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Structure-HDS reactivity relationship of dibenzothiophenes based on density functional theory

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Perpendicular adsorption of alkyl-substituted dibenzothiophenes on a $Mo_{10}S_{18}$ cluster was studied using density functional theory. The Mayer bond order between the sulfur atom of dibenzothiophene and the molybdenum atom of the $Mo_{10}S_{18}$ cluster was calculated from the optimized adsorption complex. Depending on the position of the alkyl substitution in dibenzothiophene, the values of the Mayer bond order were classified into three groups, and compared with the experimental hydrodesulfurization (HDS) rate constants measured at 320 °C, 70 atm, and 1.6 h^{-1} over a $NiMo/Al_2O_3$ catalyst using a light cycle oil.

KEY WORDS: alkyl-substituted dibenzothiophenes; HDS, density functional theory; S–Mo bond order.

1. Introduction

The sulfur content in on-road diesel fuel will be reduced to 15 ppm in the US (2006) and Canada (2007) from the current level of 500 ppm. This stringent sulfur specification has led to renewed interest in exploring the relationship between the molecular structure and reactivity of sulfur compounds, especially alkyl-substituted dibenzothiophenes (DBTs), the major refractory sulfur species to be removed in deep hydrodesulfurization (HDS). Extensive efforts have been made to understand the HDS mechanism of MoS_2-based catalysts. It is generally accepted that two reaction pathways are involved in the removal of sulfur species by HDS reaction–direct sulfur removal by hydrogenolysis and hydrogenation of one or both aromatic rings followed by carbon–sulfur bond cleavage [1–3]. The molecular size and structure of sulfur compounds are the key factors affecting the rate of their removal by HDS reaction. For alkyl-substituted DBTs, the HDS rate depends critically on the position of the alkyl substituents. HDS rates of DBTs with alkyl substituents at positions other than 4 and 6 are similar or slightly higher than that of DBT, while alkyl substituents at the aromatic carbon adjacent to the sulfur atom (4 and 6 positions) substantially reduce the HDS rate of the DBTs [4,5]. It has been reported that over a $CoMo/Al_2O_3$ catalyst, at 350 °C and 50 bar, the first-order rate constants for the hydrogenation of DBT, 4-methyldibenzothiophene (4-MDBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) were very close–15, 15 and 11 h^{-1}, respectively. The first-order rate constants for hydrogenolysis of DBT, 4-MDBT, 4,6-DMDBT were, however, significantly different–126, 26 and 6 h^{-1} [4]. These results demonstrate that the rate of sulfur removal via hydrogenation route is very similar for the alkyl substituted DBTs, and that alkyl substitutions at the 4- and 6-positions affect the direct sulfur removal by hydrogenolysis. This finding is consistent with a density functional theory (DFT) study of adsorption of alkyl-substituted DBTs over a $Mo_{10}S_{18}$ cluster [6]. Results showed that in optimized perpendicular adsorption mode (which is assumed to be the main adsorption mode for direct sulfur removal), there was a complete overlap between electron densities of the sulfur atom in the sulfur compound and the molybdenum atom in the catalyst cluster for 2-, 3-, 7-, and 8-methyl substituted DBTs. A small gap was observed for the S–Mo bond in 4-MDBT, and a significant lack of overlap of the electrons was observed for 4,6-DMDBT. The Mayer bond order value decreased as the S–Mo bond electron overlap decreased [6].

A number of groups have studied catalysis and reaction mechanisms of desulfurization at the molecular level [7–13], but only a few of them related the desulfurization reactivity of DBTs with their quantum chemical properties. One early example of the correlation of molecular orbital properties with hydroprocessing reactivity was reported by Nag [10], when he demonstrated that ionization potentials of hydrocarbons, including aromatic and heterocyclic compounds, have a linear correlation with their HOMO (Highest Occupied Molecular Orbital) energies. Since the correlation of hydrogenation rate and ionization potential was known, the HOMO energy and hydrogenation rate correlation seemed to exist as well. Ma *et al.* [11] reported that hydrodesulfurization reactivities of heterocyclic sulfur compounds could be correlated with molecular orbital properties, such as electron density and bond orders. The authors related the hydrogenation

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reactivity of sulfur compounds with the bond order of the most unsaturated bond in the aromatic or sulfur rings, and the hydrogenolysis reactivity with the electron density of the sulfur atom (or the sulfur atomic charge). This correlation failed to account for the most important sterically hindered alkyl substituted dibenzothiophenes. Based on the coordination mechanism of the sulfur lone-pair of sulfur compounds with the Mo atom of MoS_2 catalyst in HDS reaction, Isoda *et al.* [12] calculated the electron density of the sulfur atom on the HOMO and HOMO-5 orbitals (sigma orbital 5 levels below Highest Occupied Molecular Orbital) for a series of alkyl-substituted DBTs using the WinMOPAC-PM3 method. A correlation was found between the electron density of the sulfur atom in the HOMO-5 orbital and the HDS rate constant obtained over a $CoMo/Al_2O_3$ catalyst. No correlation was found between the HDS rate of alkyl-substituted DBTs and the sulfur electron density on the HOMO orbital.

In these publications, properties on the sulfur compound alone were used to interpret desulfurization reactivity that depended on the structure of the sulfur compound, the active sites on the catalyst surface, and their mutual interactions. To overcome this problem, the interaction of specific sulfur compounds with a $Mo_{10}S_{18}$ cluster has been considered in this work to establish a correlation between structure and HDS reactivity. Since the hydrogenation rates of DBTs are similar and have little dependence on the position of the alkyl substituents [4], the changes in hydrogenolysis rate will have the most impact on the overall HDS rate. This paper examines the perpendicular adsorption of 18 alkyl-substituted dibenzothiophenes over a $Mo_{10}S_{18}$ cluster using density functional theory. The adsorption energy, S–Mo bond order (between the sulfur atom of the sulfur compound and the middle Mo atom of the $Mo_{10}S_{18}$ cluster in the optimized sulfur molecule-$Mo_{10}S_{18}$ complex), electron density of the sulfur atom in HOMO, and the HOMO-5 molecular orbitals of optimized free sulfur compounds were calculated. Pseudo-first-order HDS rate constants of those sulfur compounds were determined experimentally using a $NiMo/Al_2O_3$ catalyst and compared with the calculated properties.

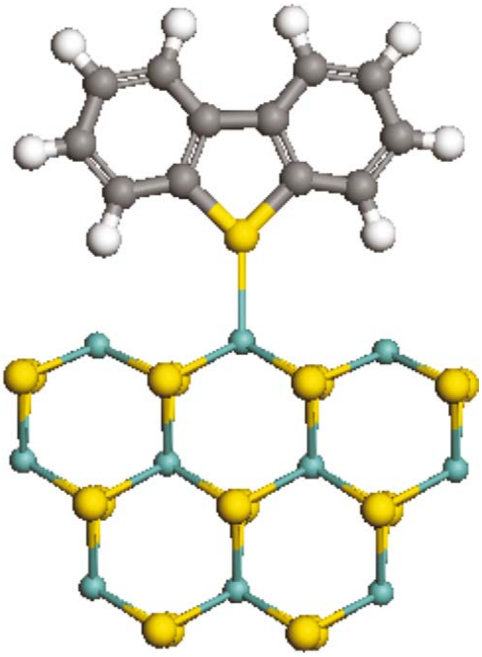


Figure 1. Perpendicular adsorption of DBT over $Mo_{10}S_{18}$ cluster. (Large yellow circles:sulfur atom; small blue circles:molybdenum; small light circles:hydrogen; larger dark grey circles:carbons).

2. Experimental

2.1. Catalyst model and computational method

A single layer $Mo_{10}S_{18}$ cluster with the coordinatively unsaturated metal sites on the Mo-edge was used as the catalyst model. This cluster was proposed by Ma and Schobert [14] as a simplified representation of a larger stoichiometric $Mo_{27}S_{54}$ cluster. Both clusters have the same Mo-edge planes. The sulfur molecule was perpendicularly adsorbed on the $Mo_{10}S_{18}$ cluster through the interaction of the sulfur atom and molybdenum atom through sulfur (η^1 S) bonding (figure 1) [15]. The calculations were performed with the DMol^3 simulation package (Accelrys Inc., San Diego, CA, USA). Individual sulfur compounds, a $Mo_{10}S_{18}$ cluster, and sulfur compound-$Mo_{10}S_{18}$ complexes were subjected to geometry optimization before energy calculation. The surface molybdenum atoms of the $Mo_{10}S_{18}$ cluster and the adsorbed molecules were allowed to relax during the calculation, while the rest of the slab was held at the fixed bulk MoS_2 geometry. The total energy of the system was determined by self-consistent density functional theory calculation, and the exchange-correlation energy was approximated by nonlocal generalized gradient corrections (BP). DFT Semi-Core Pseudopots (DSPP) was used for core treatment, and double numerical plus d-functions (DND) was used as the basis set. The real space cutoff of the atomic orbital was set at 4.0 Å, and a smearing of 0.005 Ha was used to count the orbital occupancy. The adsorption energy of the sulfur compound on the $Mo_{10}S_{18}$ cluster is given by equation 1:

$$\Delta E(\text{kcal/mol}) = E_{\text{S-Cat}} - (E_{\text{S}} + E_{\text{Cat}}) \qquad (1)$$

where $E_{\text{S-Cat}}$ is the total energy of the sulfur compound-$Mo_{10}S_{18}$ complex, E_{S} is the total energy of the free sulfur compound and E_{Cat} is the total energy of the $Mo_{10}S_{18}$ cluster. More information can be found in the work of Yang *et al.* [6].

2.2. Hydrodesulfurization kinetics

Hydrodesulfurization experiments were conducted in an automated fixed-bed microreactor (0.635 ID and

30.5 cm length) operated in continuous up-flow mode and heated by a three-zone electric furnace. A commercial sulfided $NiMo/Al_2O_3$ hydrotreating catalyst was crushed and particles in the size range of 0.28–0.50 mm (6 mL) were loaded into the reactor without dilution. The feed was a commercial fluid catalytic cracking light cycle oil (LCO) derived from a conventional crude oil. Sulfur compounds in the feed and reaction products were determined by high-resolution capillary gas chromatography using an atomic emission detector (GC-AED). Eighteen specific mono-, di-, and tri-alkyl-substituted dibenzothiophenes with measurable quantities in both feed and liquid product were identified using the retention time database collected at NCUT. Table 1 presents the feed properties and experimental conditions. Nitrogen and sulfur contents were analyzed by GC-NSD and GC-SCD. Saturate and aromatic contents of the feeds were determined by low-resolution mass spectrometry using a modified Robinson method. Density was determined by ASTM D4052. Details on analytical method and experimental procedures may be found elsewhere [16,17].

3. Results and discussion

The geometry-optimized sulfur compound was placed perpendicularly through sulfur (η^1 S) bonding to the $Mo_{10}S_{18}$ cluster, as shown in figure 1. The sulfur compound-$Mo_{10}S_{18}$ complex was optimized to obtain the structure with the minimum total energy. The adsorption energies of the 18 alkyl-substituted DBTs calculated using equation (1) are shown in Table 2, along with the Mayer bond order of the resulting S–Mo bond, which is a quantitative estimation of the electron density overlap between the sulfur and molybdenum. Figure 2 shows the plots of volumetric total density for DBT-$Mo_{10}S_{18}$ complex (left) and 2,4,6-DMDBT-$Mo_{10}S_{18}$ complex (right). There was complete electron overlap of sulfur and molybdenum for the DBT-$Mo_{10}S_{18}$ complex and practically no overlap in the 2,4,6-DMDBT-$Mo_{10}S_{18}$complex. Consequently, high Mayer bond order (1.1466) was obtained for DBT and low bond order (0.8815) was obtained for 2,4,6-TMDBT.

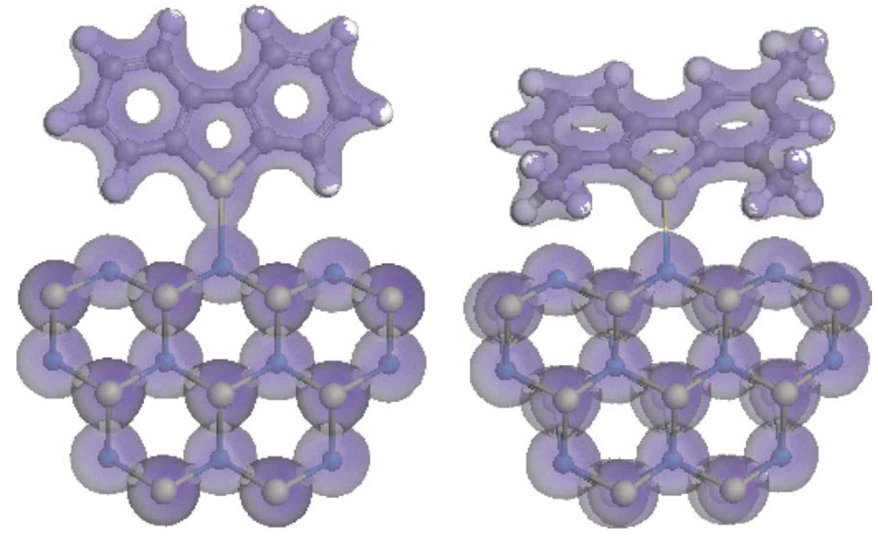
Table 1
Feed properties and HDS reaction conditions

Feed properties	
Nitrogen (mg/kg)	28.5
Sulfur (wt%)	1.18
Saturates (wt%)	28.73
Aromatics (wt%)	71.27
Density (15 °C, g/mL)	0.9353
Reaction conditions	
Catalyst (0.28–0.50 mm)	$NiMo/Al_2O_3$
Temperature (°C)	320
Pressure (atm)	70
LHSV (h^{-1})	1.6
H_2/Liquid rate (NL/L)	1000

Figure 3 presents the plots of $\ln(C_0/C)$ against 1/LHSV for DBT, 4-DBT and 4,6-DMDBT at 320 °C, where C_0 and C are the concentrations of sulfur compounds in the feed and product, respectively, and LHSV is the hourly liquid space velocity. Similar linear relationships were observed for all the alkyl-substituted dibenzothiophenes studied in this work. The first-order HDS rate constants derived from the slopes of the plots are presented in table 2. The electron densities of the sulfur atom in HOMO and HOMO-5 molecular orbitals were calculated for the free sulfur compound, in order to compare these densities with the published results. The $3P_z$ atomic orbital contributed over 99% of the valence orbitals ($3P_x$, $3P_y$, $3P_z$ and $3S$) for the sulfur atom in the HOMO molecular orbital, and $3P_x$, $3P_y$ and $3Z$ contributed over 99% of the electron density for the HOMO-5 orbital. The 3D volumetric images (not given) of the two orbitals showed that HOMO forms S π bonding and HOMO-5 forms S σ bonding, as indicated by Isoda *et al.* [12]. The eigenvalues of HOMO and HOMO-5 orbitals for the free sulfur compounds were also calculated. The results are summarized together with adsorption energy, Mayer bond order and HDS rate constants in table 2. The first observation to be made is that the HDS rate constants of the dibenzothiophenes studied can be classified into three groups based on the position of the alkyl-substituents. Group one consists of dibenzothiophene itself and DBTs with substituents at positions other than 4 or 6; group two consists of DBTs with at least one substituent at either the 4- or 6-position; and group three consists of DBTs with substituents at both 4- and 6-positions. There is a clear distinction between the values of the rate constants in these three groups. Group one (4 sulfur compounds) has HDS rate constants in the range of 3.8–4.8 h^{-1}, group two (10 substituted dibenzothiophenes) has rates within the range of 0.69–1.10 h^{-1}, and group three (4 substituted dibenzothiophenes) has rate constants between 0.33 and 0.63 h^{-1}. The HDS rate constant order is consistent with numerous published results, which all indicate that alkyl substituents at the aromatic carbon adjacent to the sulfur atom (4 and 6 positions) sterically hinder the adsorption of these compounds on the catalyst surface, resulting in a reduction of the HDS rate [4–6]. The adsorption energies for these 18 alkyl-substituted dibenzothiophenes are in the range of 21–38 kcal/mol, in good agreement with the results obtained for the perpendicular adsorption in previous work [6]. There is no simple correlation between the adsorption energies and HDS rate constants. Similarly, there are no apparent trends between the HDS rate constants and the electron densities of the sulfur atom at either HOMO or HOMO-5 orbitals. The same is true for the energy level of sulfur at the HOMO orbital. As for the energy levels

Table 2
DFT calculated properties and HDS rate constants of alkyl-substituted dibenzothiophenes

	ΔE kcal/mol	S–Mo BO	Rate constants h^{-1}	Electron density		Eigenvalues (ev)	
				HOMO	HOMO-5	HOMO	HOMO-5
Group 1							
DBT	−28.9	1.1466	3.84	0.4827	0.3950	−5.316	−8.197
2-MDBT	−35.3	1.1538	4.79	0.4510	0.3547	−5.084	−8.011
3-MDBT	−35.6	1.1569	4.23	0.4819	0.3615	−5.254	−8.102
3,7-DMDBT	−30.7	1.1602	4.69	0.4827	0.3609	−5.192	−8.027
Group 2							
4-MDBT	−34.6	1.0301	0.88	0.4591	0.4008	−5.25	−8.084
4-EDBT	−35.2	0.9331	0.69	0.4560	0.3134	−5.234	−7.95
2,4-DMDBT	−35.1	0.9070	0.89	0.4534	0.3779	−5.105	−7.991
2,6-DMDBT	−35.2	0.9822	0.90	0.4453	0.3812	−5.143	−8.022
3,6-DMDBT	−35.5	1.0269	0.89	0.4600	0.3887	−5.19	−8.007
1,4-DMDBT	−38.3	1.0948	0.75	0.4252	0.3036	−5.072	−7.949
3,4-DMDBT	−35.0	0.8982	0.76	0.4619	0.3749	−5.155	−7.96
2,4,8-TMDBT	−36.2	0.9387	0.94	0.4413	0.3496	−5.023	−7.941
2,4,7-TMDBT	−35.8	0.9736	1.10	0.4546	0.3751	−5.048	−7.918
3,4,7-TMDBT	−34.81	1.0762	1.08	0.4544	0.3788	−5.095	−7.89
Group 3							
4,6-DMDBT	−21.4	0.7900	0.33	0.4514	0.4134	−5.157	−7.955
4-E-6-MDBT	−31.4	0.8682	0.63	0.4396	0.3454	−5.177	−7.878
2,4,6-TMDBT	−31.5	0.8815	0.37	0.4411	0.3948	−5.055	−7.898
1,4,6-TMDBT	−26.5	0.8542	0.53	0.4141	0.3299	−5.024	−7.848



DBT 2,4,6-TMDBT

Figure 2. Volumetric plots of total density distribution for DBT and 2,4,6-TMDBT. The symbols for different atoms are the same as in figure 1.

of sulfur in HOMO-5 orbitals, the HDS rate constant decreases with the increase of the eigenvalues, except for two crossovers between the groups–4-MDBT and 4,6-DMDBT. The eigenvalue of 4-MDBT is closer to those of dibenzothiophene and 2-, 3- and 7-substituted DBTs, whereas the eigenvalue of 4,6-DMDBT is closer to those of 4- or 6-substituted DBTs.

Interestingly, an apparent relationship exists between the S–Mo bond order and the HDS rate constant. Dibenzothiophene and 2-, 3-, and 3,7-substituted DBTs that have the highest HDS rate constants possess the highest S–Mo bond orders (1.1466 to 1.1602); 4- or 6-substituted DBTs that have the second highest HDS rate constants possess the second highest bond order (0.8982 to 1.0948); and 4- and 6-disubstituted DBTs have the lowest HDS rate constants and lowest S–Mo bond order (0.79 to 0.8815). Figure 4 shows the plot of HDS rate constants against the S–Mo bond order. An increase in S–Mo bond order is related to an increase in HDS rate. This work is the first attempt to consider the interaction

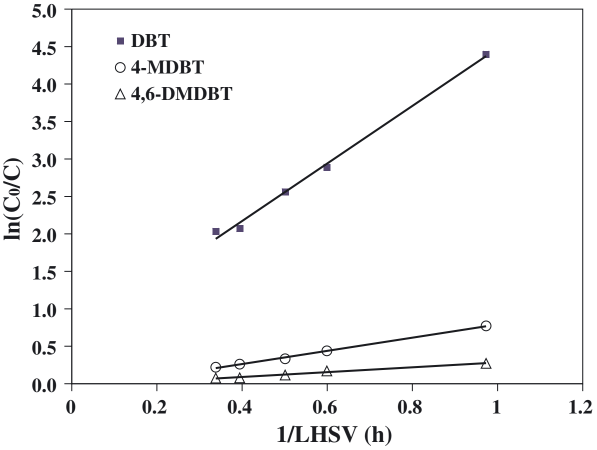


Figure 3. Plots of ln(C_0/C) as function of 1/LHSV for DBT, 4-MDBT and 4,6-DMDBT (HDS condition in table 1).

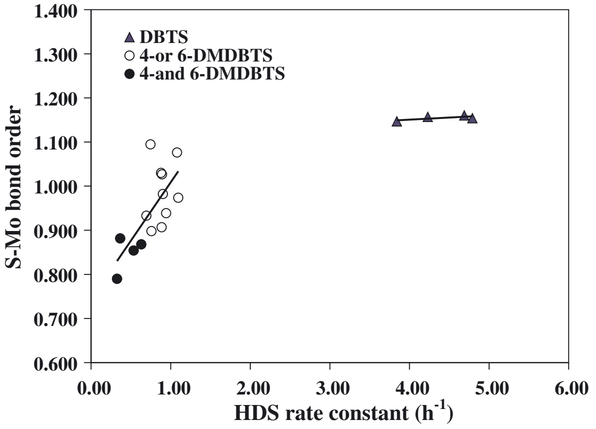


Figure 4. Plots of S–Mo bond order against HDS rate constants (HDS condition in table 1).

of the sulfur compound with an active site on the catalyst surface, leading to a correlation between the structure of dibenzothiophenes with their HDS reactivities. The increase in S–Mo bond order is a combination of electronic and steric effects. Since there is no steric hindrance for the perpendicular adsorption of dibenzothiophenes without 4- and 6-substituents, the S–Mo bond order only depends on the electron density of the S-atom in the sulfur compound and this is enriched by electron donor groups such as methyl groups. This is confirmed by the values of the Mayer bond order in our study:DBT $<$ 2-MDBT $<$ 3-MDBT $<$ 3,7-DMDBT.

The results also show that in this group of substituted dibenzothiophenes, the closer the methyl group is to the sulfur atom, the larger is the electronic contribution (3-MDBT versus 2-MDBT). Two methyl groups have more effect than one methyl group (3,7-DMDBT versus 3-MDBT). For 4- and/or 6-substituted dibenzothiophenes, both electronic and steric effects influence the S–Mo bond order. This may explain why there is no clear relationship between the position and the number of substituents with the values of the S–Mo bond order for these dibenzothiophenes. The lowest bond order and lack of electron overlap in the case of 2,4,6-TMDBT indicate that the direct sulfur removal of 4- and 6-disubstituted dibenzothiophenes by hydrogenolysis is unlikely and hydrogenation must occur before hydrogenolysis. This conclusion agrees with published results that indicate that different reaction pathways dominate the removal of those two groups of dibenzothiophenes. Direct sulfur removal by hydrogenolysis is the major reaction pathway for sulfur removal from dibenzothiophenes without 4- and 6- substituents while hydrogenation followed by carbon–sulfur bond cleavage is the major reaction path for 4-and/or 6-substituted dibenzothiophenes [3–5].

The HDS rate constants obtained in this work are the total rate constants of hydrogenation and hydrogenolysis. In our correlation, however, we assumed that perpendicular adsorption of the sulfur molecule on the $Mo_{10}S_{18}$ catalyst cluster through sulfur (η^1 S) bonding is the major configuration that contributes to direct sulfur removal by hydrogenolysis. The S–Mo bond order, therefore, represents the reaction rate of hydrogenolysis more than that of hydrogenation. We assumed that the hydrogenation rates of all DBTs are similar and that the change in total HDS rate is mostly caused by the hydrogenolysis rate. A better correlation would be expected if we could separate the contributions of hydrogenation and hydrogenolysis in our pseudo-first-order HDS rate constant and correlate the hydrogenolysis rate constant with the S–Mo bond order. This approach can only be realized by using model compounds. However, the interactions of other hydrocarbons such as aromatics and nitrogen compounds in a real feedstock would be neglected by the use of a model compound study. Finally, the HDS rate constants of 4- and/or 6-substituted DBTs are much more sensitive to the S–Mo bond-order than those of other dibenzothiophenes as observed from figure 4. This phenomenon can be explained from two perspectives. Firstly, different reaction pathways contribute to the removal 4- and/or 6-substituted DBTs and other substituted DBTs:hydrogenation followed by carbon–sulfur bond cleavage is the major pathway for the removal of sulfur in the former group and direct hydrogenolysis is the major pathway for the removal of sulfur in the latter. Secondly, hydrogenolysis and hydrogenation are competitive pathways for sulfur removal; the reaction rate of hydrogenolysis is much higher than that of hydrogenation [4,5]. In the case of dibenzothiophenes without steric effects, the direct hydrogenolysis route is more important than hydrogenation followed by hydrogenolysis. Therefore, an increased hydrogenolysis rate due to the increased S–Mo bond order would not cause significant improvement of the total HDS rate (flat slope in figure 4). For dibenzothiophenes with 4- and/or 6-substituants, hydrogenation is the main contributor to the total HDS rate constant, since sulfur removal via the hydrogenation route is much slower than via direct hydrogenolysis. Even a small increase in the hydrogenolysis rate due to increased S–Mo bond order would significantly improve the total HDS rate constant (steep slope figure 4).

4. Conclusions

The interactions of the sulfur atom of alkyl-substituted dibenzothiophenes with the coordinatively unsaturated molybdenum atom of a $Mo_{10}S_{18}$ catalyst cluster were estimated by the S–Mo bond order in perpendicular adsorption configuration. Pseudo-first-order HDS rate constants of the alkyl-substituted dibenzothiophenes were determined experimentally using a NiMo/Al_2O_3 catalyst at 320 °C and 70 atm. Good correlation was obtained between the S–Mo bond order and the HDS rate constant. A higher value of the S–Mo bond order indicated strong interaction of sulfur with the active site of the catalyst, and higher HDS rate constant. The values of the S–Mo bond order and HDS rate constants can be classified into three groups depending upon where the alkyl-substituents are located. The highest S–Mo bond order and HDS rate constants were obtained for dibenzothiophene and DBTs without 4- or 6-substituents, followed by DBTs with at least one substituent at either the 4- or 6-position; and by DBTs with both 4- and 6-substituents with the lowest S–Mo bond orders and HDS reaction rates.

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