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Catalysis Today 98 (2004) 67–74
CATALYSIS TODAY
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Competitive effects of nitrogen and sulfur content on activity of hydrotreating $CoMo/Al_2O_3$ catalysts: a batch reactor study

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Abstract

The effect of sulfur and nitrogen contents on the activity of $CoMo/Al_2O_3$ hydrotreating catalyst was investigated using model reactants such as dibenzothiophene (DBT) for hydrodesulfurization (HDS), 2,6-dimethylaniline (DMA) for hydrodenitrogenation (HDN), and 1-methylnapthalene (1-MN) for hydrodearomatization (HDA) in a batch reactor at 4 MPa and 340 °C. The effect of sulfur (0–2 wt.%) and nitrogen (0–0.2 wt.%) contents was studied by changing the concentrations of DBT and DMA, respectively. The presence of sulfur and nitrogen compounds together in a feed illustrated the way produced H_2S and NH_3 influence the catalyst properties. The sulfur content was varied at fixed nitrogen content vis-à-vis variation of nitrogen at fixed sulfur content. Interestingly, the observed relative decrease in activity at high concentrations of DBT or DMA followed similar trend. The conversion of model feed was used to find out better insight for the inhibition in hydrotreating functionalities such as C–S and C–N hydrogenolysis and hydrogenation. Among these, all catalytic functionalities were not affected at similar magnitude with added sulfur or nitrogen content. The results indicated that adsorbed S and/or N species, which caused a decrease in hydrogenolysis activities, inhibited a part of the catalytic sites. The results also indicated opposite effects of the produced H_2S and NH_3 on selectivity. H_2S improves slightly the selectivity for hydrogenation contrary to NH_3 that causes a strong decrease in hydrogenation selectivity.

Keywords: Hydrodesulfurization; Hydrodenitrogenation; Hydrogenation; Sulfided catalyst; Inhibition; Active sites; Effect of hydrogen sulfide; Effect of ammonia; Competitive reactions

1. Introduction

An ultra-clean transportation fuel is a topic of enormous interest in petroleum and automotive industries, and this is a strong incentive for the hydroprocessing research community worldwide. There has been growing interest in developing highly active catalysts for deep hydrotreating to satisfy the environmental norms that limit the amount of sulfur in gas oil to less than 50 wppm or below, i.e. as low as 15 wppm in coming years [1–3]. Deep hydrodesulfurization (HDS) and hydrodearomatization (HDA) of middle distillate plays a crucial role in obtaining the above said specifications, because the remaining sulfur compounds in diesel fuel at 500 wppm level are refractory sulfur in nature [4,5]. These refractory sulfur compounds are alkyldibenzothiophenes with one or more alkyl groups as substituants that strongly hinder the catalyst HDS activity [6–8].

Situation gets complicated when highly active catalysts (apart from the catalyst composition and material) are used for high conversion of sulfur compounds in oil feed stocks, which produce a large quantity of H_2S that can amount up to 0.3 MPa (≥90% conversion) at the exit of the hydrotreating reactor [9,10]. In industrial trickle bed reactors, HDS produces large amount of H_2S, which is responsible for severe inhibition on catalyst activity along the reactor length. The importance of inhibition effects on hydrotreating catalysts were taken up for H_2S [10–15] as well as for nitrogen compounds including ammonia [14–25]. It is difficult to obtain a low level of sulfur in gas oils without considering the effect of inhibitors as a real problem for practical deep desulfurization of middle distillates. On the other hand, these streams are rich in refractory sulfur compounds and

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doi:10.1016/j.cattod.2004.07.020

aromatics and contain high nitrogen contents. Thus, the influence of nitrogen and sulfur compounds will become relatively more important at low level of hydrodesulfurization. In this regard, particular attention has been focused on the effect of S- and N-containing model compounds considering competitive adsorption of those compounds and that of their products on catalyst surface. In addition, the role of H_2, H_2S and NH_3 adsorption on catalyst is of prime importance because these molecules and their dissociative species control the number and nature of active sites on hydrotreating catalyst. Recently, detailed reviews [11,15] were published discussing role of H_2, H_2S and reactive H species issued from their dissociation. Thus, it would be interesting to compare the effect of sulfur molecules together with that of nitrogen model compounds. Such study will give fundamental insight on the inhibition effect and it will help in understanding the industrial hydrotreating operations.

In our present investigation, we focused on studying the effect of nitrogen and sulfur contents on several hydrotreating reactions occurring in the middle distillate range: HDS of dibenzothiophene (DBT), hydrodenitrogenation (HDN) of 2,6-dimethylaniline (DMA), and HDA of 1-methylnapthalene (1-MN). Variation of S (0–2 wt.%) and N (0–0.5 wt.%) contents was studied by changing the concentration of DBT and DMA, respectively. The effects of H_2S and NH_3, modification of catalyst surface in presence of inhibiting species, and the reaction pathway of model molecules are discussed. The effect of S and N contents on catalytic activities and selectivities of a catalyst are reported, and results are discussed under the influence of H^+, H^-, and SH^- species adsorption on vacancy and sulfur-saturated sites [11].

2. Experimental

2.1. Catalyst and sulfidation

The oxidic commercial HR306-C1.2 catalyst (Co, 2.3 wt.%; Mo, 9.4 wt.%) from Axens, having BET-specific surface area 200 $m^2\ g^{-1}$ and pore volume 0.53 mL g^{-1}, was crushed and sieved between 0.2 and 0.5 mm. Before use in the batch reactor, a mass of catalyst (0.88 g) was dried at 400 °C for 1 h, then sulfided ex-situ in a mixture of 12% H_2S in H_2 (v/v) at 400 °C (heating rate 2.5 °C min^{-1}) for 2.5 h in a fixed bed glass reactor operating at atmospheric pressure; the temperature was decreased to 25 °C, and finally the sulfided catalyst was flushed with argon for 5 h.

2.2. Feed composition

A typical procedure was followed to prepare feed composition—DBT (0–0.65 mol L^{-1}) was dissolved in a mixture of *cis*- (55%) and *trans*-decalin (45%), DMA (0–0.36 mol L^{-1}), 1-MN (0.1 mol L^{-1}), and decane (0.05 mol L^{-1}) as an internal reference. The synthetic feed mixture (175 mL) was poured into the batch reactor, and the sulfided catalyst was transferred into the steel grids basket under Ar atmosphere at 25 °C.

2.3. Catalytic activity measurements

Hydrotreatment of the complex feed was performed in a 500-mL autoclave-type Robinson–Mahoney reactor equipped with a sampling port. The reactor was closed and pressurized with hydrogen and heated to 340 °C at the heating rate of 2.5 °C min^{-1}. The reaction began when the agitation (700 rpm) started at 340 °C and 4 MPa. Liquid samples were removed periodically and analyzed by GC. The liquid remaining in the sampling line (1/16'') was flushed back to the reactor with H_2. In this way H_2 pressure remained constant throughout the experiment. Reaction mass balances were found to be more than 95% in all experiments, for each reactants using decane as internal reference for analysis. In a typical experiment, about 12 liquid samples of approximately 0.5 mL each were withdrawn, so that the volume feed could be considered constant throughout the experiment. The liquid samples were diluted in ethanol (500 mL) and analyzed by GC using an FID detector and an OV101 capillary column at a temperature programmed from 40 to 150 °C (12 °C min^{-1}). Conversions were calculated according to the disappearance of reactant or the formation of products. The conversions for DBT, DMA and 1-MN are reported here after 4 h reaction-on-time.

3. Results

The results obtained on sulfided CoMo catalyst are shown for DBT in Fig. 1 and for DMA in Fig. 2. These results were obtained for the highest sulfur content used, i.e. 2.0 wt.% sulfur, and for 0.2 wt.% nitrogen using DBT and DMA as a

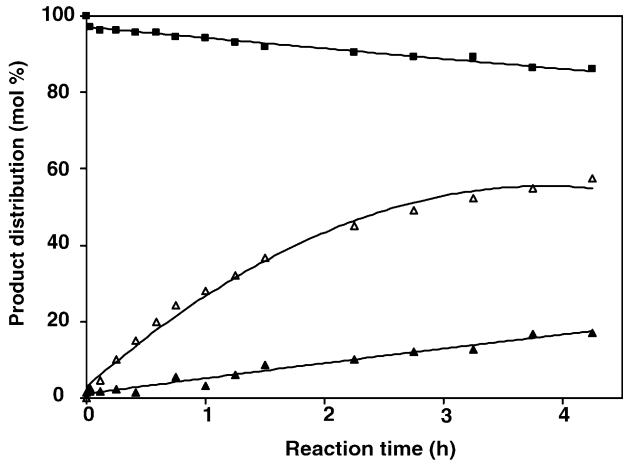


Fig. 1. Product distribution in the reaction of dibenzothiophene in presence of 2.0 wt.% S and 0.2 wt.% N content: (■) DBT; (△) BP × 5; (▲) CHB × 10.

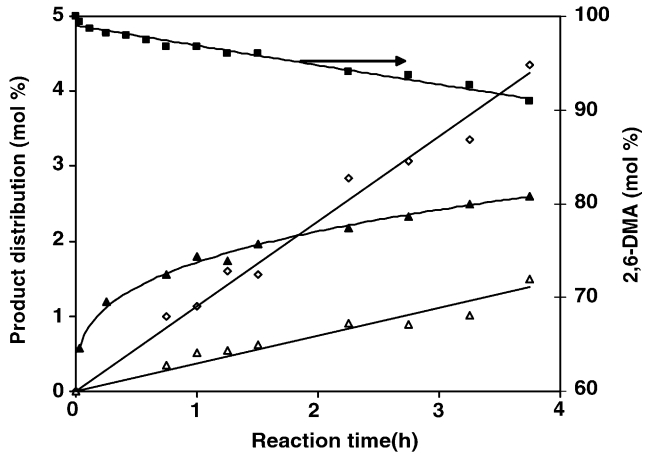
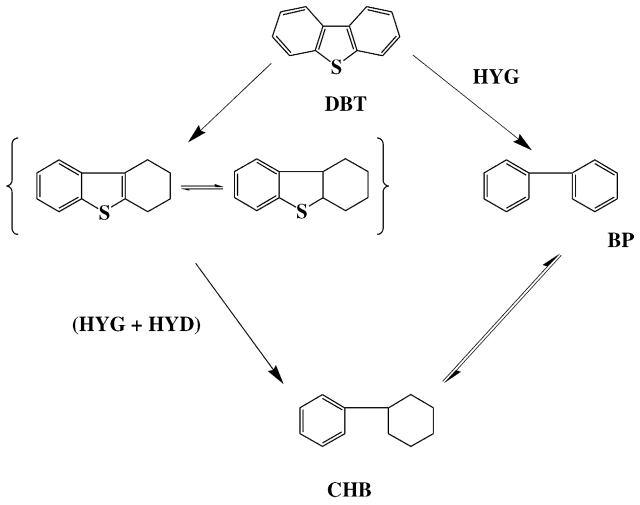


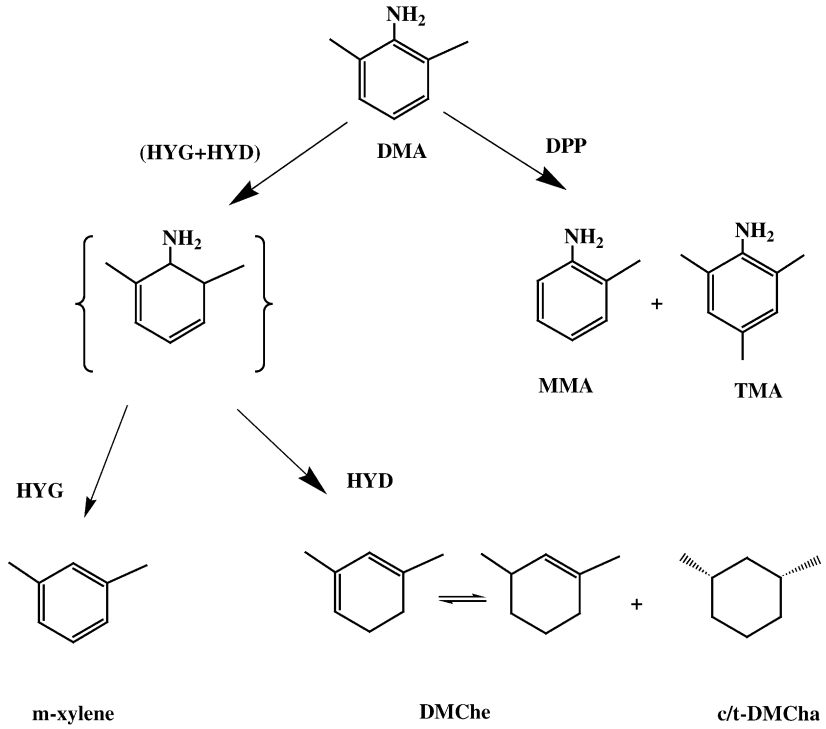
Fig. 2. Product distribution in the reaction of 2,6-dimethylaniline in presence of 2.0 wt.% S and 0.2 wt.% N content: (■) 2,6-DMA (◇) HYD; (△) HYG; (▲) DPP.



Scheme 1. Dibenzothiophene reaction network.

source for S and N, respectively. The two major products of DBT conversion are biphenyl (BP) produced by direct desulfurization or via the hydrogenolysis (HYG) route, and cyclohexylbenzene (CHB) produced via the hydrogenation (HYD) route. BP appears as the main product and the reaction pathway is shown in Scheme 1. Negligible amounts of tetrahydrodibenzothiophene and dicyclohexylbenzene could be detected after 3-h reaction time. Decalin and decane, contained in the feed as solvent and internal standard respectively, remained unconverted under our reaction conditions, except for an isomerization from *cis*- to *trans*-decalin.

The m-xylene, dimethylcyclohexenes (DMChe), dimethylcyclohexanes (DMCha), and monomethyl- and trimethylaniline (MMA, TMA) are major products for DMA conversion. The reaction pathway of 2,6-dimethylaniline conversions consists of three parallel reactions: hydrogenation (DMChe + DMCha), direct C–N bond hydrogenolysis (m-xylene) and disproportionation (MMA + TMA) [18,26]. The DMA reaction products distributions are shown in Fig. 2 and the reaction pathway in Scheme 2. DMA was first hydrogenated to cyclohexylamine, which rapidly underwent C–N bond breakage (HYG) along with the parallel hydrogenation route (HYD). Apart from these



Scheme 2. 2,6-Dimethylaniline reaction network.

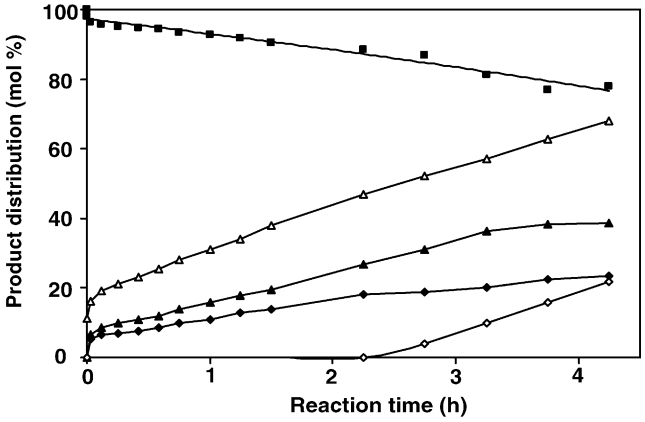


Fig. 3. Product distribution in the reaction of 1-methylnaphthalene in presence of 2.0 wt.% S and 0.2 wt.% N content: (■) 1-MN; (△) 5-MT × 8; (▲) 1-MT × 8; (◆) 2-MT × 8; (◇) MD.

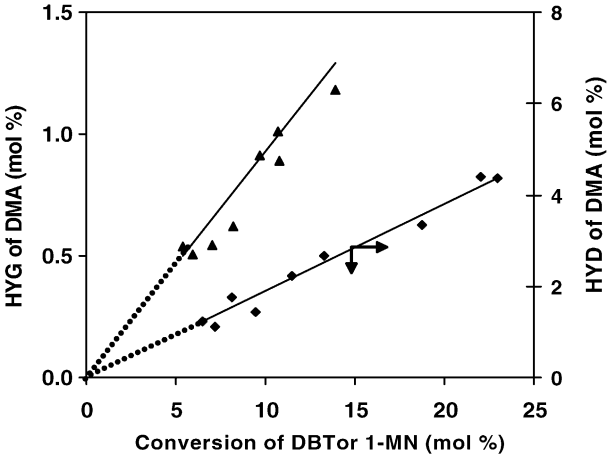


Fig. 4. Relationship between the hydrogenolysis (HDS vs. HYG) and hydrogenation (HDA vs. HYD) functionalities: (▲) HYG-DMA vs. × DBT; (◆) HYD-DMA vs. × 1-MN.

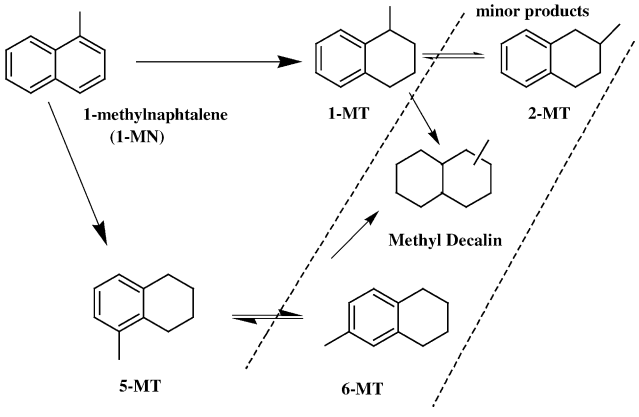
reactions, a significant disproportionation (DPP) reaction was observed with equimolar amounts of MMA and TMA being produced under our reaction conditions. However, in all cases, conversion into DPP products was found to be much less important than conversion due to both HYG and HYD routes, so that conversion of DMA characterizes essentially the HDN activity of the sulfided catalyst.

Fig. 3 shows the 1-MN conversion to 1-methyltetralin (1-MT) and 5-methyltetralin (5-MT) as major products and to 2-MT, 6-MT and methyldecalin in minor quantities as shown in Scheme 3. The secondary hydrogenated compound methyldecalin was notably formed after 2-h reaction time.

As shown in Fig. 4, a nice correlation can be established between conversions of DMA into m-xylene obtained at various reaction times and conversions of DBT. Since the reaction of DBT proceeds mainly through the hydrogenolysis route yielding biphenyl, it can be concluded that both hydrogenolysis catalyst activities for C–N and C–S bond breakages involve the same kind of site. In the same figure, the conversion of DMA into DMChe and DMCha, i.e. via the hydrogenation route, was correlated with the hydrogenation conversion of 1-MN. Thus, both hydrogenation activities for DMA conversion and HDS most probably proceed on the same kind of site. Moreover, H_2S and NH_3 that are produced in increasing amounts during the reaction because of HDS of DBT and HDN of DMA seem to affect similarly both hydrogenolysis and hydrogenation activities whatever the nature of the used model reactant.

3.1. Influence of sulfur content

Effect of sulfur content variation at fixed nitrogen content (0.2 wt.%) on the conversions of DMA and 1-MN model compounds at 4-h reaction time is shown in Fig. 5. The DBT conversion decreased with the increase in DBT concentration in the mixed liquid feed; this agrees with a reaction order close to 1 with respect to DBT. Moreover, the concentration of the produced H_2S in the liquid feed [12], which is proportional to f_{HDS} [DBT]°, where f_{HDS} is the molar fraction of converted DBT and [DBT]°, the initial concentration of DBT, increased therefore with the sulfur content in Fig. 5.



Scheme 3. Reaction network of 1-methylnaphthalene.

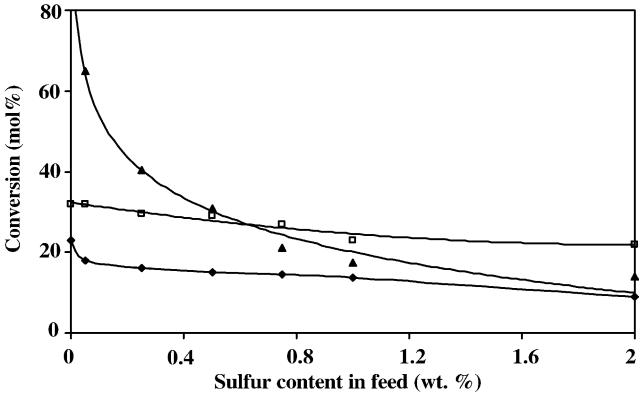


Fig. 5. Inhibition effect of sulfur content in hydrotreating (HDS, HDA and HDN) reactions: (▲) HDS; (□) HDA; (◆) HDN.

The conversions of DMA and 1-MN decreased with increasing sulfur content, most probably due to adsorption of S-compounds: DBT, H_2S and dissociated sulfur species. Fig. 5 shows that low amounts of S in the feed caused a fast decrease in DMA conversion; this has been reported previously for the same reaction carried out in the gas phase [18]. Then, upon sulfur addition, HDN conversion was found to decrease slowly but regularly. These results suggested that only a part of vacancy sites were inhibited by competitively adsorbed sulfur compounds, which make obvious to the behavior of catalyst polyfunction with respect to HDN. Regarding HDA, the conversion of 1-MN was slightly and regularly affected by the presence of increasing amounts of sulfur in the feed; but conversion remained high even for the high sulfur content studied. Thus, H_2S does not appear to be a strong inhibitor for 1-MN hydrogenation. The high sulfur contents (above 0.5 wt.%) attributed to the progressive saturation of catalytic sites as shown in Fig. 5. Kasztelan [29] reported a descriptive model for surface species of supported MoS_2 phases, which illustrates the formation of vacancy sites M–H (with hydridic species) and sulfur-saturated sites (with sorbed SH species). It has been further documented [27,28] that H_2S adsorbs dissociatively on anion vacancy site (coordinatively unsaturated metallic sites) and that those sites change subsequently into sulfur-saturated sites. This is a reversible process, which depends on reaction conditions as well as feed composition [11].

The changes in selectivity for BP formation (hydrogenolysis route) and for CHB formation (hydrogenation route) does not appear important with variation in S content as shown in Fig. 6(a) and (b). However, one can observe that the presence of sulfur compounds does improve selectivity into CHB and on the opposite has a negative effect on selectivity into BP. This is obvious at high concentration of DBT and consequently of the formed H_2S, which can be explained by a modification of the catalyst surface because of the increase in concentrations of sulfur-saturated sites and active H species [12,17].

The DMA product selectivities is shown in Fig. 7(a–c) as a function of sulfur content. The HYD selectivity remained almost constant as a function of the sulfur content, whereas the HYG selectivity decreased significantly. Therefore, the hydrogenolysis function of the catalyst appeared to be depressed by the presence of S compounds, and not its hydrogenation function. In addition, selectivity into m-xylene became constant at higher sulfur content, which indicates the saturation of active sites. The increase in DPP products yield with sulfur content may be due to an increase in concentration of surface sulfhydryl (–SH) groups [34–36].

Fig. 8(a) and (b) shows the selectivity of HDA of 1-MN into 1-methyltetralin (1-MT) and 5-methyltetralin (5-MT) as a function of S content. Up to ∼10% conversion of 1-MN, both conversions into 1-MT and 5-MT strictly follow parallel route, and the initial selectivities are found not to be

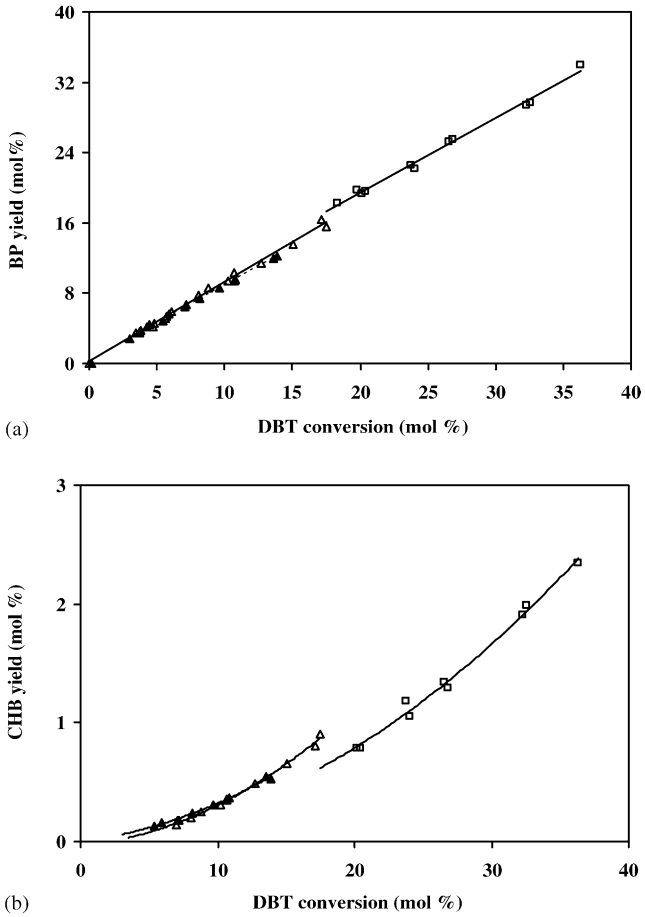


Fig. 6. (a) Hydrogenolysis selectivity for direct desulfurization of DBT to BP with variation of sulfur content: (□) 0.56 wt.% S; (△) 1.1 wt.% S; (▲) 2.0 wt.% S. (b) Hydrogenation selectivity for DBT to CHB with variation of sulfur content: (□) 0.56 wt.% S; (△) 1.1 wt.% S; (▲) 2.0 wt.% S.

affected by the presence of sulfur compounds Interestingly, at high conversions of 1-MN, the 1-MT and 5-MT selectivities decreased in the same magnitude with the increase in S content; this results from the increase in secondary hydrogenation to methyldecalin (Scheme 3). This further reveals the saturation of the catalyst surface by S species. The saturation is most likely due to the increasing concentration of SH groups, which produce active protonic centers in larger amounts at high sulfur content.

3.2. Influence of nitrogen content

Inhibition due to the nitrogen compound is well discussed with regards to kinetic dependency [30,31] or surface-site poisoning [23,32,33], and reports indicated that at least two kinds of sites are involved for HDN. The use of DMA as limiting reactant is interesting because the molecule provides three different kinds of information about the catalyst performance. Such information is difficult to obtain with basic molecules such as quinoline or indole because those molecules strongly adsorb on the catalyst surface, which

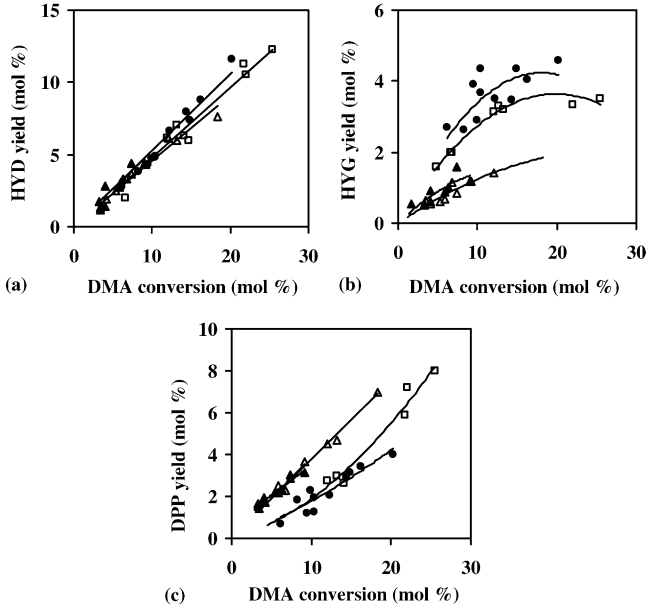


Fig. 7. (a) Hydrogenation selectivity for DMA to HYD with variation of sulfur content: (●) 0 wt.% S; (□) 0.56 wt.% S; (△) 1.1 wt.% S; (▲) 2.0 wt.% S. (b) Hydrogenolysis selectivity for DMA to HYG with variation of sulfur content: (●) 0 wt.% S; (□) 0.56 wt.% S; (△) 1.1 wt.% S; (▲) 2.0 wt.% S. (c) Disproportion selectivity for DMA to DPP with variation of sulfur content: (●) 0 wt.% S; (□) 0.56 wt.% S; (△) 1.1 wt.% S; (▲) 2.0 wt.% S.

results in a stronger inhibition for the other reactions. It is thus difficult to assess the effect of sulfur content [37,38].

Fig. 9 shows the effect of nitrogen content at a fixed sulfur concentration (0.5 wt.% S). Similarly, as in the case of DBT (Fig. 5), DMA conversion was found to decrease with increasing DMA concentration in the mixed liquid feed, and it results in an increase in concentration of the produced NH_3 ($\propto f_{HDN}$ [DMA]$^{\circ}$).

The presence of basic nitrogen compounds and N species appears to poison more hydrogenation of 1-MN than HDS of DBT (Fig. 9). In all cases, the DBT conversion followed the typical product distribution shown in Fig. 1. The selectivity for BP and CHB is shown in Fig. 10(a) and (b). Selectivity into BP marginally changed with increasing nitrogen contents except at high concentration of nitrogen (0.5 wt.%) where it decreased substantially. Thus, the hydrogenolysis function of the catalyst is hardly affected by N species. On the other hand, the effect on the hydrogenation route is evidenced by the decrease in selectivity into CHB. A 10-fold increase in nitrogen concentration in the feed suppressed the CHB selectivity by a factor of about 3. Thus, such finding shows undoubtedly that the hydrogenation function was strongly inhibited in presence of NH_3 and nitrogen compounds. Similarly, the hydrogenation route for DMA conversion appears to be more strongly inhibited with increase in nitrogen content than hydrogenolysis to m-xylene.

In conclusion, the basic nitrogen compounds or NH_3 present stronger inhibition of the catalyst hydrogenation function than sulfur compounds or H_2S.

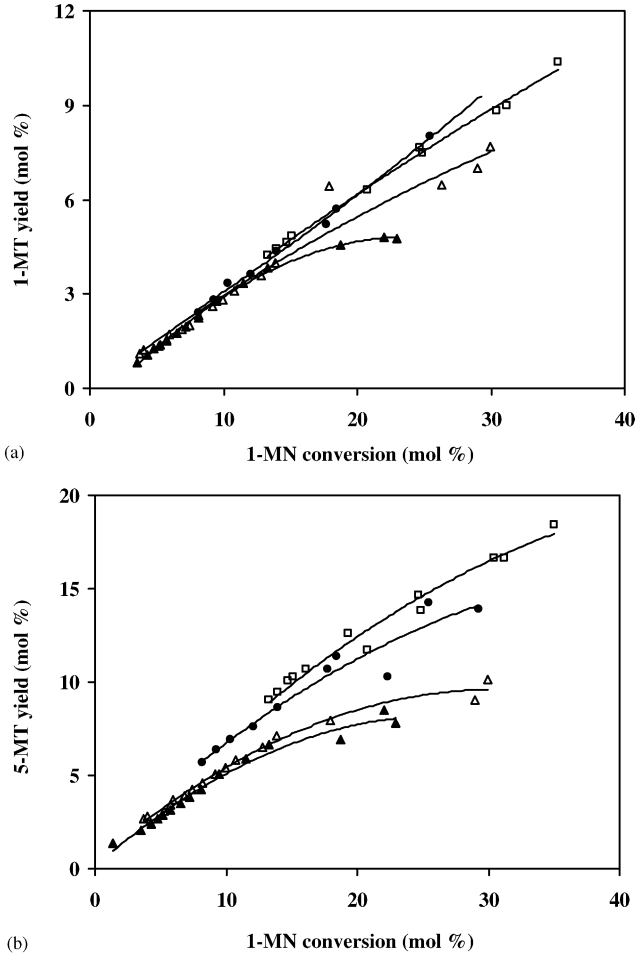


Fig. 8. (a) Hydrogenation selectivity for 1-MN to 1-MT with variation of sulfur content: (●) 0 wt.% S; (□) 0.56 wt.% S; (△) 1.1 wt.% S; (▲) 2.0 wt.% S. (b) Hydrogenolysis selectivity for 1-MN to 5-MT with variation of sulfur content: (●) 0 wt.% S; (□) 0.56 wt.% S; (△) 1.1 wt.% S; (▲) 2.0 wt.% S.

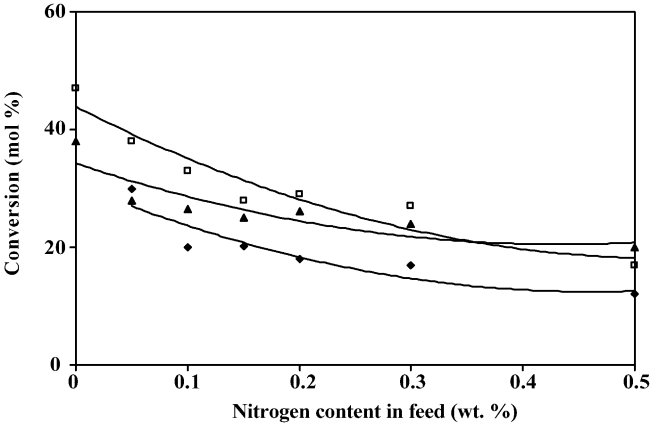


Fig. 9. Inhibition effect of nitrogen content in hydrotreating (HDS, HDA and HDN) reactions: (▲) HDS; (□) HDA; (◆) HDN.

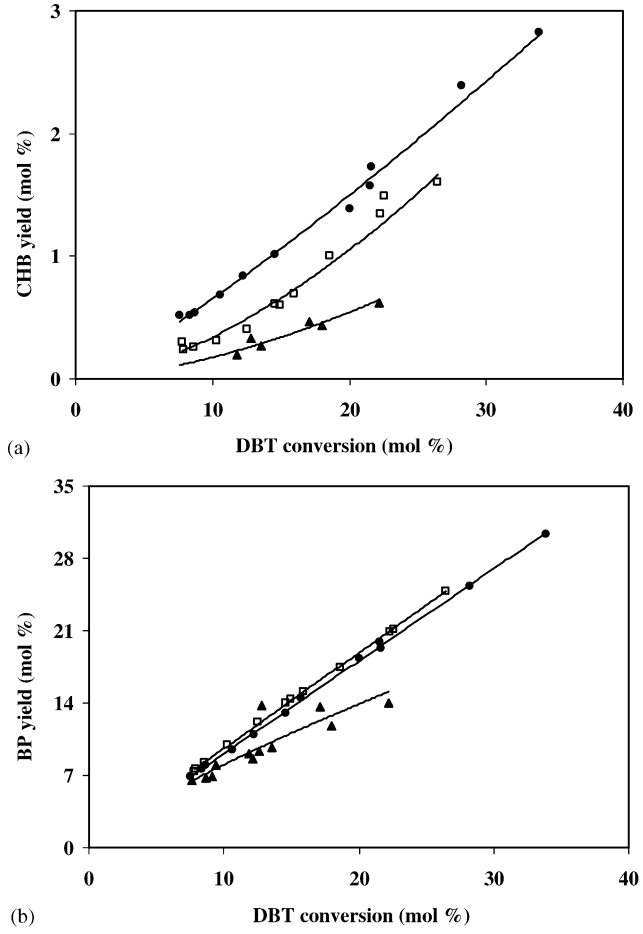


Fig. 10. (a) Hydrogenolysis selectivity for direct desulfurization of DBT to BP with variation of nitrogen content: (●) 0.05 wt.% N; (□) 0.1 wt.% N; (▲) 0.5 wt.% N. (b) Hydrogenation selectivity for DBT to CHB with variation of nitrogen content: (●) 0.05 wt.% N; (□) 0.1 wt.% N; (▲) 0.5 wt.% N.

4. Discussion

The present investigation is an effort to understand the combined inhibition effects of S and N compounds as well as those of the produced H_2S and NH_3 during the conversion of DBT and DMA. Besides adsorption of heteroaromatic molecules, it is assumed that the inhibition is occurring due to the accumulation of H_2S and NH_3 in the batch reactor. In general, inhibition must be stronger in presence of nitrogen compounds. The hydrogenolysis reactions take place on coordinatively unsaturated sites on the catalyst surface, and H_2S or NH_3 is released in a following step. The hydrogenation reaction can also take place through π-electron interaction on the vacancy site. Thus, hydrogenation is expected to be moderately inhibited as a function of S content. Hydrogenolysis (direct C–N breakage) was strongly inhibited at very low amount of H_2S and becomes constant at high H_2S content (Fig. 7b). It was thus deduced that most of the active sites are converted to sulfur-saturated sites in presence of small amounts of H_2S [28], and it is assumed that the remaining hydrogenolysis activity is due to the contribution of few vacancies that cannot be blocked by S compounds or SH groups. Therefore, sulfur species are playing a key role in controlling the vacancy as well as sulfur-saturated sites, depending on the conditions and compositions of the reactants.

The inhibition can be explained in view of H_2 as well as H_2S dissociation on catalyst surface. The dissociative species H^- and SH^- issued from H_2 and H_2S, respectively, competitively adsorb with sulfur molecule on the surface of catalyst. Indeed, without H_2S, only H^+ and H^- species are formed by heterolytic dissociation of H_2 on catalyst surface, while in presence of H_2S the H^+ to H^- ratio increases due to simultaneous heterolytic dissociation of H_2S into H^+ and SH^-. This explains the observed improvement in hydrogenation activities compared to hydrogenolysis with sulfur content (Fig. 6). Obviously, the inhibition mechanism depends on the H_2S and H_2 concentrations. We further infer from previous studies [14,18] that H^+ species are responsible for hydrogenation reaction, and H^- are responsible for hydrogenolysis reaction. The following equations are proposed to give a better insight about the role of the various H species:

$$H_2 \rightarrow H^+ + H^-$$
$$[H^-(\text{hydrogenolysis})\, H^+(\text{hydrogenation})] \quad \text{(a)}$$

$$H_2S \rightarrow H^+ + SH^- \quad [HS^-(\text{competitive adsorbent})]$$
$$\rightarrow \text{hydrogenolysis route inhibition} \quad \text{(b)}$$

$$HS^- \rightarrow S^{2-} + H^+ \quad \text{(b2)}$$

$$NH_3 + H^+ \rightarrow NH_4^+ \quad [NH_3(\text{consumption of } H^+\text{ions})]$$
$$\rightarrow \text{hydrogenation route inhibition} \quad \text{(c)}$$

NH_3 is the by-product of HDN conversion; it consumes H^+ ions and it produces NH_4^+. Results showed that the hydrogenation route was strongly inhibited in presence of nitrogen (Fig. 9). This is further supported from cumene hydrogenation data from literature, with inhibition by a factor of 7 upon addition of NH_3 (partial pressure = 0.013 MPa) [39]. Therefore, this corroborates our previous works where hydrogenation reactions were reported to require H^+ ions [14,18].

In case of H_2S dissociation, the higher concentration of H^+ as compared to H^- (SH^-) species limited the hydrogenolysis function as compared to hydrogenation function. However, in some instances, small amount of H_2S has a promotional effect on HDS, e.g. at high temperature and low H_2 pressure [40]. An increase in H_2S concentration resulted in stronger inhibition of hydrogenolysis reaction, while the hydrogenation was not affected in the same magnitude. Inhibition role of N and S species may slightly vary on catalyst composition, but strong inhibition by H_2S must be taken into account when nitrogen compounds are available in the feed.

5. Conclusion

A systematic study of S and N contents shows the behavior of the catalyst ($CoMoS/\gamma$-Al_2O_3) with respect to HDS, HDN, HDA reactions and their inhibition effect on reaction routes. The observed relative decrease in activity follows a similar trend against the added sulfur or nitrogen content in the feed. However, it should be noted that all catalytic functionalities are not affected in the same magnitude. The hydrogenation function of the catalyst is strongly inhibited in presence of N compounds and slightly improved in presence of S compounds. The hydrogenolysis (C–S and C–N bond breakages) function of the catalyst is in all cases inhibited by S or N compounds. The results revealed that only a part of the catalytic sites are inhibited by adsorbed S and N species, and that sulfur-saturated sites are present on the catalyst surface in presence of H_2S and NH_3. Two major types of catalytic sites were thus evidenced. The first type of site is a sulfur vacancy that is formed due to un-saturation on CoMoS; these sites are responsible for hydrogenolysis and hydrogenation. Second type of site is a sulfur-saturated site, which is responsible for hydrogenation and later acts as accelerator for formation of previous type of active sites.

The degree of inhibition was explained with the help of H_2 and H_2S adsorption/dissociation as well as NH_3 adsorption on the catalyst surface. The competitive adsorption of H_2S strongly depends on H_2S concentration and H_2S/H_2 ratios. Dissociated SH^- species competitively adsorbs on active sites with sulfur molecule. With an increase in sulfur content, the H^+ to H^- ratio increases because of dissociation of produced H_2S. H_2S dissociation only changed the H^+ and H^- (SH^-) species concentration, which limits the hydrogenolysis function as compared to the hydrogenation. With an increase in nitrogen content, NH_3 consumes H^+ ions, which caused the inhibition of hydrogenation reactions.

Acknowledgement

R.N. thanks ATOFINA for financial support and M.S.R. thanks the Conseil Régional de Basse-Normandie (France) for providing postdoctoral fellowship.

References

[1] K.G. Knudsen, B.H. Cooper, H. Topsøe, Appl. Catal. A: Gen. 189 (1999) 205.
[2] C. Song, Appl. Catal. B 1267 (2003) 1.
[3] R. Safi, G.J. Hutchings, Catal. Today 59 (2000) 423.
[4] D.D. Whitehurst, T. Isoda, I. Mochida, Adv. Catal. 42 (1998) 345.
[5] C. Song, in: C. Song, C.S. Hsu, I. Mochida (Eds.), Chemistry of Diesel Fuels, Taylor & Francis, New York, 2000, pp. 1–60.
[6] M. Houalla, N.K. Nag, A.V. Sapre, D.H. Broderick, B.C. Gates, AIChE J. 24 (1978) 1015.
[7] G.F. Froment, G.A. Depauw, V. Vanrysselberghe, Ind. Eng. Chem. Res. 33 (1994) 2975.
[8] M. Breysse, G. Djega-Mariadassou, S. Pessayre, C. Geantet, M. Vrinat, G. Perot, M. Lemaire, Catal. Today 84 (2003) 129.
[9] W.H.J. Stork, Stud. Surf. Sci. Catal. 106 (1999) 41.
[10] J.F. Le Page, et al. Applied Heterogeneous Catalysis, Design, Manufacture, Use of Solid Catalysts, Technip, Paris, 1987.
[11] J. Leglise, L. Finot, J. van Gestel, J.C. Duchet, Stud. Surf. Sci. Catal. 127 (1999) 51.
[12] J. Leglise, J. van Gestel, L. Finot, J.C. Duchet, J.L. Dubois, Catal. Today 45 (1998) 347.
[13] J. Ancheyta-Juarez, E.A. Rodriguez, D.S. Sotelo, G.M. Sanchez, Stud. Surf. Sci. Catal. 127 (1999) 343.
[14] M.J. Girgis, B.C. Gates, Ind. Eng. Chem. Res. 30 (1991) 2021.
[15] M. Breysse, E. Furimsky, S. Kasztelan, M. Lacroix, G. Perot, Catal. Rev. Sci. Eng. 44 (4) (2002) 651.
[16] V. La Vopa, C.N. Satterfield, J. Catal. 110 (1988) 375.
[17] S. Kasztelan, D. Guillaume, Ind. Eng. Chem. Res. 33 (1994) 203.
[18] J. van Gestel, J. Leglise, J.C. Duchet, Appl. Catal. A: Gen. 92 (1992) 143.
[19] E. Furimsky, F.E. Massoth, Catal. Today 52 (1999) 381.
[20] T.C. Ho, Catal. Rev. Sci. Eng. 30 (1988) 117.
[21] T.C. Ho, J. Catal. 219 (2003) 442.
[22] U.T. Turaga, X. Ma, C. Song, Catal. Today 86 (2003) 265.
[23] S.D.S. Murti, H. Yang, Ki.-H. Choi, Y. Korai, I. Mochida, Appl. Catal. A: Gen. 252 (2003) 331.
[24] I. Mochida, S. Shi, K. Sakanishi, D. Grudoski, J. Shinn, Stud. Surf. Sci. Catal. 127 (1999) 187.
[25] V.M. Kogan, R.G. Gaziev, S.W. Lee, N.N. Rozhdetvenskaya, Appl. Catal. A: Gen. 251 (2003) 187.
[26] J. van Gestel, C. Dujardin, F. Maugé, J.C. Duchet, J. Catal. 202 (2001) 78.
[27] M. Echard, J. Leglise, Catal. Lett. 72 (2001) 83.
[28] M. Echard, J. Leglise, Thermochim. Acta 376 (2001) 241.
[29] S. Kasztelan, Langmuir 6 (1990) 590.
[30] G.C. Laredo, E. Altamirano, J.A. De los Reyes, Appl. Catal. A: Gen. 243 (2003) 207.
[31] T. Kabe, A. Ishihara, W. Qian, Hydrodesulfurization and Hydrodenitrogenation, in: Chemistry and Engineering, Wiley-VCH-Verlag and Kodansa, Tokyo, 1999.
[32] M. Nagai, T. Sato, A. Aiba, J. Catal. 97 (1986) 52.
[33] F. Pedraza, S. Fuentes, M. Vrinat, M. Lacroix, Catal. Lett. 62 (1999) 121.
[34] N.Y. Topsøe, H. Topsøe, F.E. Massoth, J. Catal. 119 (1989) 252.
[35] M.S. Rana, S.K. Maity, J. Ancheyta, G. Murali Dhar, T.S.R. Prasada Rao, Appl. Catal. A: Gen. 258 (2004) 215.
[36] M.S. Rana, B.N. Srinivas, S.K. Maity, G. Murali Dhar, T.S.R. Prasada Rao, J. Catal. 195 (2000) 31.
[37] C. Moreau, L. Bekakra, R. Durand, N. Zmimita, P. Geneste, Stud. Surf. Sci. Catal. 50 (1991) 447.
[38] G. Perot, Catal. Today 10 (1991) 447.
[39] S. Gultekin, S.A. Ali, C.N. Satterfield, Ind. Eng. Chem. Process Des. Dev. 23 (1984) 179.
[40] J. Leglise, J. van Gestel, J.C. Duchet, J. Chem. Soc. Chem. Commun. (1994) 611.