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# Competitive adsorptions between thiophenic compounds over a CoMoS/ Al<sub>2</sub>O<sub>3</sub> catalyst under deep HDS of FCC gasoline



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Hydrodesulfurization FCC gasoline 2-methythiophene 3-methylthiophene Benzothiophene Kinetic modeling	benzothiophene: BT) representative of sulfur compounds in FCC gasoline was investigated over a CoMoS/Al2O3 catalyst. More specifically, a quantitative reactivity scale was established with BT being more reactive than 3MT and 2MT. In mixture, their reactivity was reduced due to the presence of the other sulfur compound, the scale of reactivity being preserved. BT strongly inhibits the transformation of 2MT. With a single kinetic model based on a Langmuir Hinshelwood formalism, kinetic and adsorption parameters were calculated and the results explained by mutual competitive adsorption between 2MT and BT with a higher adsorption constant for BT

# 1. Introduction

Due to increasing environmental concerns, constraints relative to exhaust gas compositions have been reinforced worldwide. China V and US Tier 3 regulations have thus imposed a 10 ppm maximum of sulfur in commercial gasoline since 2017 [1]. Commercial gasoline is blended from gasoline streams mainly produced by isomerization, reforming and fluid catalytic cracking (FCC) units in refineries. In particular, catalytic cracked gasoline represents 40–80% of the total gasoline composition but accounts for almost all of the total sulfur amount present in non-hydrodesulfurized commercial gasoline [2,3]. Consequently, there is a strong need for achieving ultra-deep HDS of FCC gasoline, which comes with developing highly active HDS catalysts. Meanwhile, these catalysts should also exhibit a high selectivity to minimize olefins hydrogenation (HDO) and preserve high octane values.

The FCC gasoline is a complex blend of more than 400 compounds, mainly including paraffins, olefins, naphtenes and aromatics. The sulfur compounds in FCC gasoline are represented in various families: mercaptans, thiophenes, benzothiophenes and their alkyl derivatives. The repartition and the total amount of these sulfur compounds depend on the origin of the feedstock and the operating conditions of the FCC unit. As reported in literature [4,5], for a typical feedstock, C<sub>1</sub>-thiophenes –i.e. methylthiophenes–, C<sub>2</sub>-thiophenes and benzothiophenes correspond to more than 50% of total sulfur compounds present in the mixture (Table 1). Therefore, the sulfur compounds selected in model feeds as single

representative of sulfur contents in a FCC gasoline are thiophene [6], alkylthiophenes [2,7], benzothiophene and its alkylated derivatives [8,9]. However, a major drawback of such approach lies in a lack of representativeness of the reactivity of a real catalytically cracked gasoline where relative reactivities of reactants and potential competitive adsorptions between reactants and products dictate the overall feed reactivity.

The reactivity of these different sulfur molecules have been ambiguously reported in the literature with different rankings. This apparent contradiction may originate from different operating conditions. At their operating conditions -100ppmS in toluene, 1.3 MPa, 150 °C, LHSV =  $3.5 \text{ h}^{-1}$ -, Hatanaka et al. [10,11] established the following reactivity scale: benzothiophene > thiophene > 3-methylthiophene > 2-methylthiophene > 2-ethylthiophene > 2,5-dimethylthiophene. The reaction rate of benzothiophene was approximatively twice that of thiophene. These results also confirmed the relative reactivities of 3-methylthiophene and 2-methylthiophene over a CoMoS/Al<sub>2</sub>O<sub>3</sub> catalyst, as reported by Desikan et al. [12] at atmospheric pressure and temperatures of 305 and 414 °C. However, in a review on hydrodesulfurization processes, Song et al [13] suggested a reverse reactivity order with thiophene being more reactive than benzothiophene. This assumption was based on results originally published by Nag et al. [14] on the hydrodesulfurization of benzothiophene and thiophene at 7,1 MPa and 300  $^\circ \text{C}.$  In this study, the reactivity of thiophene was higher by a factor of 1.7 as compared to benzothiophene.

In addition, the potential competitive adsorptions over the catalyst surface between reactants and products in complex feeds such as a real

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#### Table 1

Amount of sulfur compounds present in a feed containing 1.05 wt% of sulfur [4].

Sulfur Compounds	Sulfur Compound	ds
	ppmS	%
Mercaptans	34	4.5
Thiophene	37	4.9
C1-thiophenes	106	14.1
Tetrahydrothiophene	24	3.2
C2-thiophenes	118	15.6
C3-thiophenes/thiophenol	76	10.1
C4-thiophenes/C1-thiophenol	83	11.0
Benzothiophene	276	36.6
Total Sulfur	754	100

catalytically cracked gasoline have never been thoroughly investigated. Indeed, most relevant articles focused on the inhibiting effect of H<sub>2</sub>S on the transformation of single sulfur compounds in model feeds. Thus, Fontaine et al. [15] evidenced that the presence of H<sub>2</sub>S had a weak impact on the transformation of 2-methylthiophene over an unsupported CoMoS catalyst at 2 MPa and 250 °C A similar effect was observed by Dos Santos et al. [7] during the hydrodesulfurization of 3methyl-thiophene over a CoMoS catalyst supported on alumina at 2 MPa and 185 °CA decrease in the kinetic apparent constants as a function of H<sub>2</sub>S partial pressure was attributed to a competitive adsorption of 3-methylthiophene and H<sub>2</sub>S on the active sites of the catalyst. To develop highly efficient catalysts and bridge the gap between model feed and real catalytically cracked gasoline reactivities, there is consequently a strong need for a proper understanding of the reactivity scale of sulfur compounds under selective HDS operating conditions as well as their interplay in mixture.

This paper deals with the comparison of the reactivity of sulfur model molecules representative of various families in FCC gasoline alone and in mixture in order to determine the most refractory sulfur compounds and to quantify their competitive adsorption. The transformations of 2-methylthiophene (2 M T), 3-methylthiophene (3 M T) and benzothiophene (BT), -the selected model molecules- over a supported CoMoS catalyst under selective HDS conditions (250 °C and 2Mpa of total pressure) were thus studied alone, and then in mixture. Following a combined experimental and theoretical approach, a kinetic modeling based on a Langmuir-Hinshelwood formalism was then developed to explain these experimental results and provide quantitative elements of reactivity of sulfur compounds in selective HDS conditions in place of the more qualitative information that is found in the available literature (Table 1).

## 2. Experimental part

## 2.1. Catalyst and chemicals

Table 2 reports the main characteristics of the CoMoS/Al<sub>2</sub>O<sub>3</sub> catalyst provided by IFPEN. The catalyst was crushed and sieved to size range between 250 and 315  $\mu$ m and then sulfided *in situ* under H<sub>2</sub>S/H<sub>2</sub> flow (10 mol% H<sub>2</sub>S) for 10 h at 400 °C at atmospheric pressure. 2-methylthiophene (98% purity), 3-methylthiophene (98% purity), benzothiophene (95% purity) and n-heptane (> 99% purity) were purchased from Sigma-Aldrich. They were used without further purification. Hydrogen sulfide (1 vol% in mixture with H<sub>2</sub>) was purchased from Air Liquide.

#### Table 2

Characteristics of the	CoMoS/Al <sub>2</sub> O <sub>3</sub> catalyst.
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CoO (wt%)	MoO <sub>3</sub> (wt%)	Co/Mo (at./at.)	$S_{BET}$ (m <sup>2</sup> /g)
3	10	0.57	122

#### 2.2. Reaction conditions

Catalytic activity measurements were carried out in a fixed bed reactor at 250 °C under a total pressure of 2 MPa with a ratio  $H_2$ /feed of 360 N L/L [16–18]. The sulfur model feed (0.3 wt%, 1000 ppmS), diluted in n-heptane was injected in the reactor by a HPLC Gilson pump (307 series, pump's head volume: 5 cm<sup>3</sup>). The mass of catalyst used was 50 mg of CoMo/Al<sub>2</sub>O<sub>3</sub> and the contact time varied from 0 to 30 s.

Different types of feeds were used to study the transformation of the sulfur model molecules alone or in mixture:

- 1) Single component feed including a sulfur model molecule alone (corresponding to 1000 ppmS) (0.3 wt% of 2 M T or 3 M T or 0.42 wt % of BT) in n-heptane.
- 2) Feed consisting of a mixture of two sulfur components including 0.3 wt% of 2 M T (1000 ppmS) and various amounts of BT (corresponding to 500, 1000 and 1500 ppmS) in n-heptane.
- 3) Feed consisting of a mixture of either 2 M T or BT (1000 ppmS) and  $H_2S$  (from 0.2 to 1.45 kPa) in n-heptane. These  $H_2S$  partial pressures correspond to the amount of  $H_2S$  produced by the transformation of BT (or 2 M T) in mixture with 2 M T (or BT). These latter experiments were carried out in order to identify the real inhibitor of the transformation of a given sulfur compound (the other sulfur molecule present or the  $H_2S$  produced by its transformation).

The different partial pressures of the reactants,  $H_2S$  and,  $H_2$  introduced are reported in Table 3 for the sulfur molecules alone and in mixture, respectively. n-heptane was not converted under these experimental conditions. No catalyst deactivation was observed for all the experiments.

# 2.3. Products analysis

The reaction products were injected on-line by means of an automatic sampling valve into a Varian gas chromatograph equipped with a PONA capillary column and a flame ionization detector as in previous works [16–18]. Desulfurized products, resulting from the transformation of 2-methylthiophene, 3-methylthiophene and benzothiophene are designated as HDS products. The contact time is defined as the ratio between the total amount of feed and the mass of catalyst in the oxide form. 2 M T, 3 M T and BT reactivities are defined as the number of moles of HDS products formed per hour and per gram of catalyst and were calculated at conversion lower than 30% in a differential regime.

## 2.4. Kinetic modeling

The obtained experimental results were confirmed by a theoretical approach using the Langmuir-Hinshelwood model and the Arrhenius equation. Kinetic and adsorption parameters were first set from single component experiments using ReactOp software<sup>\*</sup> and were then used to fit binary experimental results without further adjustment.

# 3. Results

## 3.1. Transformation of single sulfur compounds

In order to draw an unambiguous reactivity ranking of 2 M T, 3 M T and BT, the hydrodesulfurization of single sulfur compounds was first studied. The conversion of 2 M T, 3 M T and BT measured separately are reported in Fig. 1. The distribution of the products are reported in Fig. 2 for 2 M T, in Fig. 3 for 3 M T and in Fig. 4 for BT. For the three sulfur compounds, a linear dependence of conversion with contact time was observed for conversions lower than 60%, thus corresponding to a differential regime. At equivalent contact time, the conversion of BT was systematically higher than those of 2 M T and 3 M T, as reported in Table 4. In other words, the reactivity order observed under these

#### Table 3

Partial pressures (kPa	<ul> <li>a) of the different</li> </ul>	compounds for	the sulfidation step	and the	transformation	of the	different feeds.
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Feed Pressure (kPa)	A Sulfidation	B 3 M T/2 M T	C BT	D 2 M T + BT	$\frac{E}{2 M T} + H_2 S$	F BT + H <sub>2</sub> S
P <sub>H</sub> 2S	10	0	0	0	0.8 - 1.45	0.2 - 0.37
P <sub>2MT</sub> or P <sub>3MT</sub>	0	2	0	2	2	-
P <sub>BT</sub>	0	0	2	1-3	0	2
P <sub>H2</sub>	90	1360	1360	1360	1360	1360
P <sub>nC7</sub>	0	638	638	633-635	637.2-636.55	637.8-637.63
P <sub>TOT</sub>	100	2000	2000	2000	2000	2000

(T = 250 °C, P = 2 MPa, CoMoS/Al<sub>2</sub>O<sub>3</sub>, H<sub>2</sub>/feed = 360 N L/L).



Fig. 1. Conversion of 2 M T, 3 M T and BT as a function of contact time. (T = 250 °C, P = 2 MPa, H<sub>2</sub>/feed = 360 N L/L, CoMoS/Al<sub>2</sub>O<sub>3</sub>).



**Fig. 2.** Transformation of 2 M T. Distribution of the products as a function of 2 M T conversion (T = 250 °C, P = 2 MPa, CoMoS/Al<sub>2</sub>O<sub>3</sub>, H<sub>2</sub>/feed = 360 N L/L). t-P2N: trans-pent-2-ene, c-P2N: cis-pent-2-ene, P1N: pent-1-ene, nC5: n-pentane.

operating conditions is in agreement with the results previously obtained by Hatanaka et al. [10,11] who reported that 2-methylthiophene was less reactive than 3 M T and BT at a total pressure of 1.3 MPa and temperatures ranging between 130 and 170 °C.

Regarding the product distribution of the transformation of 2-MT, the main products observed are pent-1-ene, cis-pent-2-ene and transpent-2-ene as primary products and n-pentane as a secondary product (Fig. 2). In agreement with the reaction scheme proposed previously (Scheme 1) [2], there are two main potential pathways: direct desulfurization (DDS) -leading to the formation of cis and trans-pent-2ene- and the hydrogenation (HYD) pathway -leading to the formation of pent-1-ene- which both end up into the hydrogenation product (npentane). However, the intermediates proposed in the reaction scheme for 2 M T were not observed under selective HDS operating conditions.

Similar to 2 M T, the transformation of 3 M T also leads to the formation of alkenes (i.e. 2-methylbut-1-ene, 2-methylbut-2-ene and 3methylbut-1-ene) as primary products and to the formation of



**Fig. 3.** Transformation of 3 M T. Distribution of products as a function of 3 M T conversion. (T =  $250 \,^{\circ}$ C, P = 2 MPa, CoMoS/Al<sub>2</sub>O<sub>3</sub>, H<sub>2</sub>/feed =  $360 \,$  N L/L). 2MB2N: 2-methylbut-2-ene, 2MB1N: 2-methylbut-1-ene, iC5: isopentane, 3MB1N: 3-methylbut-1-ene.



Fig. 4. Transformation of BT. Distribution of products as a function of BT conversion. (T = 250 °C, P = 2 MPa, CoMoS/Al<sub>2</sub>O<sub>3</sub>, H<sub>2</sub>/feed = 360 N L/L). EB: ethylbenzene, DHBT: dihydrobenzothiophene.

# Table 4

Transformation of sulfur compounds. Comparison of the activity.

	2 M T	3 M T	BT
Conversion (%)	28.2	23.1	33.4
Activity (mol. $h^{-1}$ . $g^{-1}$ )	0.376	0.597	0.833

(iso-conversion around 30% from feed B or C) (T = 250 °C, P = 2 MPa, CoMoS/  $Al_2O_3,\,H_2/feed$  = 360 N L/L).

isopentane as secondary product resulting from the hydrogenation of alkenes (Fig. 3 according to the proposed reaction scheme in the literature (Scheme 2)) [7]

The transformation of BT leads to dihydrobenzothiophene (DHBT) -resulting from the hydrogenation of the thiophenic ring- which appears as a primary product. The formation of ethylbenzene (EB) is also observed as an apparent secondary product although it can be also



Scheme 1. Transformation of 2-methylthiophene (2 M T): 2-methyltetrahydrothiophene (2 M THT), pent-1,3-diene (P13DN), pent-1-ene (P1N), pent-2-ene (P2N), n-pentane (nP).



Scheme 2. Transformation of 3-methylthiophene (3 M T), 3-methyltetrahydrothiophene (3 M THT), 2-methyl-but-1-ene (2MBN1), 2-methyl-but-2-ene (2MBN2), 3MBN1 (3-methyl-but-1-ene), isopentane (iC<sub>5</sub>).

formed directly from BT (Fig. 4). Consequently, the reaction scheme established from these results can involve two pathways for the formation of EB: a direct DDS pathway from BT involving a C–S bond rupture and the hydrogenation pathway involving the formation of DHBT and a subsequent C–S bond rupture (Scheme 3).

In order to evaluate a mutual inhibiting effect between the different sulfur compounds, the transformation of a feed containing 1000 ppmS from 2 M T and different amounts of BT (from 500 to 1000 ppmS) was studied. The contact time was varied in order to obtain a large range of conversions (from 15 to 80%) of 2 M T and BT. A mutual inhibiting

effect between 2 M T and BT was noticed. Moreover, the inhibition on the transformation of 2 M T resulting from BT was higher (Fig. 5a) than the opposite (Fig. 6a). At a contact time of 2 s, the decrease in conversion for the transformation of 2 M T was equal to 54% while only 15% for the transformation of BT. This inhibiting effect is due to the unconverted other sulfur compound (2 M T or BT) and not to the H<sub>2</sub>S produced by its transformation. Indeed, if 2 M T or BT were substituted by the amount of H<sub>2</sub>S produced by the conversion of both sulfur compounds, the inhibiting effect observed was much lower in the transformation of 2 M T (i.e. lower than 5%) (Table 5) and zero in the



Scheme 3. Transformation of benzothiophene (BT): Dihydrobenzothiophene (DHBT), Ethylbenzene (EB).



Fig. 5. Transformation of 2 M T: Comparison of simulation results (dotted lines) and experimental data (points) a) for the conversions of 2 M T alone and in presence of BT and b) for the distribution of HDS products (pentane and pentenes). (T = 250 °C, P = 2 MPa, CoMoS/Al<sub>2</sub>O<sub>3</sub>, H<sub>2</sub>/feed = 360 N L/L).

transformation of BT (Table 6). Consequently, the decrease in the conversion of 2 M T (around 60%) observed in mixture with BT corresponds to an inhibition effect of the unconverted BT. Indeed, when BT is present at high concentration (1500 ppm S) in the feed, its conversion is low (i.e. 47%), which leads to an inhibition of the transformation of 2 M T around 66.5% (i.e. a conversion of 10.2% of 2 M T in the feed as compared to a conversion of 28.2% in the absence of BT). In the opposite, for the conversion of BT, the presence of 2 M T leads to an inhibition of only around 15% whereas the concentration of unconverted 2 M T remains high due to its low conversion (maximum 17%) (see in Table 5).

# 3.2. Kinetic modeling

Conversion (%)

In order to understand and quantify the strong mutual inhibiting effects observed experimentally, a kinetic model was developed to determine the kinetic and adsorption parameters of 2 MT, 3 MT and BT transformations. As reported previously [17,18] the following assumptions were made: a Langmuir-Hinshelwood model involving reactions between adsorbed molecules, competitive adsorptions between sulfur compounds, alkenes, alkanes and H<sub>2</sub>S, a unique type of site and an heterolytic dissociation of H<sub>2</sub> and H<sub>2</sub>S. The corresponding elementary steps were reported previously under similar operating conditions [17,18].

For the transformation of 2 M T and 3 M T, different reactions were



Transformation of 2 M T. Effect of the amount of H<sub>2</sub>S or BT.

BT (ppmS)	BT Conv. (%)	P <sub>H</sub> 2S from BT (kPa)	Inhibiting effect		
(ppins)			Total (%)	By H <sub>2</sub> S (%)	By BT (%)
500 1000 1500	80.0 60.3 47.0	0.80 1.20 1.45	63.1 68.3 70.3	1.7 2.8 3.8	61.4 65.5 66.5

(conversion of 2 M T of 42% from feed E and D, T = 250 °C, P = 2 MPa, H\_2/feed = 360 N L/L, CoMoS/Al\_2O\_3).

## Table 6

Transformation of BT. Effect of the amount of  $H_2S$  or 2 M T.

2 M T Conv. (%)	$P_{\rm H}$ 2S from 2 M T (bar)	Inhibiting effect		
		Total (%)	By H <sub>2</sub> S (%)	By 2 M T(%)
10.0	0.2	17.2	0	17.2
15.4	0.31	15.5	0	15.5
18.9	0.37	14.2	0	14.2

(conversion of BT of 30% from Feed D and F, T = 250 °C, P = 2 MPa,  $H_2/feed = 360 N L/L$ , CoMoS/Al<sub>2</sub>O<sub>3</sub>).



**Fig. 6.** Transformation of BT: Comparison of simulation results (dotted lines) and experimental data (points) a) for the conversion of BT alone and in mixture with 2 M T and b) for the distribution of HDS products (Ethylbenzene: EB and Dihydrobenzothiophene : DHBT). (T =  $250 \degree$ C, P = 2 MPa, CoMoS/Al<sub>2</sub>O<sub>3</sub>, H<sub>2</sub>/feed = 360 N L/L).

taken into account, respectively named  $R_1$  or  $R_3$  for the formation of olefin intermediates and  $R_2$  and  $R_4$  for the formation of alkanes from olefins.



The rate equations are as follows:

$$r = k_{5}. \ e^{-\frac{Ea}{RT}} \frac{K_{BT}P_{BT}\sqrt{K_{H2}S}P_{H2}S}{\left(1 + K_{BT}P_{BT} + \frac{P_{H2}S}{K_{S}P_{H2}} + \frac{K_{H2}P_{H2}\sqrt{\frac{P_{H2}S}{K_{S}P_{H2}}}}{\sqrt{K_{H2}S}P_{H2}S} + \sqrt{K_{H2}S}P_{H2}S}\sqrt{\frac{P_{H2}S}{K_{S}P_{H2}}}\right)^{2}}$$

$$r = k_{6}. \ e^{-\frac{Ea}{RT}} \frac{K_{DHBT}P_{DHBT}\sqrt{K_{H2}S}P_{H2}S}{\left(1 + K_{DHBT}P_{DHBT} + \frac{P_{H2}S}{K_{S}P_{H2}} + \frac{K_{H2}P_{H2}\sqrt{\frac{P_{H2}S}{K_{S}P_{H2}}}}{\sqrt{K_{H2}S}P_{H2}S} + \sqrt{K_{H2}S}P_{H2}S}\sqrt{\frac{P_{H2}S}{K_{S}P_{H2}}}\right)^{2}}$$

 $r = k_{1(3)}$ .

$$e^{-\frac{Ea}{RT}} \frac{K_{2MT(3MT)}P_{2MT(3MT)}\sqrt{K_{H_2S}P_{H_2S}}\sqrt{\frac{P_{H_2S}}{K_SP_{H_2}}}}{\left(1 + K_{2MT(3MT)}P_{2MT(3MT)} + \frac{P_{H_2S}}{K_SP_{H_2}} + \frac{K_{H_2}P_{H_2}\sqrt{\frac{P_{H_2S}}{K_SP_{H_2}}}}{\sqrt{K_{H_2S}P_{H_2S}} + \sqrt{K_{H_2S}P_{H_2S}}\sqrt{\frac{P_{H_2S}}{K_SP_{H_2}}}\right)^2}$$

 $r = k_{2(4)}$ .

$$e^{-\frac{E\alpha}{RT}} \frac{K_{PN}P_{PN}\sqrt{K_{H_2S}P_{H_2S}}\sqrt{\frac{P_{H_2S}}{K_SP_{H_2}}}}{\left(1 + K_{PN}P_{PN} + \frac{P_{H_2S}}{K_SP_{H_2}} + \frac{K_{H_2}P_{H_2}\sqrt{\frac{P_{H_2S}}{K_SP_{H_2}}}}{\sqrt{K_{H_2S}P_{H_2S}}} + \sqrt{K_{H_2S}P_{H_2S}}\sqrt{\frac{P_{H_2S}}{K_SP_{H_2}}}\right)^2}$$

Regarding the transformation of BT, the proposed reaction scheme includes two pathways for its transformation: HYD of BT into dihydrobenzothiophene (DHBT) and then HDS of DHBT into ethylbenzene (EB). The second pathway corresponds to the formation of ethylbenzene directly from BT. Therefore, the consecutive reactions proposed to model the transformation of BT are given below:

$$H_2 + 3H_2 \rightarrow H_2S$$

$$H_2S = H_2S$$

$$H_2S = H_2S$$

$$H_2S = H_2S$$

The corresponding equation rate are as follows:

$$r = k_{7}.$$

$$e^{-\frac{Ea}{RT}} \frac{K_{BT}P_{BT}\sqrt{K_{H_{2}S}P_{H_{2}S}}\sqrt{\frac{P_{H_{2}S}}{K_{S}P_{H_{2}}}}}{\left(1 + K_{BT}P_{BT} + \frac{P_{H_{2}S}}{K_{S}P_{H_{2}}} + \frac{K_{H_{2}}P_{H_{2}}\sqrt{\frac{P_{H_{2}S}}{K_{S}P_{H_{2}}}}{\sqrt{K_{H_{2}S}P_{H_{2}S}}} + \sqrt{K_{H_{2}S}P_{H_{2}S}}\sqrt{\frac{P_{H_{2}S}}{K_{S}P_{H_{2}}}}\right)^{2}}$$

To explain the order of reactivity observed experimentally as well as the mutual inhibition of sulfur compounds, a kinetic modeling of the sulfur compounds alone initially and then in a mixture was carried out. The kinetic parameters (for the hydrodesulfurization and hydrogenation reactions) and the adsorption constants calculated from single component experiments are reported in Table 7. A good fit of the transformation of 2 M T, 3 M T and BT is obtained. The modeling (dashed curve) and the experimental results (points) for the conversion of 2 M T, BT and 3 M T alone and their product distribution are respectively reported in Figs. 5–7.

It can be seen that the rate constants of the desulfurization step (olefin formation) (k = 2.8  $10^{12}\,h^{-1}$  and 5.5  $10^{12}\,h^{-1}$  for 2MT and

Table 7

Kinetic parameters and adsorption parameters for the reaction of sulfur compounds, H<sub>2</sub>S and H<sub>2</sub> (HDS: Hydrodesulfurization, HYD: Hydrogenation).

		k x $10^{12}$ (h <sup>-1</sup> )	K <sub>ads</sub> (bar <sup>-1</sup> )
2 M T	R1 (HDS)	$2.8 \pm 0.1$	$7.1 \pm 0.3$
	R2 (HYD)	$6.9 \pm 0.3$	
3 M T	R3 (HDS)	$5.1 \pm 0.2$	$10.6 \pm 0.5$
	R4 (HYD)	$5.8 \pm 0.3$	
BT	R5 (HYD)	$12 \pm 0.6$	$12.4 \pm 0.6$
	R6 (HDS)	$19 \pm 0.9$	
	R7 (HDS)	$3.4 \ 10^{-3} \pm 2 \ 10^{-4}$	
$H_2$	-	-	$1.8 \ 10^{-7} \pm 9.0 \ 10^{-9}$
$H_2S$	-	-	$0.5~\pm~0.02$

 $(T = 250 \degree C, P = 2 MPa, H_2/feed = 360 N L/L, CoMoS/Al_2O_3).$ 



Fig. 7. Transformation of 3 MT: Comparison of simulation results (dotted lines) and experimental data (points) a) for the conversion of 3 MT and b) for the distribution of products ( $C_5$  alkenes and isopentane i $C_5$ ). (T =  $250 \degree$ C, P = 2 MPa, CoMoS/Al<sub>2</sub>O<sub>3</sub>, H<sub>2</sub>/feed = 360 N L/L).

3 M T respectively) are lower than those of the corresponding saturated hydrocarbon formation (k =  $6.9 \ 10^{12} \ h^{-1}$  and  $5.8 \ 10^{12} \ h^{-1}$  for 2 M T and 3 M T respectively) (Schemes 1 and 2). In addition, modeling confirmed that the direct formation of ethylbenzene from BT was a minor pathway in selective HDS operating conditions. Indeed, the rate constant is much lower (k =  $3.8 \ 10^8 \ h^{-1}$ ) than that via the formation of DHBT (k =  $12 \ 10^{12} \ h^{-1}$ ) (Scheme 3). Moreover, the scale of reactivity of the three model sulfur molecules was confirmed from the rate constants of the desulfurization steps where those of BT is higher than those of  $3 \ M T$  and  $2 \ M T$ . Similarly, the BT adsorption constant is higher than those of  $3 \ M T$  and  $2 \ M T$  (K<sub>BT</sub> =  $12.4 \ bar^{-1}$ , K<sub>3MT</sub> =  $10.6 \ bar^{-1}$ , K<sub>2MT</sub> =  $7.1 \ bar^{-1}$ ).

In addition, when components are in mixture, the experimental results are also well modeled considering the same model without further adjustments of the parameters fitted on single component experiments. Indeed, the same parameters (kinetic and adsorption constants) determined with the single sulfur compounds were used for the modeling in mixture. The very good fit obtained confirms the validity and the robustness of the chosen model and evidences the soundness of the obtained adsorption and kinetic parameters. The mutual inhibiting effect observed when 2 M T and BT were in mixture is well represented. Indeed, the BT adsorption constant was higher ( $K_{ads} = 12.4 \text{ bar}^{-1}$ ) than that of 2 M T (7.1 bar<sup>-1</sup>). The transformation of 2 M T (Fig. 5) was thus impacted by the presence of unconverted BT, whereas conversely BT was little impacted by 2 M T (Fig. 6). This confirmed competitive adsorptions of the sulfur model molecules on the catalyst surface.

## 4. Conclusion

Under selective HDS operating conditions, the experimental approach developed in this study demonstrated an unambiguous reactivity scale of sulfur compounds representative of FCC gasoline. Thus, benzothiophene is 2.4 times more reactive than 3-methylthiophene which 1.8 times more reactive than 2-methylthiophene when considering single component experiments. By kinetic modeling based on a Langmuir-Hinshelwood formalism, the reaction schemes for the transformation of 2-methylthiophene, 3-methylthiophene and benzothiophene were validated.

In mixture, the reactivity ranking of these sulfur compounds was preserved. In addition, a mutual inhibiting effect between sulfur compounds was evidenced from the experiments mixing 2-methylthiophene and benzothiophene. Besides, the influence of unconverted BT on the transformation of 2 M T was much higher than that of 2 M T on the transformation of BT, due to a stronger adsorption of the latter. These results were confirmed by kinetic modeling where the calculated BT

adsorption constant was 40% higher than that of 2 M T, thus explaining the stronger adsorption of BT on the catalytic sites. This also allowed us to identify the most refractory sulfur compounds that are present in FCC gasoline feed under deep HDS operating conditions. Notably, the transformations of sulfur model compounds alone and in mixture could be fitted from a single kinetic model based on a Langmuir-Hinshelwood formalism. This clearly validated our combined experimental and theoretical approach and also demonstrated that inhibition phenomena observed experimentally between sulfur molecules were due to competitive adsorption on the catalyst surface.

To further narrow the representativeness gap between model molecules feeds and real catalytically cracked gasoline and get a deeper understanding of complex feed reactivities, a similar approach will be applied to understand the mutual influence of sulfur compounds and olefins on their reactivity.

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