ELSEVIER

Catalysis Today 84 (2003) 129–138

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Deep desulfurization: reactions, catalysts and technological challenges

Michèle Breysse [a,*], Gérald Djega-Mariadassou [a],
Stéphanie Pessayre [b], Christophe Geantet [b],
Michel Vrinat [b], Guy Pérot [c], Marc Lemaire [d]

[a] *Laboratoire de Réactivité de Surface, UMR 7609 CNRS, Université P. et M. Curie, 4 place Jussieu, 75252 Paris Cedex, France*
[b] *Institut de Recherches sur la Catalyse, UPR 5401 CNRS, 2 Avenue Albert Einstein, 69626 Villeurbanne Cedex, France*
[c] *Laboratoire de Catalyse en Chimie Organique, UMR 6503 CNRS, Université de Poitiers, 40 avenue du Recteur Pineau, 86022 Poitiers Cedex, France*
[d] *Laboratoire de Catalyse et Synthèse Organique, UMR 5622, UCBL, 43 Bd du 11 Novembre 1918, 69622 Villeurbanne Cedex, France*

Abstract

Very stringent regulation in the maximal S content of gas oil have led to an intense activity of research dealing with all the aspects of desulfurization. The design of future processes is based on the identification of the refractory sulfur compounds and the knowledge of their individual reactivity and in the presence of inhibitors, as illustrated in this paper. This knowledge have oriented the research towards new catalysts such as molybdenum sulfide supported on zeolites, combination of sulfide and noble metal catalysts, and molybdenum carbides. Non-catalytic approaches like charge transfer complex were also examined. This paper summarises these various aspects of desulfurization.

Keywords: Hydrodesulfurization; Kinetics; Hydrotreating catalysts; Zeolite; Charge transfer complexes

1. Introduction

Environmental concerns are forcing dramatic changes in motor fuel specifications. It is clear today that motor fuel quality will continue to be modified to improve both combustion quality and post-combustion gas clean-up performance. Stringent regulations are becoming increasingly severe to minimize air pollution. For instance, present EC regulations for the sulfur content of diesel fuels is 350 ppm and is expected to be below 50 ppm in 2005 and circa 10 ppm around 2008 [1].

In order to eliminate sulfur compounds in fuels until the very low value required by the new regulations, several proposals can be made. For example, to reduce the concentration of a gas oil from 500 to 10 ppm of sulfur, it is necessary either

- to enhance considerably the activity of the present catalysts, by a factor of 4–5, which would correspond to very high conversion (higher than 99.9% for many gas oils),
- to increase the process severity, especially to increase the hydrogen pressure (from 1.5 to 2 times),

---

[*] Corresponding author. Tel.: +33-1-4427-5533; fax: +33-1-4427-6033.
E-mail address: breysse@ccr.jussieu.fr (M. Breysse).

0920-5861/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/S0920-5861(03)00266-9

- or by a better knowledge of the reactions in the process conditions, find new catalysts combinations and synergies with non-catalytic processes.

The second option, increase of the process severity, is efficient in the short-term range but expensive for the refiners because it implies the building of new units working under high-pressure conditions. Moreover, this leads to an increase in the hydrogen consumption which availability is now limited and the building of units of hydrogen production is very costly. Besides, this will increase CO_2 emission.

The objective of this paper is to give an overview of studies performed in some French laboratories on:

- The chemical aspects of deep desulfurization, i.e. the identification of the refractory compounds present in hydrotreated gas oils of various sulfur concentration, the reactivities and conversion schemes of the most refractory molecules, the competitive effects with nitrogen and aromatics compounds.
- The strategies for desulfurization using unconventional catalysts, acidic support, metal/sulfide combination and carbides.
- The elimination of sulfur by non-catalytic process such as the elimination by charge transfer complex formation.

2. Chemical and kinetic aspects of deep desulfurization

2.1. Nature of the refractory compounds

During the last decade numerous efforts have been made for the identification of the sulfur molecules in gas oil [2–4]. The most difficult sulfur molecules to eliminate by hydrogen treatment belong to the alkyl dibenzothiophene (DBT) family. Indeed, these molecules were identified in partially desulfurized gas oil as illustrated in Fig. 1. It is often considered that 4,6-dimethyldibenzothiophene (4,6-DMDBT) is the representative molecule of refractory compounds because it is the most abundant. However, other kinds of substituted DBT such as 4,6-diethyldibenzothiophene (4,6-DEDBT) or 4,6-diisopropyldibenzothiophene (4,6-DiPrDBT) contribute together at least to an equivalent part of the S remaining content (see Fig. 1).

2.2. Reactivity of the refractory compounds

In order to estimate the magnitude of chemical transformation that will be required to meet deep or ultra-deep desulfurization, it was necessary to investigate the reactivity of such compounds. For instance, individual rate constants of more than 60 sulfur

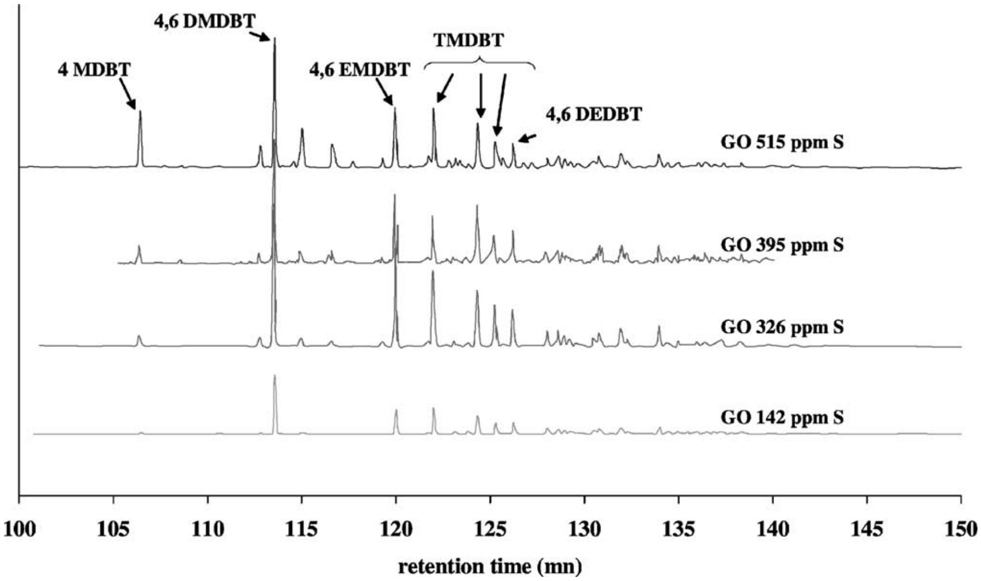


Fig. 1. GC-AED chromatograph of desulfurized SR gas oils.

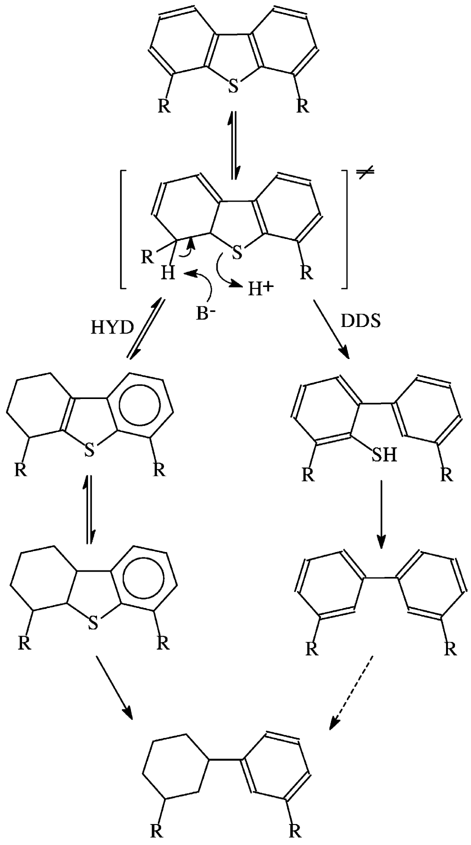
Table 1
Relative catalytic activities for the conversion of substituted DBT on a NiMo/Al_2O_3 catalyst. Adapted from [6]

	Molecule			
	4,6-DMDBT	4,6-DEDBT	4,6-DiBuDBT	4,6-DiPrDBT
Transformation rate (relative to 4,6-DMDBT)	100	75	40	1.5

compounds were roughly determined during the hydrotreatment of a diesel fuel by Ma et al. [5]. Then, some of these substituted DBTs were synthesized at the laboratory scale and their individual or combined reactivities established in a batch reactor. These kinetic studies demonstrated that a large range of activity exists among the substituted DBT [6]. Table 1 summarizes the activity scale toward HDS of these molecules. Thus, the conversion of 4,6-DiPrDBT was found seven times smaller than that of 4,6-DMDBT. Competitive experiments with 4,6-DMDBT and these substituted DMDBT demonstrated also that the origin of the refractory properties are linked to the steric hindrance in the elimination reaction involved in the C–S bond breaking. As a matter of fact, it is now admitted that the reactivity of these molecules proceeds via two routes corresponding to the reaction Scheme 1 for the transformation of alkyl DBT [2,7–9]. After a first common step of partial hydrogenation, a so called direct desulfurization (DDS) leads to direct C–S bond breaking without further hydrogenation and the other route (HYD) involves at least the complete hydrogenation of one aromatic cycle before C–S bond breaking. It is well-documented that the DDS route is deeply inhibited in the case of substituted DBT. In fact, the presence of substituents in the 4,6 positions hinder the β-elimination step required for desulfurization. To overcome this problem, attempts were made to modify the catalyst and the various strategies developed are described below.

2.3. Role of nitrogen and aromatic compounds

Another aspect of the reactivity of the refractory compounds concerns the inhibiting effect of aromatic and nitrogen compounds also present in the feed. If the inhibiting role of nitrogen compounds and especially ammonia and basic nitrogen compounds is well recognized, the effect of aromatic compounds has been less studied [10,11]. When high levels of desulfurization are reached, both kinds of compounds and especially aromatics may become dominants and compete in the adsorption or reaction processes. A similar approach as described above using 4,6-DMDBT and various aromatic or nitrogen compounds was applied [12]. The strong inhibiting effect of fluorene, carbazole and acridine is clearly illustrated in Fig. 2. In fact, the reactivity of each molecule being studied, inhibition appears to be related to some partially hydrogenated molecules rather than to the parent ones. Furthermore, the inhibiting effect of fluorene, which



Scheme 1. Mechanism of desulfurization of substituted DBT.

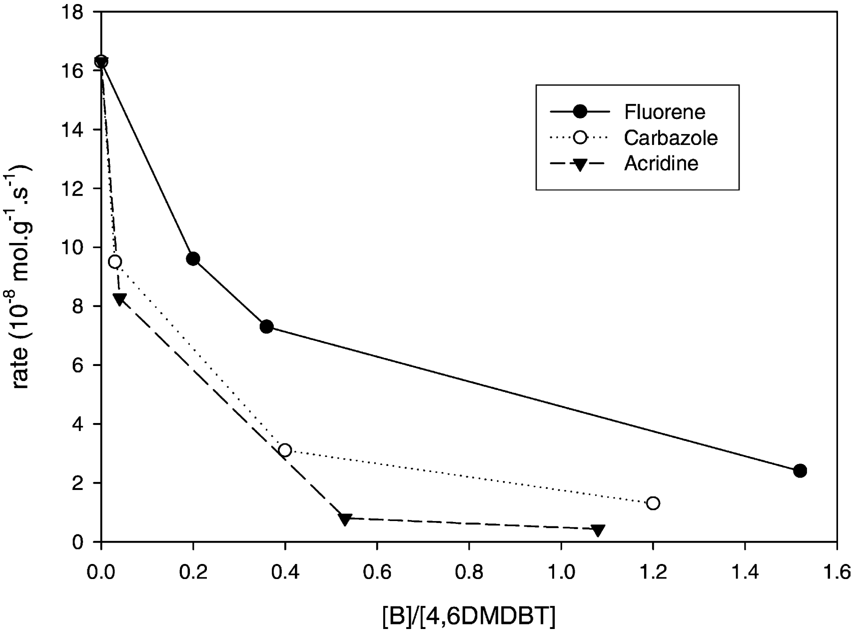


Fig. 2. Rate of transformation of 4,6-DMDBT as a function of the amount of inhibiting compounds (B), adapted from [12].

may be present in the same order of concentration as DBTs, was attributed to a competition shape effect also due to the geometrical (and electronic) similarity of the two compounds.

2.4. Reactivity of real feeds

Such fundamental studies illustrate the complexity of deep desulfurization, evidencing that compounds more refractory than 4,6-DMDBT exist and that complex inhibition phenomena occur with the other molecules present in the feed. An estimate of the reactivity scale of the S-containing molecules and the role of inhibitors in the conversion of a real feed can be obtained by the determination of the kinetic order with respect to sulfur of various untreated or partially desulfurized gas oils. Table 2 summarises the properties of these feeds. The reactions were performed at 613 K, 30 × 10^5 Pa, in a trickle described in [13,14] using various space velocities.

For conventional feeds (containing 10 000–30 000 ppm of S), it is well-documented that the reaction presents an apparent second-order behavior. Such a behavior originates from the complex composition of sulfur compounds in the feedstock, including thiophene, benzothiophene, and substituted DBT. Actually, the pseudo-second-order reaction observed corresponds to the summation of several first-order reactions related to the reactivity of each family of S compounds. After a relatively deep desulfurization, one can expect that the overall reaction order will tend to 1, since only the refractory family of alkyl DBTs remains in the feed. On the contrary, as shown in Table 3,

Table 2
Composition and physical properties of straight run (A) and hydrotreated gas oil feeds (B and C)

	Gas oil A	Gas oil B	Gas oil C
Density (288 K) g/l	850	846	852
Sulfur content (ppm)	13200	515	142
Aromatics (wt.%)	27	36	30

Table 3
Kinetic order with respect to S for various feeds determined on a NiMo catalysts at 613 K

Initial S content	Conversion (%)	Order (s)
1.32 wt.%	20–75	2.2
530 wt. ppm	13–63	2.9
142 wt. ppm	24–50	3.8

the reaction order increases as the sulfur content decreases. These high orders express the large reactivity scale of the various S compounds as shown above and may indicate the increasing role of inhibitors. However, a distribution function model regarding every refractory sulfur component would be more relevant than an *n*th order model for the designing of an ultra-deep desulfurization process [15] but requires a deep knowledge of the reactivity of each sulfur compound. In fact, reaching 10 ppm S level from a starting point of 12 000 ppm, in one step, means to reach a conversion higher than 99.999. Such a conversion level requires either new processes or catalysts and the following part summarizes some potential solutions.

3. Improvements of catalytic processes

Following the mechanistic studies described above, the design of active catalysts might be achieved by several approaches: (i) development of catalysts with enhanced acidic properties to favor the migration of the alkyl groups in positions where there is no steric hindrance for the C–S bond scission; (ii) development of catalysts with enhanced hydrogenation properties to favor the hydrogenation route not inhibited by the presence of alkyl groups in 4,6 positions. The first objective might be achieved by using other supports than alumina such as zeolites. The second one implies a modification of the active phase and the properties of non-conventional catalysts such as association of metal and sulfide or carbide can be examined.

3.1. Acid catalysts

Recently, attempts were made to increase the conversion of 4,6-DMDBT by transforming it into a more reactive compound, either through demethylation [16] or through isomerization [17,18]. These reactions are acid-catalyzed, and consequently were carried out on bifunctional catalysts, such as mechanical mixtures of the alumina-supported sulfide catalyst with an acidic component, silica–alumina or zeolite, or by associating a hydrotreating catalyst such as CoMo/alumina to a Ni/HY catalyst [19]. On such mixed catalyst, the conversion of the 4,6-DMDBT was significantly increased but a rapid deactivation of the acidic function was observed during the first hours of the reaction [17], which was not the case with sulfide catalysts, deposited on alumina–zeolite mixtures [20,21]. Indeed, it is well known that the activity and the stability of bifunctional hydrogenating-acid catalysts depend on the balance between both functions [22,23]. Taking these information into account, we were interested in studying the properties of molybdenum sulfide catalysts promoted by cobalt or nickel dispersed in a dealuminated HY zeolite (from PQ zeolites, Si/Al ratio = 19). With this kind of support, we expected a good distribution of the acidic and hydrogenating sites brought about by the sulfide phase [24].

With the zeolite-supported catalysts the reaction goes through the two expected pathways (DDS and HYD), but additional reactions were observed as illustrated in Scheme 2. The global activity of the unpromoted Mo/Z catalyst was much higher than that of the corresponding Mo/A catalyst even if one considers only the DDS and HYD reactions (see Fig. 3.) This might be ascribed to a better dispersion of the molybdenum sulfide on the zeolite support than on alumina or to an enhancement of the hydrogenation properties of the sulfide phase when it is in close vicinity to acid sites as was observed for ruthenium sulfide dispersed within acidic zeolites [25].

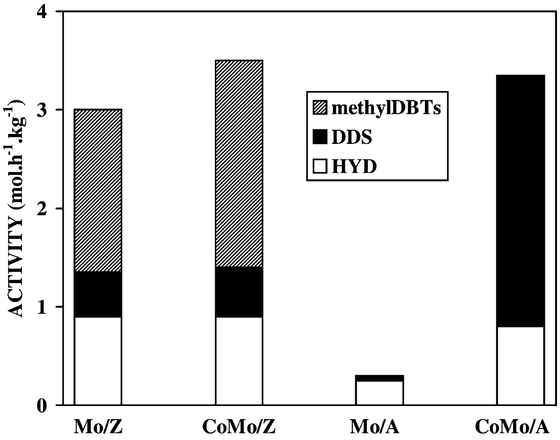
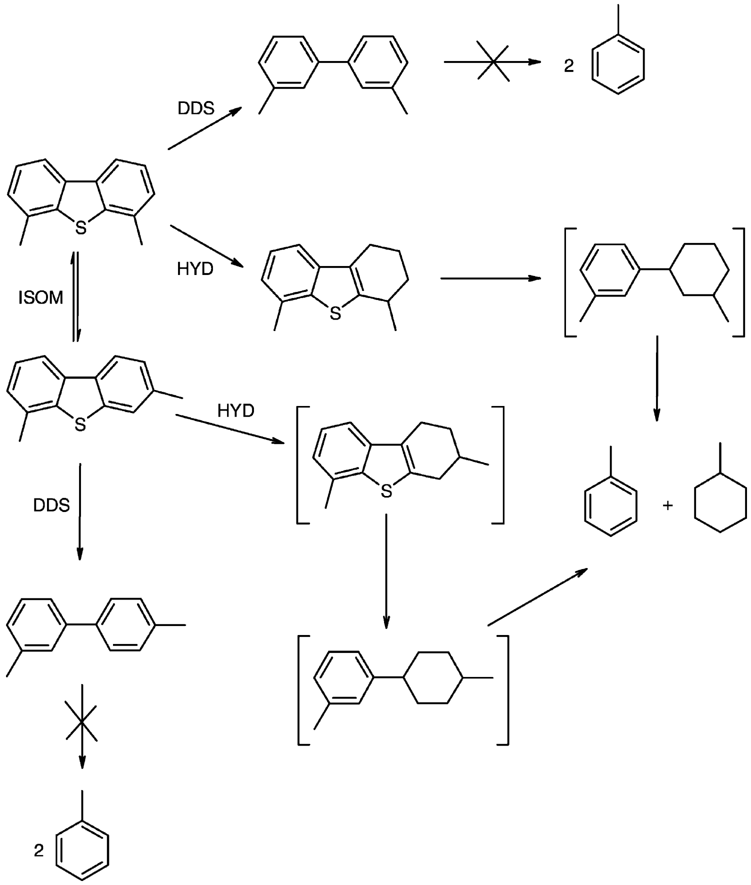


Fig. 3. Transformation of DBT on zeolite- or alumina-supported sulfided catalysts. Fixed bed reactor, 603 K, 30 × 10^5 MPa H_2; Mo/Z: 8.3% Mo; CoMo/Z: 8.5% Mo, 2.2%; CoMo/A: 9.3% Mo, 9.3% Mo, 2.5% Co.



Scheme 2. Transformation of 4,6-DMDBT on zeolite-supported sulfide catalysts. Isomerization (ISOM), DDS, hydrogenation (HYD) pathways.

As observed previously [9,26], and as generally reported in the literature [8,27,28] cobalt exerted a promoting effect on the activity of the Mo catalysts, whatever the support. This effect was very small with the zeolite-supported catalyst as compared to alumina-supported catalyst (Fig. 3). It was suspected that the promoter was not well-associated to molybdenum on the zeolite support, and that the active “CoMoS” phase was not well formed [29–31]. As pointed out [32] the DDS/HYD selectivity in the transformation of DBT is indicative of the association of Co with Mo to form the “CoMoS” phase. This is also what was observed in Fig. 3 with the alumina-supported catalysts (the values of the DDS/HYD selectivity and of the CHB/THDBT molar ratio were multiplied by 12 when Co was added to the Mo/A catalyst). It can therefore be concluded that when the active “CoMoS” phase is well formed, the promoter increases the rate of the C–S bond cleavages compared to the rate of the hydrogenation steps. A possible explanation for the absence of the “CoMoS” phase could be that cobalt, which was introduced as Co^{2+} ions, was presumably well-dispersed in the zeolite [30,33], and could therefore be very difficult to sulfide or at least to maintain in the sulfided state [34,35].

The total activity of Mo/Z in the transformation of 4,6-DMDBT was again much higher than that of Mo/A, and the activity in isomerization of 4,6-DMDBT was quite significant as illustrated in Fig. 4. However, the side reactions (transalkylation and formation of the methyl DBTs) represented about half of the total activity of the catalyst. By contrast to

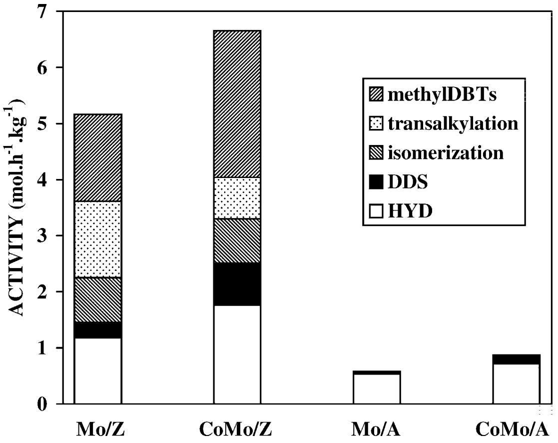


Fig. 4. Transformation of 4,6-DMDBT on zeolite- or alumina-supported sulfided catalysts. Fix bed reactor, 603 K, 30×10^5 MPa H_2; Mo/Z: 8.3% Mo; CoMo/Z: 8.5% Mo, 2.2%; CoMo/A: 9.3% Mo, 9.3% Mo, 2.5% Co.

what was observed in the case of DBT (Fig. 3), the total activity of CoMo/Z was clearly higher than that of CoMo/A.

Although, the CoMoS association is not properly formed on zeolites, which limits the interest of this catalyst for DBT conversion, these catalysts appear promising for the conversion of 4,6-DMDBT. Progresses are still expected in the preparation of mixed catalysts and in the control of the acidity in order to reduce side reactions.

3.2. Metal-sulfide association

As stated above, another way to overcome the low reactivity of 4,6-DMDBT in presence of conventional alumina-supported catalysts would be to favor the hydrogenation pathway by doping conventional systems with small amounts of Pt. The properties of such combination were reported in the literature by Vanhaeren [36] who found a favorable effect of Pt or Rh on a CoMo catalyst. Exxon also patented the introduction of Pt by means of S-containing precursor on a NiMo catalyst [37]. Taking into account the low amount of H_2S in the second reactor of a two-stage process [38–40], it appears more adequate to use the NiW system which is more stable under these conditions [41,42]. The properties of Pt/Al_2O_3, NiW/Al_2O_3 and combination of both active phases on alumina were studied in tetralin and DBT conversion and hydrotreated gas oil desulfurization. An improvement of the catalytic hydrogenation activity in the conversion of the model molecule as well as in the conversion of the real gas oil was observed (see Table 4) with a convenient activation process, i.e. a sulfidation step before impregnation of the noble metal. The optimal Pt concentration was found close to 0.25–0.3% for both reactions. HRTEM micrographs combined with EDS analysis demonstrated that there were separated Pt–S and NiWS phases on the support and no quaternary association. The enhancement of activity was probably due to the additive contribution of the two active phases homogeneously dispersed on the alumina.

3.3. Molybdenum carbides

The interest for transition metal carbides and nitrides, supported by carbon [43] or alumina or non-supported as catalysts for hydrotreatment applications is due to their high hydrogenating properties. As already mentioned above, a strong hydrogenating function is required for the first step of the conversion of alkyl DBT (Scheme 1) and would be interesting for the further hydrogenation steps of the HYD route. Molybdenum carbide, for instance, is as active as ruthenium in liquid or gas phase hydrogenation reactions [44,45] and appears resistant to sulfur poisoning in a second-stage process configuration where the H_2S

Table 4
Rate constants in the conversion of tetralin hydrogenation (500 ppm of H_2S, 45×10^5 Pa, 613 K), DBT (no added H_2S, 35×10^5 Pa, 523 K and desulfurized SR gas oil (142 ppm of S, 30×10^5 Pa, 613 K) of NiW/Al_2O_3, Pt/Al_2O_3 and their combination PtNiW/Al_2O_3

	Reactant	Pt (0.3 wt.%)	NiW/Al_2O_3	PtNiW/Al_2O_3
Rate (10^{-7} mol g^{-1} s^{-1})	Tetralin	0.3	3.7	4.1
Rate constant (10^{-3} l g^{-1} s^{-1})	DBT	0.8	2.5	3.5
K_{app} (10^7 g$^{2.8}$ mmol$^{-2.8}$ h^{-1})	Gas oil	1.3	1.4	2

concentration is rather low (circa 250 wt. ppm S). With alumina-supported molybdenum carbide, the general pathways for HDS were quite similar to those observed over conventional industrial sulfide catalysts but the selectivity was different [46,47]. The active site design is also different from that of sulfide catalysts, i.e. carbon, oxygen being present in the neighborhood of molybdenum or tungsten atoms instead of sulfur.

The activity of molybdenum carbide can be improved by phosphorus addition and it was shown that the activity of a $Mo_2CP(0.4)/Al_2O_3$ catalyst containing 0.4 wt.% of P was more active than a

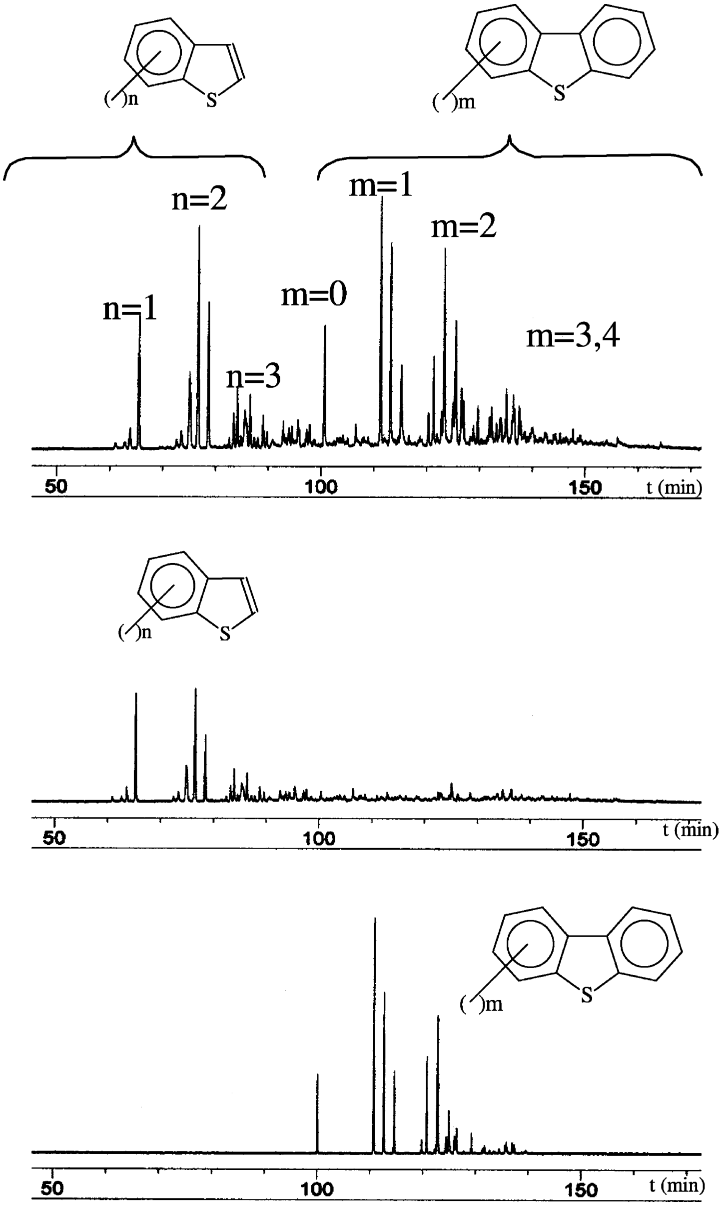
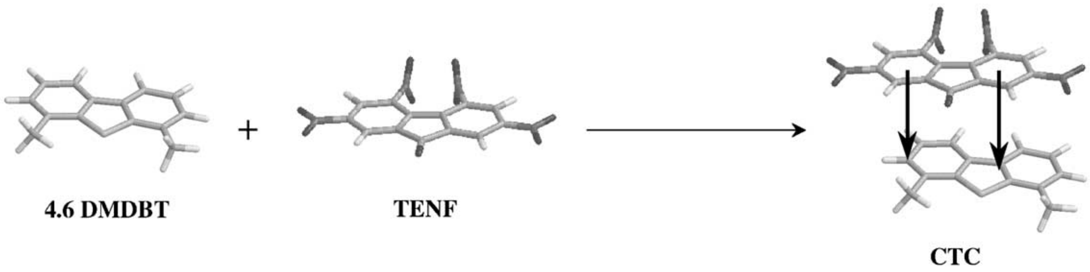


Fig. 5. Sulfur containing compounds in initial oil (top), resulting oil after the CTC process (middle) and from the aromatic compounds trapped by complexation (bottom)

conventional CoMo/Al_2O_3 catalyst for the conversion of 4,6-DMDBT present in an hydrotreated gas oil containing 135 ppm of sulfur [48].

4. Non-catalytic processes

Recently, new processes appeared based on adsorption instead of catalysis. For instance, Philips proposed the S-Zorb-Diesel process based on the decomposition of the S molecules, adsorption of the heteroatom and regeneration by further oxidation of the adsorbent [49]. Another alternative to catalytic desulfurization has been proposed [50]. Considering the electron-rich structure of these refractory alkylated DBTs, the formation and subsequent removal of insoluble charge transfer complexes between these sulfur molecules and suitable π-acceptors was envisaged. Indeed, charge transfer complex could be easily formed between DMDBT and π-acceptors as benzoquinone (BQ), 2,3-dichloro-5-dicyanobenzoquinone (DDQ) or tetranitrofluorenone (TENF). The scheme of the reaction is given below:



Considering the promising results obtained on model molecules, the possible selective complexation of DBTs in gas oil was examined. That was performed at room temperature by adding TENF to high sulfur content gas oil (11 300 ppm). After stirring during few hours, the precipitate was filtered and analyzed as well as the resulting oil. Gas chromatographs obtained with a sulfur-specific Flame Photometric Detector for the starting gas oil, the produced gas oil after the CTC process and for the compounds trapped by complexation are given in Fig. 5. These results demonstrated that the sulfur elimination procedure was specific for DBTs compounds with respect to benzothiophene ones. The complexation capacities and selectivities were correlated to an optimal overlap of the frontier molecular orbitals between the two molecules [51].

However, such an elimination process appeared to be more easily industrialized using supported electron acceptors. Polymer-grafted π-acceptors were prepared by sequential reaction of Merrifield resin (chloromethylated polystyrene) with acetone oxime and TENF, and tested in synthetic and real feeds [52].

5. Conclusion

This paper illustrates in some aspects the challenge of ultra-deep desulfurization. During the last decade, the refining industry has demonstrated its capability to adapt the hydrotreatment to the stringent regulations required by the authorities. The knowledge of the nature and the reactivity of the refractory molecules will allow the design of new catalysts, or combination of catalytic and non-catalytic processes. Besides, other routes such as biodesulfurization or selective oxidation of S molecules and further separation of the sulfones might be envisaged. The problem of hydrogen and energy consumptions as well as CO_2 emissions has to be considered for selecting new processes. Furthermore, the development of FC vehicles may require also fuels for reforming containing sulfur levels below ppm. At this stage adsorption processes will certainly be required. In conclusion, it appears that the ultra-deep desulfurization of diesel fuel is still a challenging area, which has great benefit from the multidisciplinary approach developed during the last years.

Acknowledgements

These studies were carried out within the framework of several collaboration programs between the CNRS and TotalfinaElf, IFP and Procatalyse.

References

[1] European Union, EU Directive 98/70/EC, 1998.
[2] D.D. Withehurst, I. Takaaki, I. Mochida, Adv. Catal. 42 (1998) 345.
[3] H. Schulz, W. Böhringer, F. Ousmanov, P. Waller, Fuel Proc. Technol. 61 (1999) 541.
[4] G.A. Depauw, G.F. Froment, J. Chromatogr. A 761 (1997) 231.
[5] X. Ma, K. Sakanishi, I. Mochida, Ind. Eng. Chem. Res. 33 (1994) 218.
[6] M. Macaud, A. Milenkovic, E. Schultz, M. Lemaire, M. Vrinat, J. Catal. 193 (2000) 255.
[7] G.H. Singhal, R.L. Espino, J.E. Sobel, G.A. Huff, J. Catal. 67 (1981) 457.
[8] V. Meille, E. Schulz, M. Lemaire, M. Vrinat, J. Catal. 170 (1997) 29.
[9] F. Bataille, J.L. Lemberton, P. Michaud, G. Pérot, M. Vrinat, M. Lemaire, E. Schulz, M. Breysse, S. Kasztelan, J. Catal. 191 (2000) 409.
[10] F. van Looij, P. van der Laan, W.H.J. Stork, D.J. DiCamillo, J. Swain, Appl. Catal. A 170 (1998) 1.
[11] T.C. Ho, Catal. Rev.-Sci. Eng. 30 (1988) 117.
[12] T. Koltai, M. Macaud, A. Guevara, E. Schultz, M. Lemaire, R. Bacaud, M. Vrinat, Appl. Catal. A 231 (2002) 253.
[13] D. Letourneur, M. Vrinat, R. Bacaud, Stud. Surf. Sci. Catal. 106 (1997) 491.
[14] D. Letourneur, R. Bacaud, M. Vrinat, D. Schweich, I. Pitault, Ind. Eng. Chem. Res. 37 (1998) 2662.
[15] S. Inoue, T. Takatsuka, Y. Wada, S. Hirohama, T. Ushida, Fuel 79 (2000) 843.
[16] E. Lecrenay, I. Mochida, Stud. Surf. Sci. Catal. 106 (1997) 333.
[17] P. Michaud, J.L. Lemberton, G. Pérot, Appl. Catal. A 169 (1998) 343.
[18] (a) E. Lecrenay, K. Sakanishi, I. Mochida, Catal. Today 39 (1997) 13;
(b) T. Isoda, S. Nagao, Y. Korai, I. Mochida, Am. Chem. Soc. Prepr. Div. Petrol. Chem. 41 (1996) 559;
(c) T. Isoda, S. Nagao, Y. Korai, I. Mochida, Am. Chem. Soc., Prepr. Div. Petrol. Chem. 41 (1996) 563.
[19] T. Isoda, S. Nagao, Y. Korai, I. Mochida, Sekiyu Gakkaishi 41 (1998) 22.
[20] F. Fujikawa, O. Chiyoda, M. Tsukagoshi, K. Idei, S. Takehara, Catal. Today 45 (1998) 307.
[21] T. Isoda, S. Nagao, X. Ma, Y. Korai, I. Mochida, Energy Fuels 12 (1998) 493.
[22] M. Guisnet, F. Alvarez, G. Gianetto, G. Pérot, Catal. Today 1 (1987) 415.
[23] G. Giannetto, G. Pérot, M. Guisnet, Ind. Eng. Chem. Prod. Res. Dev. 25 (1986) 481.
[24] F. Bataille, J.L. Lemberton, G. Pérot, P. Leyrit, T. Cseri, N. Marchal, S. Kasztelan, Appl. Catal. A 220 (2001) 191–205.
[25] M. Breysse, M. Cattenot, V. Kougionas, J.C. Lavalley, F. Maugé, J.L. Portefaix, J.L. Zotin, J. Catal. 168 (1997) 143.
[26] J. Mijoin, V. Thévenin, N. Garcia Aguirre, H. Yuze, J. Wang, W.Z. Li, G. Pérot, J.L. Lemberton, Appl. Catal. A 180 (1999) 95.
[27] M. Houalla, D.H. Broderick, A.V. Sapre, N.K. Nag, V.H.J. De Beer, B.C. Gates, H. Kwart, J. Catal. 61 (1980) 523.
[28] H. Topsøe, B.S. Clausen, F.E. Massoth, Hydrotreating Catalysts, in: J.R. Anderson, M. Boudart (Eds.), Catalysis—Science and Technology, vol. 11, Springer, Berlin, New-York, 1996.
[29] M. Laniecki, W. Zmierczak, Stud. Surf. Sci. Catal. 69 (1991) 331.
[30] R. Cid, F. Orellana, A. Lopez Agudo, Appl. Catal. 32 (1987) 327.
[31] R. Cid, F.J.G. Llambias, M. Gonzales, A. Lopez Agudo, Catal. Lett. 24 (1994) 147.
[32] J. Mijoin, G. Pérot, F. Bataille, J.L. Lemberton, M. Breysse, S. Kasztelan, Catal. Lett. 71 (2001) 139.
[33] R. Cid, J. Villasenor, J.L.G. Fierro, A. Lopez Agudo, Appl. Catal. 18 (1985) 357.
[34] M.J. Vissemberg, P.W. de Bont, E.M. van Oers, R.A. de Haan, E. Boellaard, A.M. van der Kraan, V.H.J. de Beer, R.A. van Santen, Catal. Lett. 40 (1996) 25.
[35] M.J. Vissemberg, P.W. de Bont, J.W.C. Arnouts, L.J.M. van de Ven, R.A. de Haan, A.M. van der Kraan, V.H.J. de Beer, J.A.R. van de Veen, E. Boellaard, Catal. Lett. 47 (1997) 155.
[36] X. Vanhaeren, Ph.D. Thesis, Université catholique de Louvain, 1997.
[37] US Patent 5 152 885 (1992).
[38] S.T. Sie, Fuel Process. Technol. 61 (1999) 149.
[39] W.H.J. Stork, Hydrotreatment and Hydrocraking of Oil Fractions, Elsevier, Amsterdam, 1997, p. 41.
[40] H.R. Reinhoudt, R. Troost, A.D. van Langeveld, S.T. Sie, J.A.R. van Veen, J.A. Moulijn, Fuel Process. Technol. 61 (1999) 133.
[41] H. Yasuda, M. Higo, S. Yoshitomi, T. Sato, M. Imamura, H. Matubayashi, H. Shimada, A. Nishijima, Y. Yoshimura, Catal. Today 39 (1997) 77.
[42] S. Pessayre, Ph.D. Thesis, Université de Lyon, 2000.
[43] D. Mordenti, D. Brodzki, G. Djéga-Mariadassou, J. Solid State Chem. 141 (1998) 114.
[44] S.T. Oyama, Catal. Today 15 (1992) 179.
[45] S.T. Oyama, G.L. Haller, G.C.B. Webb (Ed.) Catalysis, Special Periodic Reports, vol. 5, Springer-Verlag, Dordrecht, 1983, p. 443.
[46] P. Da Costa, C. Potvin, J.-M. Manoli, J.-L. Lemberton, G. Pérot, G. Djéga-Mariadassou, J. Mol. Catal. 184 (2002) 323.
[47] P. Da Costa, C. Potvin, J.-M. Manoli, M. Breysse, G. Djéga-Maraidassou, submitted for publication.
[48] P. Da Costa, J.-M. Manoli, C. Potvin, G. Djéga-Mariadassou, P. Da Silva, S. Kasztelan, F. Diehl, M. Breysse, US Patent 6,372,125 B1 (1999).
[49] World Patent 0132805 (2001).
[50] V. Meille, E. Schulz, M. Vrinat, M. Lemaire, Chem. Commun. (1998) 305.
[51] A. Milenkovic, E. Schulz, V. Meille, D. Lofreda, M. Forissier, M. Vrinat, P. Sautet, M. Lemaire, Energy Fuels 13 (1999) 881.
[52] World Patent WO 024837 (2002).