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Influence of nitrogen compounds on deep hydrodesulfurization of 4,6-dimethyldibenzothiophene over Al_2O_3- and MCM-41-supported Co-Mo sulfide catalysts

Uday T. Turaga[1], Xiaoliang Ma, Chunshan Song*

Department of Energy and Geo-Environmental Engineering, The Energy Institute, The Pennsylvania State University, 209 Academic Projects Building, University Park, PA 16802, USA

Abstract

The present work focuses on the effect of nitrogen compounds on the activity of MCM-41- and γ-Al_2O_3-supported Co-Mo catalysts for the deep hydrodesulfurization of 4,6-dimethyldibenzothiophene (4,6-DMDBT) in a fixed-bed flow reactor. Sulfur removal to the depths required by new specifications will require knowledge of the influence of non-sulfur diesel fuel components on deep hydrodesulfurization. The main objective of this paper is to examine the activity of hydrodesulfurization catalysts during and, most importantly, after exposure to basic and non-basic nitrogen. Quinoline (basic nitrogen) inhibits catalytic activity of both γ-Al_2O_3- and MCM-41-supported catalysts. It strongly inhibits hydrogenation and hydrogenolysis activity as evidenced by decreased selectivity for cyclohexylbenzene and biphenyl derivatives, respectively. To a certain extent, the long-term effects of quinoline are reversible. Carbazole (non-basic nitrogen) has little effect on the γ-Al_2O_3-supported Co-Mo catalyst but significantly inhibits the activity of the MCM-41-supported Co-Mo catalyst. The inhibition of the MCM-41-supported catalyst is reversible following removal of carbazole from the feedstock. Molecular modeling was also conducted to derive the bond order and electron charges of the nitrogen and sulfur compounds, which are helpful to understanding the experimental results.

Keywords: Hydrodesulfurization; 4,6-Dimethyldibenzothiophene; Co-Mo catalysts; MCM-41; Diesel fuel

1. Introduction

The subject of inhibition of hydrodesulfurization (HDS) activity has been studied extensively [1] and some of the inhibitors include aromatics, nitrogen-containing compounds, hydrogen sulfide, ammonia, saturated hydrocarbon solvents, and even water. Of these, nitrogen-containing compounds were identified as having the most severe inhibiting effect [2]. Atmospheric gas oil, which is frequently used as a diesel feedstock, typically, contains nitrogen compounds 70% of which are non-basic (e.g. carbazole type) while the rest are basic (e.g. quinoline type). Light cycle oil (LCO), a feedstock used for diesel fuel and thermally stable naphthenic jet fuels [3,4], contains much higher nitrogen, predominantly non-basic in nature [5]. Diesel and some jet fuel feedstocks, therefore, have enough nitrogen species to significantly influence deep HDS.

Nitrogen's effects on HDS catalytic activity could become all the more important because the US

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* Corresponding author. Tel.: +1-814-863-4466; fax: +1-814-865-3248.
E-mail address: csong@psu.edu (C. Song).

[1] Present address: ConocoPhillips, Bartlesville Technology Center, Bartlesville, OK 74006, USA.

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Environmental Protection Agency requires that diesel fuels have sulfur content no more than 15 parts per million by weight (ppmw) by 2006 [6]. Further lower sulfur contents may be required in the next decade. Sulfur removal to such depths will require knowledge of the influence of non-sulfur diesel fuel components on deep hydrodesulfurization. Furthermore, the reactivity of nitrogen-containing heterocompounds is much lower than those of polyaromatic sulfur compounds (PASCs) [7]. Therefore, nitrogen compounds will be present in appreciable quantities even at very low sulfur levels and could significantly influence the deep HDS of PASCs. In other words, the influence of nitrogen will become more important at lower level of sulfur content.

Several researchers have clearly established the inhibiting effect of basic nitrogen compounds on the HDS of thiophene and DBT [8,9]. A much smaller body of work has dealt with the effect of non-basic nitrogen on HDS and the results seem to be inconclusive. For example, La Vopa and Satterfield [10] and, more recently, Furimsky and Massoth [11] have reported on the inhibiting effects of carbazole and indole, respectively, for the HDS of dibenzothiophene (DBT). Similarly, Laredo et al. [12] found the inhibiting effects of carbazole and indole comparable to that of basic nitrogen compounds such as quinoline. However, Zeuthen et al. [7] in a very recent study found carbazoles having little negative effect on the HDS of DBT and substituted DBTs found in their blend of gas oil and light cycle oil. They, however, determined carbazoles and substituted carbazoles as the least reactive nitrogen compounds.

In addition to such ambiguity, little is known about the exact mechanism of nitrogen poisoning. Kwak et al. [13] found interesting influences of carbazole and quinoline on the HDS of DBT, 4-methyldibenzothiophene (4-MDBT), and 4,6-dimethyldibenzothiophene (4,6-DMDBT) over a Co-Mo/γ-Al_2O_3 catalyst in a batch reactor. While both nitrogen compounds inhibited conversion of all three PASCs, the HDS of DBT was only mildly poisoned till at least 500 ppm of the nitrogen compound was present in the feedstock. More profoundly, the nitrogen compounds inhibited different types of sites on the catalyst. For example, the HDS of DBT occurred less through the hydrogenation route when poisoned with nitrogen compounds. Nagai et al. [14] also obtained similar results with the HDS of DBT on a sulfided Mo/γ-Al_2O_3 catalyst. In the case of the substituted DBTs, however, Kwak et al. [13] noticed that conversion was achieved mainly through the hydrogenation pathway, i.e. the hydrogenolysis route was inhibited.

This paper reports the effect of two nitrogen compounds—one basic and the other non-basic—on the deep HDS of 4,6-DMDBT, the most refractory PASC. In addition to measuring the catalysts' activity for HDS during the presence of nitrogen-containing compounds, this work also evaluates the "long-term" effect of nitrogen compounds on HDS catalysts. More specifically, the activities of the catalysts exposed to nitrogen are also evaluated after nitrogen's removal from the feedstock. In other words, the extent and duration of deactivation, if any, caused by nitrogen on the HDS of nitrogen-free feedstocks are evaluated. In addition to determining the effects of nitrogen on a typical Co-Mo/γ-Al_2O_3 HDS catalyst, the stability of a MCM-41-supported Co-Mo catalyst is also obtained. This extends our previously reported studies on MCM-41-supported HDS catalysts [3,15–18].

2. Experimental

2.1. Catalyst synthesis and characterization

The MCM-41 support was synthesized with a SiO_2/Al_2O_3 ratio of 50 using a method based on our early work [18] and the report by Cheng et al. [19]. The method uses sodium-free reagents because sodium has been found to result in MCM-41 material with poor hydrothermal stability [20]. The MCM-41-supported catalyst, with 27.0% molybdenum oxide (MoO_3) and 5.8% cobalt oxide (CoO) loadings, was prepared via wet co-impregnation of ammonium heptamolybdate (Aldrich, 99.98%) and cobalt nitrate hexahydrate (Aldrich, >98%). It is designated Co-Mo/MCM-41(50). The catalyst synthesis procedure has been described in greater detail elsewhere [17]. The activity of the MCM-41-supported catalyst was evaluated in comparison to a Co-Mo/γ-Al_2O_3 commercial catalyst supplied by Criterion Catalyst Corporation, Houston, TX. This catalyst is referred to in this study by its trade name, C-344. Table 1 shows the properties of the catalysts.

Table 1
Properties of catalysts used in this study

Catalyst sample	Surface area (S_{BET}, m^2/g)	Pore volume (V_T, cm^3/g)	Particle density[a] (g/ml)
Co-MoO$_3$/γ-Al$_2$O$_3$ (C-344)	190	0.56	0.74
High CoO-MoO$_3$/MCM-41(50)	564	0.56	0.24

[a] Rough estimate of density measured for catalyst particles of 0.5–1.0 mm diameter.

A typical catalyst evaluation experiment used 1 g of the catalyst. All catalysts evaluated in the flow reactor were particles of 0.5–1.0 mm in diameter. The commercial catalyst was supplied as trilobe-shaped extrudates. So the commercial catalyst samples were crushed and sieved using sieves of mesh sizes 18 and 35 (0.5–1.0 mm). In the case of the MCM-41-supported catalysts, the final catalyst was in powder form. Therefore, the MCM-41-supported catalyst was first pressed into pellets, which were then crushed and sieved to particles of 0.5–1.0 mm diameter. Five percent by catalyst weight of γ-Al$_2$O$_3$ was used as a binder for pellet preparation.

X-ray diffraction and the adsorption–desorption isotherms of nitrogen were used to characterize the MCM-41-supported catalysts. These results are presented elsewhere [17] and suggest that the MCM-41 support was of high quality and the impregnated catalysts had expected physical properties.

2.2. Catalyst evaluation

All catalysts were evaluated in a laboratory-scale fixed-bed flow reactor which has been described elsewhere [17]. The catalyst evaluation conditions used in this work are summarized in Table 2. All catalysts were sulfided in situ at uniform conditions. The catalysts were evaluated for HDS activity over a period of 25–60 h and the reactor effluents were collected at regular intervals. A typical model compound feedstock contained 2000 ppmw of sulfur in the form of 4,6-DMDBT dissolved in hydrocarbon solvents such as *n*-dodecane (*n*-C$_{12}$) or *n*-tridecane (*n*-C$_{13}$). The selection of this sulfur concentration (2000 ppmw) is based on the facts that the concentrations of dimethyldibenzothiophenes in light cycle oils are in the same range and this concentration also allows reliable quantitative analysis of the products. The dissolution of the heterocompounds in the hydrocarbon solvent was facilitated by the use of a sonicator.

Table 2
Flow reactor experimental conditions

Catalyst sulfidation conditions	
Temperature (°C)	350
10 vol.% H$_2$S in H$_2$ flow rate (ml/min)	200
Time (h)	4
HDS reaction conditions	
Temperature (°C)	300
Pressure in psi (1psi = 6.89 kPa = 0.068 atm)	660
Weight hourly space velocity (h^{-1})	3 or 4
Hydrogen/hydrocarbon (ml/ml)	300
Catalyst particle size (18–35 mesh, mm)	0.5–1.0
Catalyst weight (g)	1

The main objective of this paper is to examine the nitrogen effects in terms of activity of HDS catalysts during and, more importantly, after exposure to basic and non-basic nitrogen. The catalyst was first evaluated for its activity in desulfurizing the nitrogen-free model PASC feedstock for several hours. Following the attainment of steady-state activity for the desulfurization of the model PASC, a feedstock containing the nitrogen and the model PASC was introduced in the reactor. Nitrogen content was always 500 ppmw. The nitrogen compounds were obtained commercially as reagent grade materials. The activity of the catalyst for the HDS of this nitrogen-containing feedstock was determined for several hours. At the end of this phase, a nitrogen-free feedstock of the model PASC was again introduced and the catalysts' HDS activity obtained over several hours. The liquid reaction products were characterized using a Hewlett-Packard 5890 Series II gas chromatograph coupled with a Hewlett-Packard 5971A quadrupole mass spectrometer (MS) per a procedure described in detail elsewhere [17].

3. Results and discussion

Figs. 1 and 2 describe the effect of basic (quinoline) and non-basic (carbazole) nitrogen, respectively,

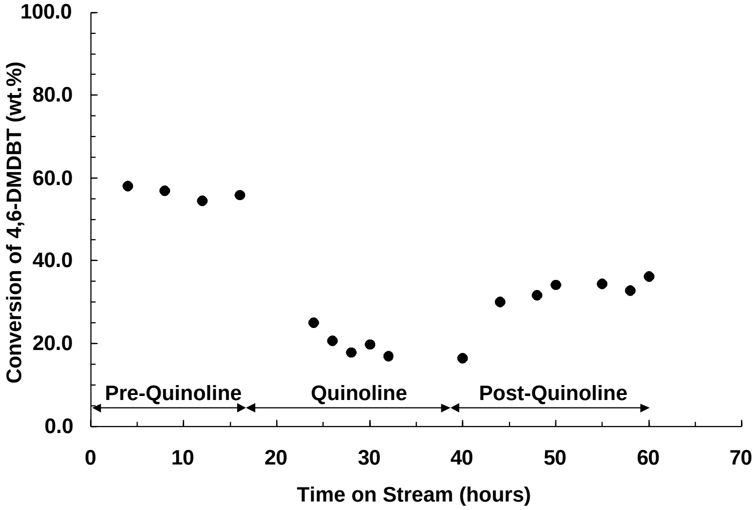

Fig. 1. HDS of 4,6-DMDBT over sulfided Co-Mo/Al_2O_3 catalyst (C-344) before, during, and after the addition of quinoline (2000 ppmw of sulfur as 4,6-DMDBT in n-C_{13}; 500 ppmw of nitrogen in the form of quinoline; temperature, 300 °C; hydrogen pressure, 45 atm; WHSV, $3\,h^{-1}$; hydrogen/hydrocarbon, 300 ml/ml).

on the activity of the sulfided Co-Mo/Al_2O_3 (commercial C-344) catalyst for the HDS of 4,6-DMDBT. Carbazole has little influence on the HDS activity of the catalyst either during or after its introduction into the reactor. As Fig. 2 shows, the conversion of 4,6-DMDBT over C-344 upon introduction of the sulfur feedstock containing 500 ppmw of nitrogen in the form of carbazole continues to remain unchanged.

Quinoline, on the other hand, severely inhibits the activity of the sulfided Co-Mo/Al_2O_3 catalyst for the HDS of 4,6-DMDBT. The catalyst regains some activity for HDS of 4,6-DMDBT after a period of 22 h

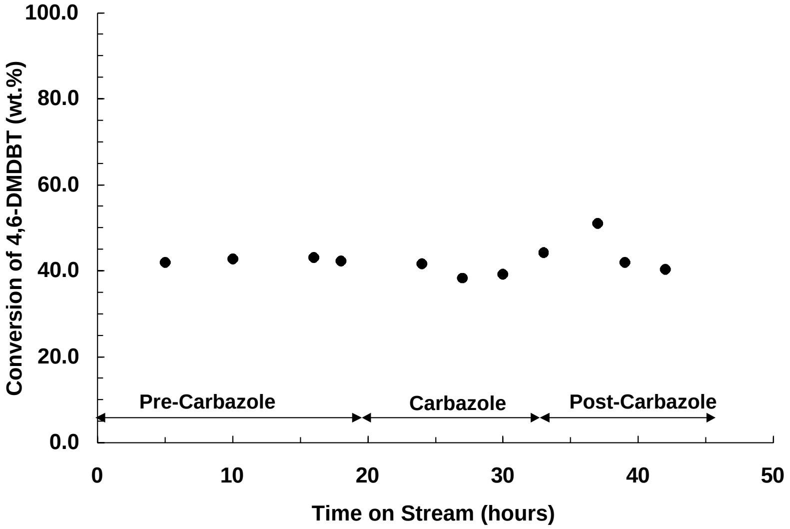

Fig. 2. HDS of 4,6-DMDBT over sulfided Co-Mo/Al_2O_3 catalyst (C-344) before, during, and after the addition of carbazole (2000 ppmw of sulfur as 4,6-DMDBT in n-C_{13}; 500 ppmw of nitrogen in the form of carbazole; temperature, 300 °C; hydrogen pressure, 45 atm; WHSV, $4\,h^{-1}$; hydrogen/hydrocarbon, 300 ml/ml).

following removal of the nitrogen compound from the sulfur-containing feedstock. While this regained activity is much lower than that of a fresh catalyst, as seen from Fig. 1, the catalyst's activity with respect to time on stream has a positive slope, suggesting the possibility of near complete regeneration of catalytic activity after several hours on stream. It should also be noted that the weight hourly space velocity (WHSV) for tests reported in Fig. 1 was $3\,h^{-1}$, while that for tests reported in Fig. 2 was $4\,h^{-1}$. As expected, higher conversion of 4,6-DMDBT was achieved at lower space velocity (longer residence time) over the same catalyst before the addition of a nitrogen compound.

The performance of the MCM-41-supported sulfided Co-Mo catalysts when subjected to nitrogen is particularly poor, as seen in Figs. 3 and 4. While the commercial catalyst did not demonstrate any susceptibility to the presence of non-basic nitrogen in the form of carbazole, the activity of the MCM-41-supported catalyst was highly affected when carbazole was introduced in the feedstock (Fig. 3). Quinoline, as in the case of the commercial catalyst, continues to severely inhibit the MCM-41-supported catalyst (Fig. 4). There are, however, subtle differences in the degree to which the MCM-41-supported catalyst is inhibited by carbazole and quinoline. Quinoline has a slightly greater effect on the HDS of 4,6-DMDBT as determined by the relative decrease in conversion. The introduction of quinoline in the feedstock reduces conversion of 4,6-DMDBT by about 64%, while carbazole's reduction is 57%.

The inhibition of the MCM-41-supported catalysts by the presence of nitrogen is not unexpected. A substantial portion of the MCM-41-supported catalyst's activity stems from its acidity, as postulated in other work by the authors [15,17,18]. The product distribution over the MCM-41-supported catalysts described elsewhere strongly supports this conclusion. Nitrogen compounds are typically basic and are expected to poison acid sites in the MCM-41-supported catalyst. Further, it is also known that nitrogen compounds adsorb strongly to hydrogenation sites. Nitrogen, therefore, has a two-fold role in the deactivation of the hydrotreating catalysts used in this study.

First, in the case of the commercial catalyst, basic nitrogen (such as quinoline) adsorbs strongly on the catalyst's active sites responsible for hydrogenation and severely inhibits activity. The product distribution data presented elsewhere have shown that hydrogenation is the predominant pathway through which the commercial catalyst achieves conversion. The adsorption of quinoline on the hydrogenation

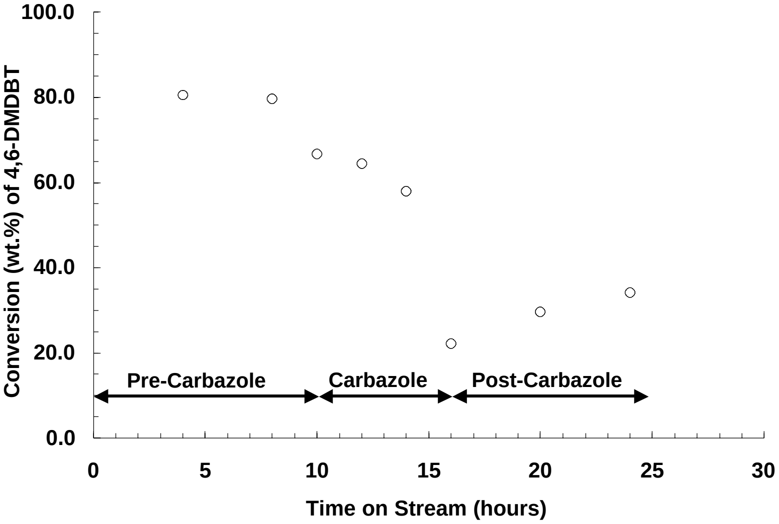

Fig. 3. HDS of 4,6-DMDBT over sulfided Co-Mo/MCM-41(50) before, during, and after the addition of carbazole (2000 ppmw of sulfur as 4,6-DMDBT in n-C_{13}; 500 ppmw of nitrogen in the form of carbazole; temperature, 300 °C; hydrogen pressure, 45 atm; WHSV, $4\,h^{-1}$; hydrogen/hydrocarbon, 300 ml/ml).

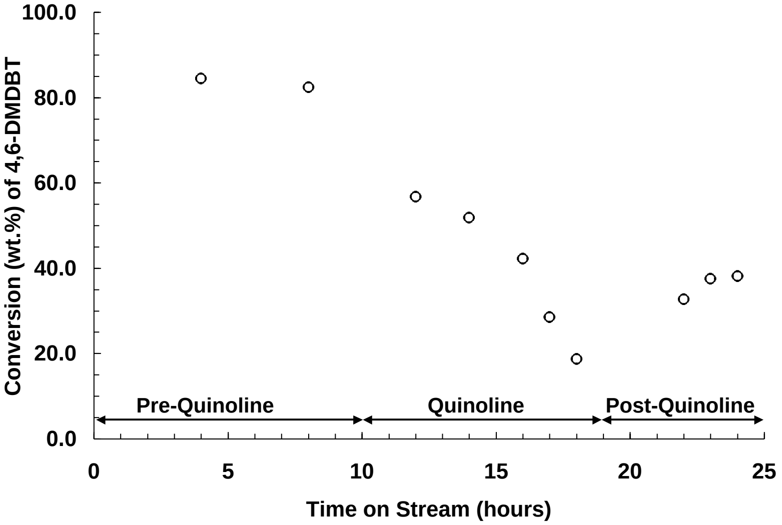

Fig. 4. HDS of 4,6-DMDBT over sulfided Co-Mo/MCM-41(50) before, during, and after the addition of quinoline (2000 ppmw of sulfur as 4,6-DMDBT in n-C_{13}; 500 ppmw of nitrogen in the form of quinoline; temperature, 300 °C; hydrogen pressure, 45 atm; WHSV, 4 h^{-1}; hydrogen/hydrocarbon, 300 ml/ml).

sites substantially reduces the contribution of these sites to the total conversion. This is substantiated by Fig. 5, which shows the selectivity change in the catalyst as a function of time on stream. The hydrogenation selectivity is defined by: 100 × ((the sum of percent yields of hydrogenation products)/(percent conversion of 4,6-DMDBT)). The hydrogenation products include hexahydro-DMDBT and methyl cyclohexyl toluene. The hydrogenolysis selectivity is defined as: 100 × ((the sum of percent yields of

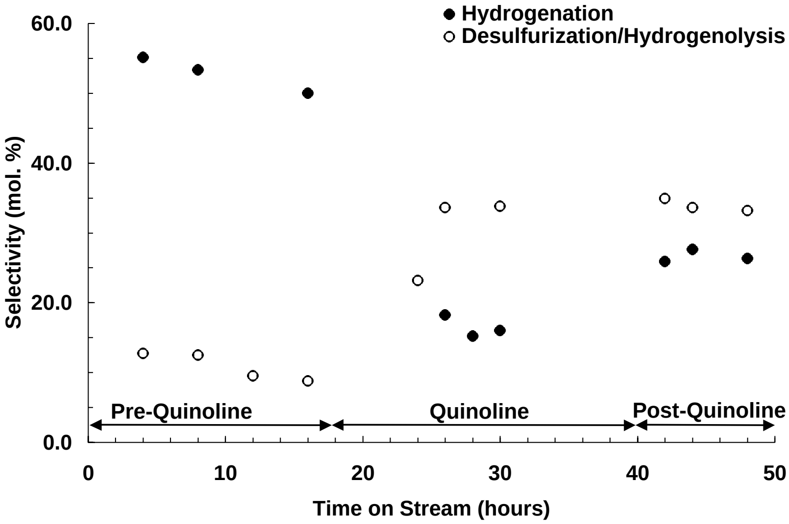

Fig. 5. Selectivity of the HDS of 4,6-DMDBT over sulfided Co-Mo/Al_2O_3 catalyst (C-344) during the presence of quinoline (2000 ppmw of sulfur as 4,6-DMDBT in n-C_{13}; 500 ppmw of nitrogen in the form of quinoline; temperature, 300 °C; hydrogen pressure, 45 atm; WHSV, 3 h^{-1}; hydrogen/hydrocarbon, 300 ml/ml).

dimethyldibenzothiophenes products)/(percent conversion of 4,6-DMDBT)).

Fig. 5 clearly shows the rapid decline in the products associated with the hydrogenation pathway after quinoline is introduced in the feedstock. This is accompanied by a small increase in the products associated with the hydrogenolysis pathway. While this may appear surprising, it has been reported in literature that the presence of basic nitrogen species increases a catalyst's selectivity for HDS via hydrogenolysis [10,21].

Besides adsorbing strongly on the hydrogenation sites of MoS_2 stacks, nitrogen compounds could also affect the acidity of the support. The passivation of support acid sites on Co-Mo/MCM-41(50) could be caused by both quinoline and carbazole. This is evident in Fig. 6 which plots the change in selectivity as a function of time on stream for the Co-Mo/MCM-41(50) catalyst before, during, and after quinoline. Fig. 6 clearly shows the rapid decline in the catalytic selectivities for both hydrogenation and hydrogenolysis. While Fig. 5 provided further evidence confirming the inhibiting effect of nitrogen species on hydrogenation sites, the reduced selectivity for hydrogenolysis products over the MCM-41-supported catalyst as shown in Fig. 6 suggests that nitrogen compounds strongly deactivate acid sites also.

The effect of non-basic nitrogen typified by compounds like carbazole is ambiguous in literature. While carbazole itself is non-basic and, therefore, considered non-inhibiting, the hydroconversion of carbazole could result in a more basic intermediate which adsorbs strongly on the catalyst and thereby poisons it [14]. It is also possible that ammonia, which is one of the products of the hydrodenitrogenation of carbazole, also inhibits deep HDS. The conversion of carbazole over both C-344 and high Co-Mo/MCM-41(50) was substantial as shown in Fig. 7. Higher conversion of carbazole was observed with Co-Mo/MCM-41(50) catalyst, probably due to its higher hydrogenation activity and/or hydrogenolysis activity compared to the Co-Mo/Al_2O_3 catalyst. This indicates that the basic intermediate or even ammonia resulting from carbazole's hydroconversion could have been produced in concentrations enough to deactivate the MCM-41-supported catalyst, although carbazole showed no impact on 4,6-DMDBT HDS over the Co-Mo/Al_2O_3 catalyst under the same conditions. This area needs further examination.

In addition to the product selectivity data, the influence of nitrogen on HDS could also be explained

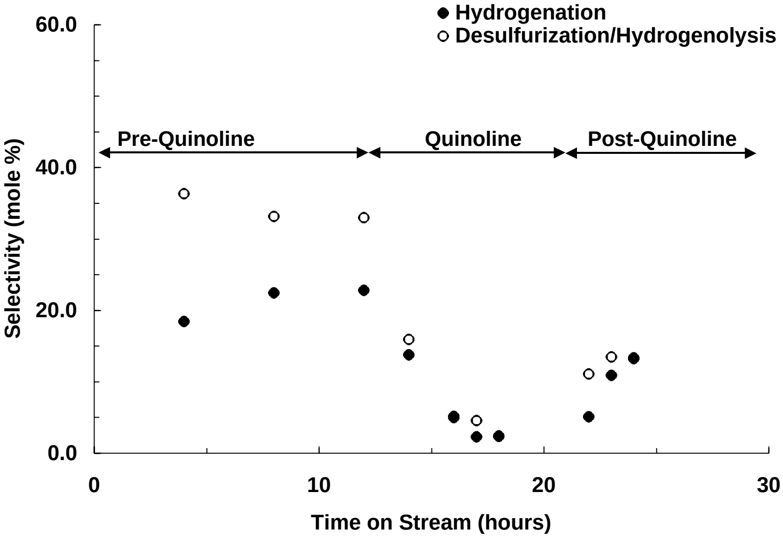

Fig. 6. Selectivity of the HDS of 4,6-DMDBT over sulfided Co-Mo/MCM-41(50) during the presence of quinoline (2000 ppmw of sulfur as 4,6-DMDBT in n-C_{13}; 500 ppmw of nitrogen in the form of quinoline; temperature, 300 °C; hydrogen pressure, 45 atm; WHSV, 4 h^{-1}; hydrogen/hydrocarbon, 300 ml/ml).

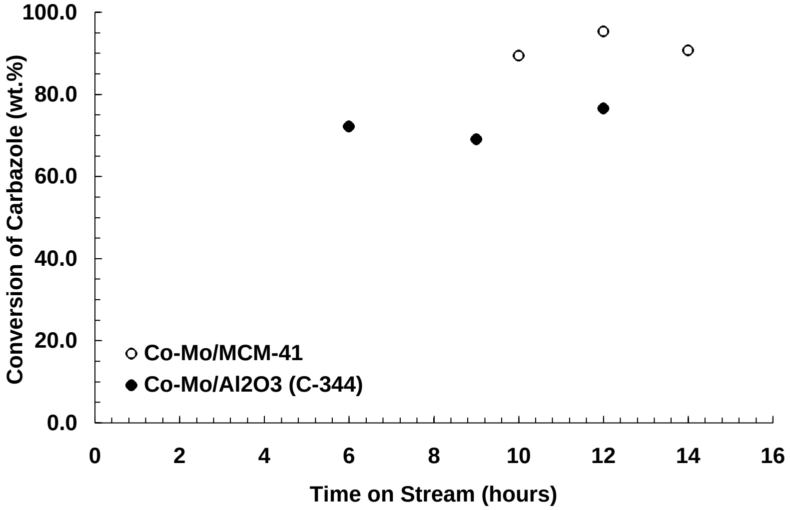

Fig. 7. Hydrotreatment of carbazole over sulfided Co-Mo/Al_2O_3 (C-344) and Co-Mo/MCM-41(50) catalysts (500 ppmw of nitrogen in the form of carbazole; temperature, 300 °C; hydrogen pressure, 45 atm; WHSV, 4 h^{-1}; hydrogen/hydrocarbon, 300 ml/ml).

using molecular modeling. Semi-empirical calculations were used to estimate the bond order and net electronic charge on the heteroatoms for nitrogen- and sulfur-containing organic compounds typically found in diesel and jet fuel feedstocks. The bond order and net electronic charge on the heteroatom have been correlated to the activity for hydrogenation and hydrogenolysis, respectively, in literature [22]. Amongst a set of molecules, the molecule having a bond with the highest order is expected to have the greatest reactivity for hydrogenation. The molecules in Fig. 8 each have one bond with the highest order relative to other bonds in the same molecule. The decreasing order of this bond is reflected in the following classification of the molecules in Fig. 8:

$$\text{acridine} > \text{quinoline} > \text{carbazole} \sim 4{,}6\text{-DMDBT}$$

Quinoline, by virtue of having a bond with the highest bond order as compared to those in carbazole and 4,6-DMDBT, could be expected to have the highest reactivity for hydrogenation. In other words, of these molecules, quinoline would be the first to undergo hydrogenation. Further, quinoline could also be expected to adsorb first and more strongly on a hydrogenation site in a catalyst. Consequently, in a feedstock containing 4,6-DMDBT and quinoline, both would compete with each other to adsorb onto hydrogenation sites and quinoline could be expected to occupy the bulk of them because of its possessing a bond with a higher order than those in 4,6-DMDBT. Since quinoline would adsorb preferentially on hydrogenation sites,

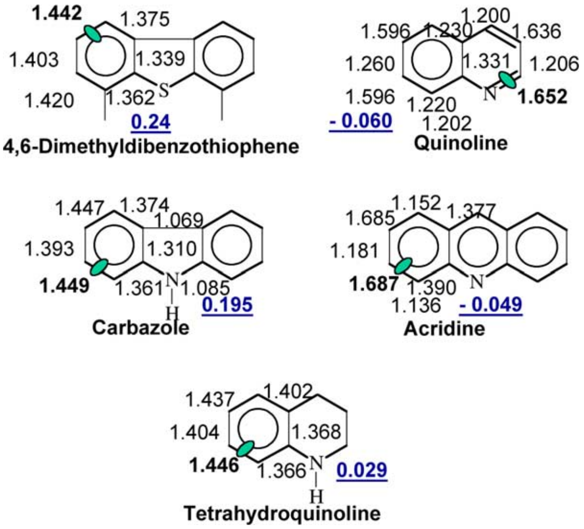

Fig. 8. Molecular modeling results for various sulfur- and nitrogen-containing organic compounds. The bond order value in bold-phase next to a symbol indicates the bond with highest bond order, while the underlined number indicates the net electronic charge on the heteroatom in a given molecule.

4,6-DMDBT's HDS would be severely inhibited—as, indeed, observed in this study's experimental data. On the basis of bond order, therefore, the inhibition of the commercial catalyst for the HDS of 4,6-DMDBT in the presence of quinoline is rational.

On the other hand, the bonds with the highest order in both carbazole and 4,6-DMDBT have similar numerical values. Carbazole's competition with 4,6-DMDBT for a catalyst's hydrogenation sites would, therefore, be much milder than demonstrated by quinoline. In addition, the nitrogen atom in carbazole is not readily available for interaction with hydrogenation sites because of shielding caused by the neighboring hydrogen atom. Furthermore, bonds in carbazole have orders that are much more homogeneous and similar to each other as compared to those in quinoline. Consequently, this does not polarize the carbazole molecule to the extent observed in quinoline thereby reducing the former's tendency to adsorb onto hydrogenation sites. This explains carbazole's little inhibition of the HDS of 4,6-DMDBT over the commercial Co-Mo/Al_2O_3 catalyst as observed experimentally in this study.

The net electronic charge on the heteroatom (nitrogen or sulfur) is another important parameter to understand the behavior of heterocyclic compounds. Similar to bond order, literature correlating the net electronic charge to the hydrogenolysis activity of a HDS catalyst has been reported [22]. The higher the electronic charge on the heteroatom, the greater is that molecule's tendency to interact with a site responsible for hydrogenolysis.

The net charge on the heteroatom in the molecules listed in Fig. 8 decreased in the following order:

4,6-DMDBT > carbazole > acridine > quinoline

The sulfur atom in 4,6-DMDBT possesses a higher electronic charge than the nitrogen atoms in carbazole and quinoline. Consequently, 4,6-DMDBT would have a much higher tendency to undergo hydrogenolysis as compared to carbazole or quinoline. This theoretical prediction is consistent with the experimental results obtained in this study, which indicate that carbazole has little influence on the HDS of 4,6-DMDBT over the commercial catalyst.

Of the molecules listed in Fig. 8, the nitrogen atom on quinoline has the lowest net electronic charge of −0.06 indicating the molecule's poor reactivity for hydrogenolysis. Product selectivity data reported earlier in this work support this conclusion by showing that the HDS of 4,6-DMDBT was inhibited primarily because quinoline poisoned the catalyst's hydrogenation—not hydrogenolysis—functionality.

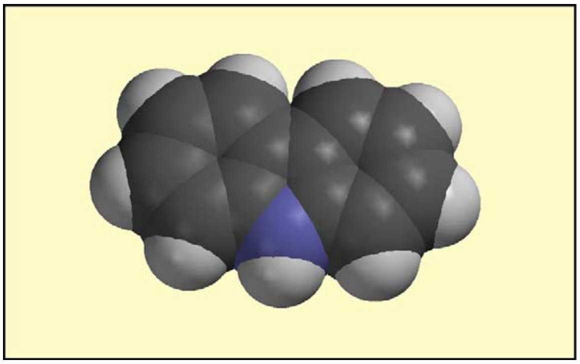

Fig. 9. Space filling model of carbazole indicating steric hindrance caused to nitrogen by hydrogen atom bound to it.

Carbazole has a higher net electronic charge on the nitrogen atom in comparison to quinoline. Therefore, carbazole should inhibit hydrogenolysis sites more strongly than quinoline. This study's experimental data, however, does not correlate with this prediction. Although the net electronic charge on the nitrogen in carbazole is higher than that in quinoline, a hydrogen atom (bound to the nitrogen) blocks carbazole's nitrogen atom. Further, carbazole has a planar molecular structure as shown in Figs. 9 and 10. The planar structure reduces the nitrogen atom's tendency to adsorb onto hydrogenolysis sites. Thus, a combination of structural and electronic factors result in lower

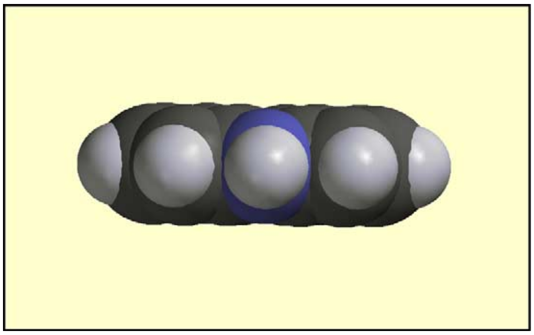

Fig. 10. Side view of space filling model of carbazole indicating steric hindrance caused to nitrogen by hydrogen atom bound to it.

hydrogenolysis reactivity for carbazole as witnessed in experimental results obtained in this work.

Finally, it should be noted that the present results provide a fair comparison on effects of two different organic nitrogen compounds on HDS of 4,6-DMDBT under comparable conditions, but the present data do not yet allow a fair analysis of effects of ammonia, which is a product of hydrodenitrogenation, on HDS of 4,6-DMDBT.

4. Conclusions

This study has elucidated the effects of nitrogen on HDS of 4,6-DMDBT over both γ-Al_2O_3- and MCM-41-supported Co-Mo catalysts. Furthermore, this study has quantified the “long-term” effects of nitrogen compounds on HDS catalysts with increasing time on stream even after the nitrogen compounds have been removed from the hydrocarbon feedstocks. Quinoline (basic nitrogen) inhibits catalytic activity of MCM-41- and γ-Al_2O_3-supported catalysts. It strongly adsorbs on hydrogenation and acid sites as evidenced by decreased selectivity for methyl cyclohexyl toluene and dimethyl biphenyl derivatives, respectively. To a certain extent, the long-term effects of quinoline are reversible. Carbazole (non-basic nitrogen) has little effect on 4,6-DMDBT HDS over the commercial γ-Al_2O_3-supported Co-Mo sulfide catalyst, but significantly inhibits the HDS activity of Co-Mo/MCM-41(50) catalyst. On the other hand, the inhibition of Co-Mo/MCM-41(50) catalyst is reversible following removal of carbazole from the feedstock.

These results were further explained by semi-empirical computational and molecular modeling data with respect to the comparison of bonds with highest bond order values in given molecules that could partially indicate relative hydrogenation reactivity of the molecules, and the comparison of net electron charges on heteroatoms in given molecules that could indicate relative hydrogenolysis reactivity of the molecules. The decreasing order of this bond order is reflected in the following ranking of the molecules: acridine $>$ quinoline $>$ carbazole $\sim$ 4,6-DMDBT. Product selectivity data reported in this work show that the HDS of 4,6-DMDBT was inhibited primarily because quinoline poisoned the catalyst’s hydrogenation—not hydrogenolysis—functionality, being consistent with the computer modeling. The net charge on the heteroatom in the molecules decrease in the order of 4,6-DMDBT $>$ carbazole $>$ acridine $>$ quinoline. A combination of structural and electronic factors result in lower hydrogenolysis reactivity for carbazole as witnessed in experimental results obtained in this work.

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