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Hydrodesulfurization of hindered dibenzothiophenes: an overview

Raheel Shafi [a], Graham J. Hutchings [b,*]

[a] Leverhulme Centre For Innovative Catalysis, Department of Chemistry, University of Liverpool,
Liverpool L69 3BX, UK

[b] Department of Chemistry, University of Wales, Cardiff, PO Box 912, Cardiff CF1 3TB, UK

Abstract

Hydrodesulfurization is a well-documented process which has been commonly used in the refining of crude oil for over 60 years. It is a process for which interest is frequently renewed due to the requirement to use new feedstocks and the application of more severe environmental legislation, for example, the need to reduce sulfur levels in fuels. Of particular importance in achieving low sulfur levels in fuels is the problem posed by a particular class of compounds, namely hindered dibenzothiophenes, e.g. dibenzothiophene, 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene. Dibenzothiophenes demonstrate resilience to hydrodesulfurization using current catalyst formulations. This overview addresses the key area of hydrodesulfurization chemistry concerning the desulfurization of highly hindered sulfur containing molecules.

Keywords: Hydrodesulfurization; Dibenzothiophene; Co/Mo/Al_2O_3 catalyst; Ni/Mo/Al_2O_3 catalyst

Abbreviations: HDS, hydrodesulfurization; BT, benzothiophene; DBT, dibenzothiophene; 4-MDBT, 4-methyldibenzothiophene; 4,6-DMDBT, 4,6-dimethyldibenzothiophene; BiPh, biphenyl; CHB, cyclohexylbenzene; DMCHB, dimethylcyclohexylbenzene; DMBiPh, dimethylbiphenyl

1. Introduction

The industrial practice of oil refining is continually changing. These changes can be either due to quality of the feeds, or due to the standards to which the products are manufactured. Both cause the refining industry to react, either by improving old technologies or by inventing new ones. For example, in the USA the average crude oil utilized has changed to a poorer quality with respect to sulfur content since sweeter USA crudes (average S=0.87 wt.%) have been largely replaced by sourer South American crudes (average S=2.20 wt.%). In addition, the overall sulfur content of crudes is also expected to rise in the USA due to increasing imports. In Western Europe, crude oil quality has remained fairly constant over the last 10 years (average S=1.02 wt.%). However, it can be anticipated that the same trend towards higher sulfur crude oils will occur due to the decreasing availability of North Sea crude (average S=0.23 wt.%).

As well as the variation in the quality of oil feedstocks, the refining industry is also under constant pressure to meet more stringent standards with respect to product specification. These specification changes are driven by environmental concerns and are summarized in Table 1 [1].

Since the amount of sulfur in crudes encountered by the refiner is expected to increase in Western Europe as well as in the USA, it can be clearly deduced that oil refining technologies, in particular desulfurization, will have to react to these changes. There is, therefore, a considerable interest in investigating

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* Corresponding author.

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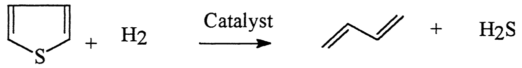
Table 1
Product specification requirements [1]

Product	1990–1994	1995–2000	Post 2000
Diesel oil	Lower sulfur content: 0.05 wt.% in USA, 0.2 wt.% in Japan and Western Europe. Lower aromatics in California and Scandinavia	Lower sulfur content in OECD countries (0.05 wt.%). Slightly lower aromatics in OECD countries	Further decrease of sulfur content in all countries. Higher cetane number, lower endpoint
Heating oil		Lower sulfur content in Western Europe (0.1 wt.%)	
Fuel oil		Lower sulfur content in Western Europe (1.5 wt.%)	

the already well-documented process of hydrodesulfurization (HDS), particularly the HDS of hindered, less reactive S containing molecules. This is because highly hindered sulfur containing molecules, such as dibenzothiophenes, are not particularly reactive under typical HDS reaction conditions. Industrial research is, therefore, aimed at improving catalyst activity with respect to the hydrogenation, and successive desulfurization of relatively unreactive sulfur containing molecules. This article aims to overview aspects of the literature concerning the HDS of hindered, less reactive sulfur containing molecules, since it is these molecules that must be desulfurized if future fuel specifications are to be met.

2. The HDS reaction

The HDS reaction for thiophene is shown below:



HDS is the process by which sulfur is removed from sulfur containing compounds by reaction with hydrogen, thereby forming H_2S. The process is widely employed throughout the world and has been used for over 60 years. The reaction has recently been extensively reviewed by Whitehurst et al. [2]. It is a catalyzed reaction usually involving a metal sulfide catalyst, in particular sulfided $Co/Mo/Al_2O_3$ or sulfided $Ni/Mo/Al_2O_3$. The resultant H_2S that is produced from the hydrogenation reaction is subsequently absorbed by reaction with ZnO to form ZnS and, in this way, sulfur is removed from the hydrocarbon feedstock.

HDS is effective for a range of sulfur containing compounds which exhibit varying reactivities towards desulfurization. The reactivity is dependent upon the local environment of the sulfur atom in the molecule, and the overall shape of the molecule. Some of these compounds have been explored experimentally in more detail than others. Particularly, important sulfur containing molecules are shown in Table 2 [3].

The HDS reaction is usually operated at moderately high temperature and pressure; typical conditions are 300–350°C and between 50 and 100 atm. As expected reaction rates for the HDS reaction vary for different sulfur containing compounds as demonstrated by Nag et al. [4] (Table 3) who have shown the order of reactivity to be as follows:

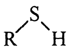
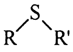
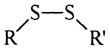
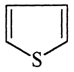
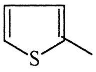
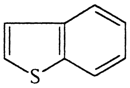
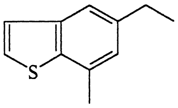
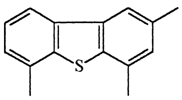
$$\begin{aligned}&\text{thiophene}>\text{benzothiophene}>\text{benzonapthothiophene}\\&>\text{tetrahydrobenzonapthothiophene}\\&>\text{dibenzothiophene}\end{aligned}$$

The reactivity is significantly affected by the degree of substitution of the thiophenic ring. In addition, the substitution of these compounds by ring alkylation further affects the reactivity. For example, Satterfield et al. [5] and Brien et al. [6] have studied the effect of ring alkylation of thiophene on the rate of the HDS reaction and have found that the reactivity varies in the following order:

$$\begin{aligned}&\text{thiophene} > \text{2-methylthiophene}\\&> \text{2, 5-dimethylthiophene}\end{aligned}$$

Interestingly, Desikan and Amberg [7] have shown that substitution at the third position enhances the rate of the HDS reaction, and so reactivity is not a simple function of ring substitution.

Table 2
Various sulfur compounds encountered in HDS reactions [3]

Sulfur compounds					
Thiols	Sulfides	Disulfides	Thiophenes	Benzothiophenes	Dibenzothiophenes
			 	 	

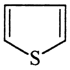
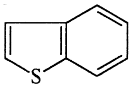
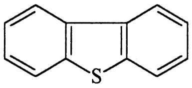
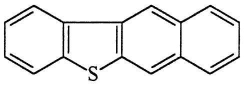
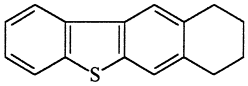
3. Reaction pathways

3.1. Reaction pathways for thiophenes

The majority of thiophene HDS studies have been performed at atmospheric pressure. It has been suggested that thiophene HDS proceeds via two parallel pathways [8]. One proposition is that hydrogenolysis of the C–S bond precedes hydrogenation of the aromatic ring [9]. Alternatively, Kolboe [10] proposed an intramolecular dehydrosulfurization pathway, whereby the hydrogen in the H_2S product originates from positions β to the sulfur atom of the thiophene. Studies by Lipsch and Schuit [11] proposed that the C–S bond was attacked by surface hydrogen, leading to bond fission and formation of 1,3-butadiene. Most researchers now consider that thiophene reacts via two parallel pathways as shown in Fig. 1 [3,12]. In the first of the parallel pathways, the thiophene ring is hydrogenated prior to desulfurization; this is known as the hydrogenation pathway. In the second pathway the thiophene ring can be split due to attack by surface adsorbed hydrogen at the sulfur atom. Sulfur is removed in the form of H_2S, leaving butadiene as the other product; this pathway is known as the hydrogenolysis pathway.

Rate equations, determined from experiments at atmospheric pressure, indicate that thiophene is an inhibitor for its own HDS. H_2S has also been demonstrated to inhibit the HDS of thiophene, as well as other sulfur compounds. Hydrogenolysis and hydrogenation are considered to occur at different sites [10]. A set of experiments performed by Van Parijs and Froment [13] suggested a reaction network in which

Table 3
Reactivities of several heterocyclic sulfur compounds [4][a]

Reactant	Structure	Pseudo first-order rate constant (l/(g of catalyst s^{-1}))
Thiophene		1.38×10^{-3}
Benzothiophene		8.11×10^{-4}
Dibenzothiophene		6.11×10^{-5}
Benzo[b]naphtho[2,3-d]thiophene		1.61×10^{-4}
7,8,9,10-tetrahydro-benzo[b]naphtho[2,3-d]thiophene		7.78×10^{-5}

[a] Catalyst: Co/Mo/Al_2O_3 (CoO, 3.7%; MoO_3, 13%; SiO_2, 1.8%); LHSV: 6 h^{-1}; reactor type: trickle bed; feed: 10 wt.% sulfur in tetralin.

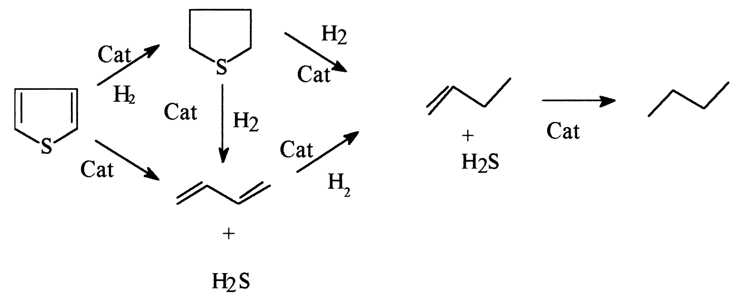


Fig. 1. Thiophene reaction pathways generally now accepted [3].

thiophene is hydrodesulfurized to give 1-butene, *cis*- and *trans*-2-butene, followed by the secondary hydrogenation of the butenes to give butane. No tetrahydrothiophene or butadiene were observed although the latter would be expected to be hydrogenated rapidly to give 1-butene and butane. Rate equations for thiophene hydrogenolysis and butene hydrogenation were determined by Van Parijs and Froment [13] and these were proposed to occur at different catalytic sites. The two rate equations from this study can be seen below and correspond to reactions occurring at different sites. Direct desulfurization occurring at σ sites and hydrogenation occurring at τ sites are as follows:

1. Thiophene hydrogenolysis on σ sites:

$$r_{\mathrm{T},\sigma}=\frac{k_{\mathrm{T},\sigma}K_{\mathrm{T},\sigma}K_{\mathrm{H_2},\sigma}P_{\mathrm{T}}P_{\mathrm{H_2}}}{\left[1+(K_{\mathrm{H_2},\sigma}P_{\mathrm{H_2}})^{1/2}+K_{\mathrm{T},\sigma}P_{\mathrm{T}}+K_{\mathrm{H_2S},\sigma}P_{\mathrm{H_2S},\sigma}/P_{\mathrm{H_2}}\right]^3}$$

   where $k_{\mathrm{T},\sigma}$ is the rate constant for thiophene hydrogenolysis on σ sites (mol/(g of catalysts)), $K_{\mathrm{T},\sigma}$ the adsorption coefficient for thiophene on σ sites (atm^{-1}), $K_{\mathrm{H_2},\sigma}$ the adsorption coefficient for hydrogen on σ sites (atm^{-1}), $K_{\mathrm{H_2S},\sigma}$ the adsorption coefficient for H_2S on σ sites (atm^{-1}), P_{T} the partial pressure of thiophene and $P_{\mathrm{H_2}}$ the partial pressure of hydrogen.

2. Butene hydrogenation on τ sites:

$$r_{\mathrm{B},\tau}=\frac{k_{\mathrm{B},\tau}K_{\mathrm{B},\tau}K_{\mathrm{H_2},\tau}P_{\mathrm{B}}P_{\mathrm{H_2}}}{[1+(K_{\mathrm{H_2},\tau}P_{\mathrm{H_2}})^{1/2}+K_{\mathrm{A},\tau}P_{\mathrm{A}}+K_{\mathrm{B},\tau}P_{\mathrm{B}}]^2}$$

   where $k_{\mathrm{B},\tau}$ is the rate constant for butene hydrogenation on τ sites (mol/(g of catalyst)), and $k_{\mathrm{A},\tau}$ the rate constant for butane on τ sites (mol/(g of catalyst)).

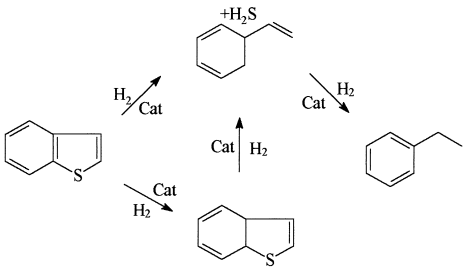
   The subscripts T, A and B denote thiophene, butane and butene, respectively.

3.2. Reaction pathways for benzothiophene

Kilanowski and Gates [8] have observed that the only product of HDS of benzothiophene is ethylbenzene. In a high pressure study by Geneste et al. [14], dihydrobenzothiophene and ethylbenzene were observed to be the only products. They also observed that when dihydrobenzothiophene was used as the substrate no benzothiophene was formed. They proposed that ethylbenzene is formed via a dihydrobenzothiophene intermediate, i.e. the hydrogenation occurs prior to desulfurization. Van Parijs and Froment [13] suggested a parallel pathway not unlike the pathways previously proposed for thiophene (see Fig. 2, [15]) and, again, proposed that hydrogenation and hydrogenolysis occur at different sites. The kinetic equations are also given in Fig. 2. As observed with thiophene HDS, H_2S was proposed to inhibit hydrogenolysis but not hydrogenation. The set of rate equations for thiophene and benzothiophene are identical and suggest equivalent mechanisms.

Geneste et al. [14] observed that methyl substitution of benzothiophene reduced its rate of partial hydrogenation, making the hydrogenolysis route more favourable. The series below shows their relative reactivities with respect to hydrogenation:

$$\text{benzothiophene (1)} > \text{2-methylbenzothiophene (0.4)} > \text{3-methylbenzothiophene (0.2)} > \text{2, 3-dimethylbenzothiophene (0.1)}$$



1. *Hydrogenolysis of Benzothiophene on σ sites*

$$r_{B,s} = \frac{k_{B,s}K_{B,s}K_{H2,s}P_B P_{H2}}{[1 + (K_{H2,s}P_{H2})^{1/2} + (K_{H2S,s}P_{H2S}/P_{H2}) + K_{B,s}(P_B + P_D)]^3}$$

2. *Hydrogenolysis of 1,2 - dihydrobenzothiophene on σ sites*

$$r_{D,s} = \frac{k_{D,s}K_{B,s}K_{H2,s}P_D P_{H2}}{[1 + (K_{H2,s}P_{H2})^{1/2} + (K_{H2S}/P_{H2}) + K_{B,s}(P_B + P_D)]^3}$$

3. *Hydrogenation of Benzothiophene on τ sites*

$$r_{B,t} = \frac{k^*_{B,t}K_{B,t}(P_B P_{H2} - P_D/K_1)}{[1 + K_{B,t}(P_B + P_D) + K_{E,t}P_E]^3}$$

Where B, D, E, and K_1 denote respectively, benzothiophene, 1,2 - dihydrobenzothiophene, ethylbenzene, and the equilibrium constant for benzothiophene giving 1,2 dihydrobenzothiophene.

Fig. 2. Parallel reaction pathway for benzothiophene HDS and rate expressions [15].

The effect of this substitution is, however, proposed to be due to electronic factors and not steric constraints.

3.3. Reaction pathways for dibenzothiophene

Gates and co-workers [16] proposed a reaction network on the basis of their studies shown in Fig. 3. They detected biphenyl (BiPh) as the major reaction product with a small amount of cyclohexylbenzene (CHB). Obolentsev and Mashkina [17] performed a study of dibenzothiophene (DBT) desulfurization in the presence of added BiPh and H_2S. It was observed that the addition of biphenyl significantly reduced the conversion, while H_2S had no effect. This suggests that the rate of DBT desulfurization is inhibited by biphenyl. Bartsch and Tanielan [18], in a study at atmospheric pressure, detected only BiPh and H_2S as the desulfurization products of dibenzothiophene. Rios [19] extended this study by using a finely divided catalyst at atmospheric pressure. It was reported that the primary reaction products were biphenyl and H_2S.

Houalla et al. [20], in a subsequent study, reported pseudo first-order kinetics for the HDS reaction of methyl substituted dibenzothiophenes. All these stud-

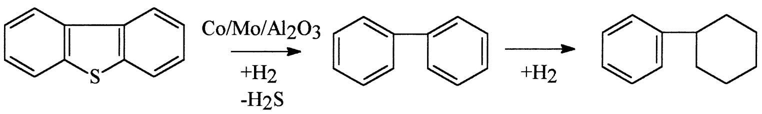


Fig. 3. Sequential mechanism [16].

Table 4
HDS studies of dibenzothiophene by Singhal et al. [23][a]

Starting material	T (°C)	P (MPa)	Conversion (%)	Products (mol%)		
				DBT	BiPh	CHB
DBT	300	3.1	40	60	37.0	3.0
	310	3.1	55	45	50.0	5.0
	325	3.1	85	15	76.5	8.5
BiPh	300	3.1	0.3		99.7	0.3
	310	3.1	0.7		99.3	0.7
	325	3.1	1.8		98.2	1.8
CHB	325	3.1	0.0			100

[a] Catalyst: $Co/Mo/Al_2O_3$ (CoO, 3.7%; MoO_3, 13%; SiO_2, 1.8%); LHSV: $6\,h^{-1}$; reactor type: trickle bed; feed: 10 wt.% sulfur in tetralin.

ies proposed a sequential mechanism for the production of small amounts of CHB, the partial hydrogenation product of BiPh in accordance with Fig. 3.

Rollman [21] studied the catalytic hydrogenation of dibenzothiophene compounds at 290–430°C and 2–10 MPa. The principal reaction for these sulfur compounds were biphenyl and H_2S together with some cyclohexylbenzene. The quantity of cyclohexylbenzene was observed to increase with temperature. Rollman concluded that the cyclohexylbenzene produced could not have been formed from the sequential hydrogenation of biphenyl. He based this upon the observation that, when biphenyl was added to the feed, no hydrogenation of the added biphenyl occurred. However, not all products were accounted for. Geneste et al. [14,22] not only explained the appearance of cyclohexylbenzene in their studies in terms of a sequential mechanism, but also reported data for the hydrogenation of biphenyl and showed that not all the cyclohexylbenzene produced could not be accounted for by the sequential mechanism of reaction. Following these investigations, a study was performed by Singhal et al. [23]. The results, summarized in Table 4, form the basis of the “parallel pathway mechanism” (Fig. 4). This mechanism does not require the cyclohexylbenzene produced to be the sequential hydrogenation product of biphenyl. Conversely, it was proposed that the majority of the cyclohexylbenzene produced was via the production of a reactive intermediate which was then desulfurized. This was consistent with the earlier study by Houalla et al. [24].

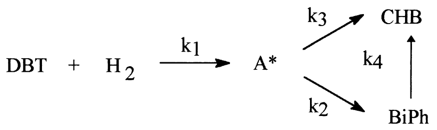


Fig. 4. Parallel pathway mechanism as proposed by Singhal et al. [23].

In the parallel pathway mechanism, the majority of the CHB is produced by the reaction of a reactive intermediate denoted as A* in Fig. 4. There is a finite contribution from the sequential reaction of BiPh which increases with temperature. This accounts for the observation by Rollman [21] that the amount of CHB increases with temperature. The proposed mechanism also accounts for the product distribution being primarily H_2S and BiPh at atmospheric pressure reported by Bartsch and Tanielan [18] and Rios [19]. The kinetic equation for DBT conversion was proposed to be in the form of a Langmuir–Hinshelwood equation:

$$\frac{-\mathrm{d}[\mathrm{DBT}]}{\mathrm{d}t} = \frac{k_1 K_{\mathrm{DBT}} K_{\mathrm{H_2}} P_{\mathrm{DBT}} P_{\mathrm{H_2}}}{(1 + k_{\mathrm{DBT}} P_{\mathrm{DBT}} + K_{\mathrm{prod}} P_{\mathrm{prod}})(1 + K_{\mathrm{H_2}} P_{\mathrm{H_2}})}$$

This expression becomes first order with respect to dibenzothiophene as the concentration of DBT decreases. This accounts for the observations of Houalla et al. [20] for HDS using low concentrations of DBT.

Houalla et al. [20] proposed a detailed reaction network for the HDS of DBT (Fig. 5). The mechanism indicates that conversion proceeds via the path of least hydrogen consumption and the hydrogenation of biphenyl and cyclohexylbenzene is slow. The rate of hydrogenation of dibenzothiophenes increased when the H_2S concentration was increased and was found to depend on catalyst composition. Houalla et al. [20] found that the CHB concentration with a $Ni/Mo/Al_2O_3$ catalyst is three times higher than that of a comparable $Co/Mo/Al_2O_3$ catalyst.

Rate equations have also been proposed by Broderick and Gates [25]. The rate equation for hydrogenolysis corresponds to a Langmuir–Hinshelwood mechanism; the rate limiting step being the surface reaction between adsorbed hydrogen on one site with DBT adsorbed on another site. In a similar manner to thiophene and benzothiophene, the rate of the dibenzothiophene HDS reaction is inhibited by the

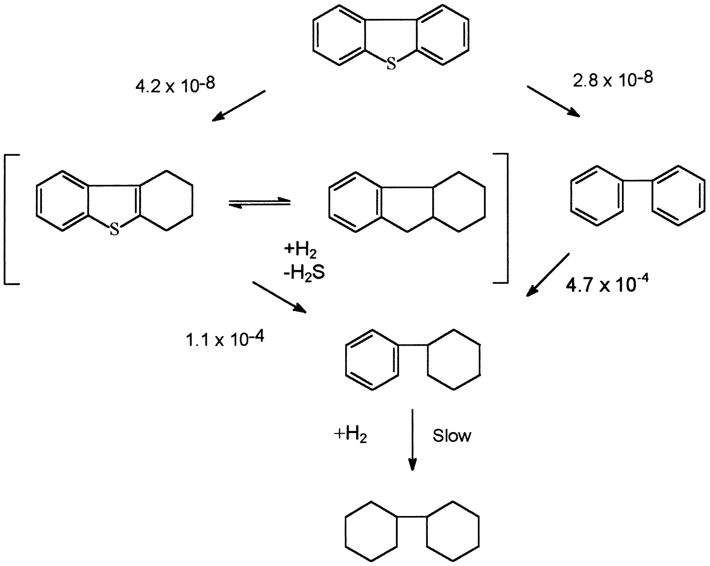


Fig. 5. Proposed reaction network by Houalla et al. [20].

reactants and by H_2S. The rate equations are analogous to those for thiophene and benzothiophene and these can be seen below:

1. Dibenzothiophene hydrogenolysis:

$$r = \frac{kK_{\mathrm{DBT}}K_{\mathrm{H_2}}C_{\mathrm{DBT}}C_{\mathrm{H_2}}}{(1+K_{\mathrm{DBT}}C_{\mathrm{DBT}}+K_{\mathrm{H_2S}}C_{\mathrm{H_2S}})^2(1+K_{\mathrm{H_2}}C_{\mathrm{H_2}})}$$

2. Dibenzothiophene hydrogenation:

$$r = \frac{k'K'_{\mathrm{DBT}}K'_{\mathrm{H_2}}C_{\mathrm{DBT}}C_{\mathrm{H_2}}}{1+K'_{\mathrm{DBT}}C_{\mathrm{DBT}}}$$

where DBT represents dibenzothiophene, k the rate constant for dibenzothiophene hydrogenolysis (mol/(g of catalyst s^{-1}), K_{DBT} the adsorption parameter for DBT (atm^{-1}), C_{DBT} the coverage of DBT on catalyst surface, $C_{\mathrm{H_2}}$ the coverage of H_2 on catalyst surface, $K_{\mathrm{H_2S}}$ the adsorption parameter for H_2S (atm^{-1}), $C_{\mathrm{H_2S}}$ the coverage of H_2S on the catalyst surface, k' the rate constant for DBT hydrogenation (mol/(g of catalyst s^{-1}), K'_{DBT} the adsorption parameter for DBT in DBT hydrogenation (atm^{-1}), and $K'_{\mathrm{H_2}}$ the adsorption parameter for H_2 in DBT hydrogenation (atm^{-1}).

3.4. The effect of solvents on the rate of the HDS reaction

One aspect which has not been discussed previously is the nature of solvent effects upon the reaction rate. Solvent systems have been found to affect the rate of reaction, as shown by Kabe et al. [26], who studied the rate of HDS of benzothiophene in a range of solvents (toluene, decalin, *n*-pentadecane and 1-methylnaphthalene). In addition, dibenzothiophene HDS was studied in *n*-heptane, xylene, decalin and tetralin. The rates of HDS in all these solvents were assessed over a range of temperatures and, at each temperature, the conversion of benzothiophene decreased in the following order:

toluene > decalin > *n*-pentadecane
> 1-methylnaphthalene

While dibenzothiophene conversion also decreased in the order

n-heptane > xylene > decalin > tetralin

The data (Fig. 6) was treated using the following rate equation which is similar to the one proposed by Kilanowski and Gates [8]:

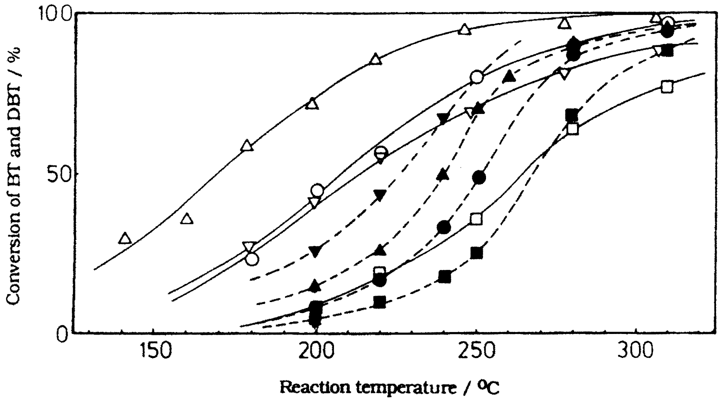


Fig. 6. The effect of solvent on the conversion of benzothiophene and dibenzothiophene [26]. BT (0.1 wt.%): (△) toluene; (○) decalin; (▽) *n*-pentadecane; (□) 1-methylnaphthalene. DBT (0.1 wt.%): (▽) *n*-heptane; (△) xylene; (●) decalin; (■) tetralin.

$$r_{\mathrm{HDS}} = \frac{kK_{\mathrm{T}}P_{\mathrm{T}}K_{\mathrm{H}}P_{\mathrm{H}}}{(1+K_{\mathrm{T}}P_{\mathrm{T}}+K_{\mathrm{S}}P_{\mathrm{S}})\quad(1+K_{\mathrm{H}}P_{\mathrm{H}})}$$

where r_{HDS} is the rate of HDS, k the rate constant of HDS, K_{T}, K_{S} and K_{H} are the adsorption equilibrium constants of benzothiophene or dibenzothiophene, hydrogen sulfide and hydrogen, respectively, and P_{T}, P_{S} and P_{H} are the partial pressures of benzothiophene or dibenzothiophene, hydrogen sulfide and hydrogen, respectively. $K_{\mathrm{S}}P_{\mathrm{S}}$ was neglected in this study as the amount of H_2S formed was minimal. The conversion of benzothiophene and dibenzothiophene were maintained constant by increasing the partial pressure of hydrogen. The HDS reactions were regarded as zero order in the partial pressure of hydrogen. The rate equation was therefore simplified as:

$$r_{\mathrm{HDS}} = \frac{k'K_{\mathrm{T}}P_{\mathrm{T}}}{1+K_{\mathrm{T}}P_{\mathrm{T}}}$$

The activation energies for r_{HDS} for benzothiophene and dibenzothiophene were 92 and 100 kJ/mol, respectively (Fig. 7) and the activation energy was not affected by the solvent. However, the heats of adsorption were significantly affected. The least inhibiting of the solvents (toluene for benzothiophene and *n*-heptane for dibenzothiophene) gave heats of adsorption values of 92 kJ/mol for each of the two substrates. Solvents for which a greater inhibition effect was observed caused the heat of adsorption to decrease. This implies that competitive adsorption for the active sites between the substrate and the solvent occurs. The inhibition on rate due to solvents was then assessed using the following equation:

$$r_{\mathrm{HDS}} = \frac{k'K_{\mathrm{T}}P_{\mathrm{T}}}{1+K_{\mathrm{T}}P_{\mathrm{T}}+K_{\mathrm{sol}}P_{\mathrm{sol}}}$$

where K_{sol} is the adsorption equilibrium constant for the solvent, P_{sol} the partial pressure of the solvent and the values of k' and K_{T} were those observed in HDS of benzothiophene with toluene and *n*-heptane with dibenzothiophene. The results are given in Table 5, which indicates that the inhibition effect of the solvents decreases in the order:

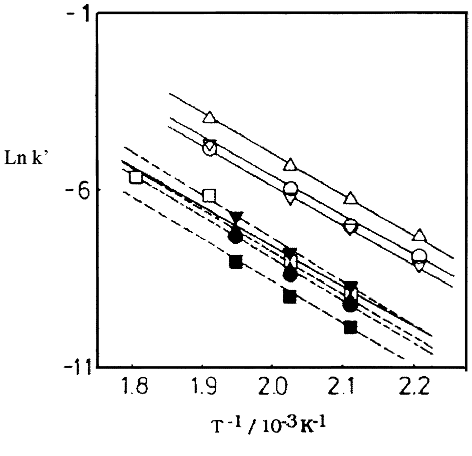


Fig. 7. Arrhenius plots of k' [26]. BT (0.1 wt.%): (△) toluene; (○) decalin; (▽) *n*-pentadecane; (□) 1-methylnaphthalene. DBT (0.1 wt.%): (▽) *n*-heptane; (△) xylene; (●) decalin; (■) tetralin.

Table 5
Heats of adsorption in deep desulfurization of benzothiophene and dibenzothiophene [26][a]

Solvent	ΔH_a (kJ mol^{-1})
Xylene	15±3
Decalin	16±2
n-Pentadecane	17±1
Tetralin	18±2
1-Methylnaphthalene	24±2

[a] Catalyst: commercial Co/Mo/Al_2O_3 (CoO, 5.0%; MoO_3, 12.5%); reactor type: trickle bed; WHSV: 70 h^{-1}; feed: 0.1–0.4 wt.% DBTs in decalin, 140–310°C, at 1 bar.

$$\text{1-methylnaphthalene} > \text{tetralin} > n\text{-pentadecane} > \text{decalin} > \text{xylene}$$

Highly aromatic solvents, such as 1-methylnaphthalene, adsorb competitively with BT and DBT. This means that comparative studies of HDS of BT and DBT performed in different solvents cannot be directly compared, or if they are, the effect of the solvents must be taken into account.

4. The effect of methyl substituents on the HDS of dibenzothiophenes

4.1. Co/Mo/Al_2O_3 and Ni/Mo/Al_2O_3 catalysts

Kilanowski et al. [27] carried out a study of HDS of methyl substituted BT and DBT with methyl substitution in different positions. The different compounds were 3-methylbenzothiophene, 3,7-dimethylbenzothiophene, 2-methylbenzothiophene, 7-methylbenzothiophene, 2,3-dihydro-benzothiophene, 4-methyldibenzothiophene, 2,8-DMDBT and 4,6-DMDBT. The catalytic experiments were carried out in a pulse microreactor at temperatures between 350 and 450°C and the results are given in Table 6 for a Co/Mo/Al_2O_3 type catalyst. It can be seen from Table 6 that the reactivity of these compounds decreases in the following order:

$$2,8\text{-DMDBT} > \text{DBT} > 4\text{-MDBT} > 4,6\text{-DMDBT}$$

Table 6
Conversion for fresh and fully sulfided catalysts [27][a]

Reactant	Reaction temperature (°C)	Fractional conversion with fresh catalyst	Fractional conversion with fully sulfided catalyst
DBT	350	0.31	0.064
DBT	400	0.23	0.1
DBT	450	0.25	0.12
2,8-DMDBT	450	0.7	0.24
4-MDBT	450	0.13	0.047
4,6-DMDBT	450	0.09	0.023

[a] Catalyst: commercial Co/Mo/Al_2O_3 (CoO, 5.6%; MoO_3, 11.2%; SiO_2, 1.8%); reactor type: pulse microreactor; feed: 0.3 wt.% sulfur in *n*-dodecane.

The enhancement in reactivity by the incorporation of the methyl groups in 2,8-MDBT was explained in terms of electronic effects. It was proposed that a combination of inductive and hyperconjugative effects of the methyl groups *para* to the two α carbons could enrich the electron density and therefore increase the activity. The decrease in the reactivity for specific methyl substituents was explained in terms of steric effects. Adsorption of the substrate onto the catalyst surface via the S atom was proposed to be hindered by the methyl groups. This study also proposed that H_2S and aromatic hydrocarbons, such as benzene, inhibit the HDS reaction. Another study performed on hindered DBTs was carried out by Houalla et al. [20] (Fig. 8). A wide range of methyl substituted DBTs were studied singly and some were employed in tandem studies. Pseudo first-order rate constants were calculated and these are given in Table 7. Most of the MDBTs and DMDBTs followed the reaction network shown in Fig. 5. 4-MDBT and 4,6-DMDBT, however, gave different reactivity. Yields of CHB from 4-MDBT and 4,6-DMDBT were 5–10 times greater than that from DBT under the same conditions. This implies that 4-MDBT and 4,6-DMDBT were more highly hydrogenated prior to sulfur removal than other substituted DBTs. It was also stated that doubling the DBT concentration decreased the pseudo first-order rate constant threefold. This implies the self-inhibition of HDS of DBTs occurs, and this has been previously discussed [28].

A subsequent study of HDS of hindered DBTs was performed by Kabe et al. [29]. In this study Co/Mo/Al_2O_3 catalysts were also employed, but the reaction was carried out under conditions similar to those employed in industry (i.e. 29 bar, 320–390°C). A gas chromatogram of the raw light oil feedstock

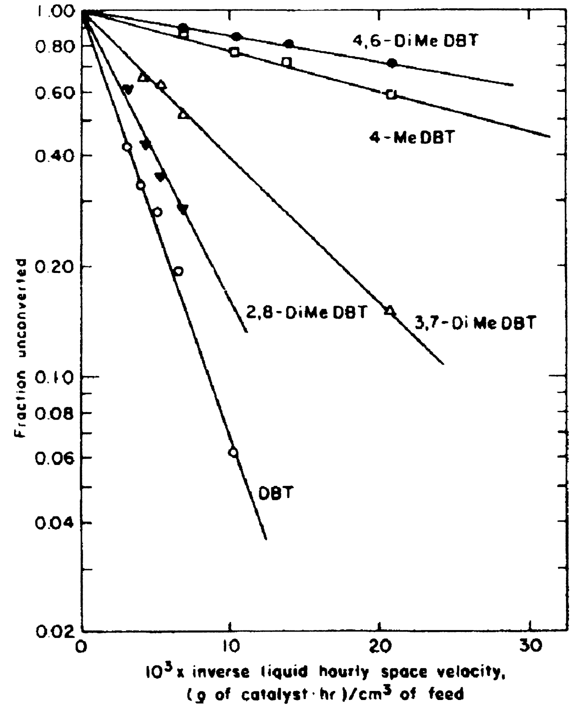


Fig. 8. HDS of DBTs [20].

prior to desulfurization is shown in Fig. 9, and it is apparent that the feedstock used contained a complex mixture of BT and DBT compounds. The results of these experiments with respect to the HDS of hindered DBT can be seen more clearly from Fig. 10, and it is apparent that some compounds are particularly resilient with respect to HDS. Particularly unreactive are 4-MDBT and 4,6-DMDBT. These results were similar to those achieved by Kilanowski et al. [27] and Houalla et al. [20], although the conversion levels observed in these studies are different due to the effect of solvents as discussed previously.

A subsequent detailed study by Kabe et al. [30] used temperatures in the range 190–340°C and the results are given in Figs. 11–13 and the rate constants are given in Table 8. The primary observation was that the reactivity decreases in the order:

DBT > 4-MDBT > 4, 6-DMDBT

This is again in agreement with the previous studies [20,27,29].

Mochida and co-workers [31] performed HDS reactions in a batch autoclave reactor for a variety of sulfur containing compounds. The majority of the compounds were alkyl BT or alkyl DBT. From the results obtained it is immediately apparent that 4-MDBT and 4,6-DMDBT were the most difficult to desulfurize. To compare the reactivities of the compounds, pseudofirst-order rate equations were calculated and these were used to classify the reactivity. The effect of H_2S partial pressure was also studied. The large amount of H_2S produced in the first few minutes of reaction originates from the most reactive BT. After 10 min, P_{H_2S} reached a constant level. When the H_2S was replaced by fresh hydrogen, the rate of HDS increased markedly and both $Co/Mo/Al_2O_3$ and $Ni/Mo/Al_2O_3$ catalysts were observed to be inhibited by H_2S.

Lamuremeille et al. [32] studied the effect of methyl substitution on the reaction pathways of HDS. The study employed Co/Mo and Ni/Mo catalysts and

Table 7
Pseudo first-order rate constants for HDS catalyzed by sulfided $Co/Mo/Al_2O_3$ at 300°C and 102 atm [20]

Substrate 1	Conc (mol%)	r_p (cm^3/(g of catalyst·hr^{-1}))[a]	Substrate 2	Conc (mol%)	r_p (cm^3/(g of catalyst·hr^{-1}))
DBT	0.058	258.4±10.3	None	–	–
DBT	0.130	77.5±11.8	None	–	–
2,8-DMDBT	0.075	241.9±23.5	None	–	–
3,7-DMDBT	0.072	126.5±10.2	None	–	–
4-MDBT	0.071	23.9±1.2	None	–	–
4,6-DMDBT	0.064	17.7±2.8	None	–	–
2,8-DMDBT	0.057	233.3±9.2	DBT	0.065	88.1±8.0
3,7-DMDBT	0.070	108.3±11.5	DBT	0.074	66.4±3.5
4-MDBT	0.073	28.4±1.9	DBT	0.081	100.8±1.4
4,6-DMDBT	0.080	21.7±5.0	DBT	0.071	213.8±48.4

[a] r_p: pseudo first-order rate constant.

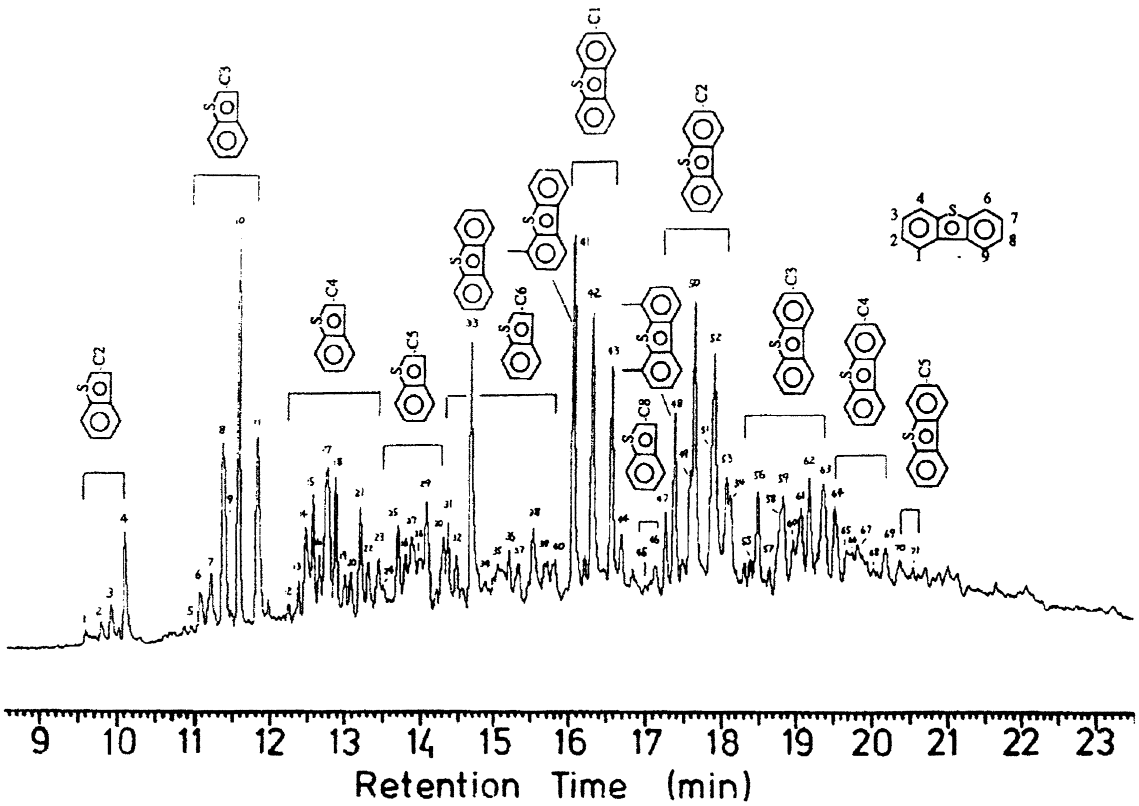


Fig. 9. GC profile of raw untreated oil [29].

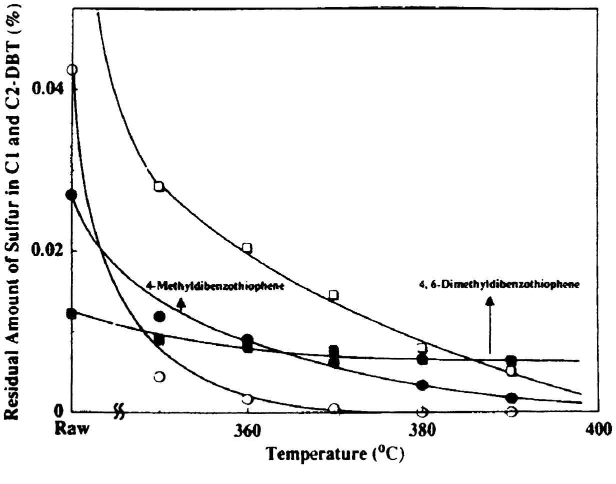


Fig. 10. Changes in residual amount of sulfur in dibenzothiophenes with temperature [29]: (●) 4-methyldibenzothiophene; (○) other C1-dibenzothiophenes; (■) 4,6-dimethyldibenzothiophene; (□) other C2-dibenzothiophenes.

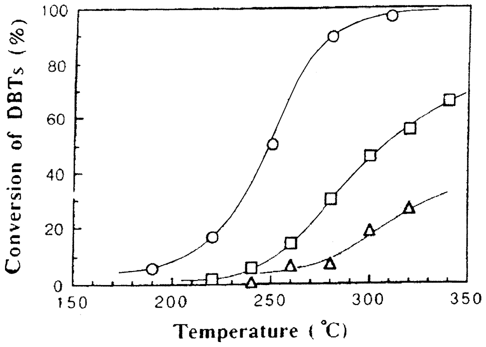


Fig. 11. The effect of temperature on the conversion of dibenzothiophenes [30]. 0.1 wt.% in decalin: (○) DBT; (□) 4-MDBT; (△) 4,6-DMDBT.

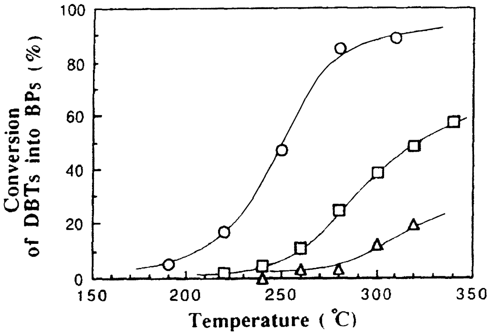


Fig. 12. Effect of temperature on the conversion of dibenzothiophenes BiPh [30]. 0.1 wt.% in decalin: (○) DBT; (□) 4-MDBT; (△) 4,6-DMDBT.

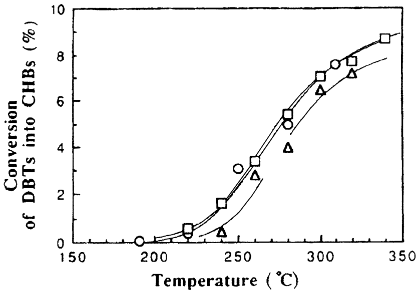


Fig. 13. The effect of temperature on the conversion of dibenzothiophenes into CHBs [30]. 0.1 wt.% in decalin: (○) DBT; (□) 4-MDBT; (△) 4,6-DMDBT.

Table 8
Rate constants as observed by Kabe et al. [30][a]

DBT (min^{-1})	4-MDBT (min^{-1})	4,6-DMDBT (min^{-1})
7.1×10^{-4}	6.9×10^{-5}	3.8×10^{-5}

[a] Catalyst: commercial Co/Mo/Al_2O_3 (CoO, 3.8%; MoO_3, 12.5%); reactor type: trickle bed; WHSV: 70 h^{-1}; feed: 0.1–0.4 wt.% DBT in decalin, 220–340°C, 1 bar.

examined the concentrations of BiPh and CHB. Their results are shown in Tables 9–11. It is apparent that the incorporation of a methyl group into the compound reduces the amount of BiPh produced. The effect of H_2S was also studied as were the reactivities of BiPh and 3-methyl biphenyl. The rate of hydrogenation of these compounds was found to be comparable with their rate of formation. Competitive adsorption was also expected, and so, hydrogenation was also studied in the presence of DBT and 4-MDBT. A DBT/BiPh (1:1) mixture was studied and the concentration of BiPh was seen to be greater than that for DBT alone. The concentration of CHB, however, remained close to that observed during HDS of DBT. A decrease in DBT concentration was observed and this shows that there is a competitive adsorption for active sites.

Kabe and co-workers [33] performed a study in which the lower reactivity of 4,6-DMDBT with respect to HDS was also observed. Steric hindrance between the methyl groups and the catalyst surface was again proposed to be the cause of this. Upon hydrogenation, this steric hindrance was considered to be decreased and this was best achieved by a Ni/Mo/Al_2O_3 type catalyst.

Mochida and co-workers [34] also demonstrated 4-MDBT and 4,6-DMDBTs to be the least reactive amongst a series of sulfur containing compounds. In computer modeling studies, electron density on the sulfur atom was shown to be hardly affected by alkyl substituents on the aromatic ring. Hydrogenation of the aromatic ring or olefinic bond adjacent to the S atom increased the electron density. As noted earlier, it was concluded that for HDS of sulfur compounds, two parallel pathways existed, hydrogenolysis and hydrogenation. The extent to which any of these were followed depended upon the nature of the substrate and the catalyst. Comparison of Co/Mo/Al_2O_3 and Ni/Mo/Al_2O_3 catalysts have been extensively studied. Mochida and co-workers [35] studied the direct comparison of the reaction pathways on the two catalysts. 4,6-DMDBT was found to be the least reactive substrate on both catalysts, but Ni/Mo/Al_2O_3 exhibited higher HDS activity for 4,6-DMDBT than

Table 9
Transformation and desulfurization rates of DBT and 4-MDBT over $Co/Mo/Al_2O_3$ and $Ni/Mo/Al_2O_3$ catalysts [32][a]

Catalyst	Compound	r_0 (10^{-8} mol^{-1} g^{-1})[b]	r_1 (10^{-8} mol^{-1} g^{-1})[c]	BiPh (%)	HN (%)	CHB (%)
$Ni/Mo/Al_2O_3$	DBT	100	100	95	Trace	5
$Ni/Mo/Al_2O_3$	4-MDBT	29	20	58	32	10
$Co/Mo/Al_2O_3$	DBT	36	35.5	95	1	4
$Co/Mo/Al_2O_3$	4-MDBT	9	7.6	60	15	25

[a] Catalyst: commercial $Co/Mo/Al_2O_3$ (CoO, 1.87%; MoO_3, 8%); commercial $Ni/Mo/Al_2O_3$ (NiO, 2.4%; MoO_3, 8%); reactor type: stirred batch autoclave; feed: 1.6 wt.% sulfur in *n*-dodecane, 190°C, 1 bar.

[b] r_0: transformation rate of reactant.

[c] r_1: desulfurization rate.

Table 10
Transformation and desulfurization rates of DBT and 4-MDBT [32][a]

Catalyst	Compound	r_0 (10^{-8} mol^{-1} g^{-1})[b]	r_1 (10^{-8} mol^{-1} g^{-1})[c]	BiPh (%)	HN (%)	CHB (%)
$Ni/Mo/Al_2O_3$	DBT	7	4.8	57	31	12
$Ni/Mo/Al_2O_3$	4-MDBT	4	1.6	17	60	23
$Co/Mo/Al_2O_3$	DBT	2.4	1.8	50	25	25
$Co/Mo/Al_2O_3$	4-MDBT	2.8	1.15	13	59	28

[a] Catalyst: commercial $Co/Mo/Al_2O_3$ (CoO, 1.87%; MoO_3, 8%); commercial $Ni/Mo/Al_2O_3$ (NiO, 2.4%; MoO_3, 8%); reactor type: stirred batch autoclave; feed: 1.6 wt.% sulfur in *n*-dodecane, 190°C, 1 bar.

[b] r_0: transformation rate of reactant.

[c] r_1: desulfurization rate.

$Co/Mo/Al_2O_3$ and this was attributed to the higher hydrogenation activity of $Ni/Mo/Al_2O_3$ catalysts. Hydrogenation of the aromatic rings was considered to alleviate the steric hindrance encountered in the HDS of 4,6-DMDBT, which was considered to be the reason for its low reactivity [36]. It was determined that 88% of the HDS of 4,6-DMDBT was shown to be carried out by the hydrogenation route. A remarkably good correlation was shown between the relative hydrogenolysis reactivity and electron density on the sulfur atom. This implies that hydrogenolysis is strongly dependent upon the electron density of the sulfur atom.

Mochida and co-workers [36] performed a study using $Co/Mo/Ru/Al_2O_3$ catalysts and compared the effectiveness with that of conventional catalysts such as $Co/Mo/Al_2O_3$, $Ni/Mo/Al_2O_3$ and also the less conventional catalyst Ru/Al_2O_3. The HDS activity for each of the catalysts was assessed as was the hydrogenation activity. Based on this study, Mochida concluded the following:

1. Hydrogenation of one of the phenyl rings on 4,6-DMDBT was demonstrated to facilitate HDS due to the reduced steric hindrance of the methyl groups.
2. 4,6-DMDBT competed for the active hydrogenation site as addition of naphthalene reduced the catalytic activity in all cases.
3. The $Co/Mo/Ru/Al_2O_3$ catalyst showed the highest rate of HDS of 4,6-DMDBT.

The role of Ru was not altogether clear. The more selective hydrogenation activity of the Ru containing catalyst may have been due to p–d interactions between the lone pair on the sulfur atom and vacant

Table 11
Hydrogenation of BiPh and 3-MBiPh [32][a]

Catalyst	Compound	r_0 (10^{-8} mol^{-1} g^{-1})[b]	r_1 (10^{-8} mol^{-1} g^{-1})[c]
$Ni/Mo/Al_2O_3$	BiPh	0.75	4
$Ni/Mo/Al_2O_3$	3-MBiPh	1.2	0.7
$Co/Mo/Al_2O_3$	BiPh	0.55	1.2
$Co/Mo/Al_2O_3$	3-MBiPh	0.3	0.35

[a] Catalyst: commercial $Co/Mo/Al_2O_3$ (CoO, 1.87%; MoO_3, 8%); commercial $Ni/Mo/Al_2O_3$ (NiO, 2.4%; MoO_3, 8%); reactor type: stirred batch autoclave; feed: 1.6 wt.% sulfur in *n*-dodecane, 190°C, 1 bar.

[b] r_0: transformation rate of reactant.

[c] r_1: desulfurization rate.

d-orbital on the metal atom. This interaction would be expected to be more pronounced with Ru than with Co, Mo or Ni. In an accompanying study [37] the optimum Ru content was found to be much lower. The ternary Ru-containing catalyst gave a similar activity for HDS of 4,6-DMDBT as $Co/Mo/Al_2O_3$, but showed higher initial rate of reaction and higher conversion levels overall. The $Ni/Mo/Al_2O_3$ proved to be inferior to both cobalt catalysts in these tests. The lower activity for $Ni/Mo/Al_2O_3$ for the HDS of 4,6-DMDBT is in contrast to a previous study by Mochida and co-workers [35] and probably reflects the importance of the reaction conditions used for the two studies. The selective hydrogenation properties of these catalysts for 4,6-DMDBT were investigated by adding naphthalene to the feed and it was found that the $Ni/Mo/Al_2O_3$ catalyst indiscriminately hydrogenated the naphthalene. $Ru/Co/Mo/Al_2O_3$ and $Co/Mo/Al_2O_3$ were much more selective to the hydrogenation of 4,6-DMDBT with less hydrogenation of naphthalene. Also no decalin was observed to be formed over $Ru/Co/Mo/Al_2O_3$ or $Co/Mo/Al_2O_3$ catalysts implying that no further hydrogenation of naphthalene occurred. Again CHB was the major reaction product, this being considered to be the product of hydrogenation prior to sulfur removal. It should be noted that the yield of CHB was sharply increased by the addition of Ru to the catalyst and the Ru/Co/Mo catalyst produced the highest yield of CHB. Ru/Co/Mo and Co/Mo gave similar yields of bicyclohexyl. Ru/Co/Mo and Co/Mo were affected much less than Ni/Mo by the addition of naphthalene. Of particular interest is the similarity between the two sets of data, again, this supports the proposal that HDS of 4,6-DMDBT preferentially occurs through hydrogenation, followed by sulfur removal.

Zhang et al. [33] investigated the HDS of 4,6-DMDBT and DBT employing $Co/Mo/Al_2O_3$ and $Ni/Mo/Al_2O_3$ catalysts under deep desulfurization conditions. The HDS of DBT, 4-MDBT and 4,6-DMDBT was investigated in the temperature range 190–340°C using $Co/Mo/Al_2O_3$. Products were BiPhs and CHBs for each of the respective substrates, i.e. BiPh and CHB for DBT, and 3,3-DMBiPh and 3,3-DMCHB for 4,6-DMDBT. Reactivities decreased in the order DBT, 4-MDBT, 4,6-DMDBT. Conversions on each of the $Co/Mo/Al_2O_3$ over the temperature range showed a remarkable similarity to the curves for the formation of BiPhs. It was implied from these data that the formation of BiPh is prevented by methyl substitution at the phenyl rings. When BiPh or 3,3-DMBiPh was added to the substrate, no increase in the formation of CHBs was observed. It was implied from this that CHBs were mainly formed through hydrogenation of DBTs prior to desulfurization. Rate constants were also calculated and no noticeable difference in HDS reaction rates was observed between any of the $Co/Mo/Al_2O_3$ catalysts investigated. This suggested that a similar mechanism was operating in all of these catalysts. Heats of adsorption were observed to decrease in the order:

$$4,6\text{-DMDBT} > 4\text{-MDBT} > \text{DBT}$$

in accordance with previous studies [30]. The difference in reactivity was therefore not considered to be due to steric hindrance with respect to adsorption onto the catalyst surface. Products using $Ni/Mo/Al_2O_3$ were mainly BiPhs and CHBs. Some tetra and hexahydro-DBTs were also detected. Again reactivity decreased in the order:

$$\text{DBT} > 4\text{-MDBT} > 4,6\text{-DMDBT}$$

$Ni/Mo/Al_2O_3$ exhibited higher activity compared with the highest activity $Co/Mo/Al_2O_3$, and $Ni/Mo/Al_2O_3$ generally required 10°C lower temperature to obtain the same conversion. Below 290°C, conversion of each of the substrates to BiPhs was similar to that for $Co/Mo/Al_2O_3$, but at higher temperatures, the conversion to BiPhs decreased rapidly, and the conversion to CHBs increased from 10 to 60%. This was explained in terms of the reaction scheme given in Fig. 5 with two mechanisms leading to CHBs being considered feasible:

1. Formation of CHBs through hydrogenation of BiPhs.
2. Formation of CHBs through desulfurization of tetra and hexahydro-DBTs.

As tetra- and hexa-hydro-DBTs are detected, it is considered that the second pathway is operating.

Mochida and co-workers [38] studied the reactivity of a series of $Co/Mo/Al_2O_3$ and $Ni/Mo/Al_2O_3$ catalysts with varying Ni and Co content in the range 0–10%. Using the $Ni/Mo/Al_2O_3$ at 300°C, 95–100% conversion was achieved with maximum activity being observed with 5% Ni content. Addition of naphthalene severely retarded the catalyst activity reducing the conversion of the 5% Ni catalyst to 77% under the same conditions. All the naphthalene was converted to tetralin regardless of Ni content. 3,3-DMCHB and 3,3-DMBiPh were the major desulfurization products from 4,6-DMDBT. The yield of 3,3-DMBiPh decreased with increasing Ni content. The formation products were retarded by the addition of 10 wt.% of naphthalene, and the 5% Ni containing catalyst gave the highest yield of 3,3-DMCHB. Co/Mo/Al_2O_3 gave ca. 100% conversion of 4,6-DMDBT, regardless of the Co content. Addition of 10% naphthalene was again observed to retard the HDS reaction, and 1% Co appeared to be optimal when naphthalene was present in the feed. In the presence of naphthalene, the Co/Mo/Al_2O_3 catalysts were found to be superior to the Ni/Mo/Al_2O_3 with respect to HDS activity and 3,3-DMCHB formation was observed to increase with increasing Co content. Surface analysis using X-ray photoelectron spectroscopy showed two bands, before sulfiding, at 235 and 232 eV corresponding to Mo^{VI} $3d_{3/2}$ and $3d_{5/2}$, irrespective of the nature of the catalyst. Sulfiding caused these bands to shift to 225 and 222 eV corresponding to Mo^{IV} $3d_{3/2}$ and $3d_{5/2}$ for both catalysts. This indicates that, in addition to sulfiding, the catalyst surface is also reduced.

4.2. Zeolite containing HDS catalysts

Mochida and co-workers [39] performed HDS reactor studies comparing the activity of Co/Mo/Al_2O_3, Ni/Mo/Al_2O_3 and Co/Mo/Al_2O_3-zeolite of 4,6-DMDBT and gas oil. The Co/Mo/Al_2O_3-zeolite exhibited excellent activity for the HDS of gas oil. Ni/Mo and Co/Mo/Al_2O_3 were observed to be inferior to the Co/Mo/Al_2O_3-zeolite catalyst. Model compounds were also studied, namely, DBT, 4-MDBT, 4,6-DMDBT. Again HDS reactivity decreased in the order

$$\mathrm{DBT} > \text{4-MDBT} > \text{4,6-DMDBT}$$

for all catalysts. Higher HDS activities over Co/Mo/Al_2O_3-zeolite were noted for alkyl dibenzothiophenes. For 4,6-DMDBT, Co/Mo/Al_2O_3-zeolite exhibited the best HDS activity followed by conventional Ni/Mo/Al_2O_3 and Co/Mo/Al_2O_3. The products observed over Co/Mo/Al_2O_3-zeolite, however, were quite different. Three types of products were found:

1. The product of 3,6-DMDBT following methyl group migration and its desulfurized product.
2. Tri and tetramethyl-DBTs.
3. Hydrocracking products in the boiling range 286–332°C.

Desulfurization appeared to take place after inter and intramolecular methyl group migration on the dibenzothiophene skeleton. No significant deactivation was observed over the Co/Mo/Al_2O_3-zeolite catalyst over a test period of 700 h. Ammonia temperature programmed desorption was performed on the Co/Mo/Al_2O_3-zeolite catalyst and over 20% more NH_3 was desorbed from the surface of the Co/Mo/Al_2O_3-zeolite catalyst, when compared with the conventional catalysts at the same temperature, indicating a higher Brønsted acidity for the zeolite supported catalyst, which is expected.

The HDS activity of 4,6-DMDBT was increased employing zeolite based catalysts, e.g. Co/Mo–HZSM-5–Al_2O_3 and Co/Mo/HY–Al_2O_3 when compared with Co/Mo/Al_2O_3 catalysts [40]. Of primary importance was the observation that the relative HDS rates of 4,6-DMDBT and DBT is related to the product ratio, CHB/BiPh. This can be seen in Fig. 14. The HDS rate of DBT and DMDBT was also compared for this series of catalysts. The order of activity for these series is shown in Fig. 15. The increased HDS rate observed with respect to DMDBT was explained by the activated cracking of the thiophene ring compared with demethylation, a mechanism consistent with the absence of demethylation products and the presence of cracked products. The reaction products are summarized in Table 12.

4.3. Effect of hydrogen sulfide partial pressure

The effect of H_2S partial pressure on the HDS activity of 4,6-DMDBT has also been investigated [34]. Langmuir–Hinshelwood kinetics were used to evaluate the effect of H_2S partial pressure upon the HDS of 4,6-DMDBT. HDS was observed to be zero order above 20 atm and so experiments were carried out at 50 atm hydrogen pressure, and [H_2S] was varied between 0 and 2.0 vol.%. Inhibition was observed to be more pronounced for DBT than for 4,6-DMDBT. This was due to the amount of BiPh produced being a more active inhibitor than 3,3-DMBiPh. 4,6-DMDBT was more strongly adsorbed than DBT, but H_2S

Table 12
DMDBT conversion products with Co/Mo/HY–Al_2O_3 catalyst [40][a]

Products	wt.%
Benzene	19.9
Toluene	47.5
Methylcyclohexane	5.9
Methylethylbenzene	3.0
Methylpropylbenzene	8.5
Biphenyl	1.0
Methylbiphenyl	2.1
Dimethylbiphenyl	6.5
Tetrahydrodibenzothiophene	1.1
Methyldibenzothiophene	2.7
Tetrahydromethyldibenzothiophene	0.3
Tetrahydrodimethyldibenzothiophene	0.7

[a] Catalyst: Co/Mo/HY–Al_2O_3 (CoO, 3.8%; MoO_3, 20.9%; SiO_2, 23.6%); LHSV: 10–200 h^{-1}; reactor type: trickle bed; temperature: 360°C; hydrogen pressure: 5.4 MPa.

was adsorbed most strongly. This implied that H_2S, DBT and 4,6-DMDBT all competed for the active sites of the catalysts. The effect of H_2S on the HDS of 4,6-DMDBT has been studied further by Zhang et al. [41]. HDS was carried out at varying hydrogen partial pressures (10–70 atm). [H_2S] was increased in the range 0–2 vol.%, and linear relationships were observed between $1/r_{HDS}$ and P_{H_2S}, and this implied inhibition for DBT and 4,6-DMDBT by H_2S. The effect was more pronounced for DBT than for 4,6-DMDBT.

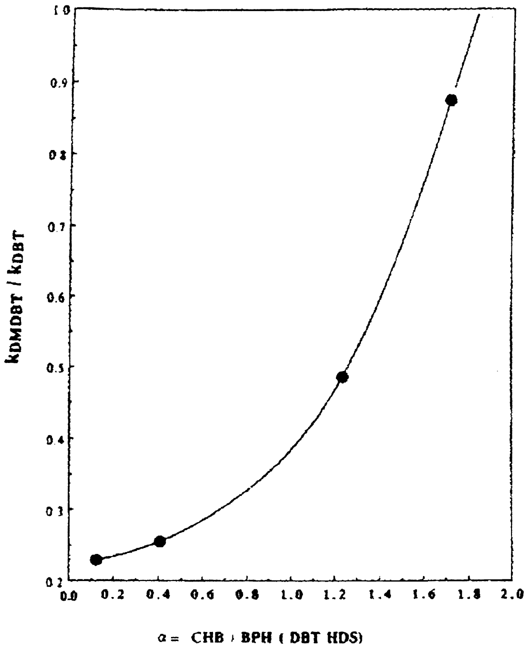


Fig. 14. Correlation between DMDBT/DBT HDS rates ratio and catalyst hydrogenation activity [40].

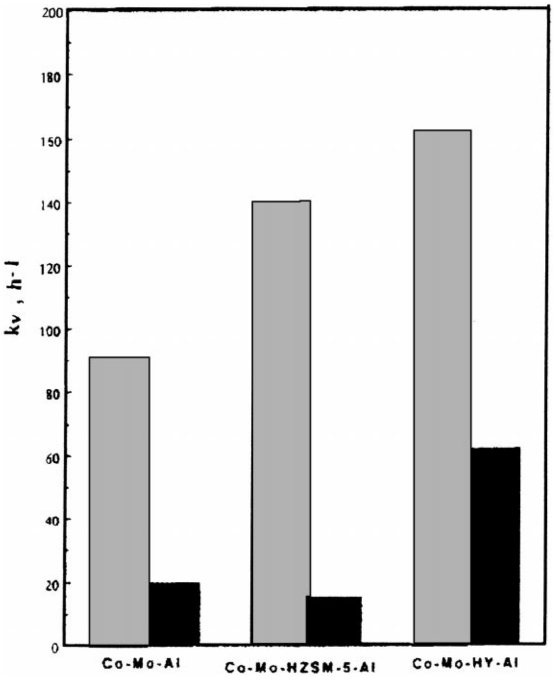


Fig. 15. Effect of zeolite addition on HDS rates of DBT and DMDBT with Co–Mo–Al_2O_3 catalyst [40]: (☐) DBT; (■) DMDBT.

4.4. HDS reactions using multistage reactors

Due to the large variety of sulfur compounds of varying reactivity required to be desulfurized in a typical crude oil feed, much research has been focused upon multistage reactors. These reactor beds are designed to utilize different catalyst types for the different types of sulfur compounds. Mochida and co-workers [42–45] have performed several studies in this area. Notably, three-stage desulfurization reactors have been studied [42]. The first stage employs a Co/Mo/Al_2O_3 catalyst at 360°C to desulfurize the most reactive sulfur compounds, e.g. thiophenes and benzothiophenes. The second stage reactor employs a Ni/Mo/Al_2O_3 catalyst at 360°C to desulfurize relatively low reactivity alkyl dibenzothiophenes, and the third stage also employs a Ni/Mo/Al_2O_3 catalyst at

Table 13
Summary of reaction conditions of HDS studies of hindered dibenzothiophenes

Reference	Catalyst	Reactor	Feed	Pressure (bar)	Temperature (°C)
[20]	Commercial Co/Mo-HDS 16A	Flow microreactor	0.058–0.130 wt.% DBT in *n*-hexadecane	102	300
[27]	Commercial Co/Mo-HDS 16A	Flow microreactor	0.3 wt.% S in $\frac{50}{50}$ *n*-heptane in *n*-hexadecane	1	350–450
[29]	Commercial Co/Mo (4.5% CoO; 17.0% MoO_3)	Flow microreactor	Distilled Arabian light crude	11	350–390
[30]	Commercial Co/Mo (3.8% CoO; 12.5% MoO_3)	Flow microreactor	0.1–0.4 wt.% DBTs	1	220–340
[31]	Commercial Co/Mo (4.4, 14.9%); Ni/Mo (3.1, 14.9%)	Batch autoclave	Diesel fuel	29	360
[32]	Commercial Co/Mo (8, 1.87%); Ni/Mo (2.4, 9%)	Batch autoclave	DBT, 4-MDBT, 4,6-DMDBT; 1 g in dodecane	50	150–190
[40]	Co/Mo (4.2, 25.1%); Ni/Mo (3.4, 24.0, 4.1%); Ni/Mo (34.0, 66.0%); Ni/Mo/Si (30.2, 58.8, 10.1%); Co/Mo/HY–Al (3.8, 20.9, 23.6%); Co/Mo–HZSM-5–Al (4.5, 24.8, 32.5%)	Flow microreactor	1 wt.% DBT, DMDBT	54	360
[33]	A: commercial Co/Mo (3.8, 12.3%); B: commercial Co/Mo (4.5, 17.0%); C: commercial Co/Mo; D: commercial Ni/Mo (3.9, 19.9%)	Flow microreactor	0.1–0.4 wt.% DBTs in decalin	50.7	190–340
[34]	Commercial Ni/Mo (3, 15%)	Batch autoclave	Vacuum gas oil	69	360
[35]	Commercial Co/Mo (4.4, 14.9%); commercial Ni/Mo (3.1, 14.9%)	Batch autoclave	Fractionally distilled gas oil	29	360
[36]	$Co/Mo/Al_2O_3$; $Ni/Mo/Al_2O_3$; $Ru/Co/Mo/Al_2O_3$; Ru/Al_2O_3	Batch autoclave	0.1 wt.% DMDBT; 0–10 wt.% naphthalene in decane	25	300
[42]	Commercial Ni/Mo; commercial Co/Mo, Co/Mo/zeolite and Ru/Al_2O_3	Batch autoclave	Diesel fuel with 4,6-DMDBT	29	Three beds: 360, 360, 260
[43]	Commercial Co/Mo (4, 15%); commercial Ni/Mo (3, 15%)	Batch autoclave	Diesel oil	19	300–340
[44]	Commercial Co/Mo (4, 15%); commercial Ni/Mo (3, 15%); Pd/Al_2O_3 (5%)	Batch autoclave	Diesel oil	11	360
[45]	Commercial Co/Mo (4, 15%); commercial $Ni/Mo/Al_2O_3$ (3, 15%)	Batch autoclave	Diesel fuel	50.7	320–340
[46]	Commercial Co/Mo (4.4, 14.9%); commercial Ni/Mo (3.1, 14.9%)	Batch autoclave	Fractionally distilled Arabian light	29	360
[37]	Co/Mo/Ru-1 (0.25, 15, 0.75%); Co/MO/Ru-2 (3, 15, 0.75%); Ni/Mo/Ru (5, 15, 0.75%); Ni/Mo (1, 15%); Co/Mo (0.25, 15%)	Batch autoclave	0.1 wt.% DMDBT; 0–10 wt.% naphthalene in decane	25	300
[38]	Mo/Al_2O_3 (15%); 3 Ni/Mo (1, 5, 10%; 15%); 3 Co/Mo (0.25, 1, 3%; 15%)	Batch autoclave	0.1 wt.% DMDBT; 0–10 wt.% naphthalene in decane	25	300
[39]	Commercial Co/Mo (4.4, 14.9%); commercial Ni/Mo (3.1, 14.9%); zeolite containing Co/Mo (3.9, 15.8%)	Batch autoclave	0.1 wt.% DMDBT in decane	30	340–380
[41]	Commercial Co/Mo (4.0, 12.0%)	Flow microreactor	0.1–0.4 wt.% DBTs in decalin	50.7	200–300

260°C to decolorize the oil which can develop a fluorescent green color following reaction at deep desulfurization conditions. Decolorization has also been achieved employing Pd/Al_2O_3 type catalysts in a similar multistage reactor [44].

A similar multistage reaction study was carried out in which the gas oil was initially fractionally distilled into five fractions [46]. Each fraction was then treated differently using commercial $Co/Mo/Al_2O_3$ and $Ni/Mo/Al_2O_3$ catalysts. The heavier fractions contained the majority of the low reactivity sulfur compounds. The $Ni/Mo/Al_2O_3$ catalyst exhibited the highest reactivity for these heavier fractions. $Co/Mo/Al_2O_3$ exhibited the highest reactivity for the lower fractions which contained the most reactive sulfur compounds (i.e. benzothiophenes and dibenzothiophenes). The higher reactivity of the $Ni/Mo/Al_2O_3$ for the heavier fractions was attributed to higher hydrogenation activity for this catalyst. The lower activity of the heavier fractions was attributed to (a) the majority of the sulfur compounds in the fractions were the least reactive, i.e. 4-MDBT and 4,6-DMDBT, (b) the heavier fractions contained more aromatic compounds which have been shown to retard HDS [36], and (c) the heavier fractions contained more nitrogen compounds which have been shown to retard HDS [47].

4.5. Other methods of desulfurization

Photochemical methods have been investigated for the desulfurization of sulfur compounds. Moza et al. [48] have studied the photodegradation of aromatic sulfur compounds, dissolved in *n*-hexane, in a thin liquid film on water using irradiation with a mercury lamp. Oxidation of the sulfur compounds to the corresponding sulfoxide occurs and the sulfoxides are transported to the water phase. This technique was applied to hindered DBTs by Hirai et al. [49] as it can demonstrate several advantages over catalytic techniques previously described, e.g.:

1. ambient temperature operation is possible;
2. no hydrogen is required;
3. it is relatively easy to operate, and control of the reaction can be readily achieved;
4. DBT, 4-MDBT and 4,6-DMDBT can all be desulfurized.

Desulfurization was found to be facilitated by the addition of an aqueous phase and by bubbling air through the reaction medium. Sulfur was found to be removed in the form of $SO_4{}^{2-}$ in the aqueous phase. DBT, 4-MDBT and 4,6-DMDBT were all studied, and the surprising reaction order was found to be as follows:

$$4,6\text{-DMDBT} > 4\text{-MDBT} > \text{DBT}$$

This is in complete contrast to the catalytic processes described earlier in this paper. After 5 h, the conversion of 4,6-DMDBT, 4-MDBT and DBT were 100, 72 and 56%, respectively. The reversal of the reactivity order was explained in terms of the expanded electron cloud of 4-MDBT and 4,6-DMDBT facilitating the excitation of DBTs. This process was also applied in the same study to predistilled crude oil but, in this case, a surprisingly low conversion was obtained. This was ascribed to a shielding effect caused by various unsaturated compounds in the crude oil. For this process to be commercially applied, unsaturated compounds would first have to be removed and this disadvantage may be more significant than the clear advantages for this method described above.

Many studies have been performed utilising microbial degradation of sulfur compounds, in particular dibenzothiophene has been studied [50–52]. However, to date, no studies have been reported on the microbial degradation of hindered DBT, e.g. 4,6-DMDBT.

5. Conclusions

The general findings for the studies of the HDS reaction of hindered dibenzothiophenes over $Co/Mo/Al_2O_3$ and $Ni/Mo/Al_2O_3$ catalysts presented in this paper are considered to be very consistent. A range of experimental conditions has been examined in the broad range of studies and these are summarized in Table 13. When compared to the reactivity of unsubstituted dibenzothiophene and other substituted dibenzothiophenes, the order of reactivity is now acknowledged as follows:

$$2,8\text{-DMDBT} > \text{DBT} > 4\text{-MDBT} > 4,6\text{-DMDBT}$$

4,6-DMDBT was observed to be the most unreactive towards HDS. The reason for this is generally considered to be ascribed to steric hindrance that occurs between the methyl groups of the dibenzothiophene molecule and the surface of the catalyst. No studies have been performed with larger substituent groups, e.g. ethyl, propyl, *t*-butyl to elucidate this further, but it is considered that the reactivity of these compounds would be considerably less than that of 4,6-DMDBT. This may, of course, be a suitable direction for future experimental work. Hydrogenation prior to sulfur removal is generally thought to alleviate this steric hindrance and, therefore, facilitate the HDS reaction. Many of the studies show that the reaction rate for 1,2,3,4,5,6,-hexahydro-4,6-DMDBT is higher than that for 4,6-DMDBT. Computer modeling by Landau et al. [40] has also supported this proposal.

Houalla et al. [20] has proposed that both 4- and 4,6-DMDBT experience enhanced hydrogenation prior to sulfur removal, and this is also supported by the study of Kabe et al. [30]. The data in this study quite succinctly show that the hydrogenation route is favoured by the hindered dibenzothiophenes. This route becomes more favourable, the more hindered the dibenzothiophene, i.e. the larger the substituent in the 4-, or 4,6-positions.

The HDS reaction, in general, has been shown to be inhibited by the partial pressure of H_2S and by the presence of the substrate, e.g. DBT. It has been shown from heats of adsorption studies, by Kabe et al. [30], that 4,6-DMDBT is more strongly adsorbed than dibenzothiophene. When this was proposed, it was assumed that the steric interaction could not be the source of the relative inactivity of the substrate, however, no discussion concerning the mode of bonding was provided. It is likely that the mode of adsorption is η^5-bonding through the aromatic ring of the molecule. If the mode of adsorption is different from that of dibenzothiophene then the two values cannot be compared. Since the hydrogenation pathway is considered to be the preferred route amongst hindered dibenzothiophenes, then it seems logical to suggest that the mode of adsorption for this class of compounds is via the aromatic part of the molecule, and not via the S atom as is considered to be the case for dibenzothiophene, benzothiophene and thiophene. Landau et al. [40], on the basis of their results, proposed that an active catalyst for the HDS reaction of hindered dibenzothiophenes should contain hydrogenation sites, to enable hydrogenation prior to sulfur removal, as well as desulfurization sites for the desulfurization of the prehydrogenated substrate. The studies by Mochida and co-workers [36,37] also indicate that HDS catalysts for hindered dibenzothiophenes require enhanced hydrogenation properties as well as desulfurization properties. This was achieved by incorporating Ru into a Co/Mo catalyst, producing a catalyst with selective hydrogenation properties for 4,6-DMDBT. Separate sites for hydrogenation and desulfurization were therefore incorporated into the catalyst by this modification procedure.

With respect to different catalyst types, Ni/Mo/Al_2O_3 evidently has a significantly higher hydrogenation activity than Co/Mo/Al_2O_3 under most reaction conditions. When used in HDS reactions, it leads to preferential hydrogenation of the thiophenic ring compared to the Co/Mo/Al_2O_3 catalysts. To provide an active HDS catalyst for industrial use, the activity must be retained for the compounds which are easier to desulfurize than 4,6-DMDBT, e.g. benzothiophenes and thiophenes. A new catalyst will probably have to be based upon the existing Co/Mo/Al_2O_3 or Ni/Mo/Al_2O_3 types, and Mochida and co-workers [36,37] have demonstrated this in their recent studies. Studies performed by Pecoraro and Chianelli [53] have demonstrated platinum to be the single most active metal in the transition metal series. This work has been investigated by Maitlis and co-workers [54,55], in which platinum complexes have been used to desulfurize dibenzothiophene. This work has only studied sequential organometallic reactions and has not yet been applied to industrially relevant conditions; it does, however, represent a promising new direction of research, which could lead to the identification of a new catalyst. In particular, to desulfurize hindered dibenzothiophenes, it has been accepted that hydrogenation followed by desulfurization will be the most likely route to reach an adequately low sulfur level. Selective hydrogenation properties, however, are required for hydrogenation of the aromatic part of substrate skeleton. In this respect, the nature of Pt and other Pt group metals could be expected to be beneficial in the design of a novel catalyst. Further work should now be directed towards the development of a catalyst which is capable of a higher degree of desulfurization activity towards 4,6-DMDBT. A fruitful area of research may be the incorporation of new metals into existing HDS catalysts in an effort to create a synergy within the existing Ni/Mo/Al_2O_3 or Co/Mo/Al_2O_3 systems.

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