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Deep desulfurization of diesel fuels: kinetic modeling of model compounds in trickle-bed

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Abstract

Five catalysts with different hydrodesulfurization (HDS) and hydrogenation activity were tested in HDS of fresh crude heavy atmospheric gas oil (HAGO) (1.33 wt% S), two partially hydrotreated HAGO (1100 and 115 ppm S) and two model compounds, dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (DMDBT), dissolved in model solvents and HAGO. Aromatic compounds in the liquid decreased significantly the HDS rate of 4,6-DMDBT, especially for catalysts with high hydrogenation activity. H_2S displayed a similar inhibition effect with all catalysts. These effects were extremely pronounced in HAGO where the DBT HDS rate decreased by a factor of 10 while 4,6-DMDBT – of 20 relative to paraffinic solvent. The feasibility of using a highly active hydrogenation catalyst for deep HDS of HAGO is diminished by the strong impact of aromatics. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Hydrodesulfurization; Diesel fuel

1. Introduction

Deep hydrodesulfurization (HDS) of heavy atmospheric gas oil (HAGO) requires removal of the polyaromatic sulfur compounds, mainly substituted on 4 or/and 6 position dibenzothiophenes (DBT) that displayed a much lower HDS rate on Co–Mo–Al catalyst compared with DBT [1–11]. Increasing the aromatics hydrogenation (HYD) activity of the mixed sulfide catalysts enhances HDS of 4-M- and 4,6-DMDBT via HYD route, but lowers HDS via direct S–C bond scission route [1,4,10]. So catalysts with improved HYD activity should display a better performance in deep HDS of gas oil compared with Co–Mo–Al. However, a correlation between activity of different catalysts in HDS of alkyl substituted DBT and their performance in deep HDS of gas oils was not found [12–14]. The discrepancy between the higher efficiency of catalysts with improved HYD activity in HDS of hindered DBT and their poor performance in deep HDS of gas oils could be a result of inhibiting effect of H_2S in the gas phase and aromatic compounds in HAGO [14].

The objective of this study is to quantify the kinetic behavior of model compounds, determine the inhibiting effect of aromatic compounds and H_2S and clarify to what extent the information about catalysts performance in HDS of model polyaromatic sulfur compounds: DBT and 4,6-DMDBT, could be used for prediction of the catalysts performance in HDS of real gas oils.

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2. Experimental

The kinetic measurements were carried out in a high-pressure, fixed-bed, mini-pilot reactor, controlled automatically by a PC and described in details elsewhere [15]. 5 cm^3 of catalyst mixed with 10 cm^3 of 0.2 mm silicon carbide were packed in a 2.2 cm i.d. reactor between two 15 cm^3 layers of silica. Two commercial Co–Mo–Al (A and B) and three proprietary catalysts: Ni–Mo–Si (C) and Ni–W–Si (D and E) were tested. Their composition and physical properties in oxide form are given in Table 1. All catalysts were sulfided for 24 h with 1.5% dimethyldisulfide–toluene mixture at LHSV=2.5 h^{-1}, 320°C, hydrogen pressure of 5.4 MPa and hydrogen to toluene ratio 500 Nl/l. All HDS measurements were carried out at 360°C, hydrogen pressure of 5.4 MPa and hydrogen to liquid ratio 500 Nl/l, while toluene HYD was conducted at 355°C, 1500 Nl/l.

Model compounds and products of their hydroconversion were analyzed by GC and GC–MS. The gas oil composition was determined by GC–MS and HPLC, organic sulfur content was measured by X-ray fluorescence.

1000 ppm of 4,6-DMDBT, prepared according to a published method [16], and DBT were dissolved in 30 wt% *n*-decane+70 wt% *n*-octadecane and 21 wt% *n*-decane+49 wt% *n*-octadecane+30 wt% tetralin mixtures. 4.5 wt% of model compounds were dissolved in fresh HAGO. H_2S was produced in situ by decomposition of dimethyldisulfide (1.33 wt% S in feed).

Three HAGO feedstocks were used in this study as listed in Table 2. Hydrotreated (HT) HAGO 1 and 2 were obtained by hydrotreating of fresh HAGO with commercial B catalyst and stripping with nitrogen to remove the dissolved H_2S.

The proper operation of the reactor for kinetic work was determined using well-established criteria [17–19]. Calculations indicated that dilution with the silicon carbide powder yields good liquid contacting, distribution and plug flow operation.

3. Results and discussion

3.1. Kinetic data fit

Hydrogenation rate of toluene as well as DBT and 4,6-DMDBT desulfurization in the paraffinic solvent was determined to be first-order with respect to the organic reactant as illustrated in Figs. 1 and 2 for catalyst B. Experiments with other catalysts and in other solvents displayed a similar kinetic behavior. Similar results for individual polyaromatic sulfur compounds in model solvents and real gas oils were obtained in previous studies [1,4,8,10].

Desulfurization of DBT yielded three organic products: biphenyl (BPH), product of desulfurization route, cyclohexylbenzene (CHB) and bicyclohexane

Table 1
Catalysts properties

	Catalyst				
	A	B	C	D	E
Chemical composition (wt%)					
Co	4.3	6.3	–	–	–
Ni	–	–	19.1	16.3	16.6
Mo	17.5	18.4	34.2	–	–
W	–	–	–	27.5	26.8
Support	Al_2O_3	Al_2O_3	SiO_2	SiO_2	SiO_2
Surface area (m^2/g)	230	280	90	180	180
Pore volume (cm^3/g)	0.41	0.49	0.15	0.35	0.37
Bulk density (g/cm^3)	0.63	0.75	1.15	1.1	1.0
Average length (mm)	5.2	5.2	–	4.8	4.8
Average diameter (mm)	1.3	1.3	1.5	1.7	1.7
Shape	Quadralobes	Quadralobes	Pellets	Cylinders	Cylinders

Table 2
Characteristics of gas oils

Feedstock	Fresh HAGO	HT HAGO-1	HT-HAGO-2
Density, 15°C (kg/l)	0.862	0.849	0.845
Distillation range (°C)	142–390	145–388	144–385
Composition[a] (wt%)			
Paraffins	30	31	31
Naphthenes	41	41.7	42.7
Aromatics			
Mono-	21	20	23.5
Bi-	7.5	7.3	2.8
Tri-	0.5	–	–
Sulfur content (wt%)	1.33	0.11	0.0115
Sulfur compounds (wt%)			
PASC[b]	2.2	0.8	0.1
Thiols and sulfides	7.2	–	–

[a] The hydrocarbons composition of HAGO was analyzed by HPLC; sulfur compounds and sulfur were separately analyzed by GC–MS and X-ray fluorescence, respectively.
[b] Polyaromatic sulfur compounds.

(BCH), products of hydrogenation route. The reaction scheme which was proved in previous studies [1,7] could be seen in Fig. 3. Similarly, for 4,6-DMDBT, dimethyl–biphenyl (DMBPH), dimethyl–cyclohexylbenzene (DMCHB), and dimethyl–bicyclohexane (DMBCH) were measured. No tetra- and hexahydro-DBTs were determined as expected from their high reactivity [1,2,7,20]. The mass balances of these experiments were 94–98%.

The molar ratio of CHBs and BCHs to BPHs products, called α, produced from both DBT and 4,6-DMDBT were calculated to determine the relative contribution of HYD route to HDS of model compounds with different catalysts. α increased slightly with DBT or 4,6-DMDBT conversion in runs with Co–Mo and Ni–Mo catalysts displaying a comparatively low HYD activity (k for HYD of toluene was 0.3–0.7 h^{-1}) in agreement with [4]. In addition, these catalysts yielded only traces of BCHs in agreement with [7] and BPhs hydrogenation occurs with relatively low rate as was reported previously [7]. Thus, the contribution of hydrogenation of aromatic rings in the desulfurized molecules to CHBs formation is low and therefore α strongly correlate with relative rates of HYD and HDS routes. However, Ni–W catalysts displayed a high HYD activity (k for HYD of toluene was 3–6 h^{-1}) and a strong dependency of α on conversion, shown in Fig. 4. Moreover, in this case about 30% of hydrogenated products (at 80% conversion of model compound in paraffinic solvent) were BCHs. It means that HYD of aromatics rings occurred with

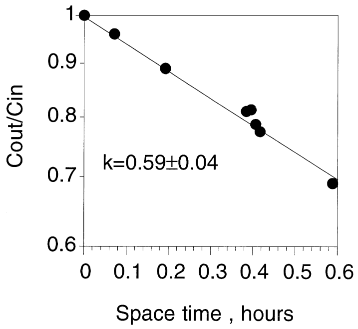

Fig. 1. Pseudo-first-order kinetics of HYD of toluene with catalyst B.

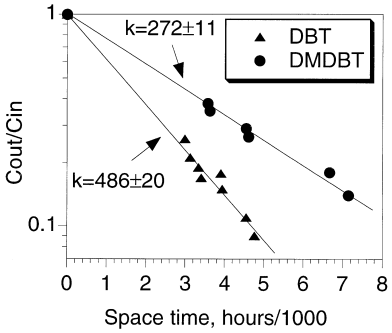

Fig. 2. Pseudo-first-order kinetics of HDS of DBT and 4,6-DMDBT with catalyst B.

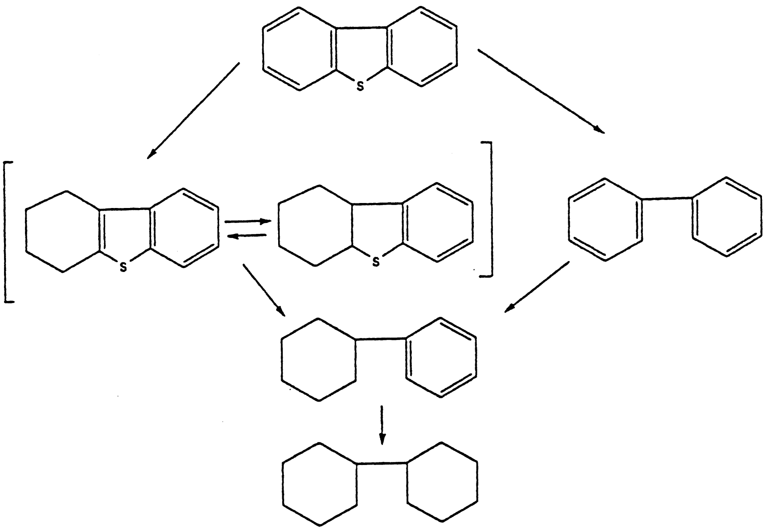

Fig. 3. Reaction scheme for DBT.

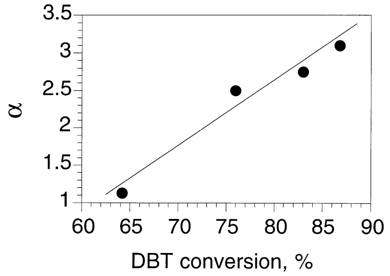

Fig. 4. Effect of DBT conversion with catalyst D on α.

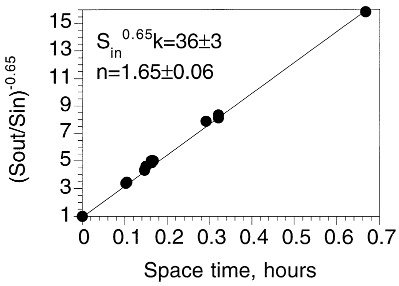

Fig. 5. HDS of fresh HAGO with catalyst B.

significant rate in parallel with HDS on this type of catalysts. However, parameter α, calculated at the same conversion for all catalysts, is a proper tool to compare the contribution of HYD route relative to direct HDS of model compounds on different catalysts.

As mentioned already, the HDS rate of individual sulfur compounds fits pseudo-first-order kinetics. However, the desulfurization rate was determined to be of 1.65 order with respect to total sulfur concentration in fresh HAGO. The formal kinetics of a non-integer order (which normally lies in the range 1.5–2.0 for similar feedstocks) is a result of superposition of pseudo-first-order rates for individual sulfur compounds with different reactivity presented in the fresh HAGO [1]. The fit of data in Fig. 5 with catalyst B supports this pseudo-kinetic expression and other catalysts displayed a similar kinetic behavior.

In other hand, HDS of HT HAGO containing 1100 (up to about 80% of sulfur conversion) and 115 ppm S fits pseudo-first-order kinetics, as illustrated in Fig. 6 with catalyst B. Other catalysts displayed a similar kinetic behavior. HAGO with such a low sulfur content contains only a sulfur species with similar HDS reactivity, thus lumping them as one pseudo-component is suitable.

The rate constant in HT HAGO containing 115 ppm S was lower than that of HT HAGO containing 1100 ppm S. The former HT HAGO was hydrotreated in more severe conditions compared to the latter and therefore it contains most refractory sulfur compounds

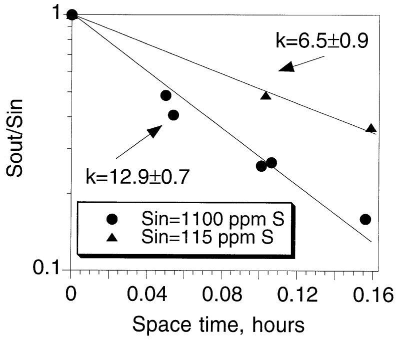

Fig. 6. HDS HT HAGO containing 1100 and 115 ppm S with catalyst B.

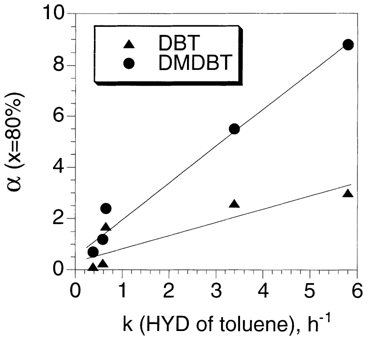

Fig. 7. A correlation between toluene HYD rate and α-values.

which react in lower rate compared to the average rate of sulfur species in HT HAGO 1.

3.2. HDS and HYD of model compounds

The hydrogenation route for HDS of refractory sulfur species was tested with a series of catalysts Co(Ni)–Mo(W) designed to cover a wide range of activity for aromatic ring hydrogenation. The HYD activity was primarily determined by hydrogenation of toluene. The activity of selected catalysts varied over a range of more than one order of magnitude, as illustrated in Table 3. As expected [1], Ni–W systems are much more active than Co–Mo systems.

The pseudo-first-order rate constants for HDS of DBT and 4,6-DMDBT in paraffinic solvent, and α values at 80% conversion are also listed at Table 3. There are no apparent correlation between the k values for HDS of DBT or 4,6-DMDBT and HYD of toluene.

Increasing the catalysts HYD activity increased the α-ratios of both DBT and 4,6-DMDBT, as shown in Fig. 7. It means that for catalysts with improved HYD activity, the HYD route becomes more important. However, the dependency of α values on HYD activity is more pronounced in case of 4,6-DMDBT compared with DBT. The contribution of HYD route relative to direct HDS route is more significant for 4,6-DMDBT than for DBT in agreement with data measured in other studies [1,2,4,5,7].

The influence of methyl groups on HDS of DBT can be defined as a ratio between observed HDS reactivity of 4,6-DMDBT and DBT. Increasing the catalysts HYD activity increases this ratio (Table 3) in agreement with [1,4]. Moreover, catalysts with improved HYD activity display values higher than unity. Interestingly, the methyl groups enhanced the HYD rate of DBT molecule, as reported previously [1,2,4,8]. A catalyst that displays a relatively high HYD activity channels the HDS reaction through the HYD route. Therefore, the 4,6-DMDBT HDS rate was higher than the DBT HDS rate in specific cases. Different active sites on the surface of sulfided catalysts perform as catalytic centers for aromatic ring saturation and S–C bond scission reactions [1,21,22]. Increasing of num-

Table 3
Catalysts performance with model compounds

Catalyst	Toluene HYD	DBT HDS		DMDBT HDS		HDS k_{DMDBT}/k_{DBT}
	k (h^{-1})	k (h^{-1})	α (x=80%)	k (h^{-1})	α (x=80%)	
A	0.38±0.04	110±8	0.12	25±1	0.7	0.23
B	0.59±0.04	486±20	0.27	272±11	1.2	0.56
C	0.65±0.05	63±4	1.7	52±5	2.4	0.83
D	3.4±0.4	377±20	2.6	380±19	5.5	1.01
E	5.8±0.5	362±17	3.0	422±21	8.8	1.16

ber of one type of active sites leads to decreasing of number of another type if the total number of active sites remains similar. Thus increasing of HYD activity of catalyst – increasing of number of HYD active sites by different methods of preparation for the same catalytic system (without increasing of total activity – total number of active sites), may decrease the direct HDS activity as result of decreasing of number of direct HDS active sites. Therefore, the ratio of the HDS activity of 4,6-DMDBT and DBT can be larger than unity also as a result of depressing of direct HDS rate – the important route for DBT HDS.

A comparison of D and E catalysts performance confirms that increasing the HYD activity of E relative to D (by different method of preparation) led to increasing of α and of the 4,6-DMDBT HDS rate, but decreased the DBT HDS rate. It appears that an effective catalysts for HDS of model compounds should contain an optimal ratio of HYD and direct HDS active sites depending on the nature of sulfur species. But the nature of active sites is still not well defined and the methods of controlling their relative amount are not available [21,22].

Fig. 8 illustrates the effect of solvent and H_2S on HDS rate of DBT and 4,6-DMDBT for two selected catalysts: the most active in DBT HDS (catalyst B) and the most active in 4,6-DMDBT HDS (catalyst E). Addition of aromatics (tetralin) to the paraffinic solvent affects the HDS rate with catalyst E more significantly than with catalyst B. Aromatics probably compete with polyaromatic sulfur compounds for adsorption sites for HYD, thus affecting the HYD route of HDS more than direct HDS route. The significant effect of aromatics on HYD HDS route is illustrated by the comparison of the inhibition effect on 4,6-DMDBT relative to DBT on both catalysts. Aromatics decrease the 4,6-DMDBT activity by a factor higher than 2.5 while DBT HDS rate drops less than by 20%. So aromatics affect mainly HYD HDS route – the most important route for 4,6-DMDBT. As a result the catalysts with improved HYD activity converting polyaromatic sulfur compounds mostly via HYD route were inhibited by aromatics more than Co–Mo catalysts.

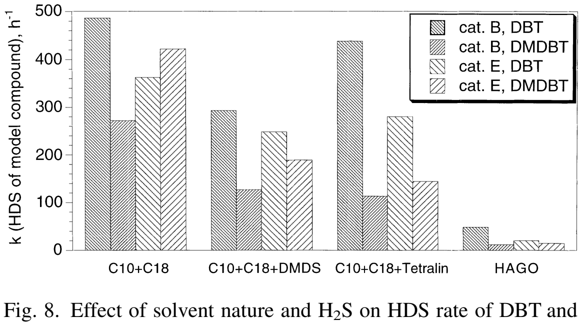

Fig. 8. Effect of solvent nature and H_2S on HDS rate of DBT and 4,6-DMDBT.

H_2S concentration at the levels corresponding to deep desulfurization simulated by decomposition of DMDS (1.33 wt% sulfur in feed) reduced the HDS rate of DBT and 4,6-DMDBT by a factor of about 1.6 and 2.2, respectively. A similar trend was reported in previous studies [1,10,23]. Little differences in the H_2S effect on activity of different catalysts were detected, undepended on their HYD activity.

HAGO has an extreme inhibition effect on HDS rate of model compounds. The rate constant decreased by a factor of 10–20 relative to the paraffinic solvent in agreement with other studies [2,9]. This can be partially explained by the presence of H_2S and especially poly-aromatics that appear to have a stronger inhibition effect on HDS of refractory sulfur compounds than mono- or naphthene-aromatics [14,24], naphthenes, nitrogen and oxygen compounds [12,25]. Inhibition effect of HAGO on the HDS rate of DMDBT was more significant than DBT. Therefore, the advantage of catalysts with improved HYD activity in 4,6-DMDBT HDS in paraffinic solvent are greatly reduced in real feedstocks.

3.3. Correlations between HDS of model compounds and HAGO

The HDS activity in desulfurization of fresh and HT HAGO containing 1100 ppm sulfur correlates with HDS of DBT measured in paraffinic solvent (see Table 3), as shown in Fig. 9. A similar plot for 4,6-DMDBT displays no correlation. The concentration of most refractory sulfur species like 4,6-DMDBT is relatively small [10] and non-thiophenic and other sulfur compounds like thiophenes, benzothiophenes react mainly via direct HDS route – the most important route for DBT. Therefore fresh HAGO HDS rate correlates with DBT HDS rate and does not correlate with 4,6-DMDBT HDS rate. HT HAGO with 1100 ppm sulfur contains only polyaromatic sulfur

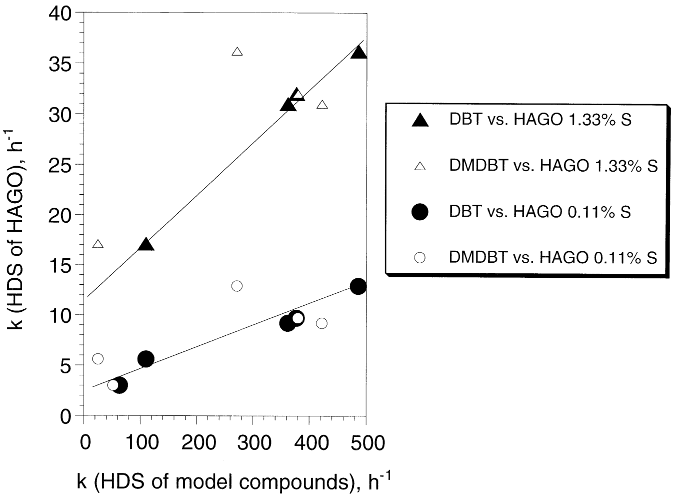

Fig. 9. A correlation between HDS rate of DBT and HAGO containing 1.33% S and 0.11% S.

compounds (Table 2), but only part of them are the least reactive sulfur compounds like 4,6-DMDBT. A correlation between HT HAGO containing 1100 ppm S and DBT HDS rate is probably a result of the strong inhibition of HYD route by aromatics, that remain almost unreacted (Table 2). Thus polyaromatic sulfur compounds may react mainly via direct HDS route that appears to be more important even for least reactive polyaromatic sulfur compounds like 4,6-DMDBT. This is also supported by the good fit of the HDS of HAGO containing 1100 ppm S to pseudo-first-order kinetics.

The opposite behavior was measured for selected catalysts in HDS of HT HAGO containing only 115 ppm S (Fig. 10). HYD route becomes more important relative to direct HDS route since the least reactive polyaromatic sulfur compounds like 4,6-DMDBT react at a very low rate via direct route. Furthermore, most of the polyaromatics were saturated (Table 2). So the HYD route was less inhibited relative to fresh HAGO and HT HAGO containing 1100 ppm S.

Pseudo-first-order constant of HDS of HAGO containing 115 ppm S with catalyst B decreases by a factor of two relative to HAGO containing 1100 ppm S. A similar comparison for catalyst E indicated a little change (Figs. 9 and 10). Catalysts with relative low HYD activity convert polyaromatic sulfur compounds like 4,6-DMDBT at a lower rate than other polyaromatic sulfur compounds in all solvents as a result of very low contribution of HYD route. The catalysts with improved HYD activity convert 4,6-DMDBT more effectively than DBT in paraffinic solvent (Table 3). In both HT HAGO, the HYD route is strongly inhibited by aromatics, so polyaromatic sulfur compounds like DBT react at a higher rate than refractory polyaromatic sulfur compounds like 4,6-DMDBT also on catalysts with improved HYD activity, but inhibition effect is lower in HT HAGO containing 115 ppm S. Thus HDS rate of two HT HAGO is nearly similar on catalysts with

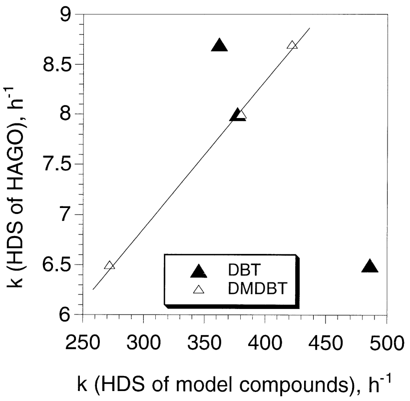

Fig. 10. A correlation between HDS rate of 4,6-DMDBT and HT HAGO containing 115 ppm S.

improved HYD activity and they are superior to catalyst B with high direct HDS activity only in HDS of HT HAGO containing 115 ppm S.

4. Conclusions

Five Co–Mo, Ni–Mo and Ni–W catalysts were tested in HDS of DBT and 4,6-DMDBT dissolved in n-C_{10}+n-C_{18}, n-C_{10}+n-C_{18}+tetralin, n-C_{10}+n-C_{18}+DMDS mixtures and industrial HAGO. Their HYD activity, determined by HYD of toluene, ranged over more than one order of magnitude. HDS performance of catalyst was tested in fresh and two partially (1100 and 115 ppm residual sulfur) HT HAGO.

The rate of HDS for both DBT and 4,6-DMDBT was first-order with respect to the organic reactant in all solvent with all catalysts, as expected. The HDS rate order was also unity with respect to sulfur in HT HAGO (1100 and 115 ppm residual sulfur) while the order was 1.65 in fresh HAGO. The similar reactivity of residual sulfur allows to lump all compounds. The rate of desulfurization of DBT was normally higher than 4,6-DMDBT, except for the catalysts with improved HYD activity. However, aromatic compounds in the liquid decreased significantly the rate of reaction of 4,6-DMDBT by the hydrogenation route diminishing the advantage of catalysts with improved HYD activity. H_2S displayed a similar poisoning effect on HDS rate for Co–Mo and catalysts with improved HYD activity. These effects are extremely pronounced in HAGO where the HDS rate decreased by more than one order of magnitude relative to paraffinic solvent. As a result of strong inhibition effect of aromatics the activity of Co–Mo and catalysts with improved HYD activity in 4,6-DMDBT HDS dissolved in HAGO become almost equal.

HDS rate of fresh HAGO and even HT HAGO containing 1100 ppm S correlate with DBT HDS rate and does not correlate with 4,6-DMDBT HDS rate, while 4,6-DMDBT HDS rate correlate with HT HAGO containing only 115 ppm S and lower amounts of aromatics.

Therefore, the feasibility of using a highly active hydrogenation catalyst for deep desulfurization of HAGO is diminished by the strong impact of aromatic compounds.

Acknowledgements

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