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Effect of the nitrogen heterocyclic compounds on hydrodesulfurization using *in situ* hydrogen and a dispersed Mo catalyst

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ABSTRACT

The hydrodesulfurization (HDS) of the highly refractory sulfur-containing compounds, dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT), and the effect of the basic and non-basic nitrogen heterocyclic compounds, such as quinoline and carbazole, on HDS using a dispersed unsupported Mo catalyst and *in situ* generated hydrogen were studied. Experimental results indicated that the dispersed unsupported Mo catalyst was effective for the HDS of 4,6-DMDBT in a mixture containing DBT. The direct desulfurization pathway (DDS) was the preferred pathway for the HDS of DBT while the hydrogenation pathway (HYD) was the preferred pathway for the HDS of 4,6-DMDBT under our experimental conditions. A strong inhibitive effect of the basic quinoline or the non-basic carbazole on the HDS of each of the sulfur-containing compounds was observed. The DDS and HYD pathways in the HDS of the refractory sulfur-containing compounds were affected to a different extent by the nitrogen-containing compounds, suggesting that different active sites were involved in these two reaction pathways.

1. Introduction

Due to the depletion of conventional oil resources, heavy oil and bitumen have become important sources for energy and fuel. Canada has large reserves of bitumen and heavy oil which play an increasingly important role in supplying the need for transportation fuels. Bitumen and heavy oil have low hydrogen/carbon atomic ratios and contain large percentages of sulfur and nitrogen heteroatoms. The recent ultra low S specifications for transportation fuels require an effective way to achieve deep hydrodesulfurization (HDS) of refractory sulfur-containing compounds, such as dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT). However, at the level of deep hydrodesulfurization, the concentration of these refractory sulfur-containing compounds is low, and other poly-nuclear molecules, especially the nitrogen-containing compounds, exhibit an inhibiting effect on the HDS due to the competitive adsorption on the active sites of the catalyst surface [1–5]. The inhibitive effect of the nitrogen-containing compounds on HDS is very strong, even at a concentration as low as 5 ppm of nitrogen in the form of quinoline or carbazole [6]. Therefore, it is necessary to investigate the effect of the nitrogen-containing compounds on the HDS of the refractory sulfur-containing compounds for achieving the recent ultra low sulfur specifications for gasoline and diesel fuels.

It has been reported that the predominant nitrogen-containing compounds in atmospheric gas oil (AGO) are carbazole, quinoline, and indole derivatives, while in light cycle oil (LCO), carbazole, indole and aniline derivatives are the main nitrogen-containing compounds [7]. In blended gas oil, alkyl-substituted carbazoles were found in large amounts and carbazoles were identified to be the most refractory organic nitrogen-containing compounds in the feed towards hydrodenitrogenation (HDN) [8]. The reactivity order for the denitrogenation of these nitrogen species was found to be: indole > methylated anilines ≥ monomethylated indole > quinoline > carbazole > methylated carbazole [9].

Based on model compound studies, basic nitrogen-containing compounds have been considered as one of the strongest HDS inhibitors due to the strong adsorption of the basic nitrogen-containing compounds on the active sites on the catalyst surface *via* donation of their lone-pair of electrons to the Lewis sites or by interaction with the protons of the Brønsted acid sites [1,10 and references therein].

Unlike the basic nitrogen-containing compounds, the effect of the non-basic nitrogen-containing compounds on HDS was less intensively studied previously. Since carbaozles are the major nitrogen-containing compounds in many hard-to-desulfurize middle distillates, the effect of carbazoles on HDS has attracted more attention recently [2,8,11–13]. Turaga et al. reported that carbazole had little effect on the HDS of 4,6-DMDBT over the commercial γ-Al_2O_3-supported CoMo sulfide catalyst, but significantly inhibited the HDS activity using the CoMo/MCM-41 catalyst [2]. Laredo et al. found that the non-basic indole and

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carbazole had a comparable inhibitive effect as the basic quinoline on the HDS of DBT using a CoMo/γ-Al_2O_3 commercial catalyst [6]. This inhibition effect was attributed to the hydrogenation reactions which converted the non-basic nitrogen-containing compounds into basic compounds, as suggested by Ho [14], or due to their polymerization on the catalyst surface [15].

The initial adsorption of non-basic nitrogen heterocycles on the catalyst surface is most likely similar to that for polynuclear aromatics, such as naphthalene, which is adsorbed *via* the aromatic ring parallel to the catalyst surface [11], therefore the hydrogenation pathway of HDS was more inhibited than the hydrogenolysis pathway.

Recently, we used quinoline and carbazole as model nitrogen heterocyclic compounds to study the effect of basic and non-basic nitrogen-containing compounds on the deep HDS of the refractory sulfur-containing compounds such as DBT and 4,6-DMDBT. Results of this investigation are reported in this paper.

We have developed a novel process for upgrading bitumen emulsions *via* the utilization of the water present in the emulsion to provide hydrogen *in situ* for upgrading [16]. Our previous research has indicated that the *in situ* hydrogen, which was produced *via* the water gas shift (WGS) reaction (Eq. (1)), was more reactive than molecular hydrogen in bitumen upgrading, HDS of DBT, and HDN of quinoline over a dispersed unsupported Mo sulfide catalyst [17–19].

$$CO + H_2O \leftrightarrow H_2 + CO_2 \quad (1)$$

In this paper, we will extend the use of *in situ* hydrogen generated *via* the WGS reaction over this dispersed Mo sulfide catalyst to study the effect of basic and non-basic nitrogen heterocyclic compounds on the HDS of DBT and 4,6-DMDBT. Quinoline and carbazole will be used as the representative basic and non-basic nitrogen-containing model compounds respectively. Although the effect of nitrogen-containing compounds on the HDS using supported CoMo, NiMo catalysts has been studied quite extensively, there is very limited data available on the effect of nitrogen-containing compounds on HDS using dispersed unsupported catalysts. This paper is the first to report on the effect of carbazole on HDS over a dispersed Mo sulfide catalyst using *in situ* generated H_2.

2. Experimental

The dispersed Mo sulfide catalyst used in this paper was prepared *in situ via* hydrothermal decomposition, reduction and sulfidation of the precursor, phosphomolybdic acid (PMA), which was purchased from Aldrich. In the reactant mixture, the molar ratio between the active transition metal, Mo, and the atomic sulfur in the model sulfur compounds, Mo:S, was 1:10. The model sulfur-containing compounds, DBT and 4,6-DMDBT, and the nitrogen-containing compounds, quinoline and carbazole, were purchased from Aldrich and used without any further purification. In the experiments carried out for studying the effect of nitrogen-containing compounds on HDS, the nitrogen-containing compounds were introduced in a molar ratio (N:S) of 1:2. A typical feedstock contained equi-molar DBT and 4,6-DMDBT (1600–1800 ppmw of sulfur in total), 340 ppmw of N in the form of quinoline or carbazole, and 500 ppmw of Mo.

Experiments were carried out in a 300 ml SS Autoclave batch reactor. The mixture of nitrogen-containing compounds with the sulfur-containing compounds was dissolved in 100 ml of toluene, while the molybdenum precursor, PMA, was dissolved in 10 ml of de-ionized water. After transferring the solutions containing the reactants into the reactor vessel, the reactor was sealed and purged three times with N_2 to remove O_2 from the solution, and then was purged three times with the reactant gas CO. 600 psi of the reactant gas mixture of H_2S/CO was introduced into the reactor vessel, and then, the reactor was heated up to the designated temperature at a rate of 2–3 °C/min. The reaction system was maintained at the reaction temperature for a designated time, and then the reactor was allowed to cool down to room temperature before samples were collected for analysis.

After the reaction, the liquid product was removed into a glass container. The finely dispersed black solid catalyst was separated from the liquid product *via* filtration using filter paper. The black solid catalyst particles have been determined to be molybdenum

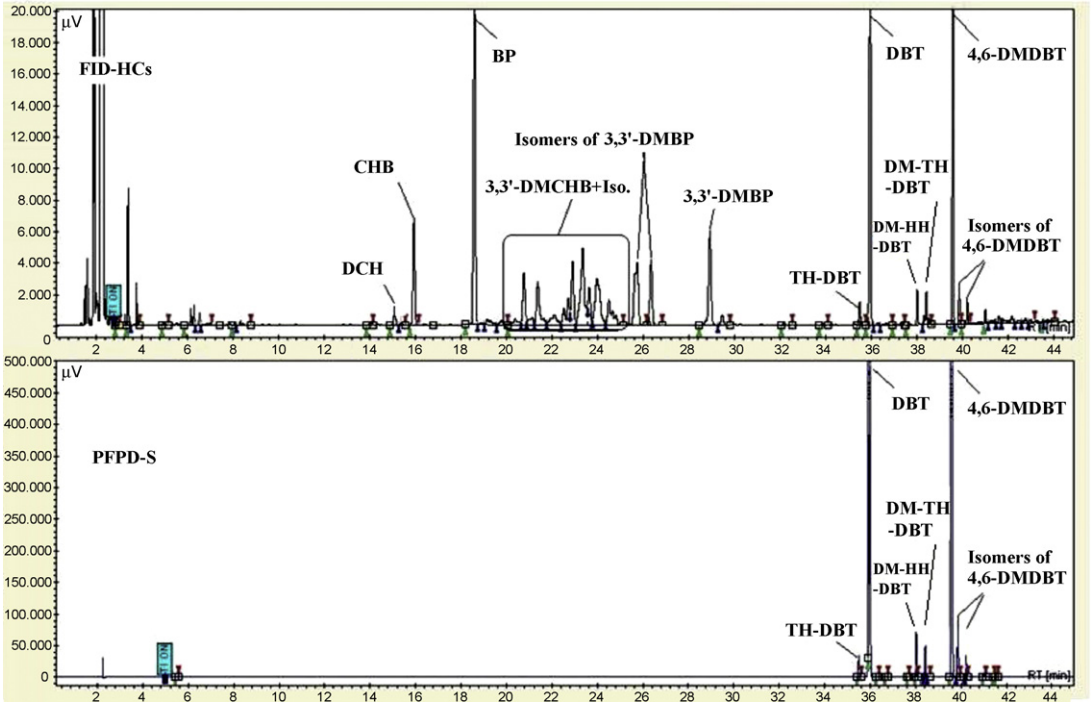

Fig. 1. GC chromatograph of the HDS products derived from DBT and 4,6-DMDBT (FID, PFPD).

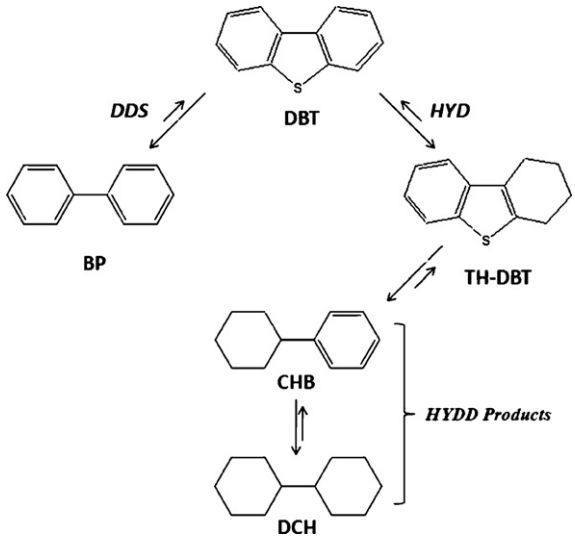

Fig. 2. Proposed reaction network of the HDS of DBT using a dispersed Mo sulfide catalyst.

sulfide *via* X-ray diffraction which indicated that during the reaction, PMA was transformed into molybdenum sulfide [18].

A gas chromatography–mass spectroscopy (GC–MS) system (Varian GC-CP3800/Saturn 2000) was used for the identification of the products. A separate GC (Varian CP-3800) was used for quantitative analysis of the liquid products. This GC was configured with a VF-05MS capillary column coated with an arylene stabilized phase equivalent to 5% phenyl and 95% dimethylpolysiloxane (30 m × 0.30 mm × 1.0 μm), which was connected to three different detectors: a flame ionization detector (FID), a thermionic specific detector (TSD, <1 ppmw of N-containing compounds), and a pulse flame photometric detector (PFPD, <0.1 ppmw of S-containing compounds). This Varian CP-3800 GC can simultaneously implement identification and quantitative analysis of S-containing compounds (*via* PFPD), N-containing compounds (*via* TSD), and hydrocarbons (*via* FID) present in the liquid products.

3. Results and discussion

It is well known that over traditional supported Mo catalysts, the HDS of sulfur-containing compounds proceeds through two reaction pathways: the direct desulfurization (DDS) pathway which yields biphenyl-type compounds by direct hydrogenolysis of the C–S bonds, and the hydrogenation (HYD) pathway where the sulfur is removed from the molecule after hydrogenation of the aromatic rings [10,18,20,21] to produce desulfurized products (HYDD). The HYDD products include only the desulfurized products obtained via the hydrogenation pathway while the HYD products include the intermediate hydrogenated products together with the HYDD products.

Fig. 1 shows the HDS products of DBT and 4,6-DMDBT, which were identified based on a comparison with the retention time of standard compounds and/or were identified using GC–MS. Since the products obtained from the HDS of DBT and 4,6-DMDBT using the dispersed Mo sulfide catalyst are similar to those reported in the literature using traditional supported catalysts, similar reaction pathways were proposed for these HDS reactions (as shown in Figs. 2 and 3).

The reaction scheme for the HDS of DBT is shown in Fig. 2, where biphenyl (BP) is the sulfur-removed product produced *via* the DDS pathway, while cyclohexylbenzene (CHB) and dicyclohexyl (DCH) are the desulfurized products obtained *via* the HYD route after DBT is partially hydrogenated to the intermediates, such as tetrahydro-DBT (TH-DBT). Fig. 3 represents the HDS reaction network of 4,6-DMDBT. The GC–MS identification showed that isomerization of 4,6-DMDBT took place during the HDS reaction and resulted in the production of isomers of the desulfurization products (as shown in Fig. 1). In the HDS of 4,6-DMDBT, the DDS reaction pathway produces 3,3-dimethylbiphenyl (3,3′-DMBP) and its isomers. In the HYD reaction route, 4,6-DMDBT was hydrogenated to 4,6-dimethyl-tetrahydro-DBT (4,6-DM-TH-DBT), and 4,6-dimethyl-hexahydro-DBT (4,6-DM-HH-DBT) firstly and then was desulfurized to generate 3,3′-dimethylcyclohexylbenzene (3,3′-DMCHB). In the present study, the totally hydrogenated intermediate 4,6-dimethyl-dodecahydro-DBT was not detected.

3.1. Simultaneous HDS of DBT and 4,6-DMDBT

Due to the different steric structures of the two sulfur-containing compounds, DBT and 4,6-DMDBT, the contribution of the two reaction pathways to the overall HDS was very different. In the HDS of DBT, the molecules adsorb mainly in the mode of σ-adsorption *via* the sulfur atom on the catalyst surface of the supported catalyst, leading to the hydrogenolysis of C–S bonds, and

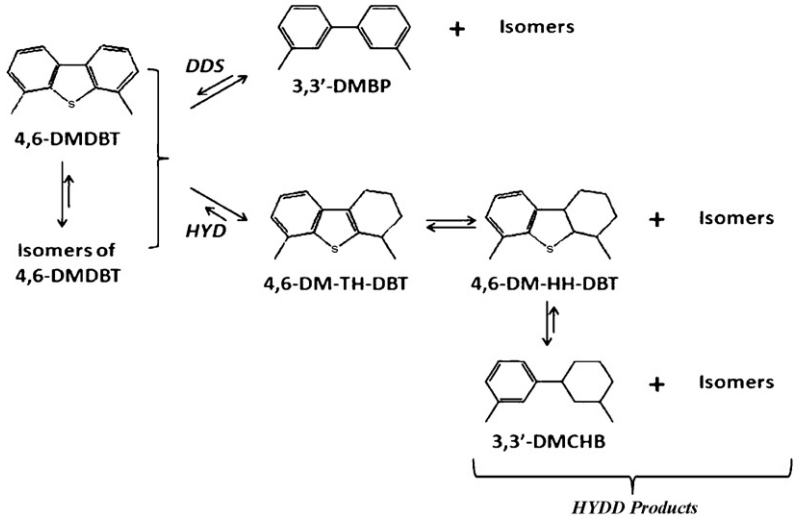

Fig. 3. Proposed reaction network of the HDS of 4,6-DMDBT using a dispersed Mo sulfide catalyst.

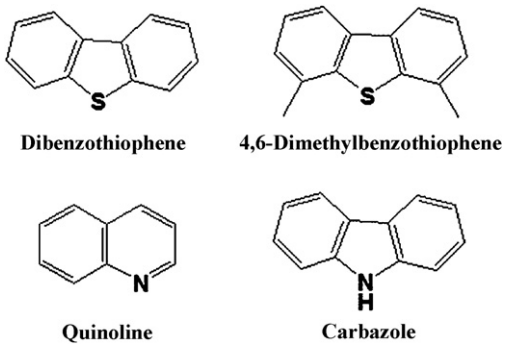

Fig. 4. Molecular structures of sulfur-/nitrogen-containing model compounds.

as a result, the DDS route is the major reaction pathway in the HDS of DBT [10,21,22]. However, in the HDS of 4,6-DMDBT, the methyl groups are adjacent to the sulfur atom (as shown in Fig. 4), hindering the σ-type adsorption of 4,6-DMDBT on the catalyst surface. Therefore, the molecule of 4,6-DMDBT prefers to adsorb on the supported catalyst surface *via* the π-orbital of the aromatic rings with the molecule lying flat on the catalyst surface to minimize steric hindrance [10,21]. After partial hydrogenation of 4,6-DMDBT, a flexible cyclohexyl ring would be produced, and hence, the steric hindrance of the methyl groups at positions 4 and 6 is decreased. This change makes the sulfur atom more accessible to adsorb *via* the σ-mode on the catalyst surface and leads to desulfurization [21]. Therefore, the HDS of 4,6-DMDBT takes place predominantly *via* the HYD route due to the π-adsorption of 4,6-DMDBT on the catalyst surface. Michaud et al. had reported that the DDS route contributed around 80% to the overall HDS of DBT, but only 20% to the HDS of 4,6-DMDBT under conventional conditions, using a supported NiMo catalyst at 340 °C [23]. Recently Wang and Prins [24] reported the HDS of DBT and 4,6-DMDBT over a Ni–MoS_2/γ-Al_2O_3 at 300 °C and they also found that the DDS route contributed to 95% of the overall conversion of DBT while the DDS route contributed to about 27% of the overall conversion of 4,6-DMDBT. Wang and Prins [25] also reported that the DDS route contributed to 76% to the overall conversion of DBT using a supported Mo/γAl_2O_3 catalyst at 300 °C.

In the present study, the dispersed Mo sulfide catalyst was unsupported and was prepared *in situ via* the hydrothermal decomposition of the Mo precursor using *in situ* generated hydrogen from the water-gas shift reaction. Table 1, Figs. 5 and 6 show the experimental results of the simultaneous HDS of DBT and 4,6-DMDBT over the unsupported catalyst using *in situ* hydrogen at different reaction times. It was observed that the HDS of DBT and 4,6-DMDBT increased gradually with increasing reaction time.

Based on the concentrations of the DBT and 4,6-DMDBT obtained from the batch autoclave experiments over the dispersed unsupported Mo sulfide catalyst using *in situ* hydrogen, the pseudo first order reaction rate constants for the conversions of the DBT and 4,6-DMDBT can be calculated as follows:

$$r = -\frac{dC_{\mathrm{DBT(or4,6\text{-}DMDBT)}}}{dt} = k \cdot C_{\mathrm{DBT(or4,6\text{-}DMDBT)}} \quad (2)$$

Upon integrating (Eq. (2)), one obtains:

$$\ln\left(\frac{C_t}{C_0}\right) = -k \cdot t \quad (3)$$

where: r is the reaction rate, M s^{-1}, k the pseudo first order reaction rate constant, s^{-1}, C_t the concentration of S compound at time t, M, C_0 the initial concentration of S compound, M.

Table 1
Conversions and product distributions for the HDS of DBT and 4,6-DMDBT over a dispersed Mo sulfide catalyst using *in situ* hydrogen at different reaction times. Equi-molar DBT and 4,6-DMDBT (1800 ppmw of S in total), 585 psi of CO and 15 psi of H_2S (at room temperature), 500 ppmw Mo, 653 K.

Reaction time, h	1	2	3
HDS of DBT			
Conversion, %	28	60	72
Product distribution, mol%			
DDS product:			
BP	16	41	47
HYD products:			
TH-DBT	5	2	2
HYDD products:			
DCH	<1	3	4
CHB	7	14	19
Desulfurization[a], mol%	23	58	70
HDS of 4,6-DMDBT			
Conversion, %	24	47	63
Product distribution, mol%			
DDS products:			
3,3′-DMBP and isomers	5	12	17
HYD products:			
DM-TH-DBT	5	3	3
DM-HH-DBT	1	2	3
HYDD products:			
3,3′-DMCHB and isomers	11	27	35
Isomerization products:			
Iso-DMDBT	2	3	5
Desulfurization[a], mol%	16	39	52

[a] Sum of DDS products (mol%) and HYDD products (mol%).

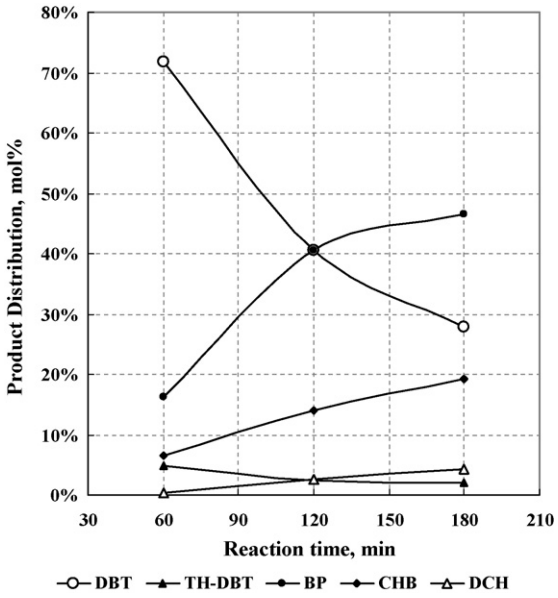

Fig. 5. Product distribution for the HDS of DBT over a dispersed Mo sulfide catalyst using *in situ* hydrogen as a function of the reaction time. Equi-molar DBT and 4,6-DMDBT (1800 ppmw of S in total), 585 psi of CO and 15 psi of H_2S (at room temperature), 500 ppmw Mo, 653 K.

Fig. 7 shows the pseudo first order plots for the conversions of DBT and 4,6-DMDBT over the dispersed Mo sulfide catalyst. Assuming that all the Mo had been converted to MoS_2, the overall rate constants for the conversion of DBT, k_{DBT}, and 4,6-DMDBT, $k_{\mathrm{4,6\text{-}DMDBT}}$, at 653 K (380 °C) were found to be $1.8 \times 10^{-3}(g_{cat}\ s)^{-1}$and $1.2 \times 10^{-3}(g_{cat}\ s)^{-1}$, respectively, where g_{cat} refers to the weight of MoS_2. Therefore, over the dispersed unsupported MoS_2 catalyst, the reactivity of DBT was 1.5 times higher than that of 4,6-DMDBT at 380 °C.

It has been reported that 4,6-DMDBT is one of the most refractory sulfur compounds present in oil fuels, and its HDS

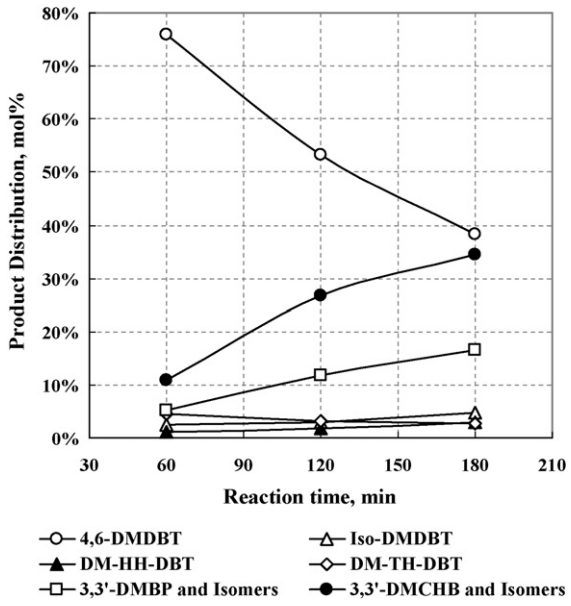

Fig. 6. Product distribution for the HDS of 4,6-DMDBT over a dispersed Mo sulfide catalyst using *in situ* hydrogen as a function of the reaction time. Equi-molar DBT and 4,6-DMDBT (1800 ppmw of S in total), 585 psi of CO and 15 psi of H_2S (at room temperature), 500 ppmw Mo, 653 K.

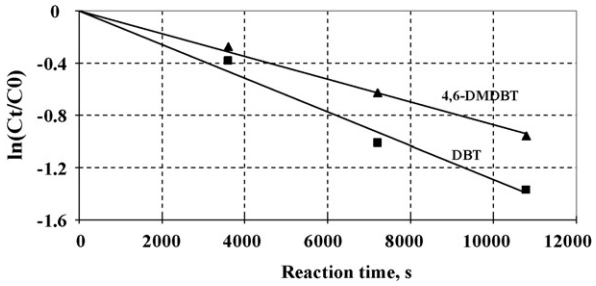

Fig. 7. Pseudo-first-order plots for the conversion of DBT and 4,6-DMDBT at 653 K. Equi-molar DBT and 4,6-DMDBT (1800 ppmw of S in total), 585 psi of CO and 15 psi of H_2S (at room temperature), 500 ppmw Mo.

reactivity was around 10 times lower than that of DBT in the HDS of a diesel fuel at 360 °C over a traditional supported CoMo catalyst [26]. More recently, Wang and Prins [24] found that 4,6-DMDBT was 7 times less reactive than DBT at 300 °C over a $NiMoS_2/\gamma$-Al_2O_3 catalyst. It is interesting to note that Yoosuk et al. [27] reported the ratio of the HDS rate constants for the conversions of DBT and 4,6-DMDBT to be 1.4 at 300 °C using an unsupported sulfided NiMo catalyst, and an unsupported MoS_2 was even more active towards the HDS of 4,6-DMDBT where the ratio of the HDS rate constants for the conversions of DBT and 4,6-DMDBT was 0.55. Hence, the dispersed unsupported Mo sulfide based catalysts apparently have a higher relative activity towards the HDS of 4,6-DMDBT than the traditional supported catalysts. Yoosuk et al. attributed the higher activity of the unsupported catalysts to their higher hydrogenation activities [27]. Another possible explanation is that the dispersed unsupported catalyst provides more effective surface area for the π-adsorption of the 4,6-DMDBT and hence is more effective for the HDS of the bulky refractory sulfur-containing compounds, such as 4,6-DMDBT.

Based on the products obtained from the HDS of DBT and 4,6-DBMBT shown in Table 1, the ratio of the selectivity between the two pathways are shown in Table 2. Two different selectivity ratios, i.e., DDS/HYD where HYD includes the hydrogenated intermediates and the desulfurized products, and the ratio of DDS/HYDD where HYDD only includes the desulfurized products were calculated (Table 2). For the HDS of DBT, the ratio of DDS/HYD or DDS/HYDD is around 2 except for the conversion data obtained at the first hour. For the HDS of 4,6-DMDBT, the ratio of DDS/HYD or DDS/HYDD is less than 1. These selectivity data clearly showed that with the dispersed unsupported Mo sulfide catalyst, the DDS pathway was the major route for the HDS of DBT, while the HYD pathway was preferred over the DDS route for the HDS of 4,6-DMDBT. This is in accordance with what has been reported using the traditional supported catalysts where the HYD pathway was the preferred pathway for the HDS of 4,6-DMDBT [18,21,23–25,28], although the reported values of the ratio between the two reaction pathways were different since this ratio is dependent on reaction conditions such as temperature and the amount of H_2S present.

Table 2
Selectivity between the two reaction pathways in the HDS of DBT and 4,6-DMDBT over a dispersed Mo sulfide catalyst using *in situ* hydrogen at 653 K. Equi-molar DBT and 4,6-DMDBT (1800 ppmw of S in total), 585 psi of CO and 15 psi of H_2S (at room temperature), 500 ppmw Mo, 653 K.

Reaction time, hr	1	2	3
HDS of DBT			
Conversion, %	28	60	72
DDS/HYD, molar	1.3	2.2	1.9
DDS/HYDD, molar	2.3	2.4	2.0
HDS of 4,6-DMDBT			
Conversion, %	24	47	63
DDS/HYD, molar	0.3	0.4	0.4
DDS/HYDD, molar	0.5	0.4	0.5

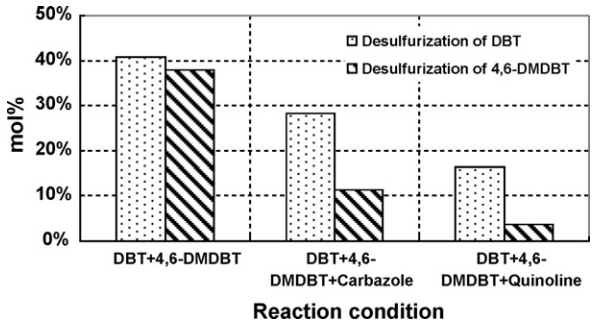

Fig. 8. Effect of the nitrogen heterocyclic compounds on the S-removal from DBT and 4,6-DMDBT over a dispersed Mo sulfide catalyst using *in situ* hydrogen. Equi-molar DBT and 4,6-DMDBT (1670 ppmw of S in total), 590 psi of CO and 10 psi of H_2S (at room temperature), 500 ppmw Mo, S:N = 2:1 (molar), 653 K.

3.2. Effect of nitrogen heterocyclic compounds on HDS

Fig. 8 and Table 3 summarize the experimental results of the effect of the basic quinoline and the non-basic carbazole on the activity of the dispersed unsupported Mo sulfide catalyst towards the HDS of DBT and 4,6-DMDBT. With the presence of the basic quinoline, the concentrations of the desulfurized products of DBT and 4,6-DMDBT decreased by 60% and 90%, respectively. In the presence of the non-basic carbazole, the concentrations of the desulfurized products of DBT and 4,6-DMDBT decreased by 31% and 70%, respectively. Comparing the two sulfur-containing compounds, the sulfur removal from 4,6-DMDBT was much more inhibited than that of DBT, especially in the presence of the basic quinoline, wherein the desulfurization of 4,6-DMDBT decreased by 90%. Therefore, it is clear that both nitrogen heterocyclic compounds had a significant inhibitive effect on the HDS, especially on the HDS of the more refractory sulfur compound, 4,6-DMDBT. The basic quinoline was a stronger inhibitor than the non-basic carbazole.

Table 3
Conversions and product distributions for the HDS of DBT and 4,6-DMDBT in the presence of the nitrogen heterocyclic compounds over a dispersed Mo sulfide catalyst using *in situ* hydrogen. Equi-molar DBT and 4,6-DMDBT (1670 ppmw of S in total), 590 psi of CO and 10 psi of H_2S (at room temperature), 500 ppmw Mo, S:N = 2:1 (molar), 653 K, 3 h.

	DBT + 4,6-DMDBT	DBT + 4,6-DMDBT + carbazole	DBT + 4,6-DMDBT + quinoline
HDS of DBT			
Conversion, %	46	33	19
Product distribution, mol%			
DDS product:			
BP	29	18	16
HYD products:			
TH-DBT	5	4	2
HYDD products:			
DCH	<1	4	0
CHB	11	7	1
Desulfurization[a] mol%	41	29	17
HDS of 4,6-DMDBT			
Conversion, %	44	19	9
Product distribution, mol%			
DDS products:			
3,3′-DMBP and isomers	16	7	3
HYD products:			
DM-TH-DBT	2	2	2
DM-HH-DBT	2	5	2
HYDD products:			
3,3′-DMDCH and isomers	22	4	1
Isomerization products:			
Iso-DMDBT	2	1	<1
Desulfurization[a] mol%	38	11	4
HDN of N-containing model compound			
Conversion, %	–	60	99
Denitrogenation, mol%	–	52	66

[a] Sum of DDS products (mol%) and HYDD products (mol%).

Because the HDN of carbazole and the HDS of DBT have common products, i.e., CHB, DCH, and BP, the effect of carbazole on the reaction pathways in the HDS of DBT could not be distinguished based on the product analysis from our experiments. Fig. 9 and Table 3 show the effect of quinoline on the HYDD and DDS products for the HDS of DBT. In the presence of quinoline, the HYDD and DDS reaction products were reduced by 93% and 46%, respectively. Cyclohexylbenzene was the only desulfurized product obtained *via* the HYD route in the presence of quinoline, while both cyclohexylbenzene and saturated dicyclohexyl were observed in the HDS of DBT without added quinoline. Hence, the basic quinoline had a more severe inhibitive effect on the HYD reaction pathway for the HDS of DBT than on the DDS route over the dispersed unsupported Mo sulfide catalyst.

Fig. 10 and Table 3 show the effect of carbazole and quinoline on the DDS and HYDD products in the HDS of 4,6-DMDBT. After introducing carbazole, the concentration of the DDS products of 4,6-DMDBT was reduced by 56%, and the concentration of HYDD products was decreased by 81%. In the presence of quinoline, the concentrations of the DDS and HYDD products of 4,6-DMDBT were decreased by 83% and 95%, respectively. Therefore, similar to the HDS of DBT, the HYD reaction pathway for the HDS of 4,6-DMDBT was more inhibited by the nitrogen heterocyclic compounds. As a result, interestingly, the DDS route became the major reaction pathway instead of the HYD pathway for the HDS of 4,6-DMDBT due to the stronger inhibitive effect of the nitrogen heterocyclic compounds on the HYD route.

The different inhibitive effects of the nitrogen-containing compounds on the two reaction pathways suggested that the DDS and HYD reactions took place on different active sites. This assumption has also been proposed by other research groups for the supported Mo catalysts [10 and references therein, 28]. Egorova and Prins studied the nature of active HDS sites and they suggested that the DDS and HYD reaction pathways occurred over separate active sites due to the different adsorption modes on the catalyst surface [29]. They proposed that the DDS reaction

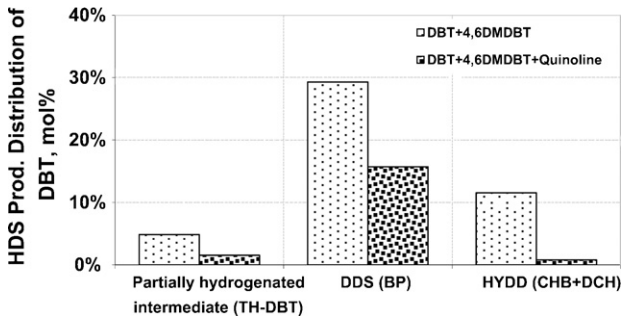

Fig. 9. Effect of the basic quinoline on the HDS product distribution of DBT over a dispersed Mo sulfide catalyst using *in situ* hydrogen. Equi-molar DBT and 4,6-DMDBT (1670 ppmw of S in total), 590 psi of CO and 10 psi of H_2S (at room temperature), 500 ppmw Mo, S:N = 2:1 (molar), 653 K.

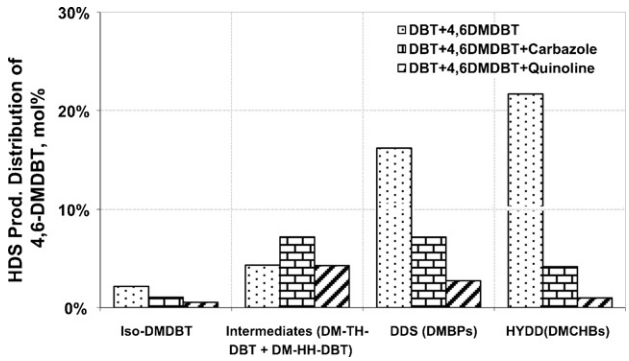

Fig. 10. Effect of the nitrogen heterocyclic compounds on the HDS product distribution of 4,6-DMDBT over a dispersed Mo sulfide catalyst using *in situ* hydrogen. Equi-molar DBT and 4,6-DMDBT (1670 ppmw of S in total), 590 psi of CO and 10 psi of H_2S (at room temperature), 500 ppmw Mo, S:N = 2:1 (molar), 653 K.

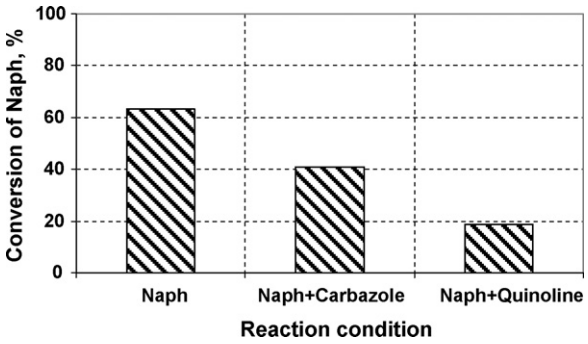

Fig. 11. Effect of the nitrogen-containing compounds on the hydrogenation of naphthalene over a dispersed Mo sulfide catalyst using *in situ* hydrogen. 590 psi of CO and 10 psi of H_2S (at room temperature), 500 ppmw Mo, 653 K.

occurred through a σ-adsorption of the refractory sulfur-containing molecule *via* the sulfur atom while the HYD route was assumed to proceed through a π adsorption of the reactant molecule *via* the aromatic ring.

The adsorption mode of the nitrogen-containing compounds on the unsupported MoS_2 catalyst probably has an important effect on the observed inhibition of HDS. The strong adsorption of the nitrogen heterocyclic compounds, quinoline and carbazole parallel to the catalyst surface *via* a π interaction of the aromatic ring would have a severe inhibiting effect on the HYD route in the HDS of DBT and 4,6-DMDBT.

Comparing the two nitrogen-containing compounds, non-basic carbazole was less harmful to the HDS of both refractory sulfur compounds. Turaga et al. used semi-empirical computational and molecular modeling data and correlated the activity towards hydrogenation to the highest bond order in the molecule to explain the difference in the inhibiting effect caused by quinoline and carbazole on the HDS [2]. They found that the highest bond order in the molecules decreased in the order of quinoline > carbazole ∼ 4,6-DMDBT and hence resulted in the preferential adsorption of quinoline on the hydrogenation active sites and caused a stronger inhibitive effect on the hydrogenation of 4,6-DMDBT than that of carbazole. Their finding is in agreement with our experimental result on the hydrogenation of naphthalene in the presence of quinoline or carbazole (Fig. 11). Similarly to the effect of nitrogen-containing compounds on the HDS of sulfur compounds, both quinoline and carbazole had a significant inhibitive effect on the hydrogenation of naphthalene, and the effect caused by quinoline was stronger than that of carbazole.

It is also important to note that the concentration of the isomerized products of 4,6-DMDBT was lower in the experiments with nitrogen-containing compounds (Fig. 10), especially in the experiment with quinoline. Isomerization during the HDS reactions is beneficial for the HDS of 4,6-DMDBT by transforming it into more reactive isomers [23,26]. The isomerization of the 4,6-DMDBT is acid catalyzed [23 and references therein]. The basicity of the nitrogen-containing compounds, especially the strongly basic quinoline, decreases the acidity of the Mo sulfide catalyst, therefore, resulting in a decrease in the concentration of the isomerized products of 4,6-DMDBT which contributed to a more severe inhibiting effect of the nitrogen-containing compounds on the HDS of 4,6-DMDBT.

4. Conclusions

A dispersed Mo sulfide catalyst was produced *in situ via* the hydrothermal decomposition of a molybdenum precursor for the HDS of DBT and 4,6-DMDBT. The activity of this unsupported Mo catalyst towards the HDS of model refractory sulfur-containing compounds and the effect of the nitrogen-containing compounds such as the basic quinoline or the non-basic carbazole, on the HDS activity of the catalyst were reported and discussed. The experimental results indicated that the dispersed unsupported Mo sulfide catalyst is effective for the HDS of 4,6-DMDBT in a mixture containing DBT. The DDS pathway was the preferred pathway for the HDS of DBT while the HYD pathway was the preferred pathway for the HDS of 4,6-DMDBT under our experimental conditions.

The nitrogen heterocyclic compounds, quinoline and carbazole, had a strong inhibitive effect on the HDS of DBT and 4,6-DMDBT. Quinoline was a stronger inhibitor than carbazole. The HYD reaction pathway for the HDS of DBT and 4,6-DMDBT was more strongly inhibited than the DDS pathway.

The nitrogen heterocyclic compounds also inhibited the hydrogenation of naphthalene and the inhibitive effect of quinoline was stronger. These results suggested that quinoline and carbazole adsorb strongly on the hydrogenation sites of the catalyst, probably *via* the π adsorption of the aromatic ring, resulting in the inhibition of the hydrogenation of naphthalene and the HYD pathway for the HDS of DBT and 4,6-DMDBT.

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