

New catalysts for deep hydrotreatment of diesel fuel Kinetics of 4,6-dimethyldibenzothiophene hydrodesulfurization over alumina-supported molybdenum carbide

P. Da Costa^a, C. Potvin^a, J.-M. Manoli^a, J.-L. Lemberon^b,
G. Pérot^b, G. Djéga-Mariadassou^{a,*}

^a Laboratoire Réactivité de Surface, UMR 7609, Université P. et M. Curie, 4 Place Jussieu, T 54-55, Case 178, 75252 Paris Cedex 05, France

^b Laboratoire de Catalyse en Chimie Organique, UMR 6503, Université de Poitiers, 40 Avenue du Recteur Pineau, 86022 Poitiers Cedex, France

Received 15 August 2001; accepted 3 January 2002

Abstract

Hydrodesulfurization (HDS) of 4,6-dimethyldibenzothiophene was investigated as a probe for the deep HDS of diesel fuel over alumina-supported molybdenum carbide catalysts. The reaction was carried out at 613 K under 4 MPa total pressure in a fixed-bed reactor, without sulfur addition to the liquid feed, H₂S being generated by the transformation of the reactant.

The reaction proceeds by two parallel routes leading either to 3,3'-dimethylbiphenyl by a direct desulfurization (DDS) pathway or to 3-(3'-methylcyclohexyl)toluene through a preliminary hydrogenation (HYD) pathway. Kinetic data can be divided into two ranges depending on the contact time. For contact times from 0 to 0.4 s (conversion < 45%), the HDS of 4,6-dimethyldibenzothiophene was found to be zeroth-order with respect to the reactant. Therefore, constant reaction rates can be measured for the two routes, the DDS pathway being the more important ($r_{\text{HYD}}/r_{\text{DDS}} = 0.7$).

All data can be interpreted in terms of kinetic coupling of the two catalytic DDS and HYD cycles through a common intermediate species. For contact times higher than 0.4 s the kinetics are more complex. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Molybdenum carbide; Hydrodesulfurization; Kinetics; 4,6-Dimethyldibenzothiophene

1. Introduction

Interest in the deep hydrodesulfurization (HDS) of gasoil has been revived by specifications concerning the sulfur content of diesel fuel. Since 1997 the maximum sulfur content of diesel fuel has been limited to 500 wt. ppm in most parts of the industrial world. However, the European Union recently proposed to reduce this further to only 50 wt. ppm by the

year 2005. The HDS of refractory S-containing compounds and the development of more active catalysts will continue to present problems to refiners.

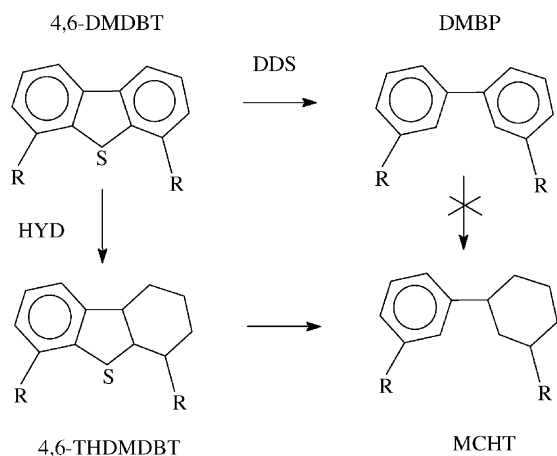
It is now well established that deep HDS stages are hindered mainly by one class of sulfur compounds, alkyldibenzothiophenes (DBT), and in particular by β -substituted alkyldibenzothiophenes: 4-methyldibenzothiophene (4-MDBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT), this latter being the most unreactive towards HDS [1–6].

Hydrodesulfurization of 4,6-dimethyldibenzothiophene has therefore often been chosen as a model to test the reactivity of HDS catalysts and has been

* Corresponding author. Tel.: +33-1-44-27-36-26;

fax: +33-1-44-27-60-33.

E-mail address: jmm@ccr.jussieu.fr (G. Djéga-Mariadassou).



Scheme 1. Hydrodesulfurization of 4,6-DMDBT ($R = \text{CH}_3$), DDS: direct desulfurization; HYD: hydrogenation.

compared to the HDS of the unsubstituted dibenzothiophene. Recent findings on the HDS of polyaromatic sulfur compounds have been reviewed by Whitehurst et al. [7].

The model compound, 4,6-dimethyldibenzothiophene (4,6-DMDBT) can be desulfurized over commercial CoMoS and NiMoS/alumina catalysts via two parallel reactions [8–10]: (i) direct desulfurization denoted DDS, which yields dimethylbiphenyl (DMBP) and (ii) desulfurization with primary hydrogenation of one ring of 4,6-DMDBT, denoted hydrogenation (HYD), which gives tetrahydrodimethylthiophene (4,6-THDMDBT) and then methylcyclohexyltoluene (MCHT) as indicated in the following Scheme 1. This reaction scheme involves partially hydrogenated intermediates (not shown on Scheme 1), some of them being common to the DDS and HYD pathways.

Many studies have been performed to develop new catalysts particularly active in the HDS of refractory molecules [6,11–13]. Conventional sulfided Co(Ni)Mo/alumina catalysts have been much improved for HDS in the past decades but there is not yet a recognized alternative to these materials. Insofar as a strong hydrogenating function is necessary in the HDS reaction [14], the HDS of refractory compounds can also be performed over molybdenum carbides [15,16]. Some studies deal with HDS over supported molybdenum carbide catalysts, where thiophene [17,18], benzothiophene [19,20] and dibenzothiophene [16] have been used as model compounds.

Several authors have found pseudo-first-order kinetics for the HDS of dibenzothiophene-type compounds [2,21,22] at a partial pressure of hydrogen disulfide sufficient to maintain the composition of the sulfide catalysts. Hougen-Watson kinetics have also been applied for the HDS of dibenzothiophene, 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene over a commercial CoMo/Al₂O₃ catalyst [23]. However, the kinetics of HDS of dibenzothiophene-type compounds over carbide catalysts has never been studied. The aim of the present study is to examine 4,6-DMDBT HDS over alumina-supported molybdenum carbide catalysts and to propose a kinetic model of this reaction. The order of reaction was determined, rates of reaction routes for HDS of 4,6-DMDBT measured, and the selectivity (MCHT/DMBP) of the process calculated.

2. Experimental

2.1. Materials

The support consisted of γ -alumina extrudates provided by Procatalyse (specific surface area, $S_g = 205 \text{ m}^2 \text{ g}^{-1}$, total pore volume $V_p = 0.7 \text{ cm}^3 \text{ g}^{-1}$). Ammonium heptamolybdate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot x\text{H}_2\text{O}$ (Acros) was used as precursor. Gases employed were CH₄, Ar, O₂ and H₂ (Air Liquide, 99.995%). Biphenyl (BP) and decalin (Aldrich, 99% purity) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) (Eburon Chemicals, 95% purity) were used as received.

2.2. Catalyst preparation

Supported molybdenum (10% w/w molybdenum loading) materials were prepared using the incipient wetness method with aqueous solutions containing the appropriate amounts of the molybdenum precursor. The alumina extrudates once impregnated were dried at 393 K for 12 h. Supported carbides (Mo₂C/Al₂O₃) were prepared by temperature-programmed carburization (TPC) using a modification of the procedure described elsewhere [24]. Carbide synthesis was divided into two steps. First the impregnated extrudates were heated in flowing argon (flow rate: $60 \text{ cm}^3 \text{ min}^{-1}$) and held at 673 K for 8 h. The material was then carburized by TPC in flowing CH₄/H₂ (20% v/v mixture,

total flow rate: $60 \text{ cm}^3 \text{ min}^{-1}$), the temperature being raised linearly from 673 to 950 K. At this final temperature the flow was switched to hydrogen and the material cooled to room temperature (RT). The flow was then switched to an O_2/Ar mixture (1% v/v) for a passivation step ($170 \text{ cm}^3 \text{ min}^{-1}$ for 1 h).

Extrudates of supported carbides were ground and sieved to between 0.25 and 0.4 mm. These powders were used for characterization and catalytic runs.

2.3. Standard reaction conditions

Hydrodesulfurization of 4,6-DMDBT was carried out in a flow reactor at 613 K and a total pressure of 4 MPa; decalin was used as solvent, the mixture being injected by a high-pressure pump (Gilson, model 307). Under standard reaction conditions the various partial pressures were: 4,6-DMDBT, 0.001 MPa; decalin, 0.888 MPa; hydrogen, 3.111 MPa. Due to the high boiling points of the reactants, on-line analysis of the reaction products was not convenient. Consequently, the reactor effluents were condensed, and liquid samples were collected about every hour and analyzed by gas chromatography. Analyses were carried out on a Varian 3400 chromatograph equipped with a 50 m DB17 capillary column (J&W Scientific) with temperature programming from 373 to 503 K (10 K min^{-1}).

Before reaction, 0.4 g of supported carbides were pretreated in situ, at 423 K and 4 MPa in flowing hydrogen ($16.7 \text{ cm}^3 \text{ min}^{-1}$) for 1 h to remove the passivation layer. The reaction mixture was then introduced and the temperature raised to 613 K.

The partial pressure of H_2S depended on the HDS conversion and ranged from 0 to 0.0009 MPa corresponding to 90% conversion of 4,6-DMDBT. The ratio of H_2 flow/liquid feed flow was set to 500. For each run, so for each contact time, a new sample of catalyst (0.4 g; 0.571 cm^3) was used. The liquid feed was totally vaporized in the hydrogen flow under our reaction conditions. The contact time was calculated from the total flow rate (4,6-DMDBT, decalin and hydrogen) and the catalyst volume.

The kinetics were studied with contact times up to 2 s. The amounts of 4,6-DMDBT reacted and of products obtained were calculated from the molar conversion of the reactant and the molar formation of products at each contact time.

3. Results

The major products of 4,6-DMDBT HDS are 3,3'-dimethylbiphenyl (DMBP) and 3-(3'-methylcyclohexyl)toluene (MCHT); 4,6-tetrahydrodimethyldibenzothiophene (4,6-THDMDBT) was detected as a minor product with a maximum molar concentration of 4% relative to unconverted reactant and other products of the reaction (Figs. 1 and 2). The HDS of 4,6-THDMDBT is very rapid and MCHT appears to be a primary product. For contact times higher than 1.5 s, 3,3'-dimethyldicyclohexyl (DMDCH) was also detected, as reported in Fig. 1.

On other catalysts [6,25,26], it was assumed that the HDS mechanism occurs via two separate pathways, leading to MCHT and DMBP as primary products of the HDS reaction of 4,6-DMDBT. No evidence for this reaction has ever been shown on molybdenum carbide catalysts. To check this point we studied the hydrogenation of BP on supported molybdenum carbide catalyst. BP was chosen because it has the same structure as DMBP and can be used to distinguish between cyclohexylbenzene (CHB) and hydrogenated dimethylbiphenyl (MCHT) coming from 4,6-DMDBT transformation.

Hydrogenation of BP was carried out at 613 K at a total pressure of 4 MPa to maintain the same experimental conditions as those used for 4,6-DMDBT HDS. In a first step, BP was hydrogenated on $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ at 613 K with a contact time of 0.75 s. BP was dissolved in decalin, the various partial pressures being: decalin, 0.880; BP, 0.009; H_2 , 3.111 MPa, and the catalyst weight 0.4 g (0.571 cm^3).

Fig. 3 shows BP hydrogenation conversion versus time on stream for the supported catalyst. After a stabilization time of 10 min, the first analysis was performed 30 min later. BP was hydrogenated to CHB with a conversion of 70% at which level it remained for at least 6 h. At this point 4,6-DMDBT was added to the liquid mixture and submitted to reaction over the supported molybdenum carbide catalyst. The partial pressures then became: decalin, 0.879; BP, 0.009; 4,6-DMDBT, 0.001; H_2 , 3.111 MPa. As observed in Fig. 3, BP hydrogenation fall sharply with a conversion of only 10%, even with a high $P_{\text{BP}}/P_{4,6\text{DMDBT}}$ (=9). This observation indicates that competitive adsorption of BP and 4,6-DMDBT occurs

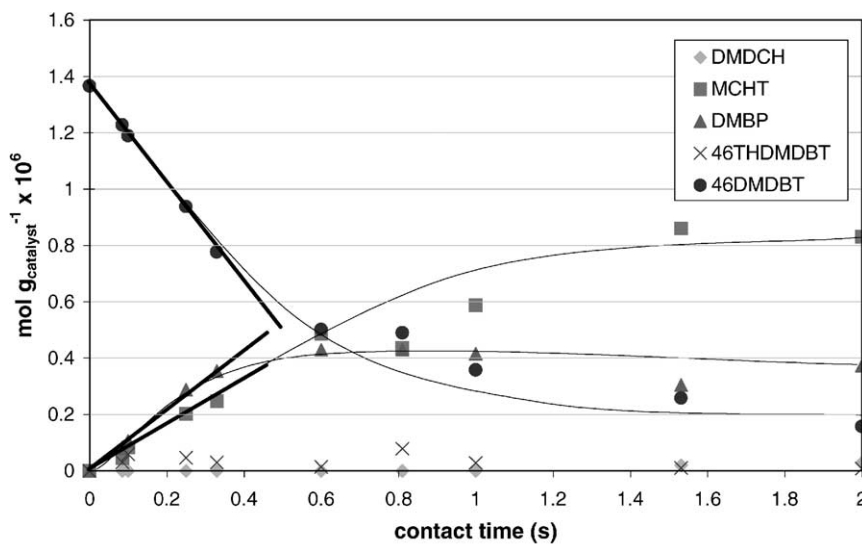


Fig. 1. Hydrodesulfurization of 4,6-DMDBT over $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$: moles of reactant and products per gram of catalyst vs. contact time.

on the active sites. It seems reasonable to assume that for low contact times and low $P_{\text{DMBP}}/P_{4,6\text{DMDBT}}$ ratios, as obtained during the HDS reaction, the hydrogenation of DMBP giving MCHT does not occur. These results show that under our experimental conditions, MCHT is produced mainly from tetrahydrodimethyldibenzothiophene (4,6-THDMDBT).

Consequently, it can be concluded that the transformation of 4,6-DMDBT occurs on $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ through two parallel reactions (Scheme 1), namely (i) direct desulfurization (DDS) yielding DMBP and (ii) desulfurization after partial HYD first yielding 4,6-THDMDBT and then MCHT, in agreement with previous work on sulfided catalysts [6].

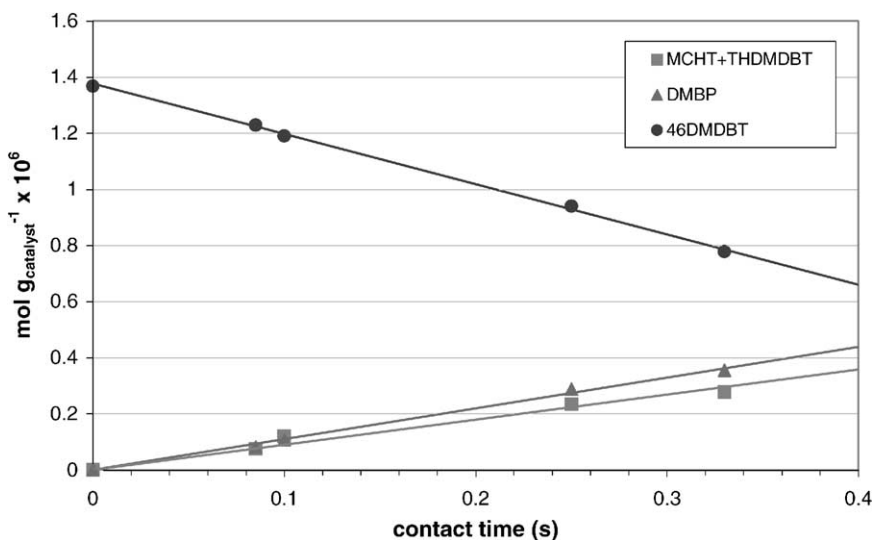


Fig. 2. Hydrodesulfurization of 4,6-DMDBT over $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ at low contact time (<0.4 s).

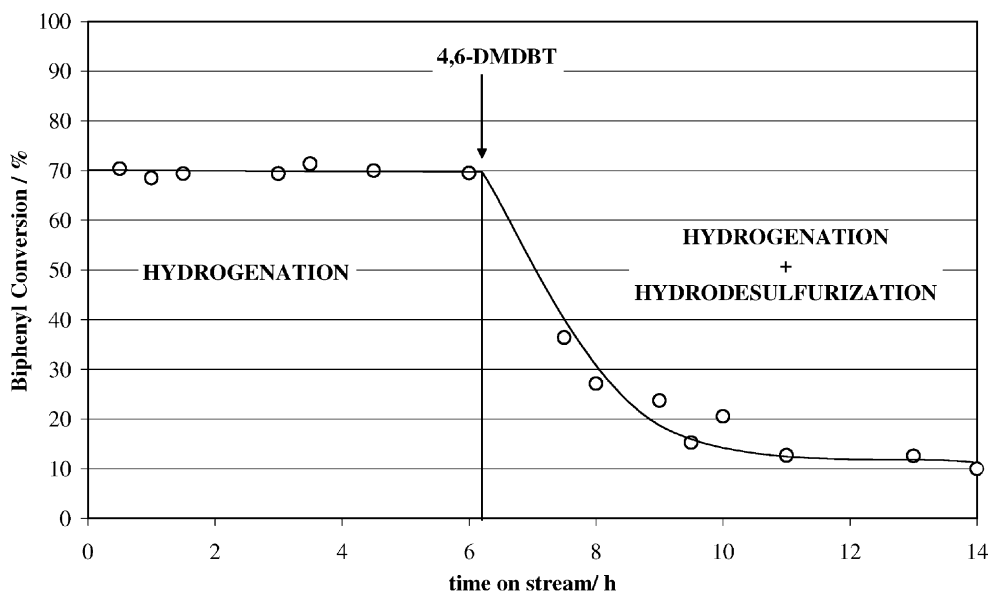


Fig. 3. Hydrogenation of biphenyl over $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ in the absence and in the presence of 4,6-DMDBT.

Fig. 1 displays moles of reactant and products versus contact time. Two zones can be observed, the first corresponding to a contact time lower than 0.4 s, i.e. conversion lower than about 45 mol%. In this case, the number of moles of 4,6-DMDBT and of the two major products were easily fitted by a linear regression.

As reported in Fig. 1, 4,6-THDMDBT, the intermediate of the desulfurization route with primary HYD, is almost constant, given the experimental uncertainty, but not negligible at low contact time, when a zeroth-order reaction is observed. The HYD rate could therefore be expressed as a sum of the 4,6-THDMDBT and MCHT formation rates. The straight lines at low conversion are fitted in Fig. 2; these linear relationships for 4,6-DMDBT transformation and for DMBP and MCHT + THDMDBT formation are characteristic of zeroth-order reactions. The reaction rates calculated from Fig. 2 are as follows: the overall 4,6-DMDBT consumption rate (r_{HDS}) is $1.87 \times 10^{-6} \text{ mol g}^{-1} \text{ s}^{-1}$, the MCHT formation rate (r_{HYD}) $0.76 \times 10^{-6} \text{ mol g}^{-1} \text{ s}^{-1}$ and the DMBP formation rate (r_{DDS}) $1.10 \times 10^{-6} \text{ mol g}^{-1} \text{ s}^{-1}$.

We conclude for alumina-supported molybdenum carbide that the DDS route is favored in the HDS of 4,6-DMDBT. The sum of r_{DDS} and r_{HYD} is equal

to the overall HDS rate corresponding to 4,6-DMDBT transformation.

For the second zone with contact times higher than 0.4 s (Fig. 1), no linear relationship can be applied and the kinetics of the reaction is more complex. At higher conversion MCHT, the major product of the HYD pathway, can also be the hydrogenation product of DMBP.

4. Discussion

In agreement with previous work on an industrial sulfided $\text{NiMo}/\text{Al}_2\text{O}_3$ catalyst [10], the HDS reaction proceeds over $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ first through partial hydrogenation of one of the two rings of dibenzothio- phene, leading to a dihydro derivative of 4,6-DMDBT which can be a common intermediate species for the DDS and HYD routes. According to Bataille et al. [10], nine dihydro isomers (divided into two groups) can be formed through partial hydrogenation of 4,6-DMDBT (Fig. 4). The first set with a $\text{C}(\text{sp}^3)\text{-S}$ bond, is presented in Fig. 4 (intermediates 1–3). The second set with a $\text{C}(\text{sp}^2)\text{-S}$ bond includes the dihydro intermediates 4–9 (Fig. 4). These two types of dihydro intermediates can be in equilibrium on the surface

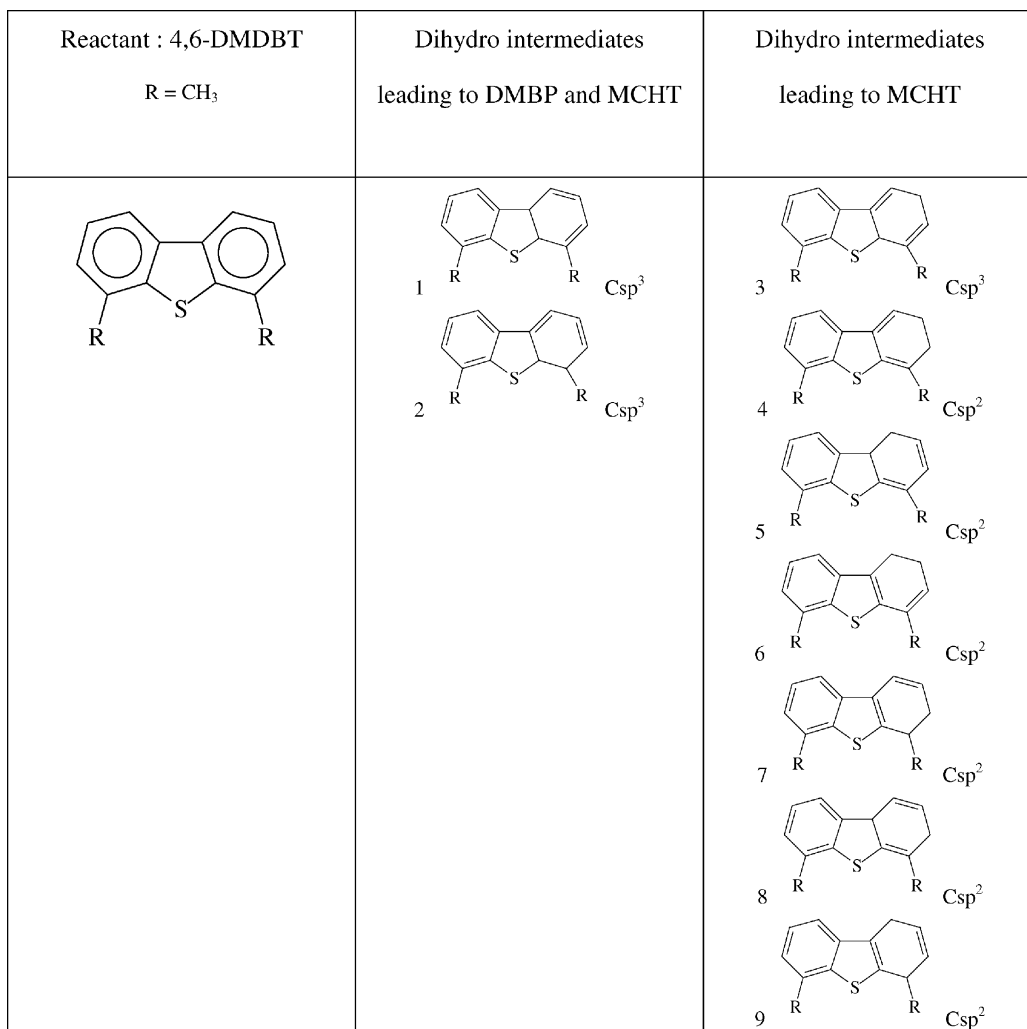


Fig. 4. Isomers of the dihydro intermediates in the hydrodesulfurization of 4,6-DMDBT.

of the catalyst. The bond energy of C(sp³)-S is lower (345 kJ mol⁻¹) than that of C(sp²)-S (610 kJ mol⁻¹). Hence, C-S bond cleavage, leading to DMBP (DDS) through an elimination step (E2), occurs preferentially at an sp³ carbon. As already reported by Bataille et al. [10] for supported nickel-molybdenum sulfide catalysts, only the dihydro isomers 1 and 2 (Fig. 4) can lead to DMBP.

Therefore, according to Bataille et al. [10], the intermediates (3–9) forming the second group will be converted by further hydrogenation to tetrahydro isomers (HYD) before C-S bond cleavage. On the other

hand, only two of the dihydro intermediates, 1 and 2, in Fig. 4, forming the first group, can undergo a direct elimination step leading to C-S bond cleavage (DDS) and regenerating an aromatic ring (production of DMBP).

Finally, two routes for HDS of 4,6-DMDBT can be considered, one leading to DDS and requiring dihydro intermediates 1 or 2, and the second leading to HYD including all dihydro intermediates reported in Fig. 4. Notice that each of the dihydro intermediates 1 and 2 can lead to both pathways and generate DMBP and MCHT.

4.1. Rate equations

Rate equations for HDS will be established for a total conversion of 4,6-DMDBT lower than 45 mol% and corresponding to a zeroth-order in 4,6-DMDBT. Two possible cases are presented.

Case 1. Rate equations in the case of two dihydrogenated intermediates and only one common species for both DDS and HYD.

To set up the kinetic equations for HDS of 4,6-DMDBT, one assumption presented before will be considered. The reaction occurs through two parallel reactions with a common intermediate: adsorbed 4,6-DMDBT. The expression of the overall reaction rate r_{HDS} deduced from Fig. 5 is the sum of the DDS (r_{DDS}) and HYD (r_{HYD}) rates:

$$-\frac{d[4,6\text{-DMDBT}]}{dt} = r_{\text{HDS}} = r_{\text{DDS}} + r_{\text{HYD}} \quad (1)$$

These reactions can be described by two coupled catalytic networks (HYD and DDS cycles) represented in Fig. 5. In each catalytic cycle, according to the steady-state approximation, all steps have the same net rate. In each cycle, the first elementary step, in the case of supported molybdenum carbide catalysts, is a dihydrogenation of the reactant leading to two different dihydrogenated derivatives of 4,6-DMDBT presented in Fig. 4. These two first elementary steps

are accessible experimentally and give the turnover rates of the two coupled cycles.

For the HDS of 4,6-DMDBT, the major species present at the surface can be considered as follows:

[*]	free active sites
[H*H]	adsorbed hydrogen
[DMDBT*]	adsorbed 4,6-DMDBT (reactant)
[THDMDBT*]	adsorbed 4,6-THDMDBT (minor product, HYD route)
[MCHT*]	adsorbed MCHT (HYD product)
[DMBP*]	adsorbed DMBP (DDS product)

We have nine dihydrogenated intermediates and nine rates for the HYD route and two dihydrogenated intermediates and two rates for the DDS routes.

If we note $k_{1\text{H}i}$ the first rate constant of the HYD route HYD and $k_{1\text{D}i}$ the rate constant of the first elementary step in the direct DDS route, the overall HDS rate law becomes:

$$r_{\text{HDS}} = \sum_{i=1,9} k_{1\text{H}i} P_{\text{H}_2} [\text{DMDBT}^*] + \sum_{i=1,2} k_{1\text{D}i} P_{\text{H}_2} [\text{DMDBT}^*] \quad (2)$$

Under our experimental conditions, the partial pressure of hydrogen is higher than that of 4,6-DMDBT and remains practically constant during the reaction.

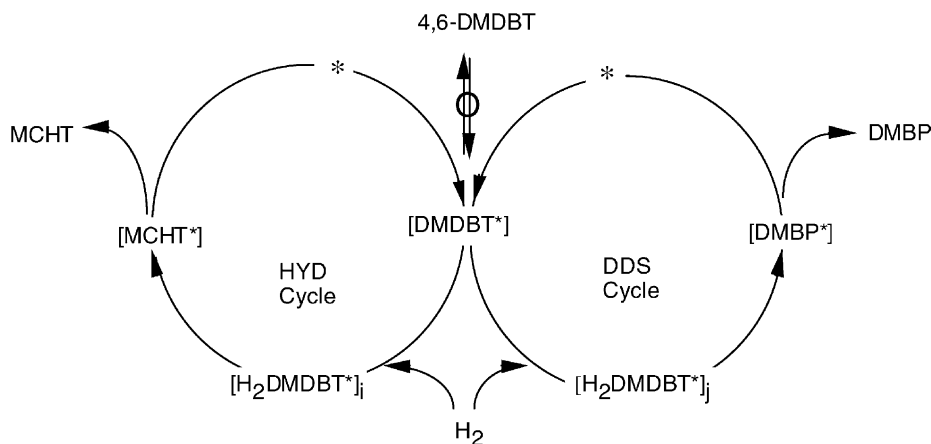


Fig. 5. Catalytic cycle for hydrodesulfurization of 4,6-DMDBT over $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ leading to a zeroth-order reaction. One common adsorbed species and two different dihydro intermediates for DDS and HYD.

Expression (2) leads to:

$$r_{\text{HDS}} = k_{1\text{H},\text{H}_2} [\text{DMDBT}^*] + k_{1\text{D},\text{H}_2} [\text{DMDBT}^*] \quad (3)$$

$$r_{\text{HDS}} = (k_{1\text{H},\text{H}_2} + k_{1\text{D},\text{H}_2}) [\text{DMDBT}^*] \quad (4)$$

with $k_{1\text{H},\text{H}_2} = P_{\text{H}_2} \sum_{i=1,9} k_{1\text{H}i}$
and $k_{1\text{D},\text{H}_2} = P_{\text{H}_2} \sum_{i=1,2} k_{1\text{D}i}$.

If we note $[L]$ the density of sites, the balance of surface species can be written as follows:

$$[L] = [*] + [\text{DMDBT}^*] + [\text{THDMDBT}^*] + [\text{MCHT}^*] + [\text{DMBP}^*] + [\text{H}^*\text{H}] + [\varepsilon^*] \quad (5)$$

$[\varepsilon^*]$ represents other species in very low concentration on the surface and can therefore be neglected. The adsorbed 4,6-DMDBT, $[\text{DMDBT}^*]$ can be calculated as:

$$[\text{DMDBT}^*] = \frac{[L]}{1 + ([*]/[\text{DMDBT}^*]) + ([\text{THDMDBT}^*]/[\text{DMDBT}^*]) + ([\text{DMBP}^*]/[\text{DMDBT}^*]) + ([\text{MCHT}^*]/[\text{DMDBT}^*]) + ([\text{H}^*\text{H}]/[\text{DMDBT}^*])} \quad (6)$$

Introducing K_X the adsorption/desorption equilibrium constant:



with X in the gas phase, X^* the corresponding surface adsorbed species and “*” a free active site, Eq. (6) leads to Eq. (8):

$$[\text{DMDBT}^*] = \frac{[L]}{1 + ((1)/(K_{\text{DMDBT}}^{[\text{DMDBT}]}) + ((K_{\text{THDMDBT}}^{[\text{THDMDBT}]})/(K_{\text{DMDBT}}^{[\text{DMDBT}]}) + ((K_{\text{DMBP}}^{[\text{DMBP}]})/(K_{\text{DMDBT}}^{[\text{DMDBT}]}) + ((K_{\text{MCHT}}^{[\text{MCHT}]})/(K_{\text{DMDBT}}^{[\text{DMDBT}]}) + ((K_{\text{H}_2} P_{\text{H}_2})/(K_{\text{DMDBT}}^{[\text{DMDBT}]})} \quad (8)$$

Therefore, the HDS rate (4) obeys the following Eq. (9):

$$r_{\text{HDS}} = \frac{(k_{1\text{H},\text{H}_2} + k_{1\text{D},\text{H}_2}) K_{\text{DMDBT}}^{[\text{DMDBT}]} [L]}{1 + K_{\text{DMDBT}}^{[\text{DMDBT}]} + K_{\text{THDMDBT}}^{[\text{THDMDBT}]} + K_{\text{DMBP}}^{[\text{DMBP}]} + K_{\text{MCHT}}^{[\text{MCHT}]} + K_{\text{H}_2} P_{\text{H}_2}} \quad (9)$$

It is seen that the reactant concentration appears in the numerator and denominator (the reactant could play an inhibitor role). The order of reaction relative to the reactant is therefore complex.

In the same way, the DDS and HYD rate laws are given by the following expressions:

$$r_{\text{HDS}} = r_{\text{DDS}} + r_{\text{HYD}} \quad (10)$$

$$r_{\text{HDS}} = k_{1\text{D},\text{H}_2} [\text{DMDBT}^*] + k_{1\text{H},\text{H}_2} [\text{DMDBT}^*] \quad (11)$$

To be consistent with the zeroth-order reactions observed in Fig. 2 for contact times less than 0.4 s and conversion lower than 45%, active sites must be saturated by the reactant.

If $[\text{DMDBT}^*]$ is the most abundant reaction intermediate (MARI) [27] the other species can be neglected and the balance of surface species can be simplified as: $[L] = [\text{DMDBT}^*]$ with $[\text{DMDBT}^*] \gg [*] + [\text{THDMDBT}^*] + [\text{MCHT}^*] + [\text{DMBP}^*] + [\text{H}^*\text{H}]$. Eqs. (9)–(11) become Eqs. (12)–(14), respectively:

$$r_{\text{HDS}} = (k_{1\text{H},\text{H}_2} + k_{1\text{D},\text{H}_2}) [L] \quad (12)$$

$$r_{\text{DDS}} = k_{1\text{D},\text{H}_2} [L] \quad (13)$$

$$r_{\text{HYD}} = k_{1\text{H},\text{H}_2} [L] \quad (14)$$

Experimentally, as expected from Eq. (13) to (14), the overall HDS, HYD and DDS rates are constant for a given catalyst, and for a density of sites $[L]$, in the presence of excess hydrogen.

Case 2. Rate equations in the case of one equilibrated reaction in the first hydrogenation step of 4,6-DMDBT and subsequent dihydrogenated intermediates in quasi-equilibrium.

A second case should be considered if a zeroth-order reaction is required. Case 2 involves an adsorbed dihydrogenated derivative. The following sequence is assumed:

(i) adsorption/desorption equilibrium



(ii) quasi-equilibrated step leading to the formation of adsorbed dehydrogenated intermediate

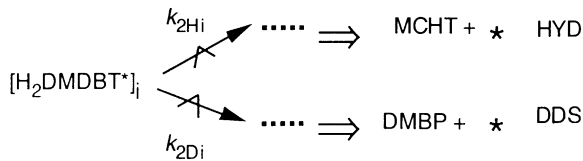


with

$$K_1 = \frac{[\text{DMDBT}^*]}{[*][4,6\text{-DMDBT}]} \quad \text{and}$$

$$K_2 = \frac{[\text{H}_2\text{DMDBT}^*]_i}{P_{\text{H}_2}[\text{DMDBT}^*]}$$

where K_1 is an adsorption/desorption equilibrium constant, and K_2 an equilibrium constant from a quasi-equilibrated hydrogenation reaction of 4,6-DMDBT.



The resulting overall HYD and DDS rates are the sum of the HYD and DDS rates for all individual adsorbed dihydrogenated species assumed to be in equilibrium:

$$\begin{aligned}
 r_{\text{HYD}} &= \sum_{i=1,9} k_{2\text{H}i} [\text{H}_2\text{DMDBT}^*]_i, \\
 r_{\text{DDS}} &= \sum_{i=1,2} k_{2\text{D}i} [\text{H}_2\text{DMDBT}^*]_i
 \end{aligned} \quad (15)$$

and

$$\begin{aligned}
 r_{\text{HYD}} &= [\text{DMDBT}^*] P_{\text{H}_2} \sum_{i=1,9} k_{2\text{H}i} K_{2i}, \\
 r_{\text{DDS}} &= [\text{DMDBT}^*] P_{\text{H}_2} \sum_{i=1,2} k_{2\text{D}i} K_{2i}
 \end{aligned}$$

The overall rate equation is:

$$\begin{aligned}
 r_{\text{HDS}} &= r_{\text{HYD}} + r_{\text{DDS}} \\
 r_{\text{HDS}} &= K_2 P_{\text{H}_2} [\text{DMDBT}^*]
 \end{aligned} \quad (16)$$

with $k_2 = \sum_{i=1,9} k_{2\text{H}i} K_{2i} + \sum_{i=1,2} k_{2\text{D}i} K_{2i}$ but if the overall order is zero, the adsorbed dihydrogenated intermediate concentration is lower than that of the adsorbed reactant:

$$[\text{DMDBT}^*] \sim [L] \gg [\text{H}_2\text{DMDBT}^*]$$

[DMDBT*] being the MARI, the HDS rate law is:

$$r_{\text{HDS}} = k_2 P_{\text{H}_2} [L] \quad (17)$$

$$r_{\text{HDS}} = k'_2 [L] \quad (18)$$

with $k'_2 = k_2 P_{\text{H}_2}$. Eq. (18) is the final expression for the HDS rate of 4,6-DMDBT when the reaction intermediate is H_2DMDBT . In this Case 2, a zeroth-order reaction relative to 4,6-DMDBT for the overall and the HYD and the DDS routes is expected.

4.2. Experimental data for reaction rates at contact time lower than 0.4 s over $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$

The results obtained for alumina-supported molybdenum carbide are:

$$r_{\text{HDS}} = 1.86 \times 10^{-6} \text{ mol g}^{-1} \text{ s}^{-1}$$

$$r_{\text{HYD}} = 0.76 \times 10^{-6} \text{ mol g}^{-1} \text{ s}^{-1}$$

$$r_{\text{DDS}} = 1.10 \times 10^{-6} \text{ mol g}^{-1} \text{ s}^{-1}$$

$$\text{Selectivity} : \frac{r_{\text{HYD}}}{r_{\text{DDS}}} = 0.7$$

For contact times lower than 0.4 s, i.e. for a conversion lower than 45%, a zeroth-order reaction is obtained. The two previous kinetic models, Eqs. (12) and (18), fit the results for alumina-supported molybdenum carbides, but the kinetics is unable to distinguish which is the more appropriate.

The most important feature of this kind of catalyst, operating at 613 K under a total pressure of 4 MPa, for conversion less than 45% is that DDS is favoured over HYD. The rate ratio ($r_{\text{HYD}}/r_{\text{DDS}}$), i.e. the selectivity, is 0.7.

Comparison with sulfided alumina-supported molybdenum oxide and sulfided commercial alumina-supported NiMo oxides is made with materials operating at same temperature (613 K) and total pressure (4 MPa), but under different sulfiding conditions (H_2S partial pressure of 0.10 MPa for sulfided materials against a maximum of 0.0009 MPa for carbide materials) required to keep sulfided catalysts sulfided. As reported [10], the main pathway for the HDS reaction of 4,6-DMDBT is hydrogenation (HYD) (90%). The promoted sulfided $\text{NiMoS}/\text{Al}_2\text{O}_3$ is twice as active with an enhancement of the rate of the DDS pathway.

Nevertheless, the HYD pathway is still the more important (80%). These results underline the difference between alumina-supported molybdenum carbides and sulfided catalysts.

4.3. Reaction rate calculations at high conversion over Mo_2C/Al_2O_3

For high contact times (conversion > 45%), the kinetics becomes more complex and corresponds to Eq. (9) (Case 1). This change could be explained by a modification of the surface molecule distribution (Fig. 1). In fact, a zeroth-order reaction implies that 4,6-DMDBT (Case 1) saturates the surface. At higher conversion, the catalyst surface is not saturated and other compounds like DMBP can be adsorbed. In this case, there is a new competitive reaction, the hydrogenation of DMBP to MCHT. Eq. (9) is justified at high conversion where the reactant does not saturate the surface.

5. Conclusion

The HDS of 4,6-DMDBT on alumina-supported molybdenum carbides occurs through two different coupled routes: a direct DDS route and a HYD one. The kinetics of HDS of the model molecule, 4,6-DMDBT, was studied at 613 K and 4 MPa with a H_2S partial pressure generated by the reactant, ranging from 0 to 0.0009 MPa. Both routes, DDS and HYD, as well as the overall conversion of 4,6-DMDBT, are zeroth-order in 4,6-DMDBT for contact times ranging from 0 to 0.4 s and for conversion lower than 45%.

From the kinetic data obtained in this work, a mechanistic scheme was devised involving a common adsorption step for both reaction paths. One proposal for coupled catalytic cycles is considered, involving a unique adsorbed species common to both cycles. The selectivity ($r_{HYD}/r_{DDS} = 0.7$) indicates that direct DDS is favoured over alumina-supported molybdenum carbides.

This contrasts with the result obtained over sulfided alumina-supported molybdenum oxides and sulfided commercial alumina-supported nickel-molybdenum oxides, operating under the same conditions of temperature (613 K) and pressure (4 MPa total pressure), but with a higher H_2S partial pressure (0.1 MPa).

For these materials, the main route for the HDS of 4,6-DMDBT is the HYD pathway (90% for sulfided Mo/Al_2O_3 , 80% for sulfided $NiMo/Al_2O_3$ which is more active).

Further work on alumina-supported molybdenum carbides promoted by phosphorus will be presented and will confirm this description of the kinetics of the HDS reaction of 4,6-DMDBT under the same conditions. Furthermore, direct relation between kinetic behaviour and acid-base or metallic properties of our materials will allow new strategies for the synthesis of improved catalysts for the HDS of alkyldibenzothiophenes.

Acknowledgements

This work was carried out in the framework of the program “Post-traitement de coupes hydrotraitées” supported by ELF, IFP, TOTAL, PROCATALYSE and CNRS-ECODEV. Thanks are due to Dr. J.S. Lomas for fruitful discussions and for correcting the manuscript.

References

- [1] D.R. Kilanowski, H. Teeuwen, V.H.J. de Beer, B.C. Gates, G.C.A. Schuit, H. Kwart, *J. Catal.* 55 (1978) 129.
- [2] 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.
- [3] T. Kabe, A. Ishihara, H. Tajima, *Ind. Eng. Chem. Res.* 31 (1992) 1577.
- [4] X. Ma, K. Sakanishi, T. Isoda, I. Mochida, *Ind. Eng. Chem. Res.* 34 (1995) 748.
- [5] V. Meille, E. Schulz, M. Lemaire, M. Vrinat, *J. Catal.* 170 (1997) 29.
- [6] P. Michaud, J.-L. Lemberon, G. Pérot, *Appl. Catal. A* 169 (1998) 348.
- [7] D.D. Whitehurst, T. Isoda, I. Mochida, *Advances in Catalysis*, Vol. 42, Academic Press, London, 1998, p. 345.
- [8] M. Houalla, N.K. Nag, A.V. Sapre, D.H. Broderick, B.C. Gates, *AIChE J.* 24 (1978) 1015.
- [9] G.H. Singhal, R.L. Espino, J.E. Sobel, G.A. Huff, *J. Catal.* 67 (1981) 457.
- [10] F. Bataille, J.-L. Lemberon, P. Michaud, G. Pérot, M. Vrinat, M. Lemaire, E. Schulz, M. Breyse, S. Kasztelan, *J. Catal.* 191 (2000) 409.
- [11] H. Topsøe, B.S. Clausen, F.E. Massoth, *Hydrotreating Catalysis*, Springer, Berlin, 1996.
- [12] H.R. Reinholdt, R. Troost, A.D. van Langeveld, S.T. Sie, J.A.R. van Veen, J.A. Moulijn, *Fuel Proc. Tech.* 61 (1999) 133.

- [13] W.R.A. Robinson, J.A.R. van Veen, V.H.J. de Beer, R.A. van Santen, *Fuel Proc. Tech.* 61 (1999) 103.
- [14] P. Da Costa, J.-L. Lemberton, C. Potvin, J.-M. Manoli, G. Pérot, M. Breysse, G. Djéga-Mariadassou, *Catal.Today* 65 (2001) 195.
- [15] B. Dhandapani, T St. Clair, S.T. Oyama, *Appl. Catal. A* 168 (1998) 219.
- [16] D.J. Sajkowski, S.T. Oyama, *Appl. Catal. A* 134 (1996) 339.
- [17] P.A. Aegerter, W.W.C. Quigley, G.J. Simpson, D.D. Ziegler, J.W. Logan, K.R. McCrea, S. Glazier, M.E. Bussell, *J. Catal.* 164 (1996) 109.
- [18] K.R. McCrea, J.W. Logan, T.L. Tarbuck, J.L. Heiser, M.E. Bussell, *J. Catal.* 171 (1996) 255.
- [19] S. Li, J.S. Lee, *J. Catal.* 178 (1998) 119.
- [20] H.K. Park, D.S. Kim, K.L. Kim, *Korean J. Chem. Eng.* 15 (1998) 625.
- [21] M. Vrinat, *Appl. Catal.* 6 (1983) 137.
- [22] V. Meille, E. Schulz, M. Lemaire, M. Vrinat, *Appl. Catal. A.* 187 (1999) 179.
- [23] V. Vanrysselberhe, R. le Gall, G. Froment, *Ind. Eng. Chem. Res.* 37 (1998) 1235.
- [24] L. Volpe, M. Boudart, *J. Solid State Chem.* 59 (1985) 332.
- [25] N. Nagai, T. Sato, A. Aiba, *J. Catal.* 97 (1986) 52.
- [26] V. Lamure-Meille, E. Schulz, M. Lemaire, M. Vrinat, *Appl. Catal. A.* 131 (1995) 137.
- [27] M. Boudart, G. Djéga-Mariadassou, *Kinetics of Heterogeneous Catalytic Reactions*, Princeton University Press, Princeton, 1984.