Mechanistic considerations on the involvement of dihydrointermediates in the hydrodesulfurization of dibenzothiophene-type compounds over molybdenum sulfide catalysts

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The mechanism of the hydrodesulfurization of dibenzothiophene-type compounds involving their dihydroderivatives as intermediates was examined in the light of previous experimental results dealing with the effect of cobalt and nickel promoters on the selectivity of the reaction. It is suggested that the orientation of the hydrodesulfurization reaction regarding the so-called "direct desulfurization" or "hydrogenation" pathways depends on various factors: the distribution of the dihydrointermediates (two of them only among nine possible isomers can lead directly from dibenzothiophene to biphenyl); the availability of dissociated hydrogen on the catalytic centers on which they adsorb and the basicity of the sulfur anions associated to the catalytic centers.

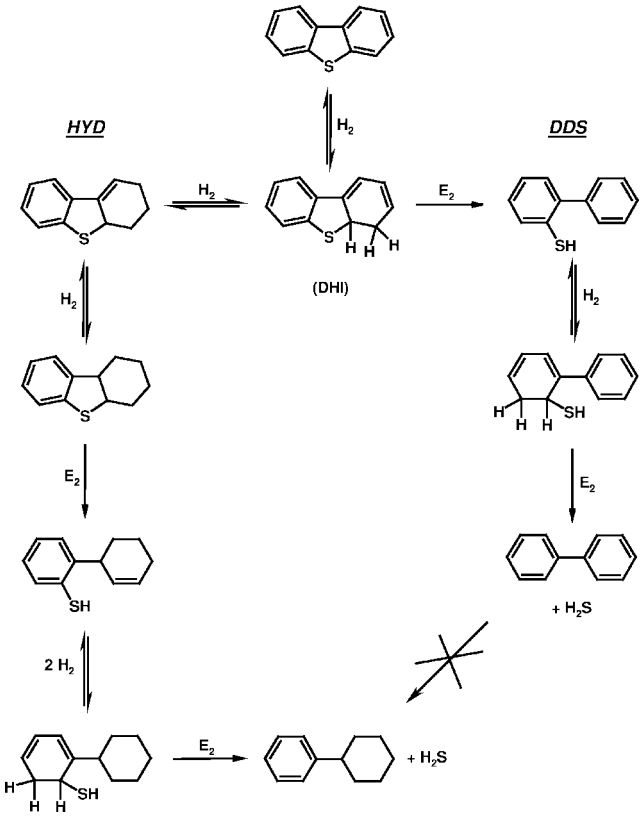
KEY WORDS: dibenzothiophene; hydrodesulfurization; sulfide catalysts; mechanism; selectivity; promoter effect

1. Introduction

The decomposition of dibenzothiophene and that of its alkylderivatives are widely used as model reactions for the deep hydrodesulfurization (HDS) of diesel fuels [1,2].

It is well established that on typical sulfided hydrotreating catalysts (CoMo and NiMo/alumina) the reaction takes place through two parallel pathways, one leading to biphenyl-type products and designated as the "direct desulfurization" (DDS) pathway, the other leading to tetrahydrodibenzothiophene-type products and eventually to cyclohexylbenzene-type products and designated as the "hydrogenation" (HYD) pathway ([2] and references therein) (scheme 1). This is based on the fact (which however is still a matter of controversy [2]) that from dibenzothiophene, both biphenyl and tetrahydrodibenzothiophene are primary products and that under HDS conditions biphenyl is not converted readily into cyclohexylbenzene. It must also be noted that the second bond cleavage in the HYD pathway does not require the second aromatic ring to be fully hydrogenated and that it occurs probably through a DDS-type process since it gives cyclohexylbenzene instead of dicyclohexyl. However, as this part of the reaction scheme is not critical for HDS it is often ignored.

On the other hand, it was shown recently [3,4] that when a promoter (Co or Ni) was associated to MoS_2/alumina, the relative contributions of the two pathways to the HDS



Scheme 1. The two possible pathways (DDS and HYD) with a dihydrodibenzothiophene of category B (see scheme 2) as intermediate.

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Table 1
Activities of Mo, CoMo and NiMo/alumina catalysts for the transformation of dibenzothiophene 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 regarding the direct desulfurization pathway, A_{HYD}: activity regarding the hydrogenation pathway, A_{HDS}: activity regarding desulfurization (mol h^{-1} kg^{-1}). S_{DDS} and S_{HYD} selectivities (%) for the DDS and HYD pathways, respectively. Conversions ∼15 mol% [4].

	Catalyst		
	Mo	CoMo	NiMo
Activity			
A_T	0.4	7.2	8.0
A_{DDS}	0.1	6.3	6.8
A_{HYD}	0.3	0.9	1.2
A_{HDS}	0.15	6.5	7.1
Selectivity			
S_{DDS}	25	87	85
S_{HYD}	75	13	15
Promoting effect			
Total		18	20
On HYD		3	4
On DDS		63	68

Table 2
Product distribution for the transformation of dibenzothiophene over Mo, CoMo and NiMo/alumina catalysts at 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 [4].

		Catalyst		
		Mo	NiMo	CoMo
Conversion (mol%)				
Total		8.7	33.0	52.2
DDS		2.0	25.7	45.2
HYD		6.7	7.3	7.0
Product distribution (mol%)				
DDS	BiP	2.0	25.7	45.2
HYD	THDBT	4.7	2.3	1.9
	HHDBT	0.6	–	–
	CHB	1.1	5.0	5.1
	DCH	0.3	–	–
THDBT/CHB		4.3	0.5	0.4

Table 3
Reactivity ratio between dibenzothiophene and 4,6-dimethyldibenzothiophene on the Mo, CoMo and NiMo/alumina catalysts at 340 °C, 3.0 MPa H_2. Reactant pressure 0.01 MPa, H_2S pressure 0.05 MPa. Total: overall reaction, DDS: direct desulfurization pathway, HYD: hydrogenation pathway. Conversions ∼15 mol% [4].

	DBT/46DMDBT		
	Total	DDS	HYD
Mo	0.6	2.0	0.5
CoMo	6.0	31.5	0.9
NiMo	4.7	22.6	0.8

of dibenzothiophene were completely inverted (table 1): on the Mo catalyst the HYD pathway was predominant whereas on the CoMo or NiMo catalysts DDS was the main pathway. Incidentally this makes the reaction a powerful tool to probe the efficiency of the promoter in hydrotreating catalysts. Actually, the presence of the promoter led to a tremendous enhancement of the rate of the DDS pathway (by a factor greater than 60). In comparison, the enhancement by the promoter of the rate of the HYD pathway was quite moderate (factor less than 5). This was attributed to a much greater enhancement of the rate of C–S bond cleavage than of the rate of the hydrogenation steps, which could also be assessed by looking at the product distribution of the HYD pathway [4]. Actually, it could be seen that when the promoter was present the ratio cyclohexylbenzene/tetrahydrodibenzothiophene (at similar conversions through the HYD pathway) was much greater than on the unpromoted catalyst (table 2). This is in accordance with the assumption that the C–S bond cleavages are much more accelerated than the hydrogenation steps. Another very important point is that on promoted HDS catalysts, 4,6-dimethyldibenzothiophene was found to be five to ten times less reactive than dibenzothiophene (table 3). Because of steric and/or electronic effects due to the methyl groups, the influence of the promoter on the DDS pathway was much less significant with 4,6-dimethyldibenzothiophene than with dibenzothiophene. Consequently both reactants had similar reactivities regarding the HYD pathway but dibenzothiophene was much more reactive than 4,6-dimethyldibenzothiophene regarding the DDS pathway.

A proposal concerning the reaction scheme and mechanism was made in the early eighties by Singhal et al. [5]. The authors suggested that both pathways could have a common intermediate, namely a dihydroderivative of dibenzothiophene. This is quite straightforward concerning the HYD pathway for which the first step is necessarily the formation of such an intermediate. This can also be considered for the DDS pathway for which it can be assumed that the cleavage of the C–S bonds occurs via an acid–base-catalyzed elimination process in such a dihydrointermediate leading to the rearomatization of the partially hydrogenated cycle, as shown in scheme 1. We will see in section 2 that several dihydroisomers can be formed from dibenzothiophene and that only two of them can lead to both pathways. Actually the elimination process is only possible if the carbon atom bearing the sulfur atom as well as one of the two carbon atoms next to it are in the sp^3 hybridization. It must be noted that this proposal does not mean that there is no other possibility of obtaining a C–S bond cleavage ending with aromatic rings in the product. In particular one could envisage the insertion of a metal in the C–S bond as proposed by several authors on the basis of organometallic chemistry [6,7].

The aim of this work was to better understand the role of the promoter in hydrotreating catalysts as well as the inhibiting effect of alkyl groups in the 4 and 6 positions in dibenzothiophene. According to the proposal made by Singhal

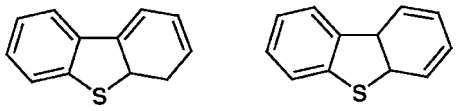
et al. [5], it can be assumed that dihydrocompounds are key intermediates in the HDS of dibenzothiophene and of its alkylderivatives. Accepting this proposal, we examined in detail the mechanism of the various steps of the reaction in order to evaluate the possible consequences of the involvement of such intermediates in the HDS of dibenzothiophene-type compounds.

2. Reaction scheme

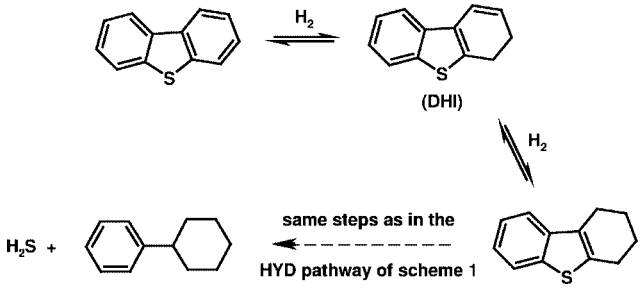
We reported recently [4] that nine different dihydrodibenzothiophene isomers could be formed from dibenzothiophene. These intermediates can be classified into two categories: those which can only undergo the HYD pathway (category A) because they do not possess a hydrogen atom available for elimination in a β-position with respect to the sulfur atom, and those (scheme 2) which can undergo both pathways (category B) because they possess such hydrogen atoms. Therefore, unless we consider that all of these nine derivatives interconvert rapidly under the HDS conditions and constitute a mixture in thermodynamic equilibrium which can behave as a single compound, we can imagine eleven parallel reactions leading from dibenzothiophene to HDS products.

Scheme 3 shows the two initial steps of a typical reaction sequence for the dihydrointermediates belonging to category A; the rest of the sequence is quite similar to the HYD pathway shown in scheme 1. Note that generally only one tetrahydroproduct is detected. For the sake of simplicity this compound is generally represented as 1,2,3,4-tetrahydrodibenzothiophene and is often considered as the intermediate in the formation of cyclohexylbenzene since the latter seems to be produced at the expense of the former. Obviously this is probably not the only tetrahydroisomer to be involved in the HDS of dibenzothiophene through the HYD pathway. However, it seems reasonable to assume that 1,2,3,4-tetrahydrodibenzothiophene which has a tetrasubstituted double bond and in which the aromatic character of the heterocycle is preserved is the one which is actually observed because it is the most stable and the less reactive among all of the possible tetrahydrodibenzothiophene isomers.

Scheme 1 describes the HDS of dibenzothiophene with one of the two compounds belonging to category B as intermediate. It shows how these intermediates can be involved in the two HDS pathways, one leading to biphenyl (the DDS pathway), the other to cyclohexylbenzene (the HYD pathway). On the unpromoted catalyst where the HYD pathway is predominant, it can be assumed that the rate-limiting step of the HYD pathway is the hydrogenation of dibenzothiophene into the dihydroproduct (which breaks the aromaticity of the ring), while for the DDS pathway the rate-limiting step is presumably the C–S bond cleavage. With the promoted catalysts, the rate of the DDS pathway is significantly enhanced. Therefore it can be concluded that C–S bond cleavage is no longer rate-limiting and that both pathways have the same rate-limiting step, i.e., the hydrogenation of dibenzothiophene into the dihydrointermediate [4].



Scheme 2. Structures of the dihydrodibenzothiophene isomers (category B) which can undergo both the HYD and DDS pathways.

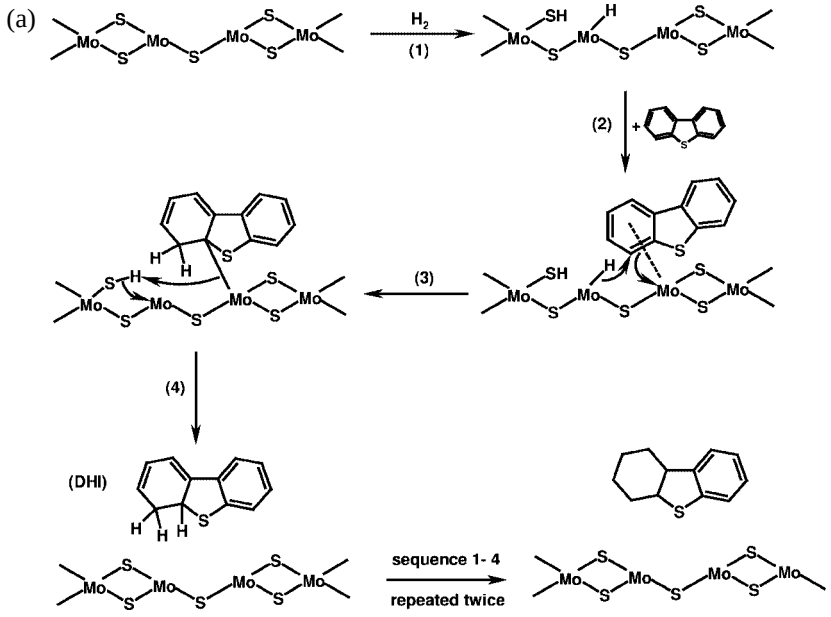


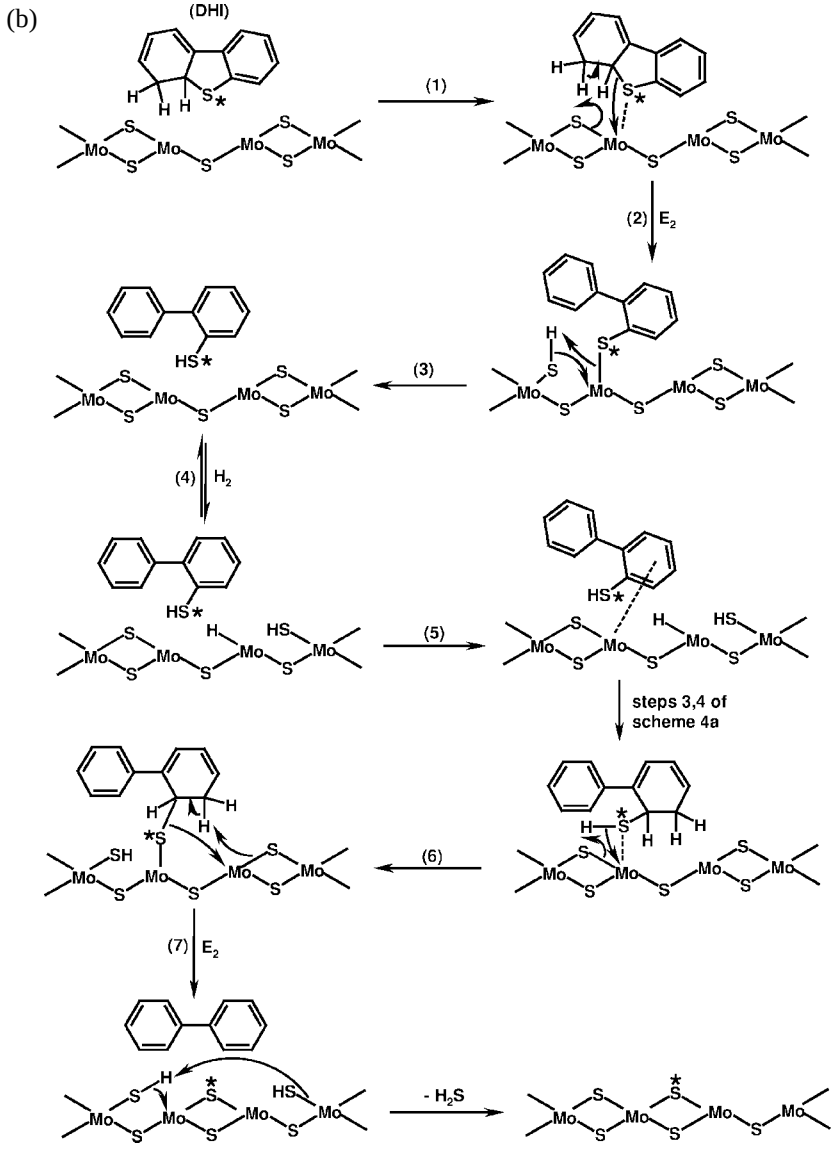
Scheme 3. The HYD pathway of the hydrodesulfurization of dibenzothiophene involving a dihydrointermediate (DHI) of category A.

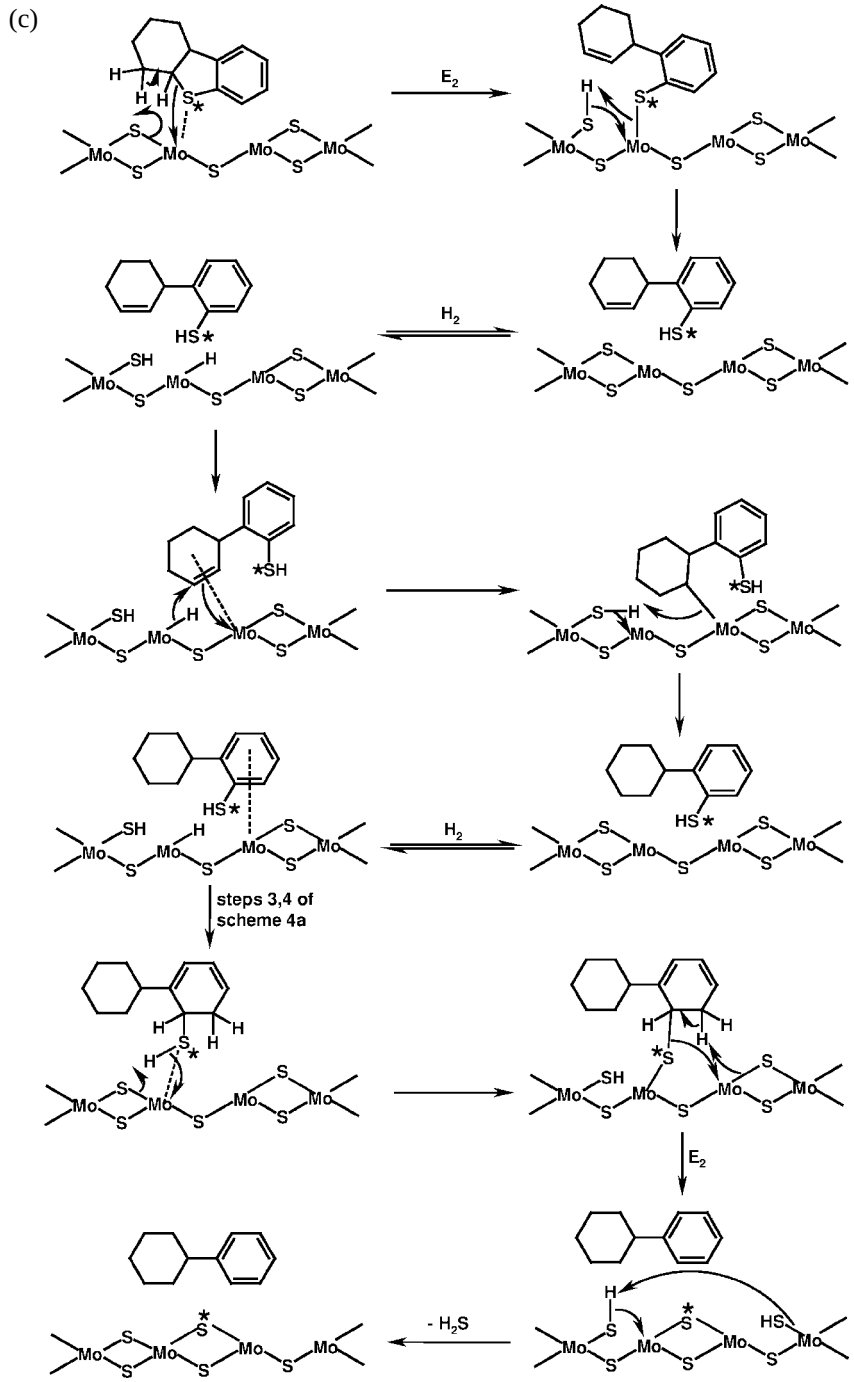
Anyhow we can conclude that in the HDS of dibenzothiophene on a promoted catalyst the reactivity of any dihydrointermediate with regard to the HYD pathway is much lower than the reactivity of the B isomers towards DDS. Actually, the DDS contribution is largely predominant despite the fact that all the isomers of both categories can contribute to the HYD pathway. As we will see in section 3, the difference in reactivity of the dihydrointermediates of category B regarding the DDS or HYD pathways may depend on the availability of dissociated hydrogen on the centers on which they adsorb. Indeed, the coverage by hydrogen atoms of the catalytic centers is not complete as indicated by the apparent kinetic order with respect to hydrogen which is not equal to 0 but is close to 1 [4]. Moreover, if the dihydrointermediates of category B react on the same center as the one on which they are produced it can be considered that there is no longer dissociated hydrogen available on this center and consequently that they are bound to react through the DDS pathway. This is probably what is occurring, otherwise these dihydrointermediates which have a conjugated diene structure would react very readily through the HYD pathway. The latter can only occur if they desorb and readsorb on a center on which dissociated hydrogen is available or if adsorbed hydrogen atoms diffuse to the catalytic center before the adsorption state of the molecule changes in order to make the DDS pathway possible (see next section). Indeed, hydrogen atoms are mobile on the surface of the sulfide catalysts under the conditions of the reaction [8]. Nevertheless, it can be assumed that because of the adsorbed dihydrointermediate, the access of new hydrogen atoms to the same center can be hindered, which would favour the DDS pathway.

3. Detailed reaction mechanism

In scheme 4 (a)–(c) we present the details of the mechanism of the HDS of dibenzothiophene on the catalyst surface. For this purpose we use a simplified representation of


(a)
H2
(1)
(2)
(3)
(4)
(DHI)
sequence 1- 4
repeated twice


(b)
(DHI)
(1)
(2) E2
(3)
(4) H2
(5)
steps 3,4 of
scheme 4a
(6)
(7) E2
- H2S



Scheme 4. Hydrodesulfurization of dibenzothiophene on molybdenum sulfide. (a) Mechanism of the hydrogenation steps leading to a dihydrodibenzothiophene isomer (DHI), then to hexahydrodibenzothiophene. (b) Mechanism of the DDS pathway leading from a dihydrodibenzothiophene isomer (DHI) to biphenyl. (c) Mechanism of the HYD pathway leading from a hexahydrodibenzothiophene to cyclohexylbenzene. (∗) Sulfur atom belonging to the organic molecule.

a catalytic center made of a sulfur vacancy associated to two Mo atoms and of an adjacent sulfur anion [4,9]. We will not consider here that a second sulfur vacancy is necessary to adsorb the reactant or product either by π-bonding of one benzenic ring or by coordinate-covalent bonding of the sulfur atom.

Scheme 4(a) describes the hydrogenation of dibenzothiophene into one of the dihydrointermediates of category B (DHI). Taking into consideration both theoretical calculations [10] and kinetic modelisation [9] as well as experimental results obtained in tracer experiments [11,12], we assume that the first step of the reaction is the heterolytic dissociation of H_2 in which the proton adsorbs on the sulfur anion and the hydride on one coordinatively unsaturated Mo atom. The second step is the adsorption of dibenzothiophene through one of its aromatic rings on the same sul-

fur vacancy (the free coordination position of the second Mo atom). This draws the π-electrons away from the aromatic ring and makes the addition of the H atom with a hydride character possible [9] (step 3). This step is then followed by the addition of the proton adsorbed on the sulfur anion (step 4) and the dihydrointermediate (DHI) can desorb.

If DHI readsorbs on a center on which H_2 is available, the HYD pathway can proceed by formation of a tetrahydro- and eventually of a hexahydrointermediate. Note that if we were dealing with a dihydrointermediate belonging to category A, the reaction would necessarily follow this pathway.

Instead of that, if DHI remains adsorbed on the same center where there is no longer dissociated H_2 available or if it readsorbs on a center where there is no dissociated H_2 available, the DDS process can occur (scheme 4(b)). After adsorption of DHI (presumably through the S atom), C–S bond cleavage with rearomatisation can take place (step 2, scheme 4(b)). Then, the intermediate thiophenol can desorb (step 3) and has to readsorb through the ring bearing the SH group on a center on which dissociated H_2 is available (step 5). After hydrogenation of the double bond bearing the SH group, the new dihydrogenated intermediate can readsorb through its S atom on a H-free center (step 6) and the second C–S bond cleavage can take place (step 7). The H-free center is recovered after desorption of H_2S. Note that according to this scheme, the S atom which is removed is not the one coming from the organic molecule but a S atom initially present on the catalyst, which is in accordance with the results of ^{35}S tracer experiments [13,14]. It has to be mentioned that the intermediate thiophenol was not detected among the products which is not surprising since *o*-phenylthiophenol was found to be very reactive under conditions similar to ours [15].

As shown in scheme 1, the HYD pathway does not lead to dicyclohexyl but to cyclohexylbenzene. This means that once the hexahydrointermediate is formed as depicted in scheme 4(a), it is not necessary that the second aromatic ring be hydrogenated to remove the sulfur atom from the molecule. A possible reaction sequence for the transformation of the hexahydrointermediate into cyclohexylbenzene is shown in scheme 4(c). This sequence leads first to a C–S bond cleavage on the side of the saturated ring, then to a second C–S bond cleavage to eliminate the SH group from the benzenic ring and involves elementary steps which are similar to the ones involved in scheme 4 (a) and (b). For reasons which are not clear yet, this second bond cleavage occurs through the same process as in the DDS pathway.

The orientation of the hydrodesulfurisation of dibenzothiophene (DDS versus HYD) will be the result of a large number of parallel reactions and will therefore depend on numerous factors:

(i) The proportion of the dihydrointermediates belonging to category A (which lead to the HYD pathway only) to the dihydroisomers belonging to category B (which can lead to both HYD and DDS). Moreover, it is very likely that the dihydroisomers can isomerize into each other under the reaction conditions.

(ii) The selectivity (DDS versus HYD) of the transformation of the B isomers. This selectivity will in turn depend on various factors which will be examined below.

However, we can assume that the factors which will influence the reactivity of the B isomers regarding the HYD pathway will be the same as the factors which govern the reactivity of the A isomers regarding the same reaction. Moreover, we can expect that for instance the presence of the promoter will have no effect on the distribution of the dihydroisomers. Consequently, we can consider that the discussion concerning the effect of the promoter on the DDS versus HYD selectivity comes down to the discussion concerning the DDS/HYD orientation of the transformation of the B isomers.

As already pointed out several factors can influence the orientation of the reaction (DDS versus HYD) of a given B isomer:

(a) the basicity of the anions in the vicinity of the vacancy and the acidity of the SH groups resulting of the heterolytic dissociation of H_2 on the vacancy–sulfur anion catalytic pairs (both properties being connected);

(b) the availability and reactivity (see item (a)) of hydrogen on the catalytic centers;

(c) steric hindrance.

Various catalytic centers can fulfil the requirements for HDS in terms of vacancies [4] but because their locations and geometries are different, they may have different acid–base properties and they may induce different steric constraints. Therefore, they can adsorb hydrogen more or less readily and they may be better adapted to adsorb the organic molecule in one way (π-bonding of one benzenic ring, for instance) or the other (S-bonding, for instance). Thus depending on which catalytic center the dihydrointermediate will adsorb on, it may react differently (through DDS or HYD).

As we have seen, the presence of the promoter (Co or Ni) has a tremendous influence on the selectivity of the reaction, especially in the case of dibenzothiophene. It is generally accepted that the promoter weakens the Mo–S bond in the catalyst [1] or increases the electron density on the sulfur atoms in the solid [16]. Consequently, the S anions of promoted catalysts can be expected to be more basic than those of the unpromoted catalyst [4] and therefore to be more active in C–S bond cleavage. However, at the same time the number of sulfur vacancies on the promoted catalysts should be higher and the S anions should adsorb hydrogen more readily [17]. Consequently, the HYD pathway should also be promoted. This is actually what is observed but to a much lesser extent than for the DDS pathway, which can be easily understood: the S anions being more basic, the corresponding SH groups (the conjugated acid) resulting from the heterolytic dissociation of H_2 are less acidic and therefore less reactive.

Moreover, we can see (table 3) that methyl groups in the 4 and 6 positions in dibenzothiophene can annihilate to a large

extent the effect of the promoter on DDS. The origin and nature of this effect were discussed in a previous paper [4].

4. Conclusion

It is proposed that the DDS/HYD selectivity of the HDS of dibenzothiophene-type compounds depends on the distribution of the dihydroisomers which are formed in the first step of the reaction as well as on the nature of the catalytic centers on which they adsorb. Considering the various steps of the reaction mechanism it is suggested that the DDS/HYD selectivity depends in particular on the basic character of the sulfur anions belonging to the catalytic centers and on the availability of hydrogen on these centers, both depending in turn on the presence or absence of the promoter in the catalyst. The HDS of dibenzothiophene which has actually been used for many years to test sulfide catalysts for HDS activity ([1,2] and references therein) can also be considered as an excellent reaction to probe through its selectivity Mo-based hydrotreating catalysts for the existence of a promotion by other elements.

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