
Acid additive added C	3.56E−02	9.10E−03
Spent C	9.12E−07	2.18E−03
D	4.80E−05	4.86E−03
Acid additive added D	1.54E−04	6.90E−03

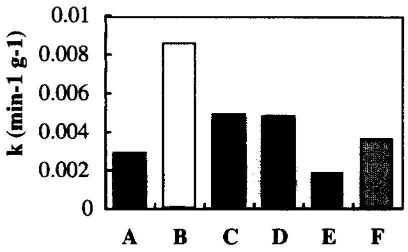

Fig. 2. Rate constant of naphthalene hydrogenation over commercial catalysts.

Interestingly, the relative ranking of the hydrogenation activities among the Co catalysts was found in the same order as that of their acidic activities, suggesting a possible relationship between these properties. Table 2 summarizes the activities of CoMo catalysts with more amounts of acid additive in the support and a spent C catalyst. The amounts of acidic additive added in the support of catalysts C and D increased their hydrogenation activity as well as the cracking activity.

The spent C catalyst lost considerably its hydrogenation activity (1/2.3) and dramatically its cracking activity (1/22 000) compared with the virgin one, suggesting a different HDS route over fresh and spent catalysts, respectively. Although acidity and hydrogenation activities are supposed to be linked, this relationship is not straightforward, suggesting an indirect participation of the acidity in the hydrogenation activity.

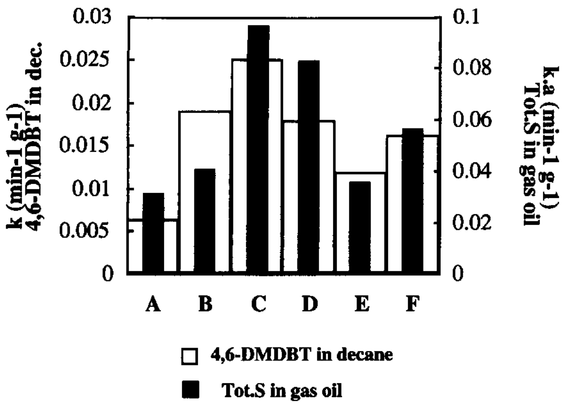

Fig. 3. HDS rate constants for GO (pseudo-1.65 order) and for 4,6-DMDBT (first order) in decane.

3.2. HDS activity for GO and 4,6-DMDBT

HDS tests of GO gave the performance ranking of A–F catalysts according to the total sulfur content (Fig. 3) C>D>F>B>E>A, the pseudo-first order rate constant of 4,6-DMDBT (also 4-MDBT, DBT) in GO C>D>F>B>E=A (Fig. 7(b)–(d)). The similarity of these rankings shows that the best catalyst is most efficient for removal of refractory sulfur species.

The ranking obtained with 4,6-DMDBT in decane (Fig. 3) is similar to that of total sulfur content in GO; but, definitely, NiMo catalysts exhibited a much higher activity for 4,6-DMDBT in decane than for GO. The inhibitors present in GO (aromatics, nitrogen compounds, etc.) and produced by the desulfurization (H_2S) retarded the HDS reaction over NiMo catalysts more severely than over CoMo catalysts.

The most active C catalyst desulfurized 4,6-DMDBT essentially through the isomerization and cracking reactions, both acid catalyzed routes, giving a number of products. Among them, mono and polyalkylated DBTs (not desulfurized products), mono and polyalkylated biphenyls and hydrogenated derivatives (desulfurized products) [5], cracked mono-ring products (benzene, toluene, xylenes, cyclohexane, methylcyclohexanes, etc.) [6] were detected.

Although silica–alumina containing catalyst D exhibited a higher acidity than conventional A CoMo, it did not offer the acidic HDS route. Nevertheless, the catalyst showed the second highest activity.

The ratios of products obtained through the hydrogenation route divided by products obtained

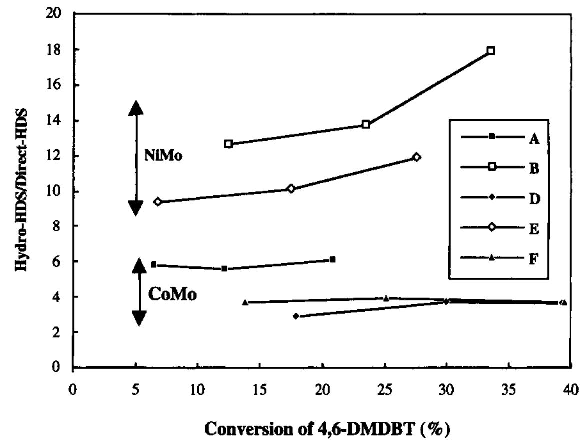

Fig. 4. Route selecivity for HDS of 4,6-DMDBT in decane over commercial catalysts.

through the direct desulfurization route are plotted in Fig. 4 for the five commercial catalysts (except for C) which promoted only two HDS routes, direct desulfurization and desulfurization through hydrogenation. NiMo B had a high activity through its high hydrogenation route, giving a higher ratio of $(\mathrm{H}_2^{\mathrm{tion}}/\mathrm{DirectDesulf.})_{\mathrm{route\ products\ at\ 270^{\circ}C}}=12$ compared to 4 for CoMo D and F catalysts. Hence, the activity difference between catalysts D and F is ascribed to the different numbers of their active sites.

At higher temperature, the direct desulfurization route is much more favored than the hydrogenation route; hence this ratio decreased to 0.3 at 360°C over CoMo and NiMo catalysts. It means that the activation energy for direct desulfurization route is larger than that for the hydrogenation route.

A computational calculation for the reaction of 4,6-DMDBT hydrogenation showed that the thermodynamics limitation of this route becomes significant at temperatures above 350°C.

3.3. HDS activity of modified C and D catalysts

3.3.1. HDS activity of C and D catalysts with more acidic additive

The effects of acidic additive content in C and D type catalysts on HDS were examined. For HDS of 4,6-DMDBT in decane over the series of C catalysts, the higher content of acidic additive increased the HDS activity slightly. According to the product distribution, it was found that the higher performance was due to an enhancement of the cracking route, giving some products without methyl groups at 4- and/or 6- position.

For HDS of 4,6-DMDBT in decane over the series of D catalysts, the higher content of acidic additive also increased slightly the HDS activity. But, in this case, the products distribution showed that the higher activity was attributed to the higher hydrogenation activity, enhancing more the hydrogenation route than the direct desulfurization route. No product from the cracking route was detected over this series of catalysts.

3.3.2. *HDS activity of spent C catalyst*

4,6-DMDBT HDS over spent C catalyst was performed in decane. The activity of spent catalyst was found to be reduced by a factor of 5 compared with the fresh one. The HDS cracking route (main route for fresh C) entirely disappeared. Furthermore, the ratio $(\mathrm{H}_2^{\mathrm{tion}}/\mathrm{DirectDesulf.})_{\mathrm{at\ 270°C}}$ for spent C catalyst is 1.5. This ratio suggests that the remaining hydrogenation route was more affected than the direct desulfurization route, since this ratio for a virgin CoMo catalyst is about 4.

3.4. *Aromatics and H_2S inhibitors in HDS of 4,6-DMDBT in decane*

3.4.1. *Aromatics inhibitors in HDS of 4,6-DMDBT in decane*

Naphthalene, tetralin and isobutylbenzene (0–40 wt% in decane) were used as aromatic model inhibitors present in the real feed.

Such aromatics inhibited the HDS in the order of naphthalene>tetralin>isobutylbenzene as shown in Fig. 5. The HDS products distribution showed that the hydrogenation route was more affected than the direct desulfurization route on NiMo catalyst. Nevertheless, the extent of inhibition by aromatic partners appeared similar regardless of catalysts. Other inhibitors in GO may deactivate NiMo catalyst more compared to CoMo catalysts.

According to a series of HDS tests of 4,6-DMDBT in decane with naphthalene over some Ni,Co–Mo catalysts with the metal weight ratios of 3 Ni, 1.5 Ni/1.5 Co, 0.75 Ni/2.25 Co, and 3 Co [7], it was found that the rate constant at the hydrogenolysis step (the C–S bond breaking of the tetra-hydrogenated 4,6-DMDBT, see Fig. 8) seems to be proportional to the %Co on the catalysts for a total metal loading of %Co+%Ni=3 wt%.

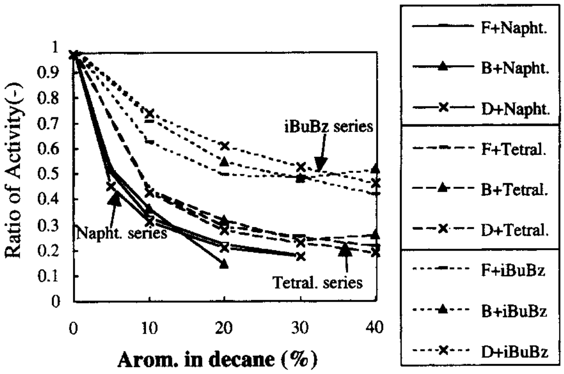

Fig. 5. Ratio of acitivity for HDS of 4,6-DMDBT in decane with aromatics.

The acidic catalyst C was very strongly inhibited by naphthalene which eliminated its major route, that of the cracking, giving the conventional 4,6-DMDBT HDS products, 3,3′-dimethylbiphenyl and 1-(3-methyl)phenyl 3-methyl cyclohexane (see Fig. 8). This strong inhibition is due to the high electron density of aromatic species which leads to a strong adsorption on acidic active sites.

3.4.2. *H_2S inhibitor in HDS of 4,6-DMDBT in decane*

Fig. 6 shows 4,6-DMDBT HDS inhibition by H_2S which was produced by dimethyldisulfide (DMDS, 0–1.5 wt% S) in decane.

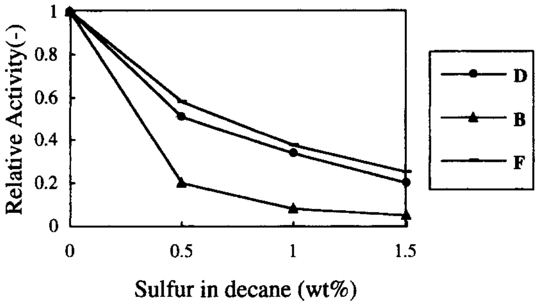

Fig. 6. Ratio of acitivity for HDS of 4,6-DMDBT in decane+dimethyldisulfide (H_2S generator).

At 270°C, H_2S is a strong inhibitor as aromatic hydrocarbons. Particularly, NiMo catalyst B is more inhibited by H_2S than CoMo, explaining partly the lower activity of NiMo in the GO. The HDS products distribution showed that the hydrogenation route is more affected by H_2S than the direct desulfurization route on NiMo. An opposite trend was found over CoMo.

According to a series of HDS tests of 4,6-DMDBT in decane under $H_2 : H_2S$ (95 : 5 vol%) atmosphere over some Ni,Co–Mo catalysts [7], it was confirmed that the hydrogenation rate constant of 4,6-DMDBT (first step in its HDS hydrogenation route) is proportional to the %Co on the catalyst, of a total metal loading %Co+%Ni=3 wt%. Ni has a low promoting efficiency in the presence of H_2S. The hydrogenolysis step rate constant (second step in its HDS hydrogenation route, see Fig. 8) is also proportional to the %Co on the catalyst, of the same total metal loading %Co+%Ni=3 wt% [7]. At least, the direct desulfurization route is more inhibited by H_2S over CoMo catalysts than over NiMo catalysts.

Except for C catalyst, H_2S behaved as an inhibitor like aromatic hydrocarbons: the direct desulfurization route on CoMo catalysts and the hydrogenation route on NiMo catalysts are the most affected. On C catalyst, where H_2S was a weak inhibitor, the aromatic hydrocarbons were relatively stronger inhibitors as reported in a previous paper [8]. In contrast, acidic catalyst D suffered similar HDS inhibition as other alumina supports.

3.5. HDS of LCO compared with that of GO

Fig. 7(a)–(d) shows the comparison between the HDS tests of LCO and GO over the six catalysts under the same conditions. Although the catalysts showed much the same activity for the desulfurization of LCO, some significant differences appeared for GO desulfurization. Acidic catalysts C and D exhibited definitely the highest activities for GO. Acidic catalyst C exhibited a comparable activity with the other catalysts, showing that isomerization and cracking routes are minor for LCO desulfurization probably because of large aromatic content and its severe inhibition.

The rate ratio $k_{\text{in LCO}}/k_{\text{in GO}}$ for particular species decreased in the order of DBT (≈0.5)>4-MDBT (≈0.25)>4,6-DMDBT (≈0.08) in case of catalyst A. It means that the high aromatic content of LCO affected more the hydrogenation route (main route for 4,6-DMDBT) than the direct desulfurization route (main route for DBT).

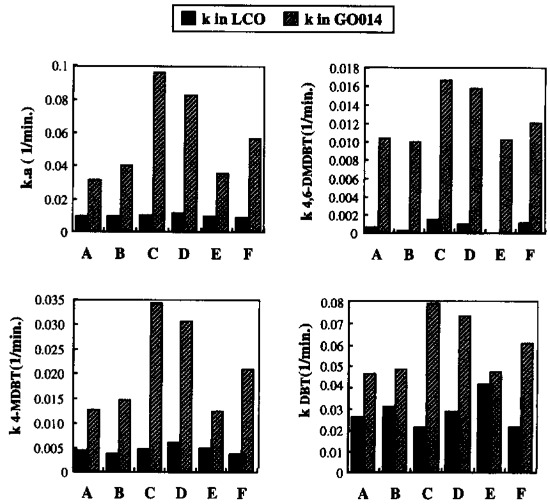

Fig. 7. (a) Total sulfur content in LCO and GO (1.65 order). (b) 4,6-DMDBT in LCO and GO (first order). (c) 4-MDBT in LCO and GO (first order). (d) DBT in LCO and GO (first order).

NiMo catalysts showed a slightly higher activity than CoMo catalysts for HDS of DBT, while CoMo are superior to NiMo for 4,6-DMDBT. It was confirmed that the direct desulfurization route was more inhibited by aromatic hydrocarbons on CoMo than on NiMo, whereas the hydrogenation route is more inhibited by aromatics on NiMo than on CoMo as observed with GO.

4. Discussion

The present study compared the catalytic activities of six catalysts for HDS of a GO and aimed to clarify the high activity of CoMo on acidic supports.

One can examine the HDS reactivity of 4,6-DMDBT in decane with inhibitors such as aromatic compounds and H_2S to evaluate the performances and schemes for the available catalysts. The schemes are summarized in Fig. 8 where three major routes are included. The present comparisons of the catalysts clarified several points of discussion. The catalysts achieved the deep desulfurization by the desulfuriza-

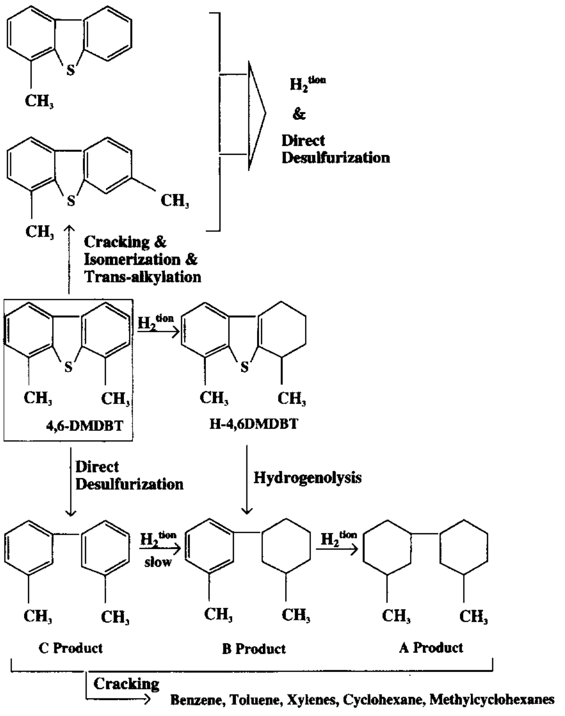

Fig. 8. HDS reaction scheme for 4,6-dimethyldibenzothiophene.

tion of 4,6-DMDBT through the hydrogenation and acidic routes, which are both inhibited severely by aromatics partners, high electron density compounds, similarly to basicity. Both routes can be evaluated by standard tests using hydrogenation of naphthalene and transalkylation of isopropylbenzene, respectively. Very acidic zeolite-containing catalyst allowed the isomerization and cracking of sterically hindering methyl groups [9], such as for 4,6-DMDBT in decane. However such catalysts suffer the decrease of these properties with the time on stream by coking and are inhibited by aromatic partners. So the importance of acidic routes decreases for HDS of real feed stocks than for that of 4,6-DMDBT in decane. Silica–alumina supported and zeolite-containing acidic catalysts exhibited a much higher HDS activity for 4,6-DMDBT in decane compared to the other catalysts, however, their activity leveled off for HDS of high aromatic content LCO or under stationary conditions where coke deposition removes the acidity.

Interestingly, it was found that acidity of the catalyst appears to enhance the hydrogenation activity of CoMo which accelerates the desulfurization. The support exhibiting increased acidity exhibits increased 'activation' of hydrogen from H_2S which results in increased reaction rate in hydrogenation reaction involved in GO desulfurization [10]. Or, the spillover hydrogen attacks the reaction intermediate which is formed on some strong Brønsted acid site [11] for the hydrogenation reaction. Lower coking acidity obtained with silica–alumina support provides a high hydrogenation activity, which is moderately inhibited by aromatic hydrocarbons, explaining the high activity for HDS of GO and the highest activity for HDS of LCO. It should be noted that the spent catalyst C containing zeolite showed quite high hydrogenation activity even if it lost completely the acidic activity as determined by transalkylation of cumene. Addition of zeolite with well-controlled acidity provides hydrogenation activity [12] which is coke resistant.

Inhibition by H_2S is important for the studies on model molecule at 270°C, although this effect may be lower at higher temperature, under practical conditions, owing to the decrease of the H_2S adsorption constant with the temperature. The stronger adsorption of H_2S on the catalyst, the higher the inhibition of H_2S [13].

Strong adsorption of aromatics and H_2S is involved in their inhibiting behavior on catalysts. The same kind of adsorption phenomenon could explain the similarity of their qualitative inhibition effects; indeed, aromatics and H_2S affected severely the direct desulfurization route on CoMo and the hydrogenation route on NiMo. CoMo suffers much less inhibitions by aromatics partners and H_2S than NiMo, being superior in the practical desulfurization. It should be noted that the inhibition of H_2S appears less on the acidic catalysts probably due to their higher hydrocracking activity against alkyldibenzothiophenes and H_2S.

Hence, the catalyst which is more active and selective for the hydrogenation of 4,6-DMDBT in presence of inhibitors can be a target of better performance. The support for CoMo catalysts can be thus explored in terms of controlled acidity and better dispersion of CoMo.

Acknowledgements

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