

# HDS of a model FCC gasoline over a sulfided CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst: Effect of the addition of potassium

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## Abstract

The transformation of a synthetic FCC gasoline (2-methylthiophene plus 2,3-dimethylbut-2-ene and orthoxylene dissolved in *n*-heptane) was studied under mild HDS conditions (total pressure, 20 bar; temperature, 200 °C) over a commercial CoMo–alumina catalyst and over the same catalyst modified with potassium. The aim of the study was to identify the factors which can favor HDS and minimize olefin hydrogenation. The modification by potassium of the commercial catalyst made it possible to improve its selectivity in HDS of the synthetic gasoline with respect to the hydrogenation of the olefins. In fact, by decreasing the acidity, the addition of potassium decreases the hydrogenation activity more than the HDS activity. This is considered to be the consequence both of a modification of the electronic properties of the sulfide phase and of the isomerization properties of the support.

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## 1. Introduction

It is well known that the gas emissions (NO<sub>x</sub> and SO<sub>x</sub>) from motor vehicles contribute widely to air pollution. To address this environmental problem, new restrictive regulations were adopted by the European Community (Directive 98/70/EC): the reduction of the sulfur levels in diesel and gasoline down to 50 ppm was planned for 2005 (10 ppm maximum on January 1, 2009 and even as soon as January 1, 2005 in some of the countries in the EEC thanks to a tax incentive) [1]. The gasoline fraction produced by the FCC process represents 30–50 vol% of the commercialized motor fuel but typically contributes over 90% of the total sulfur content of the gasoline pool. Desulfurization of this gasoline fraction is therefore mandatory. In addition to alkanes, it is mainly composed of aromatics (30 vol%), alkenes

(30 vol%), and sulfur compounds such as alkylthiophenes (up to 5000 ppm) [2–4]. To purify such fractions a high hydrotreating selectivity (corresponding to a high activity in hydrodesulfurization (HDS) and to a limited activity in olefin hydrogenation) is required.

Indeed, significant alkene saturation can occur during the HDS process, which leads to a decrease of the octane number in the final product. Consequently, it is essential to modify conventional hydrotreating catalysts in order to achieve deep HDS with a minimum of alkene saturation. Several catalytic processes are commercialized by licensors to help the refiners to meet the future stringent regulations on FCC gasoline (ScanFining from Exxon Mobil and Prime G<sup>+</sup> from Axens-IFP, for example). Moreover, several patents and papers have proposed new catalysts with reduced acidity of the alumina carrier, such as potassium-modified alumina [5–8]. The use of less acidic or basic supports such as TiO<sub>2</sub>, SiO<sub>2</sub>, or MgO was also proposed and it has been reported recently that the selectivity for HDS could be increased with CoMo

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catalysts supported on Mg–Al oxide supports [9–12]. The change in the size of the MoS<sub>2</sub> crystallites corresponding to a decrease in the number of MoS<sub>2</sub> edge sites when the magnesium content is increased leads to a decrease in the hydrogenation activity [10]. Compared to conventional catalysts, hydrotalcite-supported catalysts showed a decrease in total activity (HDS and hydrogenation) but an increase in the HDS selectivity of FCC gasoline. This could be correlated with an increase in the concentration of basic sites on the surface.

In this paper we report on the reactivity over a sulfided CoMo/Al<sub>2</sub>O<sub>3</sub> commercial catalyst, of model molecules (2-methylthiophene and 2,3-dimethylbut-2-ene) which are considered as representative of the sulfur-containing molecules and olefins found in FCC gasoline. The reactivity of the model feed was measured under conditions close to mild HDS conditions. The identification of the various reaction products is reported and reaction mechanisms are proposed. The changes in activity and selectivity due to the presence of potassium are examined and discussed. Modifications of the surface properties due to potassium addition were studied by IR spectroscopy in order to relate the changes in acid–base properties to the variations of catalytic performances.

## 2. Experimental

### 2.1. Catalyst and chemicals

The reference hydrotreating catalyst (R) was a commercial CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst (HR 306 from IFP), containing 3 wt% CoO and 14 wt% MoO<sub>3</sub>. The catalyst modified by potassium (CoMoK/Al<sub>2</sub>O<sub>3</sub>) containing 2.7 wt% K (K) was prepared by incipient wetness impregnation of the reference catalyst with an aqueous solution of potassium carbonate. The impregnated catalyst was dried at 100 °C and finally calcined at 500 °C under air flow during 10 h. The physicochemical properties of both catalysts are given in Table 1 which shows in particular that, within experimental error, the surface area of the catalyst was not modified by the presence of potassium.

2-Methylthiophene (98%) and 2,3-dimethylbut-2-ene (99%) were purchased from Aldrich, and orthoxylene (99%), 2,3-dimethylbut-1-ene (99%), and potassium carbonate (99%) from Fluka. They were used without further purification.

Table 1  
Physicochemical characteristics of the catalysts

Catalysts	Designation	S <sub>BET</sub> [m <sup>2</sup> /g]	CoO [wt%]	MoO <sub>3</sub> [wt%]	K [wt%]	Co/(Co+Mo) atomic ratio
CoMo/Al <sub>2</sub> O <sub>3</sub>	R	206	3.0	14	0	0.30
CoMoK/Al <sub>2</sub> O <sub>3</sub>	K	213	3.0	14	2.7	0.30

### 2.2. Activity measurements

Catalytic activity measurements were carried out in a high-pressure fixed-bed microreactor at 200 °C under a total pressure of 20 bar. Before the test, the catalyst samples were presulfided in situ at 400 °C for 10 h with a mixture of 10 mol% H<sub>2</sub>S in H<sub>2</sub> under atmospheric pressure and then cooled down to 200 °C.

The model feed made of 2-methylthiophene (2MT, 3 wt%: 10000 ppm S); 2,3-dimethylbut-2-ene (23DMB2N, 20 wt%) and orthoxylene (30 wt%) in *n*-heptane were injected into the reactor with a syringe pump. The reaction products were analyzed on-line by means of a Varian gas chromatograph equipped with an automatic sampling valve, a 50-m PONA (HP) capillary column (inside diameter, 0.2 mm; film thickness, 0.5 μm), a flame-ionization detector and a cryogenic system. The conditions of analysis were the following: a temperature program from 0 °C (15 min) to 20 °C (1.3 °C/min), from 20 to 50 °C (2 °C/min), and then from 50 to 250 °C (7 °C/min). The identification of the products was made possible by GC-MS coupling.

### 2.3. Characterization by infrared spectroscopy

The acidic and basic properties of the catalysts were determined by IR spectroscopy using CO and CO<sub>2</sub> as probe molecules. About 10 mg of the samples (precisely weighted) were pressed as self-supported wafers (diameter: 1.6 cm). After introduction of the wafers into the IR cell, the samples were sulfided in situ under a flow of H<sub>2</sub>–H<sub>2</sub>S (90–10%) (30 cm<sup>3</sup> min<sup>-1</sup>) using the same procedure as that used for catalyst testing. Then, the samples were evacuated for 45 min at 300 °C and cooled down to –173 °C under a residual pressure of 10<sup>-5</sup> Torr. A first spectrum of the wafer was recorded as reference. Then, given amounts of CO were introduced and IR spectra were recorded for each dose. The cell was then heated up to room temperature (RT) under secondary vacuum. A spectrum was taken in order to check that all the CO was eliminated from the catalyst surface. Adsorption of CO<sub>2</sub> was then performed at RT. The reported spectra correspond to the differences between the spectra taken in the presence of adsorbed CO or CO<sub>2</sub> and the reference spectrum of the sample. All the spectra were normalized to an equivalent sample weight of 10 mg. The FTIR spectra were recorded with a Magna spectrometer (Nicolet) using 128 scans and a resolution of 4 cm<sup>-1</sup>.

## 3. Results

### 3.1. Reaction products over CoMo/Al<sub>2</sub>O<sub>3</sub>

Orthoxylene did not transform at all under the conditions of the reaction. The sulfur compound (2MT) was the most reactive component (Fig. 1). As reported previously [13], the isomerization of 23DMB2N into 2,3-dimethylbut-1-ene

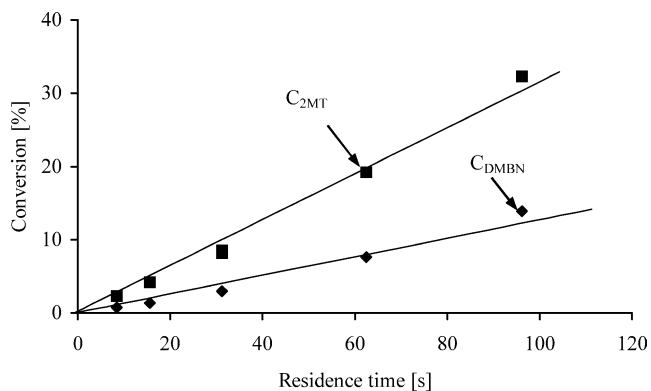


Fig. 1. Conversion of the model feed versus residence time ( $T = 200^\circ\text{C}$ ,  $P = 20$  bar,  $\text{H}_2/\text{Hc} = 200$  l/l, time on stream  $\geq 8$  h).  $C_{2\text{MT}}$ , conversion of 2-methylthiophene;  $C_{\text{DMBN}}$ , conversion of the sum of 23DMB2N and 23DMB1N into hydrogenation products.

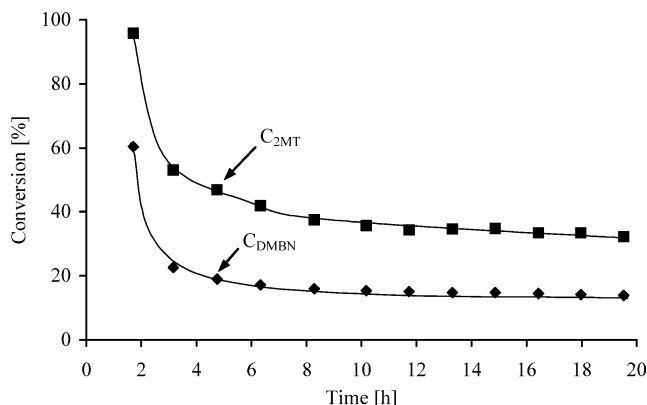


Fig. 2. Transformation of 2-methylthiophene ( $C_{2\text{MT}}$ ) and 2,3-dimethylbutenes ( $C_{\text{DMBN}}$ ) versus time on stream ( $T = 200^\circ\text{C}$ ,  $P = 20$  bar,  $\text{H}_2/\text{Hc} = 200$  l/l,  $D_{\text{Hc}} = 0.065$  ml/min, residence time = 96 s).

(23DMB1N) occurred very readily under the conditions of the reaction and the thermodynamic equilibrium between the two isomers was reached very rapidly. Consequently, the equilibrium mixture of both isomers (23DMB2N + 23DMB1N) will be considered as the reactant when measuring the hydrogenation activity of the catalysts.

The conversion of 2MT and the hydrogenation of 2,3-dimethylbutene (23DMB2N) versus time on stream are shown in Fig. 2. We can note that in both cases an initial deactivation occurred followed by stabilization after 8 h on stream. The product distributions concerning the transformation of the sulfur compound (2MT) and of the alkene (23DMB2N) were determined on the stabilized catalysts. The results will be given separately in the subsequent sections.

### 3.1.1. Transformation of 2MT

The transformation of 2MT led to the formation of a variety of products (Fig. 3):

- hydrodesulfurization (HDS) products;
- 2-methyltetrahydrothiophene (2MTHT) resulting from the hydrogenation of 2MT;

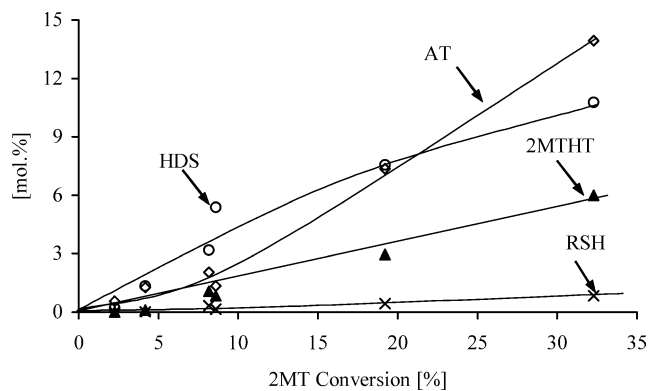


Fig. 3. 2MT transformation over  $\text{CoMo}/\text{Al}_2\text{O}_3$  ( $T = 200^\circ\text{C}$ ,  $P = 20$  bar,  $\text{H}_2/\text{Hc} = 200$  l/l). Product distribution versus 2MT conversion. HDS, hydrodesulfurization products; AT, alkylthiophenes ( $\text{C}_5$ -methylthiophenes ( $\text{C}_5\text{MT}$ ) and  $\text{C}_6$ -methylthiophenes ( $\text{C}_6\text{MT}$ )); RSH,  $\text{C}_5$ -thiols; 2MTHT, 2-methyltetrahydrothiophene.

- alkylthiophenes and alkyltetrahydrothiophenes (AT);
- $\text{C}_5$ -thiols (RSH).

2MTHT as well as the HDS products were obviously primary products. As shown by the shape of the curves in Fig. 3, part of the primary HDS products were subsequently converted into AT products which were at least in part secondary. Only small amounts of  $\text{C}_5$ -thiols (mainly pentane-1-thiol) were observed.

The HDS products included the pentene isomers (pent-1-ene (P1N), E-pent-2-ene (E-P2N), and Z-pent-2-ene (Z-P2N)) which were expected to result from  $\text{H}_2\text{S}$  elimination from 2MT. In addition to these compounds which can be considered as primary products, *n*-pentane (*n*P) resulting from their hydrogenation was also found as well as pentene skeletal isomers such as 2-methylbut-2-ene (2MB2N) and 2-methylbut-1-ene (2MB1N), and their hydrogenation product, 2-methylbutane (2MB). Moreover some of the desulfurization products underwent cracking into light products ( $\text{C}_1$ – $\text{C}_4$  hydrocarbons) and small quantities of oligomers ( $\text{C}_{10}$ – $\text{C}_{12}$ ) were also found. However no pent-1,3-diene was detected.

AT products resulted from the alkylation of 2MT by  $\text{C}_5$ -alkenes ( $\text{C}_5\text{MT}$ ) or by 23DMB2N and its isomers ( $\text{C}_6\text{MT}$ ). As shown in Fig. 4, the main alkylation products were the primary  $\text{C}_6\text{MT}$  while  $\text{C}_5\text{MT}$  which were formed in small quantities were obviously secondary products. Traces of alkylated methyltetrahydrothiophenes were also detected.

### 3.1.2. 23DMB2N transformation

23DMB2N led mainly to hydrogenation products but also to various minor products as shown in Figs. 5a and 5b:

- Hydrogenation products (HYDO): the main product was 2,3-dimethylbutane (23DMB) corresponding to the hydrogenation of 23DMB2N and of its isomer (23DMB1N). Very small amounts (about 0.5%) of 2,2-dimethylbutane (22DMB) were also detected. The hy-

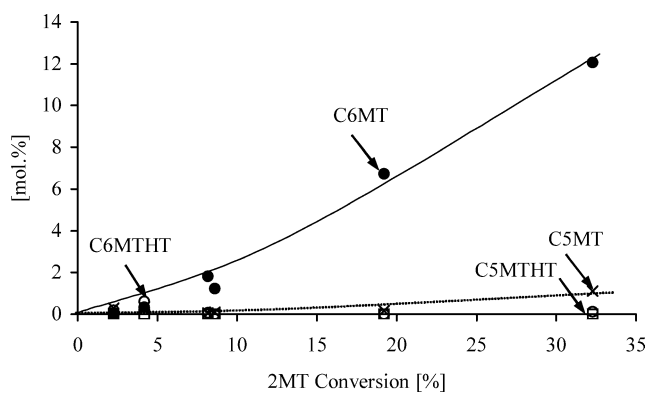


Fig. 4. 2MT transformation over CoMo/Al<sub>2</sub>O<sub>3</sub> ( $T = 200\text{ }^{\circ}\text{C}$ ,  $P = 20\text{ bar}$ ,  $\text{H}_2/\text{Hc} = 200\text{ l/l}$ ). Formation of the alkylation products versus 2MT conversion. C6MT (●) and C5MT (×), C6 and C5 methylthiophenes; C6MTHT (○) and C5MTHT (□), C<sub>5</sub>- and C<sub>6</sub>-methyltetrahydrothiophenes.

drogenation products corresponding to the other alkene isomers were in concentrations too low to be quantified.

- Isomerization products (ISO) resulting from the skeletal isomerization of 23DMB2N and 23DMB1N. The major product was 3,3-dimethylbut-1-ene (33DMB1N); 2-methylpent-1-ene (2MP1N), 2-methylpent-2-ene (2MP2N), E-3-methylpent-2-ene (E3MP2N) and E-hex-2-ene (EH2N) were also detected. All of them were formed in very small amounts;
- Alkane oligomers (OI) resulting from the condensation of C<sub>5</sub>- and C<sub>6</sub>-alkenes;
- C<sub>6</sub>-Thiols formed by addition of H<sub>2</sub>S to 23DMB2N and its isomers;
- Alkylthiophenes (ATO) including C<sub>6</sub>-methylthiophenes (C6MT) resulting from the alkylation of 2MT by 23DMB2N or its isomers and traces of C<sub>6</sub>-methyltetrahydrothiophene (C6MTHT).

As shown in Fig. 5b, the formation of C<sub>6</sub>-thiols and of the skeletal isomer of 23DMBN was very limited, presumably because of thermodynamics.

### 3.2. Modification of the acid–base properties of CoMo/Al<sub>2</sub>O<sub>3</sub> by the addition of potassium

Acidic supports are known to promote the hydrogenation activity of metals [14,15] and of sulfides [16–19]. Conversely, it is expected that basic supports can inhibit hydrogenation. This is why, in order to favor HDS and to inhibit the hydrogenation of olefins as well as the formation of secondary products such as AT products which are expected to be more difficult to desulfurize than 2MT and thiols, the standard catalyst was modified by the impregnation of 3 wt% of potassium.

#### 3.2.1. IR characterization of the effect of potassium addition

The acid properties of the sulfide catalysts with or without potassium were characterized by IR spectroscopy of CO

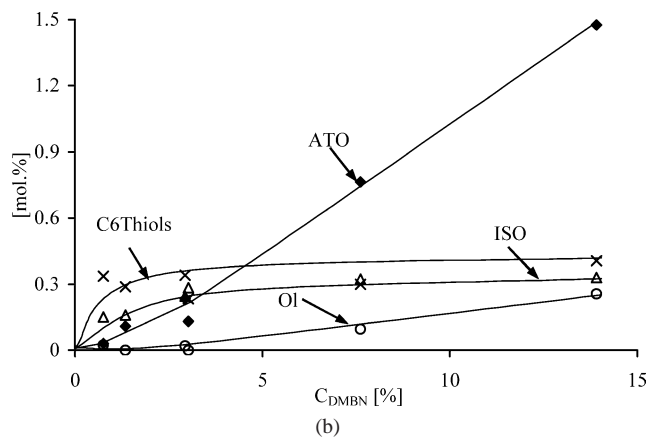
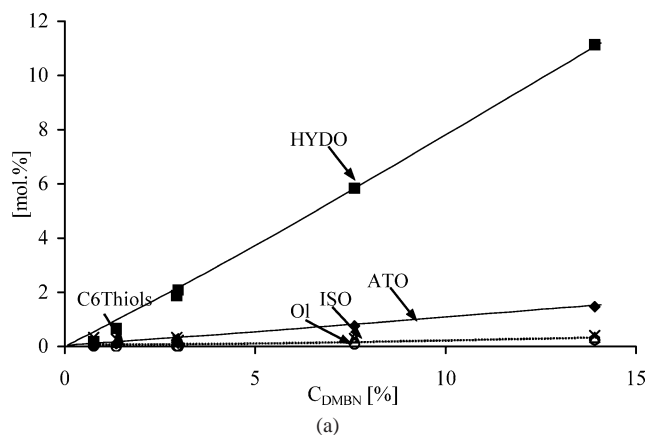


Fig. 5. (a) Transformation of 23DMB2N over CoMo/Al<sub>2</sub>O<sub>3</sub> ( $T = 200\text{ }^{\circ}\text{C}$ ,  $P = 20\text{ bar}$ ,  $\text{H}_2/\text{Hc} = 200\text{ l/l}$ ). Product distribution versus  $C_{\text{DMBN}}$  (conversion of 23DMB2N + 23DMB1N). HYDO (■), hydrogenation; ATO (◆), alkylthiophenes; ISO (△), isomerization; OI (○), alkane oligomers; C<sub>6</sub>-thiols (×). (b) Transformation of 23DMB2N over CoMo/Al<sub>2</sub>O<sub>3</sub> ( $T = 200\text{ }^{\circ}\text{C}$ ,  $P = 20\text{ bar}$ ,  $\text{H}_2/\text{Hc} = 200\text{ l/l}$ ). Distribution of the minor products versus  $C_{\text{DMBN}}$  (conversion of 23DMB2N + 23DMB1N). ATO, alkylthiophenes; ISO, isomerization; OI, alkane oligomers.

adsorbed at low temperature ( $-173\text{ }^{\circ}\text{C}$ ). By this technique, it is possible to characterize the Brønsted and Lewis acid sites of the support on one hand and the unpromoted and Co-promoted Mo coordinatively unsaturated sites (CUS) of the sulfide phase on the other hand [20,21]. The comparison of the wavenumber shifts and of the band areas made it possible to estimate the effect of potassium on the number and strength of the sites belonging to each category.

On unmodified CoMo/Al<sub>2</sub>O<sub>3</sub> (R), the interaction of CO with Lewis acid sites of the support gave rise to a band located at  $2190\text{ cm}^{-1}$  (Fig. 6). On CoMo/Al<sub>2</sub>O<sub>3</sub> modified by potassium (K), for the same amount of CO introduced, the band was shifted down to  $2181\text{ cm}^{-1}$ . This means that potassium led to a decrease of the strength of the Lewis acid sites. The interaction of CO with the OH groups of the support of the CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst is characterized by a band at  $2157\text{ cm}^{-1}$ . In the presence of potassium, this band was not shifted significantly (from  $2157$  to  $2155\text{ cm}^{-1}$  only) but presented a stronger intensity. Thus, potassium addition did not modify the strength of the weakly acid hydroxyl groups of



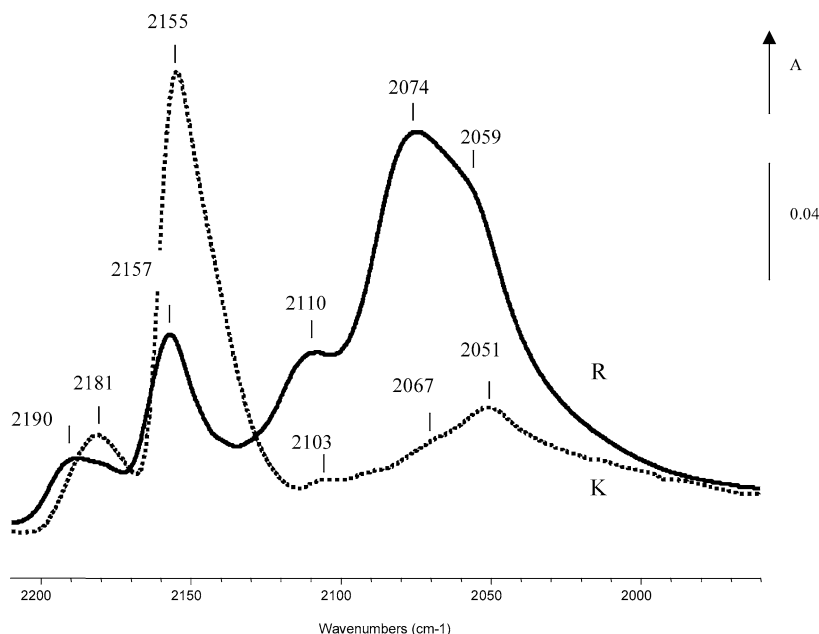


Fig. 6. IR spectra of CO adsorbed on CoMo/Al<sub>2</sub>O<sub>3</sub> (R) and CoMoKAl<sub>2</sub>O<sub>3</sub> (K) (adsorption of 580  $\mu\text{mol}$  CO per gram of catalyst;  $T_{\text{ads}} = -170^\circ\text{C}$ ).

the alumina significantly but, apparently, it increased their number.

Regarding the sulfide phase, the CO absorption bands on CoMo/Al<sub>2</sub>O<sub>3</sub> (R) were detected at 2110, 2074, and 2059  $\text{cm}^{-1}$ . They correspond to CO adsorbed on the CUS located on Mo, CoMoS, and Co, respectively [21]. The promotion level of the catalyst can be characterized by the intensity ratio of the bands of CO adsorbed on the CoMoS phase and on the unpromoted molybdenum. The low intensity of the band at 2110  $\text{cm}^{-1}$  (CO adsorbed on unpromoted Mo vacancies) compared to that at 2074  $\text{cm}^{-1}$  (CO adsorbed on vacancies of the CoMoS phase) points out a good promotion level of the R catalyst. The presence of potassium led to some important modifications on the sulfide phase. The bands corresponding to CO adsorbed on unpromoted molybdenum, promoted sites, and Co shifted from 2110, 2074, and 2059 down to 2103, 2067, and 2051  $\text{cm}^{-1}$ , respectively. On metallic and on sulfide phases, the position of the CO absorption bands depends mainly on the extent of the backdonation of the d-electron's of the adsorption center. This means that their values give information on the electronic properties of the sites. The downward shift of the frequencies of CO when adsorbed on the sulfide phase of the K-containing catalyst indicates an increase of the electronic density on the sulfide phase. This can be a consequence of the decrease in strength of the acidic sites of the support. Another effect of the presence of potassium is the decrease in intensity of the bands corresponding to CO in interaction with the sulfide phase, the band at 2074  $\text{cm}^{-1}$  being more specifically affected. This indicates that potassium atoms located on the support or on the sulfide probably lead also to direct poisoning of the various adsorption sites on the latter. In fact, the consequence of the increase in electronic density on the sulfide could be an important decrease in strength of

the adsorption centers so that CO would hardly adsorb even at  $-173^\circ\text{C}$ .

The possible modification of the support basicity due to the introduction of potassium was estimated by means of the adsorption of CO<sub>2</sub> [22–24]. On CoMo/Al<sub>2</sub>O<sub>3</sub>, CO<sub>2</sub> adsorption led to the formation of several species: hydrogen carbonates giving rise to absorption bands at 1653, 1439, and 1228  $\text{cm}^{-1}$ , and bidentate carbonates giving bands at 1585 and 1329  $\text{cm}^{-1}$  (Fig. 7). The presence of potassium led to a marked increase of the basic properties of the support. Indeed the total area of the CO<sub>2</sub> bands was multiplied by more than 3. This augmentation corresponded to an increase of the number of hydrogen carbonate as well as of carbonate species. Thus, potassium decreased the strength of the acidic sites (Al<sup>3+</sup> especially) of the support and increased the number of basic sites (O<sup>2-</sup> and OH groups). The modification of the acid–base properties of the support led to concomitant modifications of the number of sites on the sulfide phase as well as of their electronic properties.

### 3.2.2. Activity measurements

The performances of the modified catalyst (K) were compared to those of the unmodified reference catalyst (R) for the transformation of the model feed under the same conditions as described above. The presence of potassium decreased the conversion of 2MT and of the 23DMBN equilibrium mixture (23DMB2N + 23DMB1N). However the decrease in activity was less significant for the HDS of the sulfur compound (Fig. 8) than for the hydrogenation (HYDO) (Fig. 9) of the alkenes. Accordingly, the HDS/HYDO selectivity given by the ratio of the HDS reactivity of 2MT over the hydrogenation reactivity of 23DMBN was improved by the presence of potassium (Fig. 10). It was multiplied by 2 and was nearly constant in the range of HDS conversions

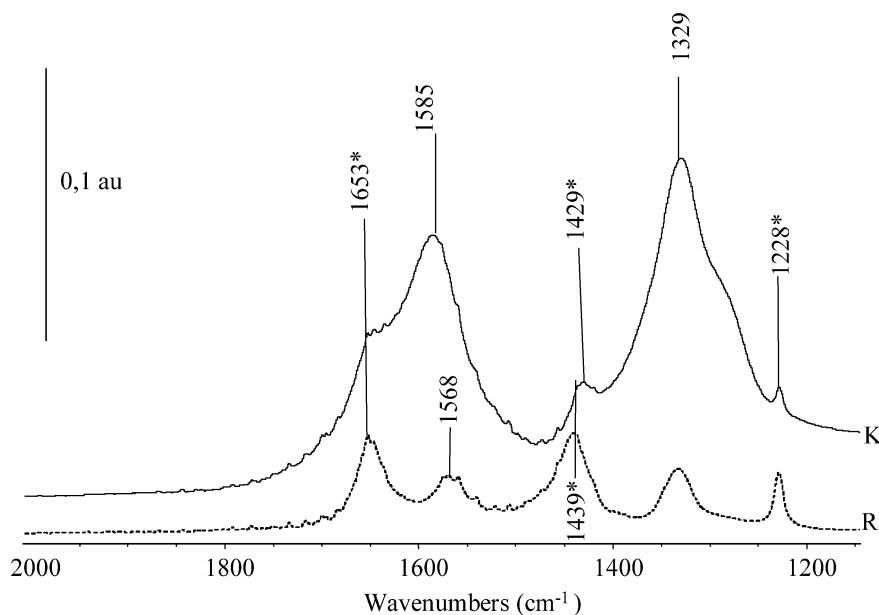


Fig. 7. IR spectra of  $\text{CO}_2$  adsorbed on  $\text{CoMo}/\text{Al}_2\text{O}_3$  catalysts ( $T = 100 \text{ K}$ ). Effect of the modification by potassium. \* Hydrogen carbonates: R,  $\text{CoMo}/\text{Al}_2\text{O}_3$ ; K,  $\text{CoMoK}/\text{Al}_2\text{O}_3$ .

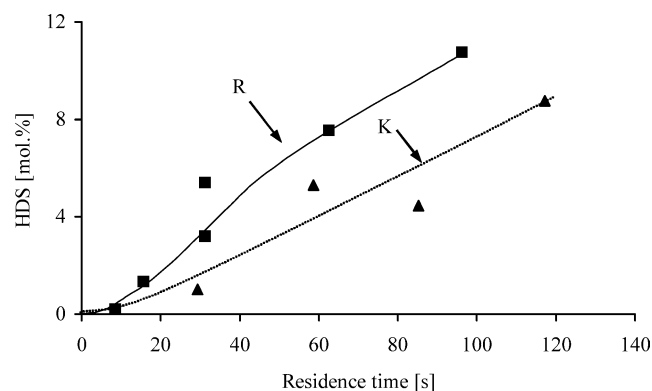


Fig. 8. Transformation of a model FCC gasoline ( $T = 200^\circ\text{C}$ ,  $P = 20 \text{ bar}$ ,  $\text{H}_2/\text{Hc} = 200 \text{ l/l}$ ). Formation of the HDS products from 2MT versus residence time. Effect of the presence of potassium. R,  $\text{CoMo}/\text{Al}_2\text{O}_3$ ; K,  $\text{CoMoK}/\text{Al}_2\text{O}_3$ .

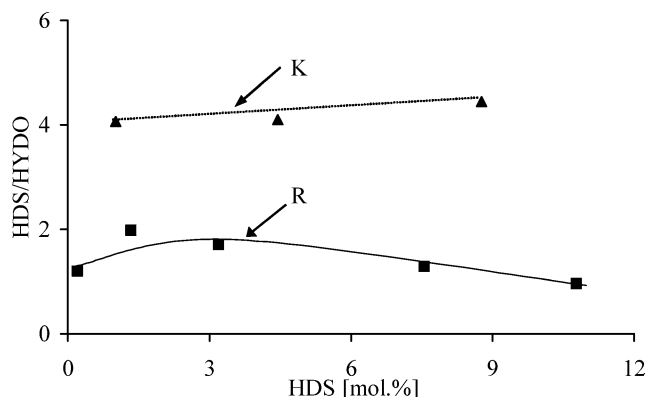


Fig. 10. Transformation of a model FCC gasoline ( $T = 200^\circ\text{C}$ ,  $P = 20 \text{ bar}$ ,  $\text{H}_2/\text{Hc} = 200 \text{ l/l}$ ). HDS/HYDO selectivity versus HDS yield. Effect of the presence of potassium. R,  $\text{CoMo}/\text{Al}_2\text{O}_3$ ; K,  $\text{CoMoK}/\text{Al}_2\text{O}_3$ .

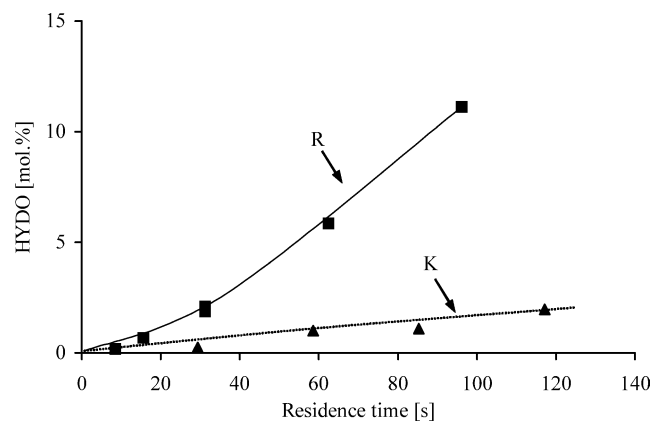


Fig. 9. Transformation of a model FCC gasoline ( $T = 200^\circ\text{C}$ ,  $P = 20 \text{ bar}$ ,  $\text{H}_2/\text{Hc} = 200 \text{ l/l}$ ). Formation of the hydrogenation products (HYDO) from 23DMBN versus residence time. Effect of the presence of potassium. R,  $\text{CoMo}/\text{Al}_2\text{O}_3$ ; K,  $\text{CoMoK}/\text{Al}_2\text{O}_3$ .

which was obtained. At the same time a decrease in the activity of the potassium-modified catalyst in the isomerization of 23DMB2N into 23DMB1N compared to that of the unmodified catalyst could be noted (Fig. 11). Actually it was found that on the unmodified catalyst, this reaction was very fast and it was also found that the hydrogenation of 23DMB1N was much faster than the hydrogenation of 23DMB2N [13]. Consequently any inhibition of the olefin isomerization activity is likely to decrease the activity of the catalyst in olefin hydrogenation. The addition of potassium led also to the nearly complete disappearance of the formation of C6MT, the alkylthiophenes resulting from the reaction of 23DMB2N or 23DMB1N with 2MT (Fig. 12). This is also a consequence of the decrease in acidity of the catalyst.

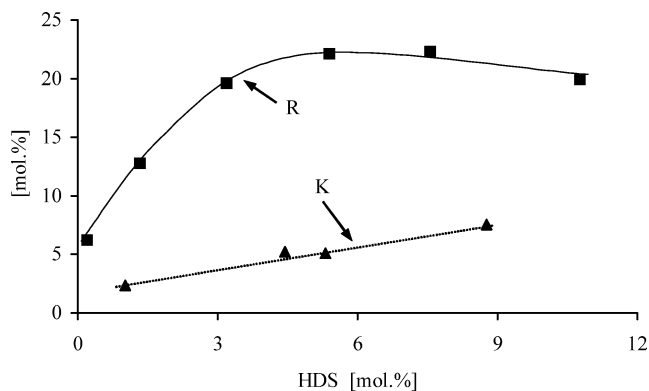


Fig. 11. Transformation of a model FCC gasoline ( $T = 200\text{ }^{\circ}\text{C}$ ,  $P = 20\text{ bar}$ ,  $\text{H}_2/\text{Hc} = 200\text{ l/l}$ ). Formation of 23DMB1N from 23DMB2N versus HDS yield. Effect of the presence of potassium. R, CoMo/Al<sub>2</sub>O<sub>3</sub>; K, CoMoK/Al<sub>2</sub>O<sub>3</sub>.

## 4. Discussion

### 4.1. Reaction mechanisms

The identification of all the products of the transformation of the model feed containing 2MT and 23DMB2N made it possible to determine the reaction schemes and to propose reaction mechanisms. Except for HDS and hydrogenation, the formation of the products involved the Brønsted acidity of the support.

Regarding the transformation of 2MT, the primary desulfurization products underwent a series of consecutive reactions leading to pentanes, cracking products, oligomers, thiols, and alkylthiophenes, which appeared as secondary products (Scheme 1). According to the literature, the desulfurization of compounds such as thiophene involves two pathways [25]. In the case of 2MT, this gives as main products P1N, E-, and Z-P2N (Scheme 2). Following this scheme, the direct desulfurization of 2MT should give penta-1,3-diene as a primary product which through hydrogenation would produce pentenes then pentane as the final product. The other pathway would involve the hydrogenation of 2MT

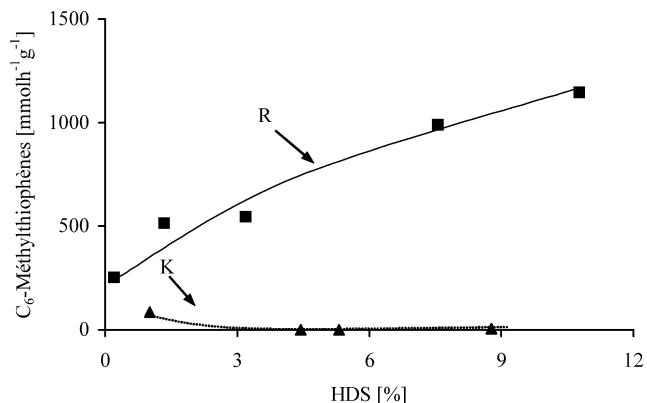
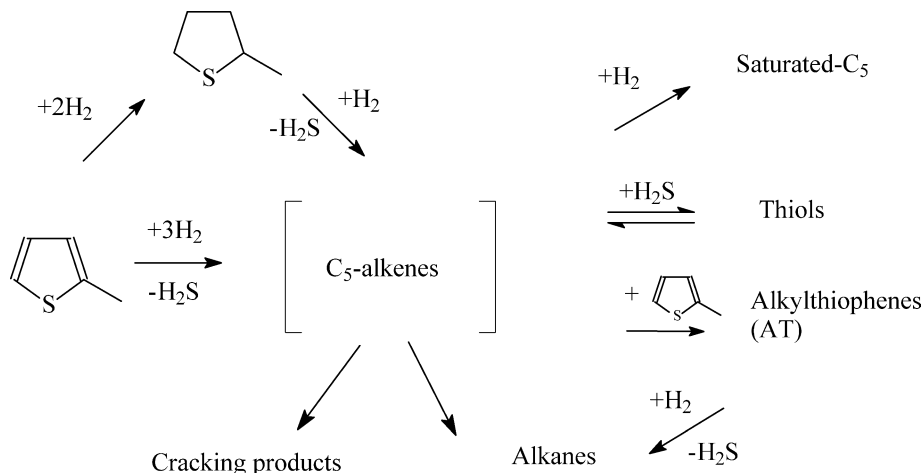


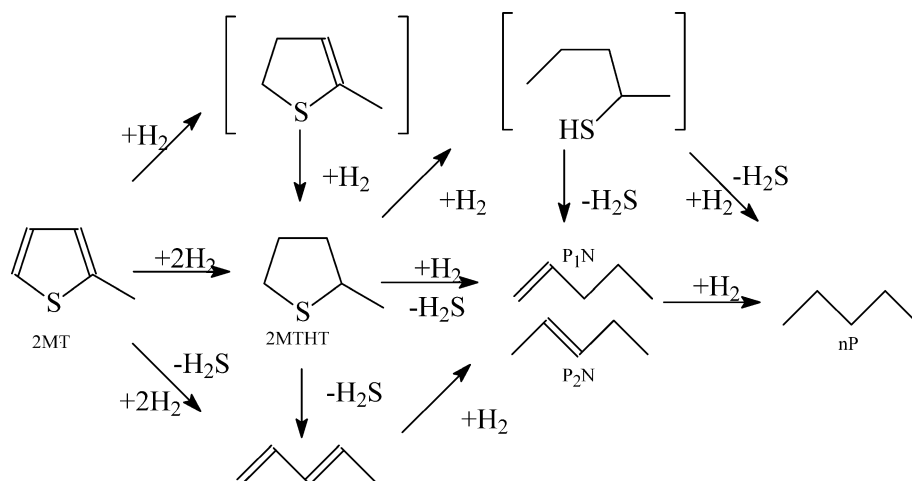
Fig. 12. Transformation of a model FCC gasoline ( $T = 200\text{ }^{\circ}\text{C}$ ,  $P = 20\text{ bar}$ ,  $\text{H}_2/\text{Hc} = 200\text{ l/l}$ ). Formation of C<sub>6</sub>MT versus HDS yield. Effect of the presence of potassium. R, CoMo/Al<sub>2</sub>O<sub>3</sub>; K, CoMoK/Al<sub>2</sub>O<sub>3</sub>.

into 2MTHT followed by the desulfurization of the latter into penta-1,3-diene. However, under our conditions we did not observe any trace of penta-1,3-diene, which was also the case in the literature for dienes in general [26–28]. Nevertheless, this does not prove that such compounds do not exist as adsorbed intermediates which, as already suggested by others, would react very fast through hydrogenation [26,27]. The possibility of a direct transformation of 2MTHT into pentane through hydrogenolysis must also be considered.

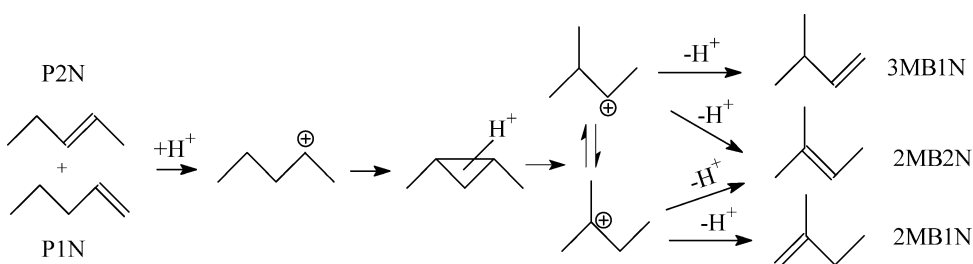
The formation of the by-products involved mainly the Brønsted acidity of the catalyst. The alkene isomers (2MB2N, 3MB1N, 2MB1N) are supposed to be produced through the protonation of P2N and P1N and the formation of protonated cyclopropane (Scheme 3). The presence of C<sub>5</sub>-thiols (pentane-1-thiol and pentane-2-thiol) could be due to the opening of the 2MTHT ring and/or to the addition of H<sub>2</sub>S to the primary pentene products (Scheme 4). Actually, 2MTHT resulting from the hydrogenation of 2MT can be protonated and undergo either the “a” or “b” rupture of the cycle through an elimination process to produce the ene-thiols which after the hydrogenation of their double bond would give the corresponding thiols. The addition



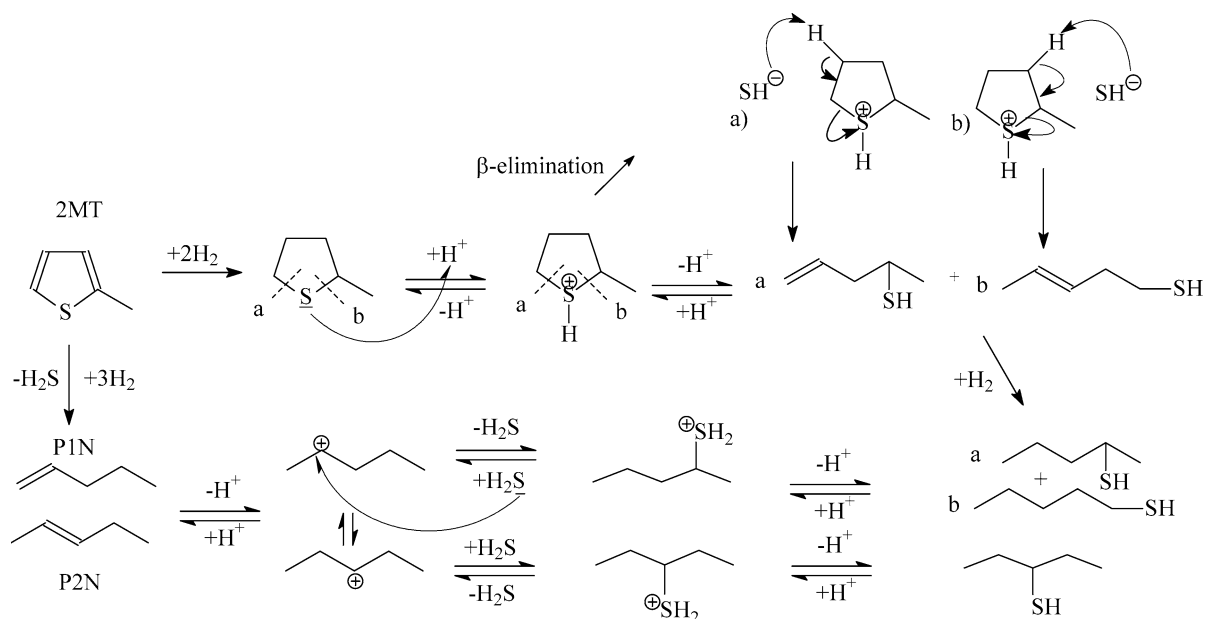
Scheme 1. Transformation of 2MT.



Scheme 2. Formation of the HDS products from 2MT. 2M, 2-methylthiophene; 2MTHT, 2-methyltetrahydrothiophene; P1N, pent-1-ene; P2N, pent-2-ene; nP, *n*-pentane.



Scheme 3. Isomerization of the C5 alkenes produced by the HDS of 2MT. P2N, pent-2-ene; P1N, pent-1-ene; 2MB2N, 2-methylbut-2-ene; 2MB1N, 2-methylbut-1-ene; 3MB1N, 3-methylbut-1-ene.

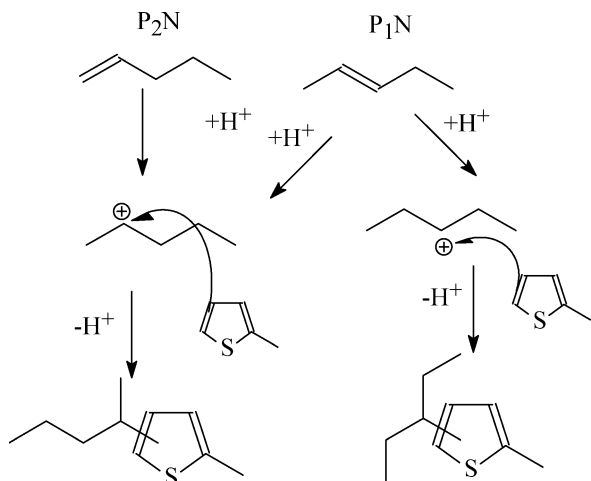


Scheme 4. Formation of C<sub>5</sub>-thiols. 2MT, 2-methylthiophene; P2N, pent-2-ene; P1N, pent-1-ene.

of H<sub>2</sub>S to the double bond of the primary pentene products involves the protonation of the latter followed by a nucleophilic attack by H<sub>2</sub>S. This reaction which is expected to follow Markownikoff's rule favors the formation of the secondary thiols. Consequently, as shown in [Scheme 4](#), the

recombination of H<sub>2</sub>S with P1N or P2N should give mainly pentane-2-thiol and pentane-3-thiol. The fact that we obtained mainly pentane-1-thiol and that no pentane-3-thiol was observed seems to indicate that pentanethiols resulted essentially from the opening of 2MTHT. In addition, the ex-

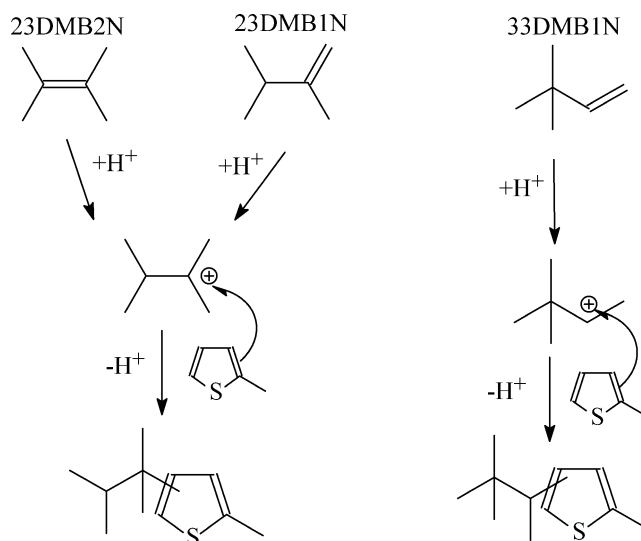




Scheme 5. Formation of C<sub>5</sub>-methylthiophenes (C5MT). P<sub>2</sub>N, pent-2-ene; P<sub>1</sub>N, pent-1-ene.

cess of pentane-1-thiol with respect to pentane-2-thiol means that the opening occurs preferentially at the carbon atom to which the methyl group is attached or that if it occurs on both sides pentane-2-thiol decomposes through HDS more rapidly than pentane-1-thiol. The C<sub>5</sub>MT and C<sub>6</sub>MT alkylthiophenes were formed in significant amounts through the alkylation of 2MT by the pentene HDS products and by the 23DMBN isomers, respectively. The C<sub>5</sub>MT products are supposed to result from the attack of the thiophenic cycle by a secondary carbenium ion formed through protonation of pentenes followed by deprotonation (Scheme 5). Similarly, the C<sub>6</sub>MT products are supposed to result mainly from the electrophilic attack of the thiophenic ring by carbenium ions formed by protonation of 23DMB2N and 23DMB1N (Scheme 6). Partial or total hydrogenation products of these AT were also observed in small amounts. The formation of heavy alkanes results from the condensation of C<sub>5</sub>- and C<sub>6</sub>-alkenes through acid catalysis. C<sub>10</sub>-, C<sub>11</sub>-, or C<sub>12</sub>-alkanes may also be produced through the desulfurization of AT. Their structure could not be determined by GC-MS.

Scheme 7 shows all the products of 23DMB2N transformation. The main products are the 23DMB1N isomer and 23DMB, the hydrogenation product. However, as indicated previously the 23DMBN isomers contribute to the formation of the C<sub>6</sub>MT products (Scheme 6) as well as to the formation of C<sub>6</sub>-thiols (through the addition of H<sub>2</sub>S) and of heavy alkanes (C<sub>12</sub> and C<sub>11</sub>). The important point is that the equilibrium between the two alkenes (23DMB2N and 23DMB1N) is very rapidly reached through double-bond migration. 23DMB, the main hydrogenation product, is mostly formed from 23DMB1N which is much more reactive than its 23DMB2N isomer [13]. The formation of the other products can be explained by skeletal isomerization involving the tertiary carbenium ion corresponding to 23DMB2N and 23DMB1N and a protonated cyclopropane intermediate (Scheme 8). The C–C bond ruptures in the protonated cyclopropane lead to the formation of 2-methylpentenes (2MP1N and 2MP2N) and

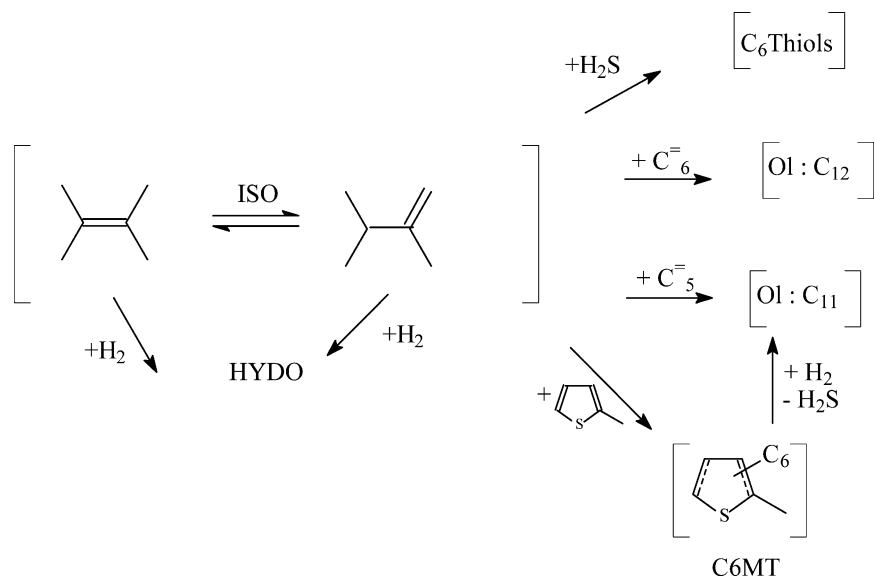


Scheme 6. Formation of C<sub>6</sub>-methylthiophenes (C6MT). 23DMB2N, 2,3-dimethylbut-2-ene; 23DMB1N, 2,3-dimethylbut-1-ene; 33DMB1N, 3,3-dimethylbut-1-ene.

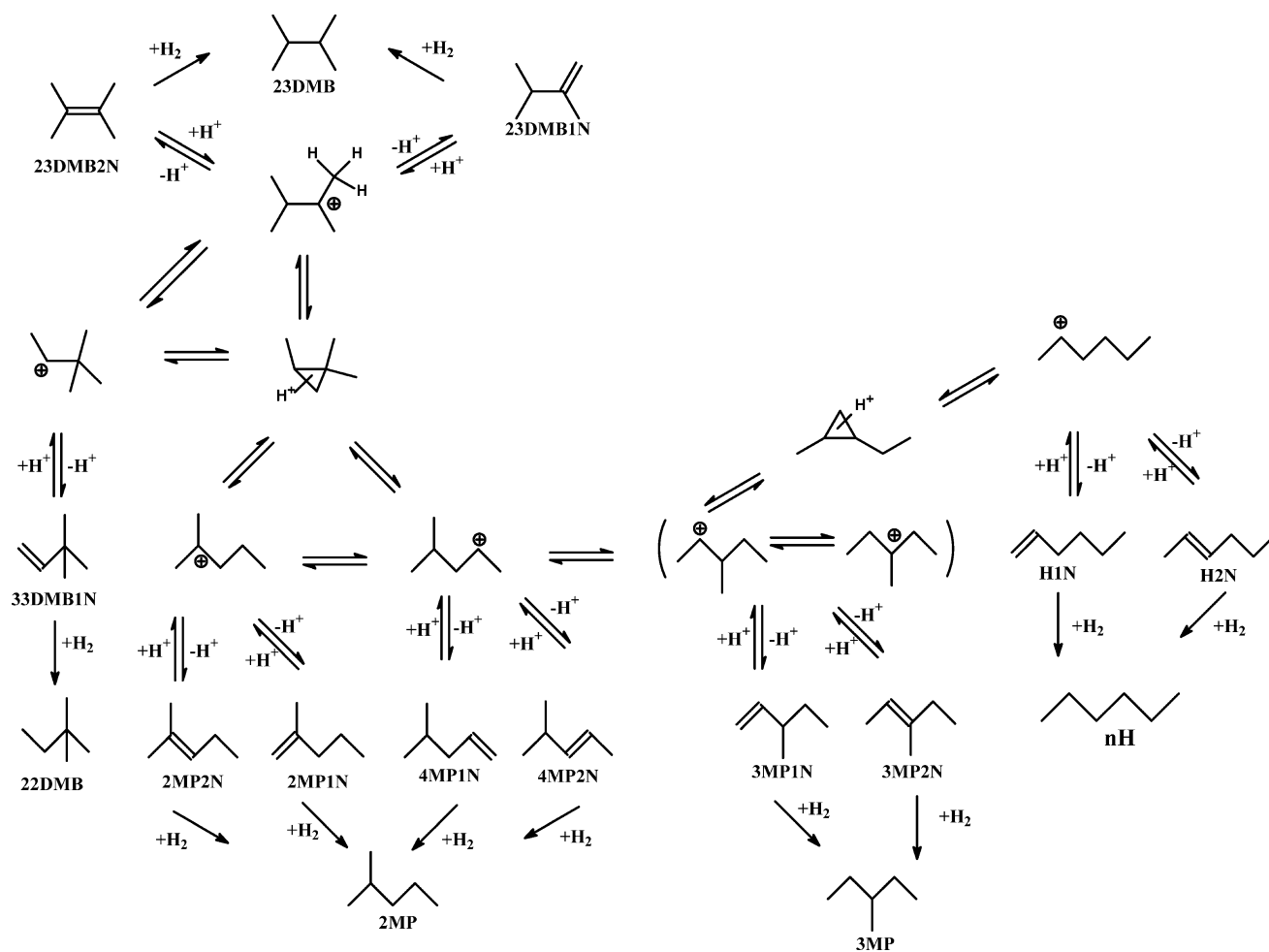
4-methylpentenes (4MP1N and 4MP2N). Successive rearrangements of the various carbenium ions can explain the formation of the other minor products. The various C<sub>6</sub>-thiols result from the nucleophilic attack of H<sub>2</sub>S on the protonated double bond of the C<sub>6</sub>-alkenes followed by the elimination of H<sup>+</sup>.

#### 4.2. Effect of potassium

It is known that acidic supports such as zeolites can promote the hydrogenation activity of metals [14,15] as well as of sulfides [16–19]. The enhancement of the activity was attributed, in part at least, to electronic transfer phenomena from the metal or sulfide to acceptor sites in the zeolite lattice. Such a transfer would favor the adsorption of the substrate and therefore the hydrogenation activity of the metal or sulfide [29]. However, this kind of effect could also be interpreted in terms of a modification of the intrinsic hydrogenation properties of the material. Evidence for the electronic transfer was found in FTIR of adsorbed CO which showed that the absorption bands were shifted toward high frequencies, indicating an electron deficiency of the catalytic centers which increased with the acidity of the support [17,19]. Conversely, it can be expected that increasing the basicity of the support should decrease the hydrogenation activity. This is indeed what was observed with Pt zeolites [29,30] and more recently by Zhao et al. [11] as well as by Hatanaka et al. who reported that potassium-modified hydrotreating catalysts were more selective in the HDS of FCC gasoline than unmodified catalysts [7,8]. Actually, the interpretation of Hatanaka et al. was not based on electronic effects; they suggested that potassium may limit the coke formation and the deactivation of the catalyst. However, it must be noted that this observation is not general and that others [31,32] found no positive effect of the addition



Scheme 7. Transformation of 23DMB2N. HYDO, hydrogenation; ISO, isomerization; Ol, C<sub>12</sub>-, and C<sub>11</sub>-alkane oligomers; C6MT, C<sub>6</sub>-methylthiophenes.



Scheme 8. 23DMB2N transformation, hydrogenation, and isomerization products. 23DMB2N, 2,3-dimethylbut-2-ene; 23DMB1N, 2,3-dimethylbut-1-ene; 33DMB1N, 3,3-dimethylbut-1-ene; 3MP1N, 3-methylpent-1-ene; 3MP2N, 3-methylpent-2-ene; 2MP1N, 2-methylpent-1-ene; 2MP2N, 2-methylpent-2-ene; 4MP2N, 4-methylpent-2-ene; H1N, hex-1-ene; H2N, hex-2-ene; nH, *n*-hexane; 2MP, 2-methylpentane; 3MP, 3-methylpentane; 22DM, 2,2-dimethylbutane; 4MP1N, 4-methylpent-1-ene.

of alkaline elements on the performances of the catalysts. For instance, Miller et al. [31] reported recently that cesium and potassium had respectively no effect on the selectivity of Mo and CoMo catalysts used in the HDS of FCC naphtha. Moreover, Muralidhar et al. [32] even found that the HDS of thiophene was more depressed than the hydrogenation of hex-1-ene when their CoMo catalyst was modified by sodium and calcium additives. However, they used separate experiments which may not be representative of the situation encountered under practical conditions. Indeed, it was found that the hydrogenation of olefins was inhibited significantly in the presence of sulfur compounds [13]. In fact, the differences in the effects which were observed may result from differences in the experimental conditions and methods. The effect of alkali metals or alkaline earth elements on the HDS/HYDO selectivity very likely depends on whether we are using FCC gasoline, model reactions, or synthetic gasoline; it may depend also on the sulfur content of the feed and consequently on the HDS conversion which is reached. For instance, Miller et al. [31] used a FCC gasoline and studied the effect of potassium and cesium in a range of sulfur content between zero and 800 ppm, which was much lower than in our case and this could explain at least partly the discrepancies in the results. On the other hand, Zhao et al. [11] studied the effect of potassium on the conversion of a synthetic gasoline made of thiophene and hex-1-ene in solution in cyclohexane under conditions where the HDS conversion with the modified catalysts was much lower than with their conventional standard catalyst, which may explain why they observed a positive effect. Actually, it is sensible to expect that when approaching 100% HDS conversion it becomes more and more difficult, even with selective catalysts, to avoid olefin hydrogenation since the inhibition of the latter by sulfur compounds which is quite significant at low HDS conversion [13] is disappearing. In practice one has therefore to adjust the experimental or process conditions carefully so that they be severe enough to get high HDS levels but mild enough so as to avoid complete olefin hydrogenation. We may conclude that alkali metals can definitely have a positive effect on the HDS/HYDO selectivity provided that the conditions may not be too severe otherwise the effect is bound to disappear.

The FTIR study carried out in this work showed that although the promotion level was apparently not strongly modified, the number of accessible sites on the sulfide phase decreased, which may explain that the activity of the catalyst regarding both the transformation of 2MT and the hydrogenation of 23DMBN decreased. However the activity in HDS decreased less than the activity in hydrogenation and consequently the HDS/HYDO selectivity increased. The FTIR results showed also that potassium had indeed an effect on the electronic properties of the sulfide. Actually, the absorption bands corresponding to CO adsorbed on molybdenum vacancies were shifted downward (from 2110 to 2103  $\text{cm}^{-1}$ ), which means that there was an increase of the electronic density on the metal. This is in accordance

with previous results in the literature. For instance a similar observation was made by De Mallmann and Barthomeuf with basic zeolites used in the case of benzene hydrogenation [29] while the reverse was obtained, for instance, with ruthenium sulfide on acidic zeolites [17]. It can therefore be concluded that the stronger decrease in hydrogenation activity than in HDS activity, hence the increase in HDS/HYDO selectivity, could be due at least in part to the modification of the electronic properties of the sulfide following the addition of potassium. However, the fact that HDS is supposed to involve hydrogenation steps prior to C–S bond cleavage makes this explanation questionable unless we suppose as several authors did [3,4,26,33–35] that the reactions occur on different catalytic centers and that potassium inhibits those involved in olefin hydrogenation mainly. One may note that this constitutes an easy way out which our results do not really support since all the sites seem to be affected by potassium. This is the reason why another explanation must be considered.

Actually, the FTIR study showed also that the acidity of the support was decreased due to the addition of potassium. CO adsorption showed that the number and the strength of the Lewis sites of the support were decreased and the adsorption of  $\text{CO}_2$  confirmed that the basic properties were promoted. This was expected to decrease the activity of the catalyst regarding the acid-promoted reactions such as in particular double-bond migration. Given the fact that terminal olefins such as 23DMB1N hydrogenate much faster than olefins with a tetrasubstituted double bond such as 23DMB2N [13], this may also explain the effect of potassium on the HDS/HYDO selectivity. With the unmodified catalyst, the isomerization was very fast so that 23DMB1N could be regenerated in concentrations close to the equilibrium as soon as it was consumed through hydrogenation, which was apparently no longer the case with the catalyst containing potassium. This could very well constitute the main explanation to the effect of potassium on the HDS/HYDO selectivity observed in our case. It was also observed that potassium inhibited the formation of by-products such as alkylthiophenes. This is also the consequence of the neutralization of the acidic properties of the catalyst.

## 5. Conclusion

The transformation, under hydrogen pressure of a synthetic feed made of 2-methylthiophene, 2,3-dimethylbut-2-ene, and orthoxylene dissolved in *n*-heptane can be a useful and predictable test reaction to discriminate between various catalysts regarding their HDS/HYDO selectivity.

Under the conditions we have used, the modification by potassium of a commercial catalyst made it possible to improve its selectivity in HDS of a synthetic FCC gasoline with respect to the hydrogenation of the olefins. In fact, the addition of potassium by decreasing the acidity decreased more the hydrogenation activity than the HDS activity. This

could be in part the consequence of the modification of the electronic properties of the sulfide phase but, more likely, is considered as being due to the change in the isomerization properties of the support.

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