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Hydrotreating catalysts containing zeolites and related materials—mechanistic aspects related to deep desulfurization

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Abstract

The deep hydrodesulfurization (HDS) of diesel fuels requires the decomposition of refractory compounds such as 4,6-dimethyldibenzothiophene (46DMDBT). There is a general agreement on the fact that the low reactivity of these compounds is due to steric hindrance of the transition state leading to C–S bond cleavage, which annihilates the effect of the promoter to a large extent. The consequence is that their so-called "direct desulfurization pathway" is particularly inhibited.

Various issues were considered to circumvent the difficulty to eliminate the HDS-resistant molecules and therefore to reach deep desulfurization. Two of them at least consist in designing new hydrotreating catalysts (in addition to the improvement of the alumina-supported conventional catalysts): (i) catalysts with improved hydrogenation properties; (ii) bifunctional catalysts containing an acid component. The main findings obtained with the first class of catalysts are summarized. On these catalysts HDS was found very sensitive to the inhibition by aromatics. The studies regarding the second category of catalysts are analyzed in more detail. Several techniques were used to introduce acid components, including mesoporous materials, in hydrotreating catalysts: physical mixing, binding, deposition of sulfide precursors on an acid–alumina support, deposition of sulfide precursors on an acidic support. Most of these catalysts were found more active than conventional catalysts in the HDS of compounds such as 46DMDBT. The various interpretations of the effect of the acid component are reported and discussed. It is however generally accepted that the improvement of the reactivity, on this category of catalysts, of the HDS-resistant compounds is due to their acid-catalyzed isomerization and disproportionation into more reactive derivatives. When acidic materials were used directly as supports it was difficult to obtain a good association of, for instance, molybdenum, with promoters. Nevertheless, in certain cases catalysts were obtained which were more active than conventional catalysts in the HDS of compounds such as 46DMDBT or of gas oils containing such impurities. However although the catalysts containing acid components proved efficient in hydrotreating various kinds of oils, they suffer several drawbacks such as deactivation by coke deposition and inhibition of HDS by aromatics. Moreover nitrogen impurities which inhibit HDS even with conventional catalysts may also impede seriously their use in practice.

Keywords: Hydrodesulfurization; Dibenzothiophene; 4,6-Dimethyldibenzothiophene; Bifunctional catalysts; Molybdenum sulfide; Cobalt–molybdenum sulfides; Nickel–molybdenum sulfides; Zeolites; Mesoporous materials

1. Introduction

The possibility of using zeolites and related materials as supports for hydrotreating catalysts has been

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considered since many years with the hope of obtaining better dispersed and hence more efficient active phases. However many difficulties were encountered regarding in particular the preparation and sulfidation of the materials as well as the introduction of promoters. As an introduction to this review dealing more specifically with deep desulfurization, we will just summarize the main observations available from the literature regarding the general aspects of the association of sulfides with zeolites and related materials.

The effect of the method of preparation of the catalysts on their activity in hydrogenation and hydrodesulfurization is one of the parameters which have been examined in detail. In this respect it was shown that when the conventional method of introduction of molybdenum (with ammonium heptamolybdate) was used a significant part, if not the totality, of the metal would stay outside the microporous structure of the zeolite [1,2]. The reason for this is that the Mo species is anionic so that it cannot exchange with the cations of the zeolite and, in addition is bulky enough not to penetrate its pores readily. Moreover the metallic species have a tendency to migrate outside the structure upon sulfidation [2,3]. In order to circumvent the inconveniences of the impregnation with ammonium heptamolybdate, vapor phase deposition of $Mo(CO)_6$ was used [1,4–6]. In general better dispersed Mo species and more active catalysts were obtained.

It is also very difficult to take advantage of the addition of promoters to Mo when zeolites are used as supports [4,7]. This was shown by Vrinat et al. [4] with catalysts obtained by introducing Co in HY and NaY zeolites by cationic exchange and Mo through vapor phase deposition of $Mo(CO)_6$. However, Cid et al. [7–9] found that Co and Mo did not interact when introduced successively by impregnation but that the catalysts were more active when Co was introduced by cationic exchange before Mo deposition although the promotion effect was much weaker than with alumina-supported catalysts. Okamoto ([10] and references therein) reported also a promotion effect with CoMo/NaY catalysts obtained by using carbonyl precursors. The synergy effect was attributed to the formation of $Co_2Mo_2S_6$ clusters inside the zeolite pores. More recently, Taniguchi et al. [11] reported a significant promotion effect in the hydrodesulfurization (HDS) of benzothiophene when Ni and Mo were introduced simultaneously in the zeolite by cationic exchange using $[Mo_3NiS_4Cl(H_2O)_9]^{3+}$ clusters.

It was also shown that the acidity of the support could play a major role in the catalytic activity. For instance, the initial activity in the HDS of thiophene of metal sulfides supported on HNaY zeolites increased with the increasing acidity of the support [12], which according to the authors could not be attributed to an increase in the metal sulfide dispersion.

Moreover in connection with the deep desulfurization of diesel fuels the pore size is also of major importance and the interest for mesoporous materials is obvious. Actually, if the metal sulfide is located inside the pores of the support, the organic sulfur molecules to be decomposed have to enter these pores, which, in the case of zeolites, may be difficult with bulky molecules like 4,6-dialkyldibenzothiophenes. For instance, it was found that the use of HZSM5 as a support had no effect on the HDS of 4,6-dimethyldibenzothiophene (46DMDBT) [13] because its pore apertures are too small.

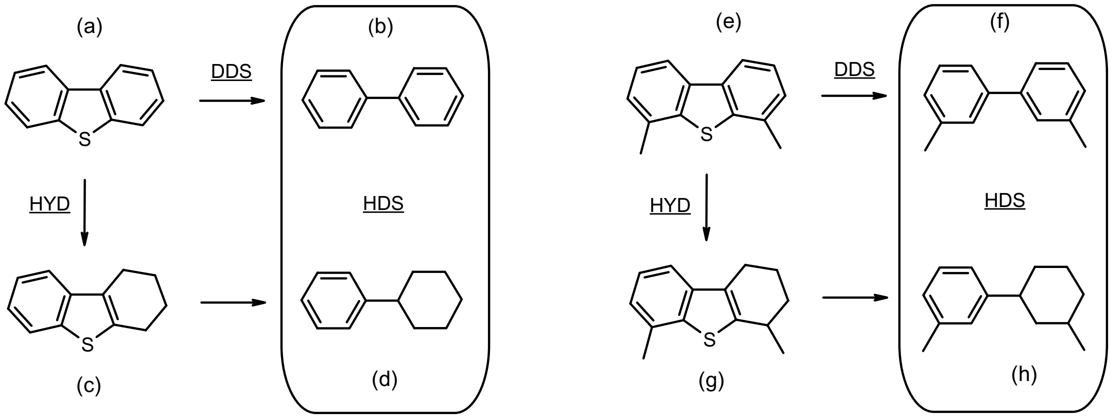
This paper will focus essentially on mechanistic studies in relation with deep HDS carried out on catalysts containing zeolites or related materials.

2. The refractory character of 4,6-dialkyldibenzothiophenes and its possible origin

In recent years the issue of associating sulfides and zeolites or related materials with an acidic character has gained a renewal of interest in relation with the necessity of deep desulfurization of diesel fuels and more specifically of the decomposition of refractory sulfur impurities.

Actually, because of the presence of resistant molecules such as 46DMDBT the complete desulfurization of gas oils is very difficult to reach with the catalysts used at present in the industry [14,15]. Indeed, while on commercial catalysts such as sulfided CoMo or NiMo/alumina, 46DMDBT is 4–10 times less reactive than dibenzothiophene (DBT) [14–23], the latter and most of the other dialkyldibenzothiophene isomers are relatively easy to convert [16–18,24,25].

Apart from this difference in reactivity, DBT (a, Scheme 1) and 46DMDBT (e) transform through the same reaction scheme composed of two parallel



Scheme 1. Transformation of DBT and 46DMDBT on hydrotreating catalysts. DDS pathway; HYD; HDS.

pathways [18,20–23,26–29]: the direct desulfurization (DDS) pathway yielding biphenyl (b) or 3,3′-dimethylbiphenyl (f), and the “hydrogenation” pathway (HYD) yielding cyclohexylbenzene (d) or 3-(3′-methylcyclohexyl)-toluene (h) with a tetrahydrogenated compound (c or g) as an intermediate. Several authors [20,23,27,30] have proposed that both pathways had a dihydrodibenzothiophene derivative as a common intermediate (Scheme 2). This intermediate can indeed transform in two different manners: (i) through further hydrogenation into tetrahydro- and hexahydrodibenzothiophene and after C–S bond cleavages eventually into cyclohexylbenzene (this constitutes the HYD pathway); (ii) through, first a C–S bond cleavage followed by the partial hydrogenation of the benzenic ring bearing the SH group to form a second dihydrointermediate which subsequently will give biphenyl through C–S bond cleavage with rearomatization (this constitutes the DDS pathway). In a recent report, Mijoin et al. [30] proposed a detailed description of the process by supposing that it involved a series of hydride and proton additions (assuming a heterolytic dissociation of H_2 [31]) and C–S bond cleavages through an elimination mechanism (as suggested by Singhal et al. [27]).

Actually if one looks into more detail at the difference in reactivity on commercial catalysts between DBT and its 4,6-substituted dialkyl derivatives, it can be seen that the reactivity along the HYD pathway is hardly affected by the presence of the alkyl groups in the 4 and 6 positions but that the DDS pathway is severely inhibited [13,19,21,23] as shown in Fig. 1. This appeared also in the activation energies reported by Kabe et al. [19] which are about the same for the

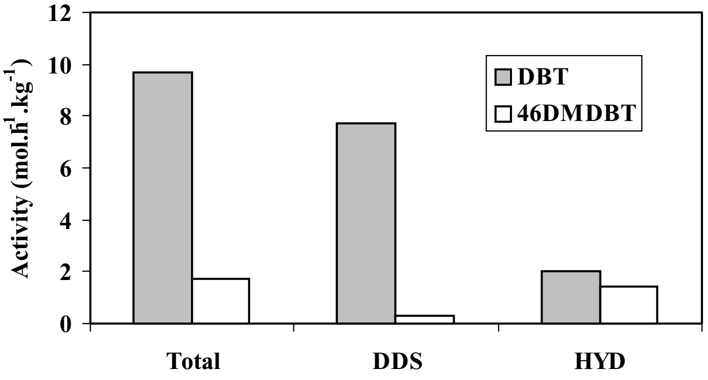
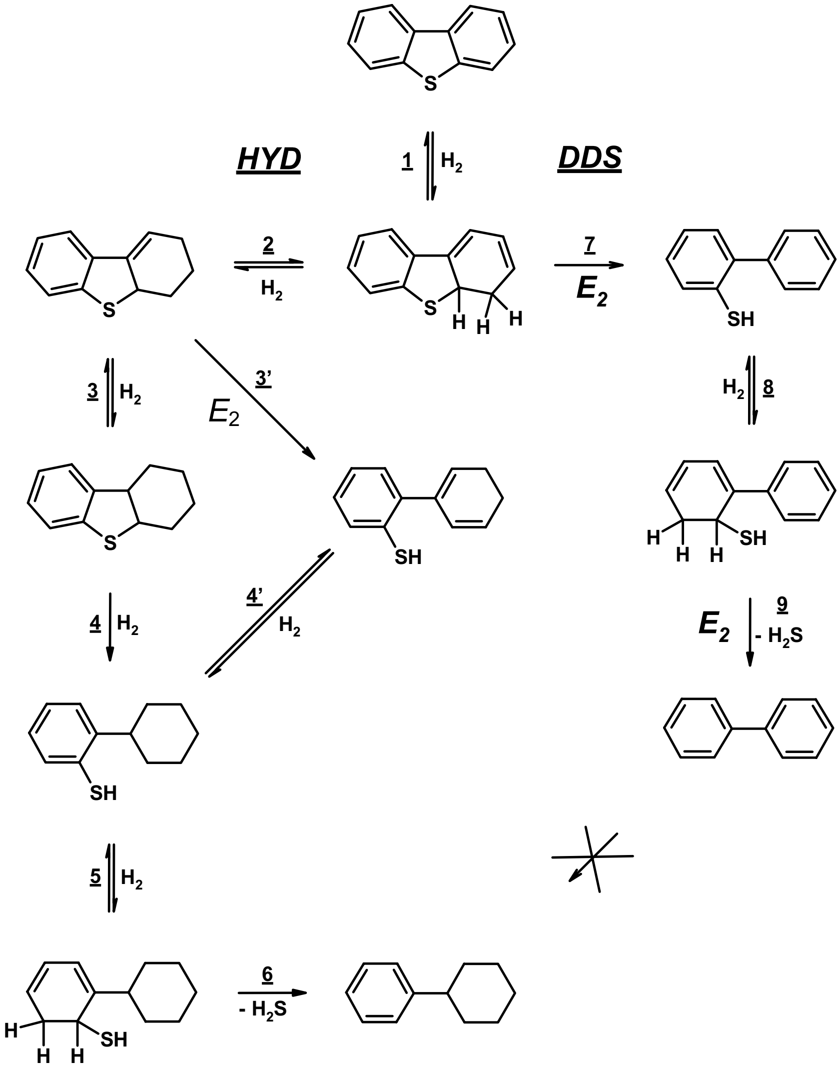


Fig. 1. HDS of DBT and 46DMDBT over sulfided NiMo/Al_2O_3 (fixed bed reactor, 340 °C, 4.0 MPa). DDS pathway; HYD. Data from [21].



Scheme 2. The various steps of the HDS of DBT through the HYD and DDS pathways. E_2: C–S bond cleavage through an elimination process involving sulfur anions as basic sites (for details, see [30]).

HYD pathway of both reactants while the activation energy for the DDS pathway is higher for 46DMDBT. We should not be mistaken on this point: the reactivity of 46DMDBT by the HYD pathway is not higher than that of DBT, the greater contribution of the HYD pathway to its decomposition is in fact due to the inhibition of the DDS pathway. According to several authors [13,19,24,32], the higher contribution of the HYD pathway to the HDS of 46DMDBT could be the result of the hydrogenation of one of the benzenic rings. This would release the steric hindrance in the adsorbed molecule [19,32]. However if as expected the rate-limiting step of the HYD pathway is the addition of the first molecule of hydrogen to the aromatic ring, the release of steric hindrance cannot be expected to influence the reactivity. Moreover it must be recalled that the reactivity of 46DMDBT through the HYD pathway is more or less the same as that of DBT so that the alkyl groups in the 4 or 4,6 positions do not seem to play a significant role in this pathway.

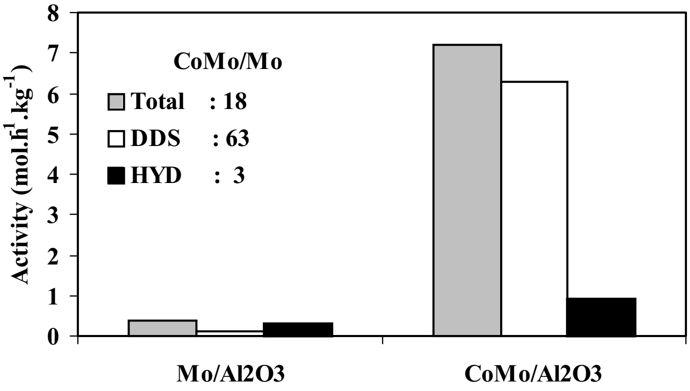


Fig. 2. Promoting effect of Co on the activity of Mo/Al_2O_3 in the HDS of DBT (fixed bed reactor, 340 °C, 4.0 MPa). Data from [23].

In fact, the difference in reactivity between DBT and 46DMDBT on commercial catalysts originates essentially in the DDS pathway and was identified as being the result of a selective promoting effect [23]. On MoS_2/Al_2O_3, DBT and 46DMDBT have roughly the same reactivity, 46DMDBT being even slightly more reactive than DBT. Their difference in reactivity on promoted commercial catalysts comes from the fact that the promoting effect on the DDS pathway which is very significant in the case of DBT is very limited in the case of 46DMDBT. Actually with DBT the promoting effect was found much more pronounced on the DDS pathway (about 60) than on the HYD pathway (about 4) (Fig. 2); the result is an overall promoting effect of about 20 [23] which can however depend on the reaction conditions [33]. Under the same conditions as for DBT, the promoting effect found with 46DMDBT was much more limited (about 2 only); it was about the same as for DBT regarding the HYD pathway but was more than 10 times smaller regarding the DDS pathway [23] (Fig. 3). This led the authors to consider that the alkyl groups in the 4 and 6 positions in DBT derivatives hindered the transition state of the elimination process which makes C–S bond cleavage possible. Actually if one accepts the mechanism described in Scheme 2, the orientation of the reaction towards one or the other of the two possible pathways is the consequence of the difference in reactivity of the common dihydrointermediate in further hydrogenation or in C–S bond cleavage through elimination. It was supposed that by increasing the basic character of the sulfur anions, which is in accordance with accepted theories [33–36], the promoter enhances the rate of C–S bond cleavage through the

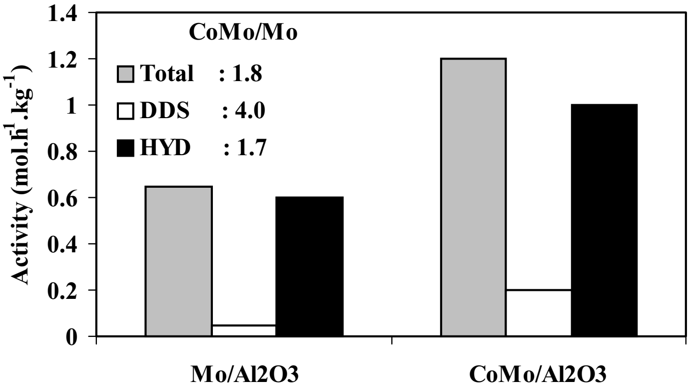


Fig. 3. Promoting effect of Co on the activity of Mo/Al_2O_3 in the HDS of 46DMDBT (fixed bed reactor, 340 °C, 4.0 MPa). Data from [23].

E_2 mechanism. Consequently, this step which in the case of DBT is rate-limiting on MoS_2/Al_2O_3 becomes fast on promoted catalysts so that the DDS route becomes prominent. With 46DMDBT, C–S bond cleavage in the common dihydrointermediate remains relatively slow because of steric hindrance, which annihilates to a large extent the effect of the promoter on the HDS. Hence while various authors [17,18,37] have proposed that the origin of the difference in reactivity between DBT and 46DMDBT was the steric hindrance of the reactant adsorption, today most of the results are in accordance with the early proposal of Kabe et al. [19] that this difference is due to other factors. These factors are rather related to the reactivity of the adsorbed reactant or to the reactivity of the intermediates involved in its decomposition [23,32], the most likely being hindrance of C–S bond cleavage in the partially hydrogenated intermediates [23]. This is perfectly sensible if one accepts the mechanism of Scheme 2, both reaction pathways involving as a first step the partial hydrogenation of one of the aromatic rings. Therefore the difference regarding the effect of the methyl groups on the two pathways has to be in a subsequent step (unless each of the two pathways occur entirely on specific catalytic centers).

3. Possibilities of improving the reactivity of refractory alkyldibenzothiophenes

With this in mind, two main different strategies were considered in order to improve the catalytic reactivity of the HDS-resistant impurities of middle distillates [22,38–40] (apart from conventional catalyst improvement, multistage or fractional desulfurization):

- One is to improve the hydrogenation properties of the hydrotreating catalysts (in order to take advantage of the HYD pathway which is not hindered by the alkyl groups in 46DMDBT).
- The other is to find the means to suppress the steric hindrance brought by the alkyl groups in 46DMDBT so as to restore the reactivity of the DBT derivatives through the DDS pathway.

In the next sections we will outline and comment briefly the main findings regarding the first option, then discuss more deeply the second issue.

3.1. Improvement of the hydrogenation activity of the catalysts

The first possibility was examined by several groups of researchers [13,14,18,32,41–48]. Actually, it can be expected that any improvement of the hydrogenation activity of the catalysts should improve the reaction rate of the HDS of DBT-type compounds through the HYD pathway. This was demonstrated by Landau et al. [13] with a series of NiMo catalysts having different hydrogenation activities.

Indeed, in their study of the HDS of DBT, Houalla et al. [18] noticed that the concentration in cyclohexylbenzene (the HYD pathway) was higher with a NiMo than with a $CoMo/Al_2O_3$ catalyst. Similarly, several authors reported that $NiMo/Al_2O_3$ catalysts were more efficient for the HDS of gas oils containing refractory compounds [14,44,45] as well as in the HDS of model compounds such as 4-methyldibenzothiophene (4MDBT) or 46DMDBT [28,41,43,46]. This is in agreement with the fact that NiMo catalysts were found more active than CoMo catalysts in hydrogenation [49,50]. According to Zhang et al. [32], the higher activity of $NiMo/Al_2O_3$ catalysts in the HDS of refractory compounds would be due to their better ability to achieve the hydrogenation of the aromatic ring(s), which would lead to a decrease of steric hindrance prior to desulfurization. However, as indicated in the foregoing discussion, this does not seem to be quite relevant to the kinetics of the reaction since the HYD pathway is apparently not much sensitive to alkyl groups in the 4 and 6 positions. In fact the better activity of $NiMo/Al_2O_3$ catalysts compared to $CoMo/Al_2O_3$ catalysts for the overall HDS of 46DMDBT seems to be simply the consequence of their better hydrogenation activity under these conditions. It should also be noticed that the difference in activity of CoMo and $NiMo/Al_2O_3$ catalysts depends very much on the H_2S partial pressure in the medium [14]. For instance, in cases where the partial pressure in H_2S produced by the reaction was high, $CoMo/Al_2O_3$ was found more active than $NiMo/Al_2O_3$ [14]. On the other hand, when H_2S (or a precursor) was added to the feed in order to maintain its partial pressure nearly constant during the reaction whatever the conversion, the activity of $NiMo/Al_2O_3$ in the HDS of DBT was only slightly superior to that of $CoMo/Al_2O_3$ [51].

Isoda et al. [41] used catalysts with added Ru which were found to be more effective for the HDS of 46DMDBT by enhancing the production of cyclohexylbenzene type compounds. This was also supposed to be due to their high hydrogenation activity. However, this was not really confirmed by a subsequent study [42] in which it was found that NiMo/Al_2O_3 was the least active for the HDS of 46DMDBT and CoMo/Al_2O_3 approximately as active as RuCoMo/Al_2O_3. Similarly, according to Isoda et al. [47], the presence of aromatics in the reaction medium can influence the difference in activity between CoMo/Al_2O_3 and NiMo/Al_2O_3 very much. They found that in the presence of naphthalene CoMo/Al_2O_3 was more active for the HDS of 46DMDBT than NiMo/Al_2O_3.

It seems in fact that the main obstacle to the use of catalysts with improved hydrogenation activity is the inhibition by aromatics which impede seriously the conversion of the least reactive DBT derivatives by the HYD pathway [48].

3.2. *The bifunctional approach: the association of zeolites and related materials with sulfides*

Several methods were used to try to improve the reactivity of refractory sulfur impurities with the help of acidic components like zeolites:

- physical mixing or two-stage processes [52–56];
- sulfides deposited on zeolite-containing alumina [13,21,57–61];
- sulfides deposited on acidic supports such as amorphous silica–alumina or zeolites [56,60–62];
- sulfides deposited on mesoporous materials [63–68].

3.2.1. *Effect of zeolites on the activity of hydrotreating catalysts*

Landau et al. [13] reported one of the first attempts to associate zeolites to hydrotreating catalysts. In particular, they compared CoMo and NiMo–alumina commercial catalysts to CoMo catalysts obtained by impregnation of alumina-containing HY or HZSM-5 zeolites in the HDS of DBT and 46DMDBT in a fixed bed reactor. The introduction of HZSM-5 in the support increased slightly the reactivity of DBT but, as expected, it did not improve the reactivity of 46DMDBT (and even decreased it slightly). As indicated by the authors, the reason was probably that such bulky molecules could not diffuse readily into the channels of the zeolite. On the other hand, the CoMo catalyst containing HY zeolite was found about three times more active than the commercial CoMo catalyst for the HDS of 46DMDBT. The positive effect of the presence of zeolites on the reactivity of DBT was attributed to a direct action of the acidity on the HDS activity and its effect on the reactivity of 46DMDBT was attributed mainly to demethylation and cracking of the C–C bond of the thiophenic ring connecting the two benzenic rings together.

Isoda et al. made a series of studies on the subject. The use of CoMo deposited on alumina-containing 5 wt.% of Y zeolite [57] led to a better activity in the HDS of a gas oil feed and in particular to a better conversion of the 4MDBT and 46DMDBT contained in the oil than CoMo and NiMo deposited on alumina. All three catalysts had practically the same activity regarding DBT conversion. Similarly the catalyst containing added zeolite was more active than the reference catalysts for the conversion of 46DMDBT dissolved in decane. Interestingly, the authors did not observe any deactivation either in the conversion of individual molecules or in the HDS of gas oil.

Following these experiments, Isoda et al. [52] reported somewhat different experiments in which they used a Ni–HY catalyst physically mixed with a CoMo–alumina catalyst for the HDS of a gas oil as well as for the conversion of 46DMDBT diluted in decane. Again the so-called “hybrid catalyst” exhibited a higher activity for the HDS of the gas oil as well as for the conversion of 46DMDBT contained in it or dissolved in decane. Moreover, the existence of a “bifunctional” process for HDS was demonstrated by the fact that the conversion of 46DMDBT with the hybrid catalyst was higher than with both of the Ni–HY and CoMo–alumina individual components. They noticed also that the desulfurized products contained a large amount of alkylated biphenyl resulting from the decomposition of 3,6-dimethyldibenzothiophene (36DMDBT), which indicates incidentally that the low reactivity of 46DMDBT is actually due to hindrance of its C–S bond cleavage leading to the DDS pathway.

In subsequent reports [53–55] the procedure was modified in order to better identify the respective roles of both catalytic ingredients. The authors conducted more or less the same experiments except that they used a "two-stage" procedure in which 46DMDBT diluted in decane was first contacted with Ni–HY and then after filtration and further dilution with decane, contacted with CoMo–alumina. Actually, the products obtained in the first stage were essentially the result of transalkylation (4MDBT and trimethylDBT) and of isomerization (36DMDBT); no HDS or cracking products were detected and there was no coke deposition. In the second stage, the reactivities of the sulfur compounds were increasing in the order: 46DMDBT $<$ DBT derivatives with one methyl in the 4 or 6 position $<$ 28DMDBT and methylDBT derivatives without methyl group in the 4 or 6 position. This again reveals steric hindrance in the 4 and 6 positions and the efficiency of the methyl migration as a means of improving the reactivity of 46DMDBT, which makes bifunctional catalysts of real potential interest in view of deep desulfurization [39]. The authors pursued their investigation by making calculations in order to establish relationships between cross-sectional areas of the σn orbitals of the S-atoms in the various alkylDBT(s) with the catalyst plane and the activation energies for their HDS [54,55]. It was actually found that the activation energies decreased with the increasing cross-sectional areas. However this relationship could be fortuitous. Indeed if as proposed by several authors [20,23,27,30], the first step of the two possible HDS pathways of DBT derivatives is the partial hydrogenation of one of the benzenic rings, then the interaction of the S-atom of the reactant itself with the surface should not play a prominent role in the reaction. On the contrary it could be the case for the dihydrointermediates in which the C–S bond cleavage is supposed to occur [19,23].

Meanwhile, Yumoto et al. [58] reported results obtained with a catalyst they developed which contained zeolite in the support. They showed that the catalyst with an alumina support containing a small amount of a zeolite with an appropriate silica/alumina ratio was more active than a conventional catalyst in the HDS of a light gas oil. They did not detect any isomer of 46DMDBT and therefore concluded that the higher activity of the catalyst containing the zeolite was due to the enhancement of its hydrogenation activity. However this would imply that the sulfide was in close interaction with the acidic component in order to induce electronic effects. This was probably not the case if Co and Mo were introduced by impregnation. In fact it was indicated in a subsequent article [59] that the catalyst was indeed prepared by pore-volume impregnation of the zeolite-containing alumina. The acidity and amount of the zeolite were tuned in order to avoid undesirable cracking and coke formation. Three catalysts were compared: a commercial CoMo/alumina; CoMo–P/alumina and CoMo–P/zeolite–alumina. It was found that the most effective catalyst was the latter, mainly because of a better conversion of 4MDBT and 46DMDBT (Fig. 4) and the authors were able to show that the zeolite–alumina support did promote the isomerization of 46DMDBT. Therefore it could be concluded that the improvement of the reactivity of 46DMDBT was indeed due to isomerization although the product of this reaction could not be detected in the preliminary work reported by the authors [58]. Moreover it was shown that the catalyst was quite resistant to deactivation on a long term period.

Lecrenay et al. [60,61] compared commercial catalysts such as conventional CoMo and NiMo/alumina or deep HDS CoMo catalysts (with zeolite-containing alumina or silica–alumina as support) as well as laboratory made catalysts with various amounts of acidic additives and also a spent catalyst. They found also that the CoMo catalysts containing either zeolite included in the support or silica–alumina as the support led to a higher activity for both the HDS of gas oil and the conversion of 46DMDBT in decane (Fig. 5). The CoMo catalysts with more acidic additives in the support were more active both in hydrogenation (measured with naphthalene) and in cracking (measured with isopropylbenzene). The silica–alumina-containing catalyst was more active in HDS than a conventional CoMo/alumina catalyst but as indicated by the product distribution its high activity did not seem to be due to a bifunctional process involving its acidity but rather to an increase of its hydrogenation activity; no products originating from a cracking route were found. An important thing from the practical point of view is that the authors noticed that the benefit resulting from the presence of the acidic ingredient was greatly impeded by aromatic inhibitors and/or by coke deposition. Indeed, the spent catalyst lost more than half of its initial hydrogenation activity and practically all of its cracking activity. In fact the activity in the HDS of 46DMDBT of the

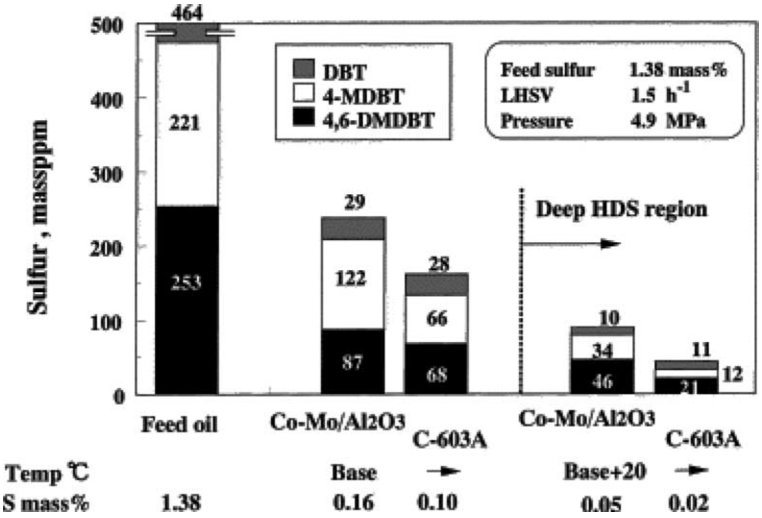


Fig. 4. HDS of a light gas oil over a CoMo–P/zeolite–Al_2O_3 catalyst (C-603A) (320–370 °C; 3–5 MPa) [59].

spent catalyst compared to that of the fresh catalyst was divided by 5 and the cracking route disappeared completely. However the HYD/DDS selectivity decreased also showing that the HYD route was more affected by deactivation than DDS.

Michaud et al. [21] carried out experiments using NiMo/alumina mixed with silica–alumina and also a NiMo/HY–alumina catalyst. They found that the addition of silica–alumina to NiMo/alumina had practically no effect on the conversion of DBT; this was expected since no acid-catalyzed reaction could occur in this case and no electronic effect on the properties of the sulfide either. On the other hand it improved the reactivity of 46DMDBT by a factor of about 2.5, which was attributed to the isomerization of the reactant into 36DMDBT. Cracking of the desulfurized products was also observed. Similarly, the use of HY–alumina as a support for a NiMo catalyst had no effect on the reactivity of DBT, which means in particular that no electronic effect on the hydrogenation properties of the sulfide existed in this case either. On the other hand, the reactivity of 46DMDBT was also multiplied by about 2 with respect to that on NiMo/alumina. By using cyclohexane instead of decaline as a solvent, it was possible to show that 46DMDBT did isomerize into 36DMDBT and that 3,4′-biphenyl as well as methylcyclohexane and toluene (cracking products) were formed. It may also be noticed that deactivation was observed in the case of 46DMDBT and not for DBT, which was attributed to the fact that the acidic component did not play any role in this latter case.

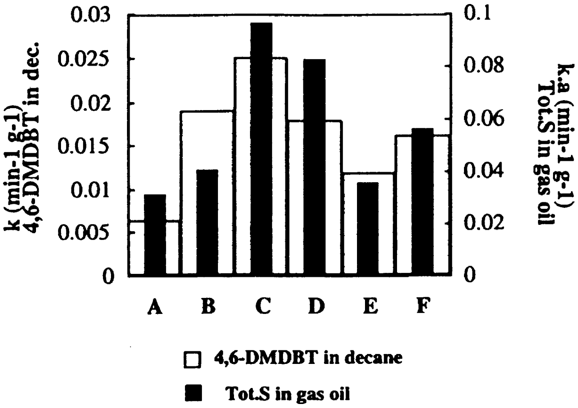


Fig. 5. HDS of 46DMDBT in decane (270–360 °C, 2.4–5 MPa) and gas oil (340 °C, 2.4 MPa). Comparison of conventional catalysts with acid-containing hydrotreating catalysts: (A) CoMo/Al_2O_3; (B) NiMo/Al_2O_3; (C) CoMo/zeolite–Al_2O_3; (D) CoMo/amorphous SiO_2–Al_2O_3; (E) NiMo (low content)/Al_2O_3; (F) deep HDS CoMo/Al_2O_3 [61].

Bataille et al. [62] reported results on the HDS of DBT and 46DMDBT on Mo/zeolite (8.3 wt.% Mo) and CoMo/zeolite (2.2 wt.% Co and 8.5 wt.% Mo) catalysts prepared by impregnation of a HY zeolite with a Si/Al ratio of 19. They found that the sulfided

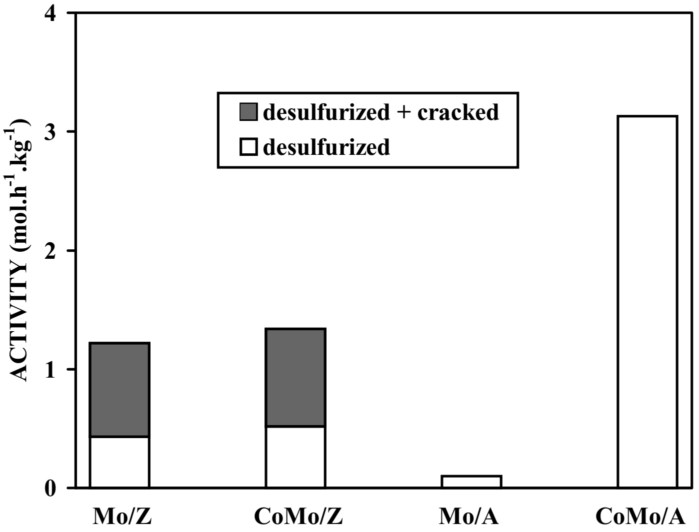


Fig. 6. HDS of DBT over zeolite-supported Mo and CoMo catalysts and over their alumina-supported counterparts (fixed bed reactor, 330 °C, 3.0 MPa H_2) [62].

Mo and CoMo/zeolite were both more active than their alumina-supported counterparts in the HDS of DBT (Fig. 6). Since no isomerization was possible in this case, the high activity was attributed to a high dispersion of the active phase and to possible electronic effects improving the hydrogenation activity of the sulfides. Furthermore, the promoting effect of Co was much more limited than with the alumina support so that the CoMo/zeolite catalyst was found less active than the CoMo/alumina catalyst. This was because Co was not well associated to Mo as was indicated by the fact that the HYD pathway was prominent with the zeolite support while on catalysts where the promoter is well associated to Mo, the DDS pathway is expected to be largely favored [30]. However, both zeolite-supported catalysts were significantly more active than the alumina-supported catalysts in the HDS of 46DMDBT although the promoting effect was also quite limited in this case (Fig. 7). This was considered as the consequence of two factors: (i) with the alumina-supported catalyst, the promoter effect on the transformation of 46DMDBT was much smaller than on the transformation of DBT; (ii) the zeolite support was able to isomerize 46DMDBT into more reactive isomers [21,52–55,59,61]. Moreover certain of the DBT derivatives containing three (or more) methyl groups resulting either from alkylation (by added dimethyldisulfide, DMDS) or from disproportionation were also expected to have a high reactivity [16,17,25]. Indeed, it was found that on the zeolite-supported catalysts 46DMDBT was more reactive than DBT. It is also worth mentioning that when DMDS was added to the feed alkylation was observed.

In a recent report, Klimova et al. [56] studied the effect of the method of introduction of a zeolite additive on the properties of NiMo hydrotreating catalysts. They prepared catalysts containing NaHY zeolite (20 wt.%) by three different methods: (i) mechanical mixing of the zeolite and NiMo/alumina; (ii) binding of NiMo/alumina and NaHY; (iii) impregnation of a NaHY–alumina support with Ni and Mo and they compared these catalysts to a conventional NiMo/alumina catalyst and NiMo/NaHY. They found that the presence of added zeolite did not improve the reactivity of DBT nor its HDS pathways (except that the desulfurized products underwent cracking), which confirms that unless the metal is deposited directly on the acidic ingredient, significant electronic effects on its hydrogenation properties cannot be expected. On the other hand the presence of zeolite increased the reactivity of 46DMDBT significantly, in particular when the zeolite and NiMo/alumina were binded together or when they were mechanically

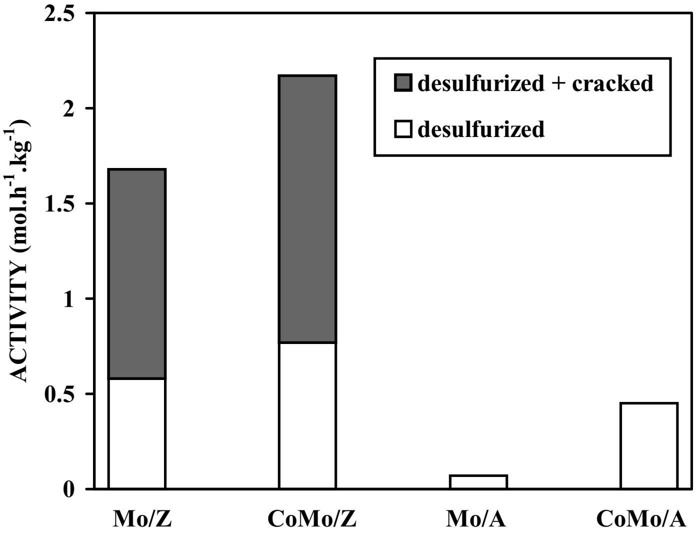


Fig. 7. HDS of 46DMDBT over zeolite-supported Mo and CoMo catalysts and over their alumina-supported counterparts (fixed bed reactor, 330 °C, 3.0 MPa H_2) [62].

mixed. However deactivation seemed to occur quite significantly.

3.2.2. Sulfides deposited on mesoporous materials

In their study of CoMo catalysts deposited on MCM-41 Song et al. [63,64] showed that it was possible to obtain high metal loading (about twice the amount of conventional catalysts) with this kind of support and therefore to obtain catalysts with higher activity for the HDS of DBT than that of a commercial CoMo/alumina catalyst. The catalyst had also a high activity for the HDS of 4MDBT and hence was considered a good potential catalyst for deep HDS of diesel fuels.

Their results were confirmed by a subsequent study [65] where it was shown that CoMo/MCM-41 with a double metal loading was about twice as active as a conventional CoMo/alumina catalyst for the HDS of a jet fuel spiked with 46DMDBT. This is in accordance with recent results published by Kaluza et al. [66] who found that a highly loaded Mo/mesoporous alumina was about twice as active as a conventional Mo/alumina catalyst in the HDS of thiophene. Nevertheless, Turaga and Song [65] recommended the use of MCM-41 with a moderate acidity (SiO_2/Al_2O_3 ratio of about 50) in order to avoid extensive cracking of the oil. The product distribution indicated that the high activity resulted both from the isomerization of 46DMDBT and the improvement of the hydrogenation route. It may also be noticed that the authors applied hydrothermal recrystallization of their MCM-41 material in order to enhance its stability.

In a more recent work, Turaga and Song [67] compared the activity of their CoMo/MCM-41 catalyst with a SiO_2/Al_2O_3 ratio of 50 to the activity of a conventional CoMo/alumina catalyst in the HDS of a LCO containing DBT and its alkylated derivatives. They found that their MCM supported catalyst was more active than the conventional catalyst especially for the conversion of alkylDBT derivatives. However the authors concluded that the presence of aromatics in the LCO inhibited the HDS of these compounds as was found for zeolite-containing catalysts.

The results reported recently by Klimova et al. [68] are in general agreement with those of Song and coworkers. They found that the most active catalysts in the HDS of DBT were those supported on MCM-41 with a SiO_2/Al_2O_3 ratio of 30.

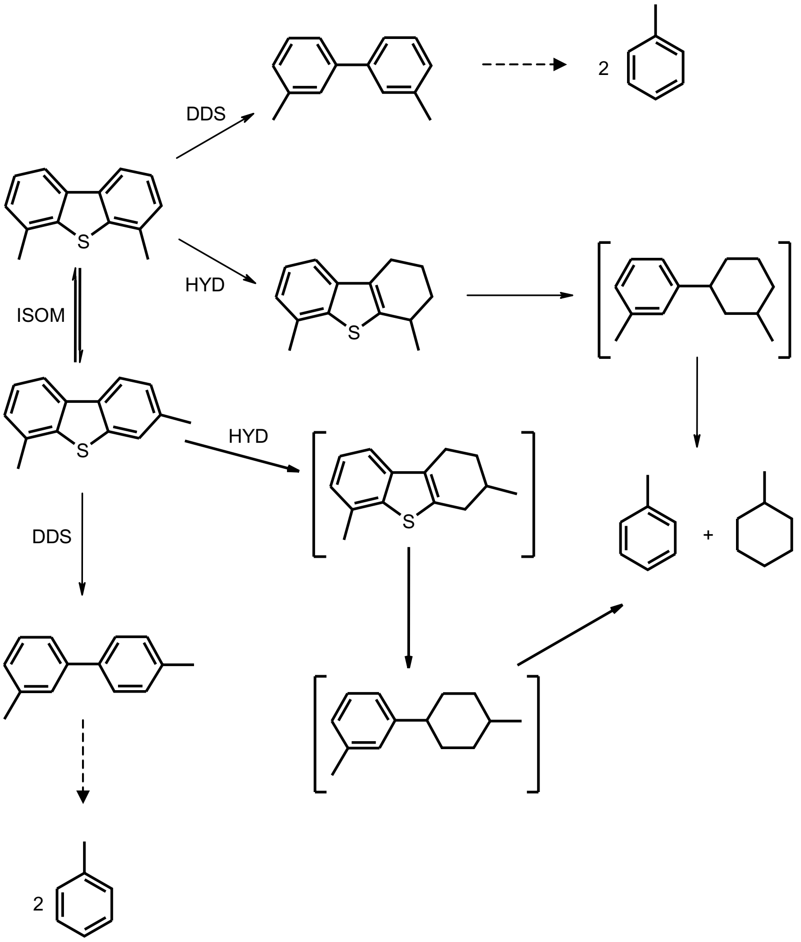
3.2.3. Effect of added zeolite and related materials on the product distribution and mechanism

Regarding the effect of acidic components on the hydrogenation properties of hydrotreating catalysts, some contradictory results were obtained. However it turns out that in the cases where the sulfide can be in direct interaction with an acidic support, the enhancement of the HDS activity can be ascribed, at least partly, to the improvement of the hydrogenation properties due to electronic effects. This was particularly clear when there was an improvement of the activity in the HDS of DBT [13,62] or when no product resulting from acid-catalyzed or bifunctional reactions were observed [60,61]. However the effect on the product distribution is not very easy to see because in this case the reaction leads essentially to the same products as conventional catalysts and because the selectivity depends also on the degree of association of the promoter with molybdenum.

On the other hand it is clear that in most of the reports the product distribution revealed the existence of acid-catalyzed or bifunctional reactions.

Landau et al. [13] explained the high activity of their HY-containing catalyst in the conversion of 46DMDBT by two different cracking reactions: the demethylation of the reactant and the C–C bond cleavage of the thiophenic ring connecting the two benzenic rings together. The argument of the authors in favor of this interpretation is that they did not observe any isomer of 46DMDBT like 36DMDBT nor desulfurized products like dimethylbiphenyl corresponding to the migration of the methyl groups. This is actually in accordance with the early work of Mochida and coworkers [45] who reported also that they did not found biphenyl derivatives (the products of the DDS pathway) corresponding to the migration of methyl groups while the methyl groups in the partially hydrogenated products did move from their initial position. This is contradictory with most of the subsequent studies on the subject showing methyl migration in the starting material. Moreover given the difference in reactivity of the various alkylDBT derivatives, if methyl migration would actually occur it should facilitate the DDS pathway rather than the HYD pathway. Anyhow, both of these reactions (C–C bond cleavage in the reactant and demethylation) are expected to be rather difficult and it must be noted that they cannot be considered as acid-catalyzed since both involve hydrogen as shown in the reaction scheme proposed by the authors. Consequently they should be considered as hydrogenolysis reactions which do not require acidity and if they do exist they should be possible on conventional hydrotreating catalysts, which was not the case. In fact the conditions under which the reaction was carried out were rather severe; no indication was given regarding the conversion but one can expect that it was very high so that it was not possible to observe the initial product distribution and therefore to identify the primary products of the reaction. It is, for instance, difficult from the results reported by the authors to ascertain whether the C–C bond cleavage they refer to, preceded HDS or was consecutive to it. In particular the dimethylphenylsulfide which would have resulted from the C–C bond cleavage in the thiophenic ring prior to desulfurization could not be detected. On the other hand the product corresponding to demethylation could as well be the result of an acid-catalyzed disproportionation reaction as evidenced in subsequent studies.

Actually most of the authors who carried out experiments involving acidic material-containing hydrotreating catalysts, agree on the fact that the improvement of the reactivity of compounds like 46DMDBT is due to the displacement of the methyl groups or to disproportionation [21,52–55,57,59,61]. Various reaction schemes were proposed to account for the product distribution [21,52,53,57,61,62]. They differ slightly but most of them can be summarized as in Scheme 3. 46DMDBT gave three main primary reaction products, 3,3′-dimethylbiphenyl (DDS pathway), 4,6-dimethyltetrahydrodibenzothiophene (HYD pathway) and 36DMDBT (isomerization: ISOM pathway) to which disproportionation should be added. In fact, several isomers were generally observed, but only 36DMDBT could be identified. 3,3′-Dimethylbiphenyl was actually found in the reaction products, but the final products of the HYD pathway (3-(3′-methylcyclohexyl)toluene) sometimes was not obtained [13,62] contrary to what occurred on the alumina-supported catalysts. Similarly, 3-(4′-methylcyclohexyl)toluene and the corresponding compounds resulting from the HDS of the disproportionation products were not detected. This was due to a rapid cracking of these compounds into toluene and methylcyclohexane (Scheme 4). In a few studies [21,60], toluene was found in excess with respect to methylcyclohexane showing that methylbiphenyls may also crack into toluene through a mechanism corresponding to the reverse of the condensation of benzene into biphenyl [21] as proposed by Gates et al.

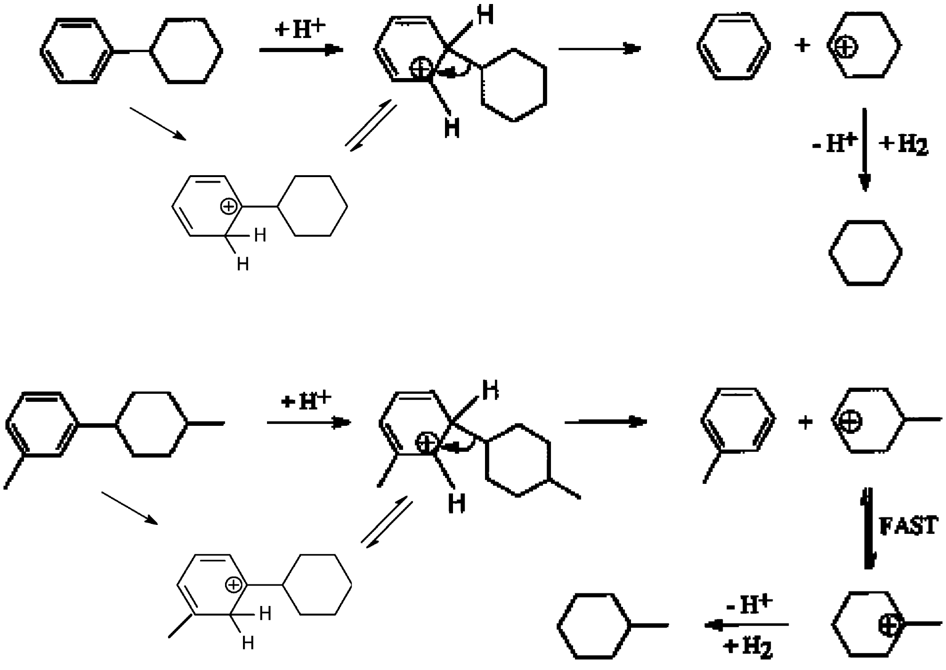


Scheme 3. Transformation of 46DMDBT acid-containing hydrotreating catalysts. Main reaction steps for the HDS of the reactant and of its 3,6-dimethylisomer. Isomerization (ISOM); DDS pathway; HYD.

[69]. This depends obviously on the reaction conditions but in most of the studies equimolar amounts of toluene and methylcyclohexane were obtained, which means that it was essentially methylcyclohexyltoluene which underwent cracking.

Both isomerization and disproportionation are acid-catalyzed since they did not occur with the alumina-supported catalysts. Like for xylenes [70], the methyl migration in 46DMDBT can occur either through acid-catalyzed intramolecular displacement (Scheme 5) or disproportionation (Scheme 6). Disproportionation itself can occur on acid centers as shown in Scheme 6A. The transalkylation (or disproportionation) of alkylaromatics such as xylenes implies the formation of benzylic carbocations and diarylmethane intermediates [71]. In the case of 46DMDBT, this reaction transforms two molecules of the reactant into one molecule of methyldibenzothiophene and one molecule of trimethyldibenzothiophene (Scheme 6A). A subsequent transmethylation reaction between trimethyldibenzothiophene and 4,6-DMDBT can also produce isomers of the latter (Scheme 6B). Consequently, such a mechanism can account for the formation of the methyl and trimethyldibenzothiophenes, but also for part of the 4,6-DMDBT isomers.

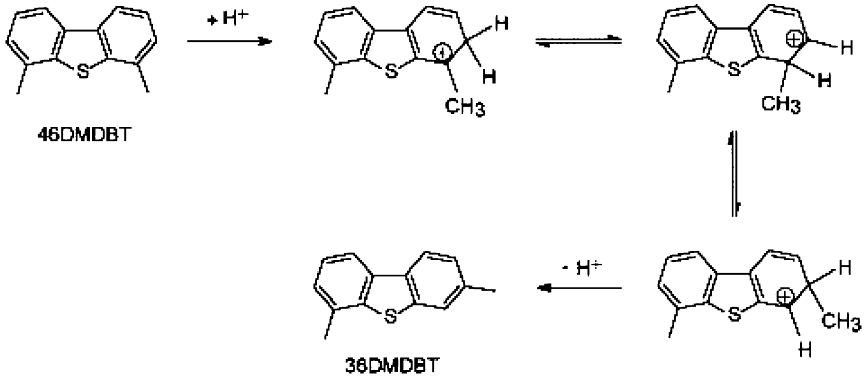
In addition when cracking of the oil or paraffinic solvent occurred or when DMDS was added to the reaction mixture or feed, alkylation could occur



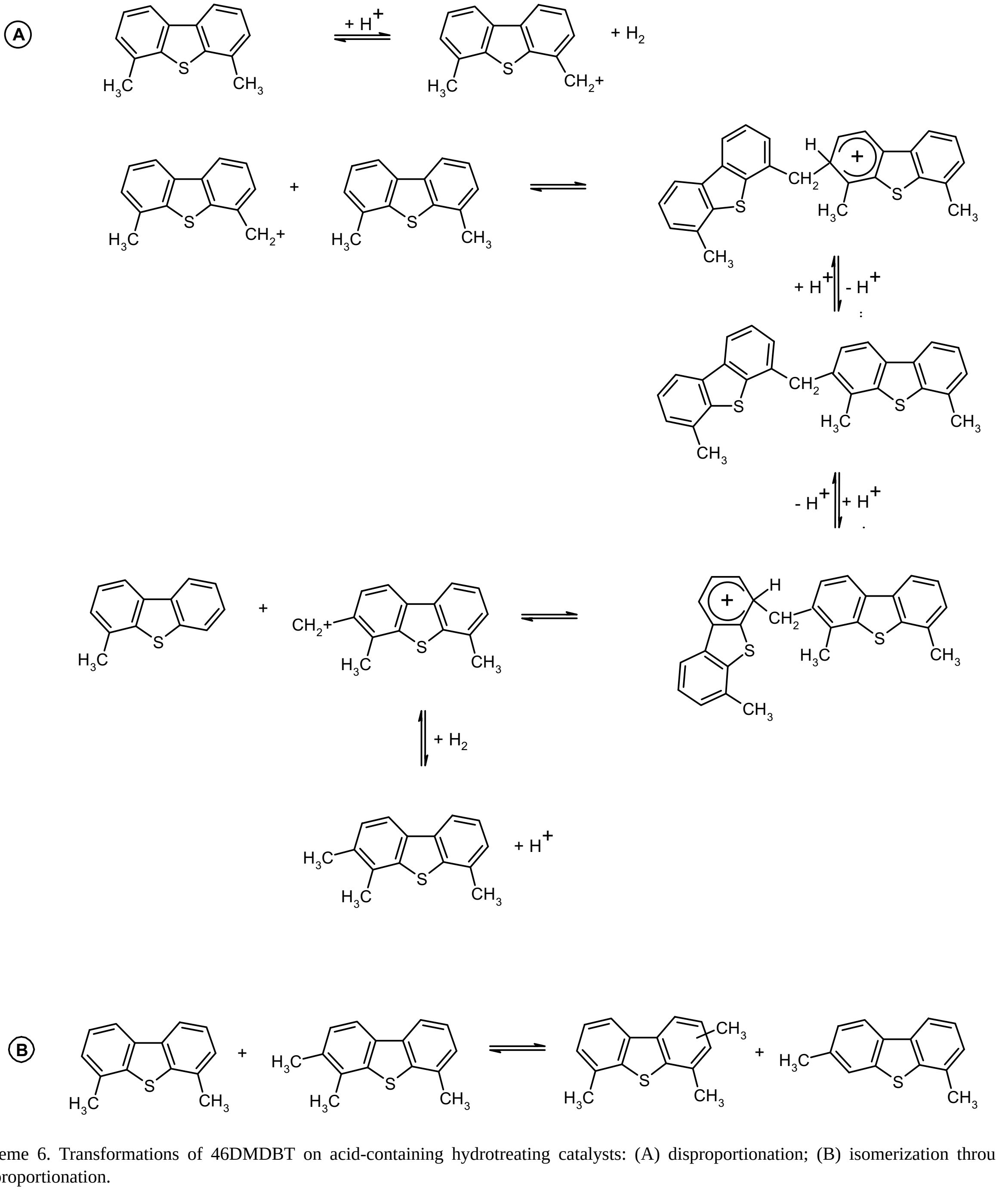
Scheme 4. Hydrocracking of cyclohexylbenzenes.

[13,52,62]. For instance, polymethylDBT derivatives were obtained in the presence of DMDS even when DBT was used as the reactant [62]. It was assumed that DMDS was able to act as a methylation agent through electrophilic substitution catalyzed by the acid component.

It should also be mentioned that the acid component could also have an influence on C–S bond cleavage itself which is considered as very difficult in the case of 46DMDBT [19,23] and is presumably rate-limiting regarding the DDS pathway on conventional hydrotreating catalysts. It was proposed recently [72], that the acid component could act as a cocatalyst by providing the proton which would make the sulfur atom a better leaving group and consequently the elimination process (with a sulfur anion as basic site) leading to C–S bond cleavage easier. One could also imagine a purely bifunctional mechanism with the formation of



Scheme 5. Isomerization of 46DMDBT into 36DMDBT through an acid-catalyzed intramolecular methyl displacement.



Scheme 6. Transformations of 46DMDBT on acid-containing hydrotreating catalysts: (A) disproportionation; (B) isomerization through disproportionation.

a dihydrointermediate on the sulfide and the whole process of C–S bond cleavage on the acid support or component.

4. Conclusions

The low reactivity of compounds such as 46DMDBT in the presence of commercial catalysts seem well understood nowadays. Most of the authors agree on the fact that it is due to steric hindrance of the transition state leading to C–S bond cleavage. The consequence is that the promoter effect which is very significant with DBT because of a tremendous enhancement of the rate of the so-called DDS pathway is almost reduced to nothing with 46DMDBT.

In certain cases the reactivity of 46DMDBT can be increased significantly by improving the hydrogenation properties of the catalysts either through a modification of the hydrogenation function itself or through the interaction with an acidic component. This is made possible by the fact that the HYD pathway of HDS is not hindered by the alkyl groups in the 4 and 6 positions in DBT derivatives. However, the main obstacle to the use of these catalysts is the inhibition by aromatics which impede seriously the HDS conversion.

On the other hand, the reactivity of compounds such as 46DMDBT through the DDS route can be at least in part recovered by the displacement (through isomerization) or transfer (through disproportionation) of the alkyl groups in the 4 and/or 6 positions. This is made possible thanks to the presence of an acid component in the hydrotreating catalyst. Various techniques can be used to introduce this component (physical mixing, binding, deposition of sulfide precursors on an acid–alumina support, deposition of sulfide precursors on an acidic support) and it is possible to obtain catalysts which are more active than conventional catalysts both in the conversion of individual refractory sulfur impurities and in the HDS of gas oils containing such impurities.

However there are a few serious drawbacks to the preparation and use of such catalysts. First it is difficult to take advantage of the promoters when the precursors of the sulfides are deposited directly on the acid support such as a zeolite. Certain catalysts containing zeolites or related materials have a tendency to deactivate rapidly due to coke formation and in certain cases, HDS can also be severely inhibited by aromatics.

Moreover nitrogen impurities which are known to inhibit HDS with conventional catalysts [73] especially under the conditions of deep desulfurization [74–82] may be even more detrimental for the acid component present in the catalyst.

Nevertheless one should remain optimistic since it was shown that a good tuning of the properties of the acid component could lead to efficient catalysts for the treatment of oils [58,59,65].

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