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Alkyldibenzothiophenes Hydrodesulfurization-Promoter Effect, Reactivity, and Reaction Mechanism

Frédéric Bataille,* Jean-Louis Lemberton,* Philippe Michaud,* Guy Pérot,*,[1] Michel Vrinat,† Marc Lemaire,‡ Emmanuelle Schulz,‡ Michèle Breysse,§ and Slavik Kasztelan‖

*Laboratoire de Catalyse en Chimie Organique, Université de Poitiers, 40 avenue du Recteur Pineau, 86022 Poitiers Cedex, France; †Institut de Recherches sur la Catalyse, 2 avenue Albert Einstein, 69626 Villeurbanne Cedex, France; ‡Laboratoire de Catalyse et Synthèse Organique, IRC, UCBL, CPE, 43 bd du 11 novembre 1918, 69622 Villeurbanne Cedex, France; §Laboratoire de Réactivité de Surface, Université Pierre et Marie Curie,Tour 54-55, Casier 178, 2è étage, 4 place Jussieu, 75252 Paris Cedex 05, France; and ‖Institut Français du Pétrole, 1&4 avenue de Bois-Préau, 92852 Rueil-Malmaison Cedex, France

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The promoter effect of Co or Ni on the hydrodesulfurization (HDS) activity of Mo/alumina was studied by using dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (46DMDBT) as reactants. The reaction was carried out at 340°C under a 4 MPa total pressure in a fixed-bed microreactor. On the Mo/alumina catalyst, both reactants had similar reactivities, 46DMDBT being even slightly more reactive than DBT. However, as generally observed, on the CoMo/alumina and NiMo/alumina catalysts, DBT was much more reactive (5 to 6 times) than 46DMDBT. This was mainly because of a tremendous enhancement of the rate of the so-called "direct desulfurization" (DDS) pathway of the HDS of DBT, whereas for 46DMDBT this effect was much more limited. It was therefore concluded that the main effect of the promoter on the HDS of DBT-type molecules was to increase the rate of the C–S bond cleavage provided this reaction was not hindered by steric constraints. This effect was attributed to an enhancement by the promoter of the basicity of certain sulfur anions in its vicinity. It was also shown that the lower reactivity of 46DMDBT compared to that of DBT measured on the promoted catalysts could not be attributed to differences in the adsorption strength of the reactants. Assuming that C–S bond cleavage occurred through a β-elimination process, several other explanations for the low reactivity of 46DMDBT were proposed and discussed: (a) steric hindrance of the adsorption of the dihydrointermediates by the methyl groups; (b) steric hindrance by the methyl groups of the C–S bond cleavage; (c) the fact that only one H atom is available for the C–S bond cleavage; (d) an effect of the methyl group on the acidity of the H atom involved in the elimination step. Proposals were also made concerning the catalytic centers involved in the hydrogenation steps and in the C–S bond cleavage steps.

INTRODUCTION

The removal of sulfur from gasoline and diesel oil is becoming more and more necessary due to the implementation of more stringent specifications in many countries. The gas chromatographic analysis of hydrotreated gas oils compared to that of the corresponding straight-run gas oils shows clearly that alkyldibenzothiophenes and particularly 4,6-dimethyldibenzothiophene (46DMDBT) are the sulfur impurities that are the most difficult to decompose (1–4). Actually, on typical CoMo/alumina and NiMo/alumina hydrotreating catalysts, 46DMDBT was found to be much less reactive than dibenzothiophene (DBT) (5–9). It has been suspected for a long time that the low reactivity of 46DMDBT was due to steric effects on adsorption (5, 6). However, recently, the measurement of the heat of adsorption of DBT and of alkyldibenzothiophenes on CoMo/alumina catalysts (7) as well as competitive hydrodesulfurization (HDS) experiments with DBT and 46DMDBT (8) indicated that the low reactivity of 46DMDBT was not due to an inhibition of the reactant adsorption, but to steric hindrance of the C–S bond scission in the adsorbed sulfur compound, although the exact origin of this inhibition remains unknown.

The product distribution obtained in DBT and in 46DMDBT HDS over typical CoMo and NiMo/alumina catalysts shows that the reaction gives essentially two families of products: biphenyl-type compounds and tetrahydrodibenzothiophene-type compounds (9–12). The latter lead in turn to cyclohexylbenzene-type products. Moreover, it has been shown that, under HDS conditions (i.e., in the presence of an organic sulfur compound), biphenyl-type compounds do not hydrogenate readily into cyclohexylbenzene (9, 13–15). Despite the fact that this point is still questioned especially with NiMo catalysts (4, and references therein), it was concluded that the HDS of DBT-type compounds occurred through two parallel reactions as indicated in Scheme 1: (i) direct desulfurization (DDS) which yields biphenyl-type compounds, and (ii) desulfurization through hydrogenation (HYD) which gives first tetrahydrodibenzothiophene and then cyclohexylbenzene-type compounds.

[1] To whom correspondence should be addressed.

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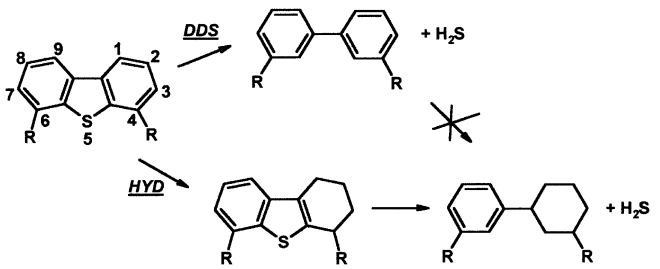
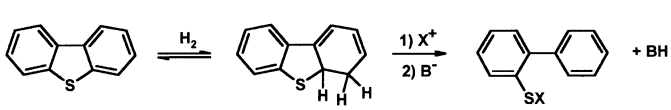


SCHEME 1. Hydrodesulfurization of DBT ($R = H$) or 46DMDBT ($R = CH_3$) on sulfided NiMo/alumina catalyst. DDS, direct desulfurization pathway; HYD, hydrogenation pathway.

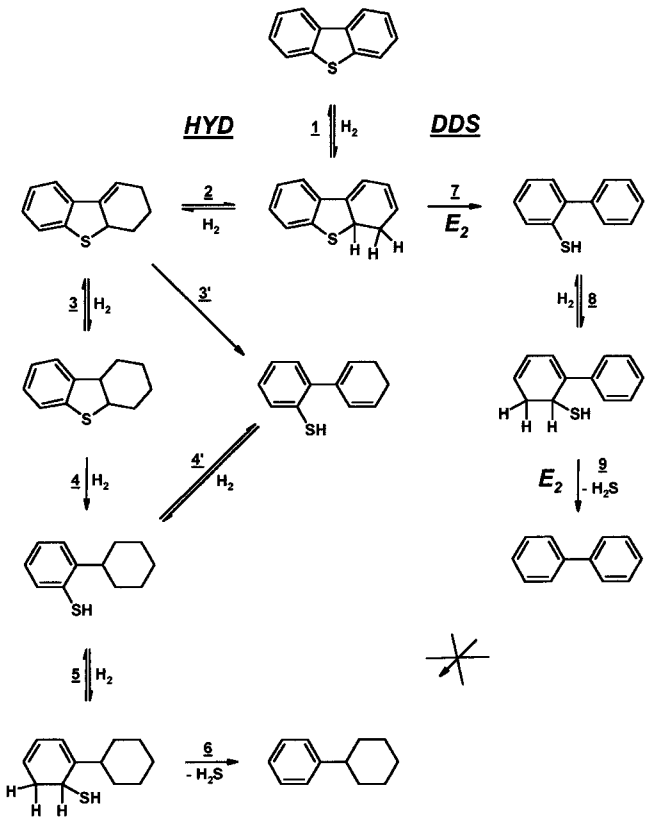
However, depending on the reactant (DBT or 46DMDBT), the contribution of the two pathways to the overall HDS was very different. Under conventional HDS conditions (9), the DDS pathway contributed 80% to the overall HDS of DBT, while only 20% to the HDS of 46DMDBT. It was also found that the presence of methyl groups in the 4 and 6 positions in 46DMDBT inhibited the DDS pathway, whereas the HYD pathway was hardly affected (7–9).

For the DDS pathway, one way to obtain a C–S bond cleavage ending with two phenyl rings in the product is to hydrogenate one of the double bonds in the vicinity of the sulfur atom to obtain a dihydrogenated product and then to open the C–S bond by an elimination process (8, 10, Scheme 2). We note that this particular double bond is not necessarily the easiest to be reduced. The second C–S bond cleavage leading to the biphenyl compound possibly occurs through the same mechanism. Accepting this mechanism, we will discuss in this paper the possible reasons why the existence of methyl groups in the 4 and 6 positions in DBT alters its reactivity. However another possibility of obtaining a C–S bond cleavage ending with aromatic rings is the insertion of a metal atom in the C–S bond (16, 17). We will not discuss this mechanism here, although it could also be sensitive to steric hindrance.

For the HYD pathway which involves the hydrogenation of one aromatic ring, it is reasonable to consider a step by step process beginning also with the hydrogenation of the substrate into a dihydrogenated intermediate. Therefore, as in earlier proposals (8, 10) we assume that the two pathways have dihydrodibenzothiophene compounds as intermediates (Scheme 3), despite the fact that this type of compound has never been observed under the usual HDS conditions. We also note that, whatever the reactant, the



SCHEME 2. Hydrodesulfurization of DBT. The first steps of the DDS pathway: C–S bond cleavage through an elimination reaction (E_2) leading to the rearomatization of the ring. X^+, vacancy or proton; B^-, basic site.



SCHEME 3. Reaction scheme for the hydrodesulfurization of DBT.

second C–S bond cleavage in the HYD pathway does not require the second aromatic ring to be fully hydrogenated and may occur through a DDS-type process leading to the production of cyclohexylbenzene instead of dicyclohexyl-type compounds. This means that the second C–S bond cleavage is not affected much by the presence of a methyl group in the vicinity of the sulfur atom in the second aromatic ring.

In the literature, many of the results reported on alkyldibenzothiophene HDS have been obtained with promoted hydrotreating catalysts, namely sulfided CoMo and NiMo/alumina catalysts. Considering the important promoter effect often measured for hydrotreating reactions, it appears of importance to know how the observations summarized above can be influenced by the presence of the promoter.

In this paper we examine the effect of Co and Ni promoters on the activity of a Mo/alumina catalyst in the HDS of both DBT and 46DMDBT under typical hydrotreating conditions. We also report complementary experiments on the competitive reaction in the gas phase of DBT and 46DMDBT as well as on the effect of hydrogen and hydrogen sulfide on the transformation of these compounds. Our aim was to propose new explanations concerning the inhibition of the reactivity of alkyldibenzothiophenes and to discuss the nature of the catalytic centers involved in HDS

on molybdenum sulfide-based catalysts and more specifically to address two questions: (i) Do the DDS and HYD pathways occur on the same or on distinct catalytic centers? (ii) What are the possible structures of these centers?

EXPERIMENTAL

Standard Reaction Conditions

The HDS of DBT and 46DMDBT was carried out in a flow reactor at 340°C under a 4 MPa total pressure (9). Decalin was used as a solvent to which dimethyldisulfide was added to generate H_2S. Under standard reaction conditions, the various partial pressures were DBT or 46DMDBT = 0.01 MPa, decalin = 0.89 MPa, H_2 = 3.0 MPa, H_2S = 0.05 MPa (plus 0.05 MPa CH_4 resulting from the dimethyldisulfide decomposition).

DBT/46DMDBT Competition Experiments

Both reactants were mixed together in decalin and injected into the reactor. To examine the effect of DBT on the transformation of 46DMDBT, the partial pressure of 46DMDBT was maintained at the standard 0.01 MPa value, while that of DBT was 0.01, 0.02, or 0.04 MPa. All the other partial pressures and the total pressure were kept constant by changing the partial pressure of the solvent. To examine the effect of 46DMDBT on the conversion of DBT, the partial pressure of DBT was kept constant at 0.01 MPa, while that of 46DMDBT was modified (0.005 or 0.01 MPa). Higher 46DMDBT partial pressures could not be obtained because of the low solubility of this compound in decalin.

Effect of Hydrogen Partial Pressure

Hydrogen partial pressures of 2, 3, and 4 MPa were used, which modified the total pressure (3, 4, and 5 MPa, respectively), but not the partial pressures of the reactant, of the solvent, and of H_2S when compared to the standard partial pressures. After each hydrogen pressure modification, the reaction was carried out again under standard reaction conditions to make sure that the catalyst had remained unaltered.

Effect of Hydrogen Sulfide Pressure

In this case, the total and the partial pressures of the reactant were kept constant. The changes in the H_2S partial pressure, obtained by modifying the amount of dimethyldisulfide in the feed, were compensated by changes in the solvent partial pressure. The H_2S partial pressures used were 0, 0.025, 0.05, and 0.1 MPa. As explained above, we also checked after each H_2S pressure change that the catalyst had not been modified.

Catalysts

The commercial NiMo/alumina hydrotreating catalyst used for the competition and the pressure effect experiments contained 3 wt% NiO and 14 wt% MoO_3. The Mo/alumina catalyst, containing 9.3 wt% Mo, was prepared (18) by incipient wetness impregnation of γ-alumina (240 $m^2\,g^{-1}$, pore volume 0.56 $cm^3\,g^{-1}$) with an aqueous solution of ammonium heptamolybdate (Fluka). The catalyst was dried at 120°C and calcined under air flow at 500°C. The NiMo/alumina and CoMo/alumina catalysts used for studies of the promoting effect were obtained (18) by impregnating the Mo/alumina catalyst with aqueous solutions of nickel or cobalt nitrates (Aldrich). They contained 2.3 wt% Ni and 2.5 wt% Co, respectively, which corresponded to a molar ratio Ni (Co)/Ni (Co) + Mo equal to 0.3. All the catalysts were dried at 120°C and calcined under flowing air at 500°C. They were then sulfided *in situ* by a mixture of 5 vol% dimethyldisulfide in *n*-heptane, under a 3.0 MPa hydrogen partial pressure and a 4.0 MPa total pressure. The H_2S partial pressure was 0.125 MPa and that of *n*-heptane was 0.75 MPa. The sulfiding feed was injected at a starting temperature of 150°C and raised to 350°C at a 5°C min^{-1} rate. After 14 h, the temperature was lowered to 340°C, and the reaction mixture was substituted for the sulfiding feed.

Products

Dibenzothiophene, decalin, and dimethyldisulfide were purchased from Aldrich, whereas 46DMDBT was synthesized as previously described (19). Owing to the high boiling point of the reactants, on-line analysis of the reaction products was not convenient. Consequently, the reactor effluents were condensed, and liquid samples were periodically collected to be analyzed by gas chromatography. Gaseous products were not formed, except for methane which was produced by dimethyldisulfide decomposition. The analyses were carried out on a Varian 3400 chromatograph equipped with a 50-m DB17 capillary column (J&W Scientific) with a temperature programming from 100 to 230°C (10°C min^{-1}). Unknown products were identified by GC-MS (Finnigan INCOS 500).

RESULTS

Simultaneous Transformation of DBT and of 46DMDBT on a Commercial NiMo/Alumina Catalyst

Table 1 shows the effect of 46DMDBT partial pressure on the activity of the catalyst for DBT transformation (total activity and activity for each pathway: DDS or HYD). The results obtained indicate that 46DMDBT inhibits the transformation of DBT. The apparent kinetic order with respect to 46DMDBT can be roughly estimated to be −0.4. On the other hand, the A_{DDS}/A_{HYD} ratio for DBT is reduced by a factor of about 2 when the 46DMDBT pressure is increased

TABLE 1

Effect of 46DMDBT on the Transformation of DBT and Vice Versa

Reactant:	DBT			46DMDBT			
Competitor:	46DMDBT			DBT			
Partial pressure of competitor (MPa)	0	0.005	0.01	0	0.01	0.02	0.04
A_T	9.7	6.9	5.7	1.7	1.1	1.0	0.8
A_{DDS}	7.7	4.8	3.8	0.30	0.20	0.20	0.15
A_{HYD}	2.0	2.1	1.9	1.40	0.90	0.80	0.65
A_{DDS}/A_{HYD}	3.85	2.28	2.00	0.21	0.22	0.25	0.23

Note. Sulfided commercial NiMo/alumina catalyst at 340°C; 3.0 MPa H_2. Reactant pressure = 0.01 MPa; H_2S pressure = 0.05 MPa. A_T = total activity; A_{DDS} = activity for the direct desulfurization pathway; A_{HYD} = activity for the hydrogenation pathway (mol h^{-1} kg^{-1}). Conversions of DBT and of 46DMDBT as reactants ≤40 and 15 mol%, respectively.

from 0 to 0.01 MPa. This means that the DDS pathway for DBT is apparently more sensitive to 46DMDBT inhibition than the HYD pathway. However, the number of experiments is not sufficient here to come to a definite conclusion.

Table 1 shows also that DBT inhibits the transformation of 46DMDBT in the same manner as 46DMDBT inhibits the transformation of DBT. The apparent kinetic order with respect to DBT is also −0.4. The two pathways (DDS and HYD) are in this case equally affected since the A_{DDS}/A_{HYD} ratio is not modified.

Effect of Hydrogen Pressure on the Transformation of DBT and 46DMDBT on a Commercial NiMo/Alumina Catalyst

Table 2 shows that an increase in hydrogen pressure enhances the conversion of DBT and of 46DMDBT. Both the reaction rates and the kinetic orders reported in Table 4 indicate that for DBT the DDS and the HYD pathways increase in a similar manner, while for 46DMDBT, the DDS pathway is much less sensitive to hydrogen pressure than the HYD pathway. Consequently, while there is almost no change in A_{DDS}/A_{HYD} selectivity in the case of DBT, there is quite a noticeable change in the case of 46DMDBT (Table 2).

TABLE 2

Effect of Hydrogen Pressure on the Transformation of DBT and 46DMDBT

Reactant:	DBT			46DMDBT		
P H_2 (MPa)	2	3	4	2	3	4
A_T	6.7	9.7	13.0	1.2	1.7	3.1
A_{DDS}	5.2	7.7	9.6	0.3	0.3	0.4
A_{HYD}	1.3	2.0	2.7	0.9	1.4	2.6
A_{DDS}/A_{HYD}	4.0	3.8	3.5	0.33	0.21	0.15

Note. Sulfided commercial NiMo/alumina catalyst at 340°C. Reactant pressure = 0.01 MPa; H_2S pressure = 0.05 MPa. (See Table 1 for abbreviations and units.) Conversions = 10–30 mol%.

TABLE 3

Effect of Hydrogen Sulfide Pressure on the Transformation of DBT and 46DMDBT

Reactant:	DBT				46DMDBT			
P H_2S (MPa)	0	0.025	0.05	0.1	0	0.025	0.05	0.1
A_T	74.7	17.7	9.7	5.4	4.0	1.9	1.7	1.3
A_{DDS}	70.9	15.8	7.7	4.2	1.9	0.5	0.3	0.2
A_{HYD}	3.8	1.9	2.0	1.2	2.1	1.4	1.4	1.1
A_{DDS}/A_{HYD}	18.6	8.8	3.8	3.5	0.90	0.36	0.21	0.18

Note. Sulfided commercial NiMo/alumina catalyst at 340°C, 3.0 MPa H_2. Reactant pressure = 0.01 MPa. (See Table 1 for abbreviations and units.) Conversions of DBT and of 46DMDBT ≤20 and 30 mol%, respectively.

Effect of Hydrogen Sulfide Pressure on the Transformation of DBT and of 46DMDBT on a Commercial NiMo/Alumina Catalyst

The influence of hydrogen sulfide partial pressure was also studied by adding dimethyldisulfide to the feed. It must be pointed out that the H_2S pressures indicated in Table 3 correspond only to the H_2S produced by the dimethyldisulfide decomposition; the H_2S produced by the HDS of the reactant was not taken into account. The results in Table 3 indicate that the addition of H_2S brings about a significant decrease in activity, especially in the case of DBT. In the presence of 0.1 MPa H_2S, the activity for DBT transformation is reduced by a factor of 14, while the activity for 46DMDBT transformation is divided only by a factor of 3.

As shown in Table 4, the kinetic order with respect to H_2S is largely more negative for DBT than for 46DMDBT. On the other hand, for the two molecules, the A_{DDS}/A_{HYD} ratio is lower in the presence of H_2S, which means that the DDS pathway is much more sensitive to H_2S than the HYD pathway. The kinetic order with respect to H_2S is more negative for the DDS pathway than for the HYD reaction. In other words, H_2S must be a better competitor for the intermediate

TABLE 4

Apparent Kinetic Orders for the Transformation of DBT and 46DMDBT

Reactant:	DBT		46DMDBT	
Effect of:	H_2	H_2S	H_2	H_2S
Global	1.0	−0.7	1.3	−0.3
DDS	0.9	−0.8	0.3	−0.3
HYD	1.0	−0.4	1.4	−0.2

Note. Sulfided commercial NiMo/alumina catalyst at 340°C, reactant pressure = 0.01 MPa. (See Table 1 for abbreviations.)

involved in the DDS pathway of HDS in the case of DBT than in the case of 46DMDBT. This explains why the HDS of DBT is more sensitive to H_2S than the HDS of 46DMDBT, the contribution of the DDS pathway to the overall HDS reaction being much more significant for DBT than for 46DMDBT.

Effect of Ni or Co Promoters on the Decomposition of DBT and of 46DMDBT

The reactivity and product distribution of DBT and of 46DMDBT were measured on a Mo/alumina catalyst and compared to those obtained with CoMo/alumina and NiMo/alumina catalysts.

Surprisingly, on the Mo/alumina catalyst, 46DMDBT is slightly more reactive than DBT. This is mainly due to a higher rate of the HYD pathway which is the prominent pathway for both compounds on this catalyst: 75% for DBT, 92% for 46DMDBT (Table 5). However, if we consider the HDS activity (products with no sulfur), DBT is about twice as reactive as 46DMDBT.

As generally reported, the CoMo/alumina and NiMo/alumina catalysts were much more active than the Mo/alumina catalyst for the HDS of DBT (Table 5). The promoting effect was around 20, which is in accordance with previous studies (20, and references therein). However the promoting effect was essentially due to the enhancement of the rate of the DDS pathway of DBT. In this case, the promoting effect for the DDS pathway was over 60, whereas it was equal to 3–4 for the HYD pathway. For DBT, the HYD pathway represented about 75% on the Mo/alumina catalyst but only 13–15% with the promoted catalysts.

TABLE 5

Activities of Mo, CoMo, and NiMo/Alumina Catalysts for the Transformation of DBT and of 46DMDBT at 340°C, 3.0 MPa H_2

Reactant:	DBT			46DMDBT		
Catalyst:	Mo	CoMo	NiMo	Mo	CoMo	NiMo
Activities						
A_T	0.4	7.2	8.0	0.65	1.2	1.7
A_{DDS}	0.1	6.3	6.8	0.05	0.2	0.3
A_{HYD}	0.3	0.9	1.2	0.60	1.0	1.4
A_{DDS}/A_{HYD}	0.3	7.0	5.7	0.1	0.2	0.2
A_{HDS}	0.15	6.5	7.1	0.08	0.6	0.7
Selectivities						
S_{DDS}	25	87	85	8	17	18
S_{HYD}	75	13	15	92	83	82
Promoting effect						
Total		18	20		1.8	2.6
On HYD		3	4		1.7	2.3
On DDS		63	68		4.0	6.0

Note. Reactant pressure = 0.01 MPa; H_2S pressure = 0.05 MPa. S_{DDS} and S_{HYD} = selectivities (%) for the DDS and HYD pathways, respectively. (See Table 1 for other abbreviations and units.) Conversions ≈15 mol%.

TABLE 6

Reactivity Ratio between DBT and 46DMDBT on the Mo, CoMo, and NiMo/Alumina Catalysts at 340°C, 3.0 MPa H_2

DBT/46DMDBT	Total	DDS	HYD
Mo	0.61	2.0	0.50
CoMo	6.0	31.5	0.9
NiMo	4.7	22.6	0.8

Note. Reactant pressure = 0.01 MPa; H_2S pressure = 0.05 MPa. Conversions ≈15 mol%.

As reported in the literature (5–9) the HDS reactivity of 46DMDBT on promoted catalysts is less than that of DBT by a factor of 5 to 6 (Table 6). This is because the promoting effect of Co and Ni for the HDS of 46DMDBT (1.8 and 2.6, respectively) is 10 times smaller than for the HDS of DBT.

The main pathway for the transformation of 46DMDBT on all the catalysts was the HYD pathway (80% on the promoted catalysts, 90% on Mo/alumina, Table 5). It can be noted that this selectivity is about the same as the one obtained with DBT on Mo/alumina. The promoting effect on the HYD pathway is small, about one-half that for DBT. The effect is greater on the DDS pathway than on the HYD pathway yet smaller than for DBT.

Table 6 reports the differences of reactivity between DBT and 46DMDBT for the various catalysts. As we have seen, on Mo/alumina DBT is less reactive than 46DMDBT, mainly because of the HYD pathway. As already reported (7–9) on the promoted catalysts both reactants have approximately the same reactivity regarding the HYD pathway (reactivity ratio between DBT and 46DMDBT equal to 0.8–0.9) but DBT is considerably more reactive than 46DMDBT regarding the DDS pathway (reactivity ratio equal to 20–30).

Table 7 compares the product distributions obtained with the Mo/alumina and with the CoMo and NiMo/alumina catalysts, either at similar total conversions or at similar conversions through the HYD pathway. In the case of DBT, we can see that the promoter changes not only the contributions of the DDS and of the HYD pathways with respect to each other but also the product distribution of the HYD pathway. The two promoted catalysts give approximately the same results. In particular, the observed amount of tetrahydrodibenzothiophene (THDBT) is much greater with the unpromoted catalyst than with the promoted catalysts. At a total conversion of about 9%, we obtain 4.7% of tetrahydrodibenzothiophene with the unpromoted catalyst and about only 1% with the promoted catalysts. We can also consider the results obtained at similar HYD conversions (compare line 1 to lines 3 and 5, Table 7) which are more relevant. We note in particular that the molar ratio tetrahydrodibenzothiophene/cyclohexylbenzene (THDBT/CHB) is much higher with the unpromoted catalyst than with

TABLE 7

Product Distributions for the Transformation of DBT and 46DMDBT over Mo, CoMo, and NiMo/Alumina Catalysts

		Conversion (mol%)			DDS	Product distribution (mol%) HYD				
Reactant	Catalyst	Total	DDS	HYD	BiP	THDBT	HHDBT	CHB	DCH	THDBT/CHB
DBT	Mo	8.7	2.0	6.7	2.0	4.7	0.6	1.1	0.3	4.3
	NiMo	8.9	7.4	1.5	7.4	1.0	—	0.5	—	2.0
		33.0	25.7	7.3	25.7	2.3	—	5.0	—	0.5
	CoMo	8.8	7.6	1.2	7.6	0.8	—	0.4	—	2.0
		52.2	45.2	7.0	45.2	1.9	—	5.1	—	0.4
Reactant	Catalyst	Total	DDS	HYD	DMBiP	THDMDBT	HHDMDBT	MCHT	DMDCH	THDMDBT/MCHT
46DMDBT	Mo	9.9	0.8	9.1	0.8	8.6	—	0.5	—	17.2
		20.0	2.8	17.2	2.8	13.4	—	2.0	1.8	6.7
	NiMo	9.0	1.5	7.5	1.5	5.5	—	2.0	—	2.8
		20.0	4.5	15.5	4.5	4.5	—	10.0	1.0	0.4
	CoMo	11.9	2.5	9.4	2.5	5.5	—	3.9	—	1.4
		23.0	4.7	18.3	4.7	2.8	—	15.5	—	0.2

Note. Reaction conditions: 340°C, 3.0 MPa H_2. Reactant pressure = 0.01 MPa; H_2S pressure = 0.05 MPa. DDS, direct desulfurization pathway; HYD, hydrogenation pathway; BiP, biphenyl; THDBT, tetrahydrodibenzothiophene; HHDBT, hexahydrodibenzothiophene; CHB, cyclohexylbenzene; DCH, dicyclohexyl; DMBiP, dimethylbiphenyl; THDMDBT, tetrahydrodimethyldibenzothiophene; HHDMDBT, hexahydrodimethyldibenzothiophene; MCHT, methylcyclohexyltoluene; DMDCH, dimethyldicyclohexyl.

the promoted catalysts. We can also see that traces of hexahydrodibenzothiophene (HHDBT) were detected in the transformation of DBT on the Mo/alumina catalyst.

Similar results were obtained with 46DMDBT except that in this case the DDS pathway was much inhibited so that there was not so much difference between the total conversion and the conversion through the HYD pathway. Nevertheless, we can see that at similar conversions through the HYD pathway, the molar ratio tetrahydrodimethyldibenzothiophene/methylcyclohexyltoluene (THDMDBT/MCHT) is much smaller on the promoted catalysts than on Mo/alumina.

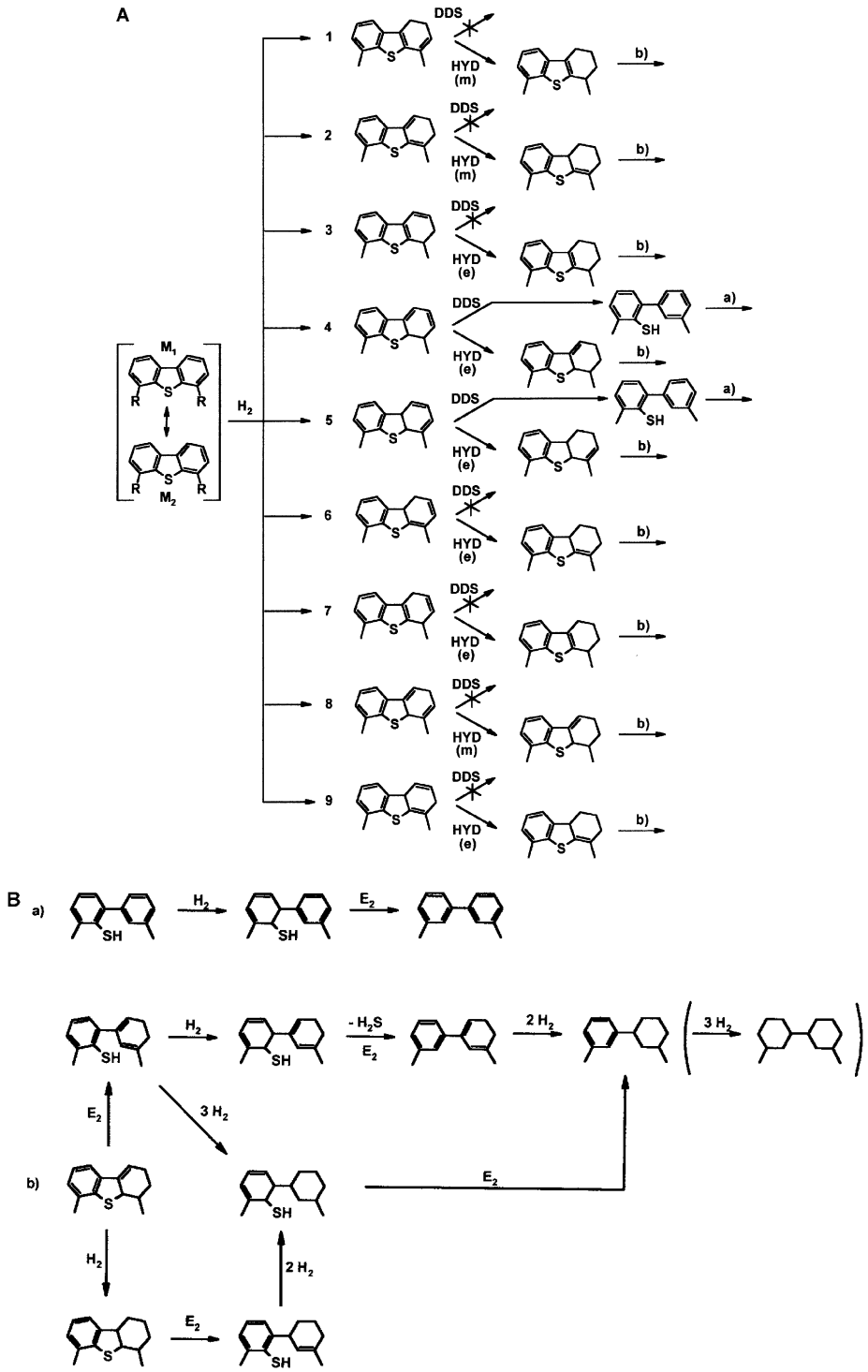
DISCUSSION

As already reported in the literature (5–9), it is found in this work that the two S compounds, DBT and 46DMDBT, have different reactivities on promoted catalysts. However it is also shown that the effect of the promoter (Co or Ni) on the activity of the Mo catalyst is notably different for the DDS and HYD pathways of the two compounds. Unexpectedly, it is found that the activity of the Mo catalyst for the HDS of 46DMDBT is almost equal to its activity for the HDS of DBT. This questions the explanation often found in the literature (5, 6) of the low reactivity of 46DMDBT based on steric hindrance of the 46DMDBT adsorption due to the presence of the methyl groups at the 4 and 6 positions.

In the following discussion we examine other possible explanations for the differences in reactivity of DBT and 46DMDBT over the Mo, CoMo, and NiMo catalysts in order to better understand the origin of the promoter effect. Then we attempt to deduce from these considerations a reasonable description of the active edge sites. However, before that it appeared useful to describe in detail the sequence of steps that are expected to occur during the transformation of alkyldibenzothiophenes.

Steps Involved in the HDS of Alkydibenzothiophenes

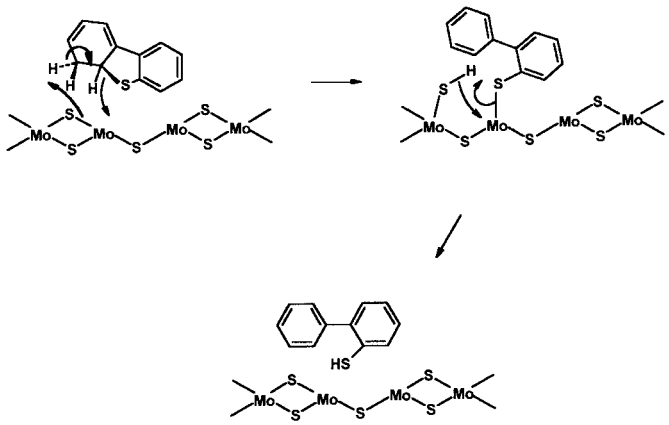
Scheme 3, a typical reaction scheme for the HDS of DBT, shows that a common dihydrointermediate could exist for the DDS and HYD pathways. However, Scheme 3 is still oversimplified. Actually, nine dihydroisomers can be formed through partial hydrogenation of either DBT or 46DMDBT as shown in Scheme 4A. One can note that this step is expected to be the most difficult hydrogenation step since it destroys the aromaticity of one benzenic ring. The dihydroisomers 1–6 can be formed by 1,2 addition of two hydrogen atoms to either of the two mesomeric structures M_1 or M_2 shown in Scheme 4A. Compounds 7–9 result either from 1,4 addition of two hydrogen atoms to DBT or 46DMDBT or from double-bond isomerization in compounds 1–6. It can be noted, however, that the double bonds in the dihydrogenated rings of compounds 7–9 are not conjugated. Consequently these compounds are probably less stable than compounds 1–6, especially compounds 8 and 9 in which the thiophenic ring is not preserved. In Scheme 4A two types of reaction can be considered for the dihydroisomers, either C–S bond cleavage (a) or further hydrogenation into tetrahydrogenated products (b). Scheme 4B decribes these two routes in detail.



SCHEME 4. (A) Various isomers of the dihydrointermediates in the hydrodesulfurization of DBT ($R = H$) and of 46DMDBT ($R = CH_3$). Reaction rates: e, easy; m, medium; a, end of the sequence for the DDS pathway; b, end of the sequence for the HYD pathway. (B) Details for sequences a and b of Scheme 4A given for compound 4 as an example.

We note immediately in Scheme 4A that only two of the dihydrointermediates can undergo directly an elimination step leading to C–S bond cleavage (DDS pathway, route "a" in Scheme 4A and 4B) and regenerate an aromatic ring. All of the other dihydroisomers will be converted by further hydrogenation to tetrahydroisomers (HYD pathway, route "b" in Schemes 4A and 4B).

The presence of the methyl groups could have an effect on most of the steps leading to the HDS of DBT and 46DMDBT, namely on: (i) the adsorption of the reactants



SCHEME 5. Mechanism of the C–S bond cleavage in the DDS pathway on MoS_2.

or intermediates (especially the dihydrointermediates); (ii) the addition of hydrogen atoms (to form the tetrahydro- and hexahydrointermediates) and (iii) the C–S bond cleavage steps through elimination (E_2 mechanism shown in Scheme 5). In particular, the presence of the methyl groups could explain why the rate-limiting steps for DBT and for 46DMDBT are not the same.

The results of Tables 5–7 indicate that the rate-limiting step of the two pathways (Table 8) depends both on the reactant and on the catalyst. This will be discussed in greater detail later (see in particular the section dealing with the effect of the promoter). It is clear, however, that on the Mo/alumina catalyst C–S bond cleavage is the rate-limiting step of the DDS pathways for both reactants. On the promoted catalysts, C–S bond cleavage is still the rate-limiting step for the DDS pathway of 46DMDBT while the formation of the dihydrointermediate is the rate-limiting step for the DDS pathway of DBT.

TABLE 8

Rate-Limiting Steps (X) for the HDS of DBT and 46DMDBT on Mo, CoMo, and NiMo/Alumina Catalysts

Reactant:		DBT		46DMDBT	
Catalyst:		Mo	CoMo or NiMo	Mo	CoMo or NiMo
DDS	Formation of the dihydroisomers 4 and 5	/	X	/	/
	C–S cleavage in the dihydroisomers 4 and 5	X	/	X	X
HYD	Formation of the dihydroisomers (1–7)	/	X	/	X ?
	Hydrogenation of the dihydroisomers (1–7)	/	/	/	/
	C–S cleavages in tetrahydro or hexahydroisomers	X	/	X	/

Regarding the HYD pathway, C–S bond cleavage is also the rate-limiting step for both reactants on the unpromoted catalyst (the hydrogenated intermediates were obtained in significant quantities) but the formation of the dihydrointermediates is most likely the rate-limiting step for the transformation of DBT on the promoted catalysts. For 46DMDBT it is not so clear: significant amounts of hydrogenated intermediates were formed, which means that the C–S bond cleavage is apparently not very rapid compared to the hydrogenation steps. In the following sections we will examine the possible effect of the methyl groups on the various steps of both pathways and try to understand why they inhibit mainly the DDS pathway.

Steric and Electronic Effects on the Reactivity of DBT-Type Compounds

(a) Effect on the adsorption of 46DMDBT. It was found that the methyl groups in 46DMDBT affected only the DDS pathway. Therefore, if we assume that the DDS and HYD pathways have a common intermediate, we can conclude that it is neither the adsorption of the reactant which is affected by the presence of alkyl groups in positions 4 and 6 nor the step leading to the common dihydrointermediate, but rather one of the subsequent steps of the DDS pathway of 46DMDBT, most probably the first C–S bond cleavage (7). Indeed, the HDS reaction of DBT and 46DMDBT carried out in competition in a batch reactor (8) showed that the adsorption coefficients of the two compounds on NiMo/alumina were similar. A value of 1.3 for the ratio of the constants of the adsorption equilibrium ($K_{DBT}/K_{46DMDBT}$) was obtained by comparing the ratio of reactivity between the two molecules in competition ($k_{DBT}/k_{46DMDBT}$) with the ratio of the rate constants ($k_{DBT}/k_{46DMDBT}$) calculated for the transformation of each molecule. In the experiments reported here, it was found that the two reactants had the same reciprocal inhibiting effect. In the present work the HDS of DBT and of 46DMDBT (alone or in competition) was carried out in a continuous flow reactor on NiMo/alumina (Table 1). Using the same method as Meille *et al.* (8), the activity values for the two reactions led to a $K_{DBT}/K_{46DMDBT}$ ratio of 1.1, which confirms that the two molecules have similar adsorption coefficients.

We must consider then the hypothesis that with 46DMDBT the two pathways could have different rate-limiting steps which would not be equally sensitive to steric hindrance. Actually, in the case of DBT the kinetic orders with respect to hydrogen of these pathways are close to 1 (Table 4). This result is consistent with the assumption (as indicated in Table 8 for promoted catalysts) that the rate-limiting step of DBT transformation is the step which is common to the two pathways, i.e., the formation of dihydrodibenzothiophene as proposed recently by Olguin and

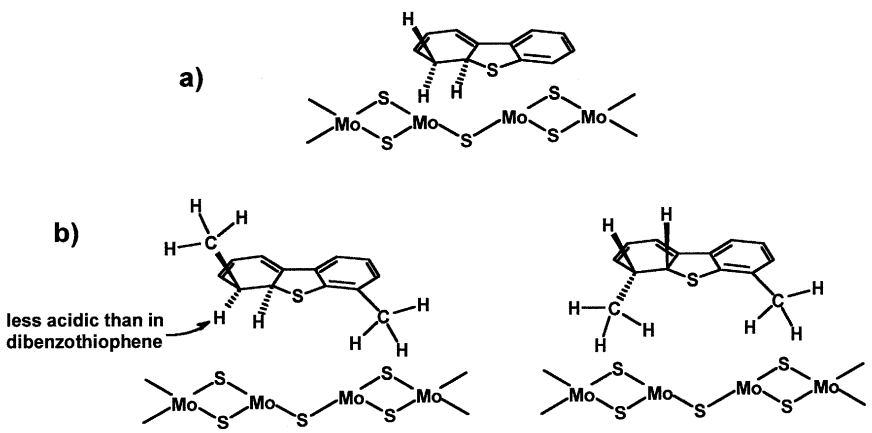
Vrinat (21). In the case of 46DMDBT, the kinetic order with respect to hydrogen for the HYD pathway is also quite high (greater than 1), but the kinetic order for the DDS pathway is only 0.3. This can be explained by supposing that the two pathways do not have the same rate-limiting step; for example, the rate-limiting step of the HYD pathway is still the formation of the dihydrointermediate (Table 8), whereas for the DDS pathway the C–S bond cleavage is now the rate-limiting step.

If we look at the mechanism of the C–S bond cleavage shown in Scheme 5, it can be seen that there are several other reasons why alkyl groups in positions 4 and 6 may alter the reactivity of DBT-type compounds and in particular regarding the DDS pathway.

(b) Steric effect of the methyl groups on the adsorption of the dihydrointermediates involved in the DDS pathway. If the alkyl groups do not inhibit the adsorption of the substrate, we must envisage that the alkyl groups can have an effect on the adsorption of the dihydrointermediates. This must be considered especially if there is desorption of these intermediates (as shown in Scheme 4), which we will assume despite the fact that they were not detected among the products (probably because they undergo subsequent hydrogenation readily).

As already pointed out, only two of the dihydrointermediates (compounds 4 and 5 in Scheme 4A) can undergo C–S bond cleavage. The adsorption of one of these compounds (compound 4) may be greatly affected by the presence of the methyl groups. Actually once the substrate has been partially hydrogenated into compound 4 the two sides of the molecule are no longer identical. Hence, while the analogous dihydrodibenzothiophene can adsorb equally on both sides, the adsorption of compound 4 on the side with the alkyl group out of the plane of the molecule can obviously be hindered (Scheme 6b). We must assume then that depending on whether the adsorption of these intermediates leads to the DDS or HYD pathway, the steric hindrance of the methyl groups would not interfere in the same manner, either because the sites are different or because of the presence or absence of hydrogen atoms on the sites (see below).

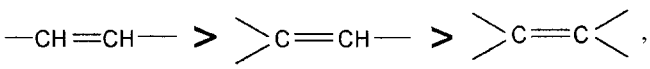
(c) Steric hindrance of the C–S bond cleavage and electronic effect on the lability of the proton involved in the reaction. For C–S bond cleavage to take place according to the DDS pathway (Scheme 5), compounds 4 and/or 5 must either undergo the elimination reaction without desorption or readsorb on their side bearing one hydrogen atom in β-position with respect to the sulfur atom. Moreover, it is reasonable to consider that in the adsorbed state the sulfur atom should be in interaction with the catalyst (which is not necessarily so in the adsorbed state for hydrogenation) in order to favor the antielimination process. However, if the catalytic hydrogenation of a double bond consists (as generally accepted) in a *cis* addition of the two hydrogen atoms, then the sulfur atom and the β-hydrogen atom in the dihydrointermediate (as shown for compound 4 in Scheme 6b) should be in a *trans* configuration. This is favorable for an antielimination despite the fact that it must be very difficult to have, at the same time, both the sulfur atom and the *trans*-hydrogen atom in β-position in interaction with the surface (if the latter is assumed to be flat). In any case, the presence of the methyl group on carbon 4 of compound 4 (Scheme 6b) can obviously hinder the elimination process by preventing either the sulfur atom or the β-hydrogen atom from approaching the catalytic centers. The methyl group in 46DMDBT can also make the β-hydrogen atom involved in the elimination process (Scheme 6b) less acidic than in DBT (22). Moreover, only one hydrogen atom is available for the elimination reaction instead of two in the corresponding dihydrointermediate for DBT (if we do not exclude the possibility that a *cis*-β-hydrogen atom could be involved in the elimination process). All these effects could lower the reactivity of 46DMDBT compared to that of DBT regarding especially the DDS pathway.



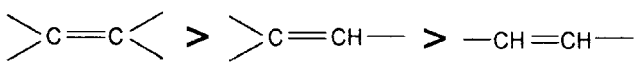
SCHEME 6. Approaches of the dihydrointermediates of DBT (a) and of 46DMDBT (b) to the catalytic center (compound 4 of Scheme 4A chosen as an example).

(d) Effect of the methyl groups on the distribution of the dihydroisomers. The presence of alkyl groups in positions 4 and 6 can modify the kinetics of hydrogenation of the substrate and the stability of the dihydroproducts. Consequently the distribution of the dihydroisomers obtained with DBT can be different from that of the analogous dihydroisomers obtained with 46DMDBT.

We can consider that the rates of hydrogenation of double bonds follow the sequence,



(the less substituted, the more reactive the double bond (22)) and that the stabilities of the dihydro compounds depend on the degree of substitution of their double bonds in the order



(the less substituted, the less stable the double bond). With this in mind and considering the fact that the thiophenic ring is preserved or not in the dihydrointermediates, we come to the conclusion that compounds 4 and 5 will most likely be disfavored both kinetically and thermodynamically (Table 9), with one of them (compound 4) even more disfavored in the case of 46DMDBT than in the case of DBT. Moreover these intermediates should be among the more reactive to undergo HYD since they possess a disubstituted double-bond (Scheme 4A). These observations could also explain why DBT is more reactive especially in the DDS pathway than 46DMDBT.

However, if this were a critical point, the addition of any cocatalyst which could help the migration of the double bonds in the dihydroisomers should in principle increase the reactivity of both DBT and 46DMDBT by producing compounds 4 and 5 as soon as they disappear through the DDS pathway. An increase in reactivity was indeed observed in the case of 46DMDBT when an acid component was added to a commercial hydrotreating catalyst, but not for DBT (9), which makes this explanation of the effect of the methyl groups less likely than the explanations based on steric hindrance (sections b and c above). Indeed, the reactivity of 46DMDBT can be improved by releasing steric hindrance through acid-catalyzed methyl migration, while no such effect can be expected with DBT (9).

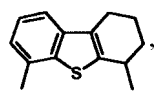
TABLE 9

Kinetics of Dihydroisomers Formation from DBT ($R = H$) and 46DMDBT ($R = CH_3$) and Expected Stabilities (See Scheme 4A for the Notation of the Dihydroisomers)

R	Kinetics	Expected stabilities
H	$1 \approx 2 \approx 3 > 4 = 6 > 5$	$1 \approx 3 \approx 7 > 2 > 4 \approx 6 > 5$
CH_3	$1 \approx 2 > 3 \approx 6 > 4 \approx 5$	$1 > 2 > 3 > 6 > 7 > 4 \approx 5$

(e) Effect of the methyl groups on the hydrogenation steps. As we have seen, the methyl groups in the 4 and 6 positions hinder the DDS pathway significantly but have practically no effect on the reactivity through the HYD pathway of DBT-type compounds.

As suggested by Schemes 4A and 4B, all the dihydrointermediates can undergo a subsequent hydrogenation step and lead to the HYD pathway. The dihydrointermediates which are expected to be the most reactive regarding subsequent hydrogenation are those with a disubstituted double bond (compounds 3–7). We note that compounds 4 and 5 which can lead to DDS can also undergo HYD quite readily. We also recall that tetrasubstituted double bonds are difficult to hydrogenate; they are also the most stable. This may explain why tetrahydrodibenzothiophene, probably the 1,2,3,4-tetrahydroisomer,



was found among the products. If we consider compounds 3, 4, and 7 formed from 46DMDBT, we could expect that the methyl group which is out of the plane of the molecule could hinder its adsorption and subsequent hydrogenation. This does not seem to be the case. The reason for this could be that in the case of a hydrogenation step the sulfur atom of the adsorbed reactant does not necessarily interact with a catalytic center which, on the contrary, is probably the case for C–S bond cleavage (the rate-limiting step of the DDS pathway).

Catalytic Centers

The foregoing discussion has shown that the numerous possible steps involved in the HDS of DBT-type molecules belong to two categories: (i) the addition of H_2 and (ii) C–S bond cleavage by elimination. It is therefore of interest to discuss the possible nature of the catalytic centers responsible for these two major steps. We will first consider a simplified representation of a MoS_2 particle neglecting possible surface reconstruction (23), a much debated matter, as well as the presence of surface carbon species (24). In addition, since it is not well known yet which of the two exposed edges ($\bar{1}010$ or $10\bar{1}0$) is the one containing the active centers, both will be considered in the following discussion. We will also consider that H_2 dissociates heterolytically on sulfide catalysts (25–28) and that hydrogen atoms (protons at least) are mobile on the surface of sulfide catalysts at temperatures as low as 80°C (28).

The main features that must be taken into account are that (i) the catalytic centers should be able to activate (adsorb) the aromatic ring(s) of the substrate molecules in order to make their hydrogenation possible, (ii) they must obviously adsorb and dissociate dihydrogen, and (iii) the catalyst should be able to retain S atoms resulting from the decomposition of the organic molecule (29, 30).

Therefore the catalytic centers should display the qualities (or functions) indicated below:

for H_2 addition

—at least one vacancy to absorb the substrate through at least one of its aromatic rings;

—one vacancy to adsorb a hydrogen atom with a hydride character;

—one neighboring S^{2-} atom to adsorb a hydrogen atom as a proton;

for C–S bond cleavage

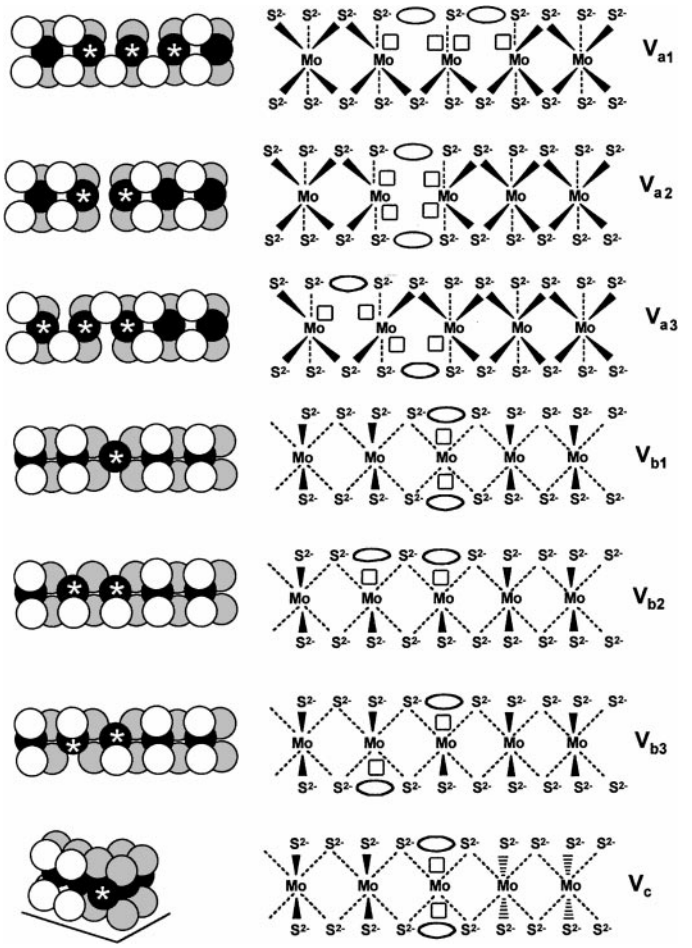
—one vacancy to adsorb the dihydro-, terahydro-, or hexahydrointermediate;

—one vacancy to "activate" (Lewis-type center) and retain the sulfur atom;

—one S^{2-} atom acting as a basic site.

Hence it could be considered that before adsorption of the reactants, the sites for the two steps should possess the same features, namely at least two vacancies and one neighboring sulfur atom. Such catalytic centers can be obtained by removing the sulfur atoms from the edges and corners of a MoS_2 slab with all its edges lined by sulfur atoms. Indeed, *ab initio* calculations indicate that the edges of a MoS_2 slab are more stable when terminated by sulfur atoms than by molybdenum atoms (31). We will consider the centers which, resulting from the removal of a minimum number of sulfur atoms, fit the requirements indicated above.

A catalytic center with at least two vacancies can be obtained by removing two sulfur atoms from the edges in the $\bar{1}010$ and $10\bar{1}0$ planes of an hexagonal MoS_2 slab (Scheme 7). For each edge plane, several configurations can be obtained. In the $\bar{1}010$ case, sites V_{a1}, V_{a2} and V_{a3} are easy to obtain according to Byskov *et al.* (31). In the $10\bar{1}0$ case, it is possible to obtain V_{b1} (or B site according to Siegel's proposal (32)), V_{b2} and V_{b3}. Other sites may also be obtained at corners. Such sites (e.g., V_c, Scheme 7) with two vacancies are like site V_{b1} except that on one side they have no S^{2-} neighbors in the front row. If we consider just these types of sites, it is clear that although they possess the same number of vacancies, they have neither the same number of S^{2-} neighbors nor the same geometry and will not generate the same steric constraints to the approaching substrate. The adsorption of H_2S on such centers will in principle inhibit the HYD pathway, but should also inhibit the DDS pathway. However, depending on whether the removed S^{2-} ions belong to the same or to different Mo atoms, the remaining S^{2-} atoms may not have the same



SCHEME 7. Catalytic centers with two sulfur vacancies on the $\bar{1}010$ and $10\bar{1}0$ edges. White or gray circles, sulfur atoms; black circles, molybdenum atoms; black circles with star, uncompletely coordinated molybdenum atoms. ⬭, sulfur vacancy; □, free coordination position.

basicity. Therefore, if the main requirement for the E_2 step (or C–S bond cleavage in general) is the basicity of the S^{2-} atoms involved in the elimination process (18, and references therein), the greater sensitivity of the DDS pathway to H_2S may be explained by supposing that H_2S (due to its acidic properties) adsorbs preferably on the most basic sites.

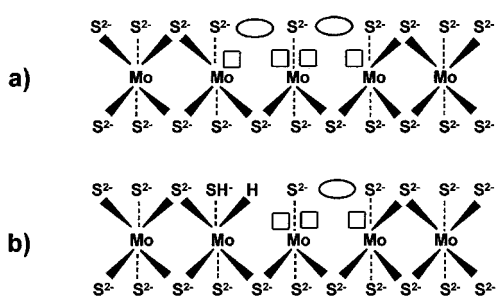
The difference between C–S bond cleavage and hydrogenation centers could also arise once the catalyst is under running conditions. Under these conditions, we could consider that the E_2 reaction (C–S bond cleavage) requires a "naked" site such as V_{a1} for instance (Scheme 8a), while the hydrogenation reaction would require the same type of center occupied, however, by dissociated hydrogen (Scheme 8b). A hydrogenating center must be capable of delivering two H atoms. This would be definitely so if, under these steady-state working conditions, dissociated hydrogen were available on the center. Interestingly, the adsorption of H_2 on a "C–S bond cleavage site" is able to transform

it into a "hydrogenation site", which is in accordance with the idea of site interconversion (33).

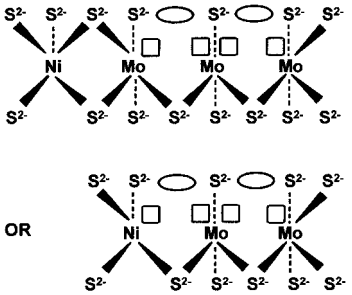
Possible Role of the Promoter

According to the interpretation of Chianelli (34) the promoter is supposed to decrease the strength of the bond between molybdenum and the sulfur atoms resulting from the decomposition of the organic molecules. In the same way it can be supposed that the promoter decreases the metal–sulfur bond in the sulfide itself (20, and references therein) and increases the electronic density on the sulfur atoms (35), which can also be interpreted in terms of an enhancement of the basicity of particular S^{2-} centers (18). This obviously has a consequence on the reactivity of both DBT and 46DMDBT as well as on their product distribution. Both depend at the same time on the properties of the catalysts (acid-base character in particular) and on the structure of the reactants (steric effects of the methyl groups for instance). A remarkable observation is that the product distribution and in particular the A_{DDS}/A_{HYD} selectivity obtained with DBT on the unpromoted catalyst are very much the same as those obtained with 46DMDBT on the promoted catalysts (Tables 5 and 7).

The main effect of the promoter is to enhance the rate of the DDS pathway (or the C–S bond cleavage activity in general). This is quite easy to understand if we assume that the C–S bond cleavage occurs through an elimination mechanism as described in Schemes 2 and 5. Such a mechanism involves the attack of a hydrogen atom (in β position relative to the sulfur atom in the organic molecule) by a sulfur anion acting as a basic site. Therefore if, as suggested, the promoter enhances the basicity of the sulfur anions, it should favor C–S bond cleavage. The effect is spectacular in the case of DBT with which there are no significant steric constraints. As explained in the foregoing discussion, on the unpromoted catalyst the C–S bond cleavage reactions involved in the HDS of DBT seem to be slow compared to the hydrogenation reactions: the DDS pathway participates to a minor degree to the overall process (Table 5), which means that step 7 (Scheme 3) is slow. Regarding the HYD pathway which is predominant, a large amount of intermediate hydrogenated compounds is found (tetrahydrodibenzothiophene and even traces of hexahydrodibenzothiophene, Table 7), which means that steps 4 (Scheme 3) is also relatively slow compared to step 2. This is even more so with 46DMDBT, the difficulty to cleave the C–S bond being amplified by steric constraints.



SCHEME 8. Examples of catalytic centers. C–S bond cleavage center, naked V_{a1} site (a); hydrogenation center, V_{a1} with adsorbed H_2 (b).



SCHEME 9. Possible promoted C–S bond cleavage centers.

When the promoter is added to molybdenum the DDS pathway becomes predominant for DBT and the amount of intermediate hydrogenated compounds (tetrahydrodibenzothiophene or hexahydrodibenzothiophene) is much smaller at similar conversion rates than with the unpromoted catalyst. The tetrahydrodibenzothiophene/cyclohexylbenzene molar ratio decreases significantly (Table 7). Hence it can be concluded, at least as far as DBT is concerned, that the C–S bond cleavage is no longer rate-limiting. It is not so with 46DMDBT probably because of steric constraints. The DDS pathway represents in this case a minor contribution even with the promoted catalysts. On the other hand, if the amount of hydrogenated intermediates is also smaller on the promoted catalysts, it can be seen that, at similar HYD conversion (about 7.5% on NiMo/alumina for instance), the tetrahydrodimethyldibenzothiophene/methylcyclohexyltoluene molar ratio is much greater than the tetrahydrodibenzothiophene/cyclohexylbenzene molar ratio. This explains why 46DMDBT behaves with promoted catalysts more or less in the same way as DBT on the unpromoted catalyst, and why we have approximately the same product distribution in both cases. The reason is that in both cases C–S bond cleavages are slow compared to the hydrogenation steps whereas with DBT on promoted catalysts the rate of the C–S bond cleavages is increased to such an extent that the hydrogenation steps become rate-limiting for the HDS.

It can therefore be concluded that a typical C–S bond cleavage center on a promoted catalyst should contain at least a promoter atom in the vicinity of a sulfide anion (Scheme 9).

CONCLUSION

The results obtained in the present work indicate that promoted and unpromoted catalysts have different

properties regarding the two main pathways (DDS and HYD) of the HDS of DBT and 46DMDBT. This means that attributing the differences in reactivity of these compounds to steric effects upon adsorption on the catalytic surface is not correct. A detailed analysis of the activities and product distributions for the transformation of DBT and 46DMDBT on sulfided Mo, CoMo, and NiMo supported on alumina catalysts indicates that the origin of these differences lies in the kinetics of transformation of these two compounds. For both reactants the DDS and HYD pathways can be decomposed into H_2 addition steps and C–S bond cleavage by elimination (or E_2) steps. Depending on the reactant and on the catalyst the rate-determining step may be different.

On the unpromoted catalyst, DBT and 46DMDBT have similar reactivites because of the fact that C–S bond cleavages are rate-limiting for both reactants. 46DMDBT is even slightly more reactive than DBT although it leads mainly to hydrogenation products.

On the promoted catalysts, DDS becomes the main pathway for the HDS of DBT. The hydrogenation of DBT into dihydrodibenzothiophene is the rate-limiting step for the two pathways. With 46DMDBT, the effect of the promoter on C–S bond cleavage is limited because of steric constraints. Consequently, C–S bond cleavage remains the rate-limiting step, for the DDS pathway in particular. The presence of the methyl groups in 46DMDBT changes considerably the reactivity regarding the two pathways. The low reactivity of 46DMDBT is mainly due to the inhibition of the DDS pathway (which in this case means C–S bond cleavage). Several explanations can be proposed for this lower reactivity:

—a steric hindrance by the methyl groups to the adsorption of the dihydrointermediates;

—the fact that only one H is available for the elimination step in 46DMDBT;

—a steric hindrance by the methyl groups during the E_2 elimination step in the dihydrointermediates;

—an effect of the methyl group on the acidity of the H atom in the position 4 (or 6).

Two types of catalytic centers can be considered to account for the results obtained, including the effect of hydrogen and of hydrogen sulfide:

—the sites involved in the hydrogenation steps would be composed of a vacancy associated with a SH group and with a hydrogen atom adsorbed on a molybdenum atom;

—the sites involved in the E_2 direct desulfurization route and more generally in C–S bond cleavage would be composed of two vacancies associated with a sulfur anion.

The two centers could be considered as basically identical (in terms of Mo and S atoms involved) except that adsorbed H_2 should be considered as part of the hydrogenation center.

The main effect of the promoter is to improve the C–S bond cleavage activity of the MoS_2 on alumina catalyst, presumably by increasing the basicity of certain sulfur anions shared between the Mo and the promoter (Co or Ni).

ACKNOWLEDGMENTS

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