



Kinetic study of olefin hydrogenation on hydrotreating catalysts

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ABSTRACT

In connection with the specific requirements of the hydrotreating of FCC gasoline, the selectivity of hydrotreating catalysts in hydrodesulfurization with respect to the hydrogenation of olefins has to be controlled and if possible improved. Hydrogenation of several olefins over CoMo/Al₂O₃ and NiMo/Al₂O₃ sulfided catalysts was studied using kinetics in order to understand both promoter and structure effects. After approximations made on the Langmuir–Hinshelwood theory, a pseudo Eley–Rideal model was obtained. Using this model, the kinetic constants have been determined and are very consistent with our experimental results.

The calculations of the adsorption constant of olefins explain differences between both promoters, Ni and Co. On CoMo catalyst, the olefin with the highest steric hindrance is less adsorbed than the others. On NiMo catalyst, the olefins are better adsorbed and there is no influence of the structure. Therefore CoMo catalysts will be more efficient in the selective hydrodesulfurization of FCC gasoline than NiMo catalysts.

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1. Introduction

New restrictions on the sulfur content of the gasoline and diesel fuel were fixed at a maximum content of 10 mg/kg of sulfur as from January 1, 2009 by the directives of the European Parliament and the council [1]. This is not only because of the harmful emissions of SO_x but also because of the noxious effect of sulfur on the effectiveness of the catalytic technologies used in the post-processing of exhaust gases. Thus, hydrotreating has become more and more important in refining with the objective of removing as much as possible of the sulfur impurities from petroleum products [2–7]. Regarding the gasoline pool, the sulfur content depends essentially on the olefin-rich fraction coming from the fluid catalytic cracking (FCC). Consequently, in order to meet the new requirements concerning gasoline, it is necessary to reduce the amount of sulfur impurities in the FCC naphtha drastically. In this particular case, the selectivity of the catalysts in hydrodesulfurization with respect to the hydrogenation of olefins has to be controlled and if possible improved in order to limit the octane rating loss [7 and references therein]. Several factors can influence this selectivity, the presence of Co and Ni promoters in particular [8–12]. The promotion effect of Co or Ni on the activity in HDS of Mo or W sulfide catalysts has been known for many years and various theories were proposed to explain it [9–12]. This effect also exists for the hydrogenation of olefins [13–21]. Several studies show that the promoter effect of

Ni on the hydrogenation of olefins is higher than the effect of Co [15,17,18,20,21]. This can explain why CoMo catalysts are generally considered as more efficient than NiMo catalysts in the selective HDS of FCC gasoline [7]. Recently, influence of olefin structure on their reactivity was also pointed out [18,19,21]. Another parameter which could play an important role in the hydrogenation of olefins is their isomerization [7 and references therein,12,18,20–23]. Actually FCC gasoline contains mostly internal olefins with di-, tri- or tetrasubstituted double bonds (about 75 wt%) [24–27]. These olefins are expected to be much less reactive in hydrogenation than terminal olefins. Therefore, their isomerization into terminal olefins may increase their reactivity in hydrogenation [19,22].

Many studies have been devoted to the kinetics and to the mechanism of the hydrogenation of olefins over metallic catalysts [28–30]. On sulfide catalysts, hydrodesulfurization of sulfur compounds [31,32] and hydrogenation of aromatics [33–37] have been extensively studied.

In a preliminary study [18,21], the hydrogenation of three olefins with different structures (cyclopentene, 1-methylcyclopentene and 3,3-dimethylbut-1-ene) was investigated over NiMo, CoMo and Mo sulfided catalysts supported on alumina. It was shown that the reactivity in hydrogenation of olefins increased with the decreasing number of alkyl groups attached to the double bond on the CoMo catalyst. This sequence is the one observed in catalysis by metals for years [28,29] and very recently on sulfided CoMo catalyst [18,19,21]. Moreover, we showed that the promotion effect of Ni was higher than that of Co whatever the olefin. Nevertheless, the order in the reactivity of the three olefins was different on NiMo and on CoMo catalysts [21].

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Table 1

Apparent rates of olefin hydrogenation over sulfide CoMo and NiMo catalysts at 150 °C. Influence of the partial pressure of olefin A (P_A) with $P_{H_2} = 85$ kPa and influence of partial pressure of dihydrogen (P_{H_2}) with $P_A = 2400$ Pa.

Olefins	Catalysts	Rate (10^{-4} mol h $^{-1}$ g $^{-1}$)							
		P_A (Pa) with $P_{H_2} = \text{constant} = 85$ kPa				P_{H_2} (kPa) with $P_A = \text{constant} = 2400$ Pa			
		400	800	1200	2400	55	65	75	85
cC ₅ [≡]	NiMo	7.9	9.6	10.6	12.0	6.3	8.8	10.1	12.0
	CoMo	0.50	0.79	0.88	1.2	0.76	0.92	1.1	1.2
1McC ₅ [≡]	NiMo	1.0	1.2	1.3	1.6	1.0	1.2	1.4	1.6
	CoMo	0.07	0.11	0.15	0.24	0.15	0.18	0.21	0.24
33DM1C ₄ [≡]	NiMo	4.6	5.5	5.9	7.1	4.0	4.6	5.7	7.1
	CoMo	1.2	1.5	1.8	2.6	1.5	2.0	2.3	2.6

The aim of this work was to develop kinetic models for the hydrogenation of the same three olefins on sulfided NiMo and CoMo catalysts to understand the differences observed between the olefin reactivities and between the promoters. Both apparent rate constants and adsorption constants were determined for each olefin.

2. Experimental

2.1. Catalysts

The CoMo/Al₂O₃ and NiMo/Al₂O₃ commercial catalysts contained 8.3 wt% Mo with 2.3 wt% Ni and 2.2 wt% Co respectively deposited on alumina (230 m² g⁻¹). The catalysts were presulfided *in situ* with a flow of H₂ (90%) and H₂S (10%) at 400 °C under atmospheric pressure for 15 h. After sulfidation, the catalyst samples (250–700 mg of NiMo/Al₂O₃ or CoMo/Al₂O₃ catalyst) were treated under helium at 350 °C for 1 h.

2.2. Transformation of olefins

Cyclopentene (95%) and 1-methylcyclopentene (98%) were purchased from Aldrich, and 3,3-dimethylbut-1-ene (98.5%) and n-heptane (99%) from Fluka. They were used without further purification. The transformation of the olefins in solution of n-heptane was carried out in a fixed-bed reactor at 150 °C under atmospheric pressure. The kinetic orders were determined by varying partial pressure of olefins or dihydrogen. The total pressure of 100 kPa was maintained constant by adjusting the partial pressure of n-heptane. Under these conditions no significant sulfur loss was detected by elemental analysis of the used samples (CE Instruments NA2100 Protein).

The reaction rate of hydrogenation or isomerization of olefin A was calculated by the formula:

$$r_A = FX_i m^{-1}$$

where F is the molar flow rate of olefin A, X_i the molar fraction of product i and m the weight of catalyst.

The reaction products were analyzed on-line by means of a Varian gas chromatograph equipped with an automatic sampling

Table 2

Apparent partial orders with respect to olefin A and with respect to dihydrogen for the hydrogenation of olefins over CoMo and NiMo sulfide catalysts at 150 °C.

Olefin A	Apparent partial orders			
	With respect to olefin A		With respect to dihydrogen	
	NiMo	CoMo	NiMo	CoMo
cC ₅ [≡]	0.23	0.48	1.4	1.1
1McC ₅ [≡]	0.26	0.69	1.1	1.1
33DM1C ₄ [≡]	0.24	0.43	1.3	1.2

valve, a 50-m CPSil-5 capillary column (film thickness, 0.4 μm) and a flame-ionization detector. The activity of each sample was measured after stabilization (120 min on stream) and under conditions where a linear relationship between conversion and residence time was obtained (conversion lower than 15%). It was checked that the reactor was inactive. Moreover, the solvent (n-heptane) has no effect on the considered reactions.

3. Results

Equilibrium constants were determined for the hydrogenation of the three olefins from the Gibbs free energy of formation of olefins and corresponding alkanes [38]. They are always higher than 5×10^6 under the conditions used in this study. Therefore, the reactions were not limited by thermodynamics. Reaction schemes of the three olefins were determined previously [21]. In our experimental conditions, cyclopentene (cC₅[≡]) was hydrogenated only into cyclopentane (cC₅). 1-Methylcyclopentene (1McC₅[≡]) underwent initially isomerization into 3-methylcyclopentene and 4-methylcyclopentene and methylcyclopentane results from the hydrogenation of the mixture of the methylcyclopentene isomers. 3,3-Dimethylbut-1-ene (33DM1C₄[≡]) underwent two parallel reactions: pathway 1: the hydrogenation into 2,2-dimethylbutane (HYD) and pathway 2: the skeletal isomerization into 2,3-dimethylbut-1-ene and 2,3-dimethylbut-2-ene (ISO). The 2,3-dimethylbutene isomers were in turn hydrogenated into 2,3-dimethylbutane. Actually, the amount of 2,2-dimethylbutane makes it possible to measure the hydrogenation activity while the amount of the three other products leads to the isomerization activity but this way will be considered in a future study.

3.1. Determination of kinetics orders

Table 1 shows the effect of the partial pressure of olefin A (P_A) and of the partial pressure of dihydrogen (P_{H_2}), respectively on the apparent rates of olefin hydrogenation.

For each hydrogenation reaction, the variations of global rate with partial pressures may be represented by a power-law:

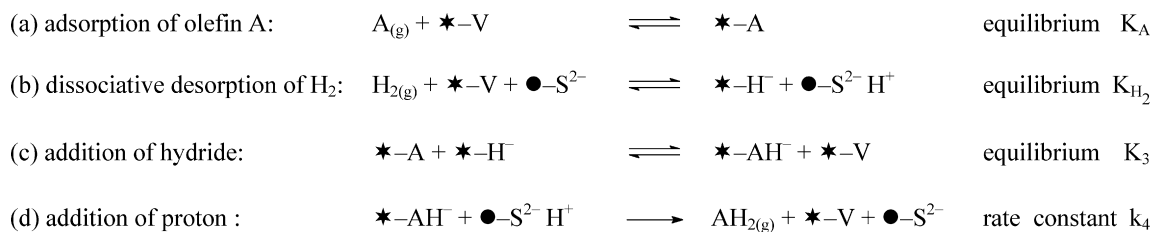
$$r_A = k P_A^a P_{H_2}^b \quad (1)$$

with r_A : global rate of hydrogenation, k : kinetic rate constant, a and b : apparent partial orders with respect to olefin A and dihydrogen respectively, P_A and P_{H_2} : partial pressures of olefin A and dihydrogen respectively.

In order to determine the apparent partial orders with respect to olefin A, the rate of its hydrogenation reaction was measured by varying the partial pressure of olefin A, the partial pressure of dihydrogen being constant ($P_{H_2} = 85$ kPa). Eq. (1) becomes:

$$r_A = k_1 P_A^a \quad (2)$$

with $k_1 = k P_{H_2}^b = \text{constant}$.



Scheme 1. Mechanism for the hydrogenation of olefin A on sulfide catalysts with heterolytical dissociation of dihydrogen.

The apparent partial order with respect to olefin A was determined by plotting $\ln r_A$ vs $\ln P_A$. The apparent partial order with respect to dihydrogen was determined by the same procedure by measuring the rate of hydrogenation of olefin A for various partial pressures of dihydrogen, the partial pressure of olefin A being kept constant ($P_A = 2.4$ kPa) (Table 2).

3.2. Theoretical treatments

The rate expression for catalytic hydrogenation is computed by the Langmuir–Hinshelwood theory. The three important steps are the adsorption of reactants on the active sites, the surface reaction between the adsorbed reactants and the desorption of products and reactants.

Various types of adsorption of dihydrogen are considered in the literature for the hydrogenation reactions such as non-dissociative or homolytic dissociative adsorption expected to occur on metal catalysts. Over sulfide catalysts, adsorption mechanisms are thought to be different and the kinetic modelling of the olefin hydrogenation was based on the following assumptions:

- (i) Only the hydrogenation reaction is considered. The isomerization of 1-methylcyclopentene ($1McC_5^=$) occurred very quickly into 3-methylcyclopentene ($3McC_5^=$) and 4-methylcyclopentene ($4McC_5^=$) under our conditions. The skeletal isomerization of 3,3-dimethylbut-1-ene depends also of the partial pressure of olefin A and of the partial pressure of dihydrogen: the partial apparent orders are always close to one (not shown in this study).
- (ii) The hydrogenation reaction occurs only on the sulfide phase. Indeed, no hydrogenation product was found in experiments carried on the support alone under the same conditions.
- (iii) Only one mechanism is proposed according to the heterolytical dissociation of dihydrogen on sulfide catalyst [12,23,31,33–37]: hydride on a vacancy of a metallic atom, symbolised by $\star-V$ and proton on a sulphur anion symbolised by $\bullet-S^{2-}$. Others mechanisms were studied but were unlikely.
- (iv) No interconversion of active sites is considered by adsorption and desorption of H_2S because all the experiments were carried out without H_2S .
- (v) The adsorption and desorption of reactants (H_2 and olefin) are considered to be much faster than surface reactions and be assumed at equilibrium.
- (vi) The adsorption of olefin is only considered on a vacancy of a metallic atom.
- (vii) The desorption of the product (alkane) and the adsorption–desorption of solvent (n-heptane) did not be considered.

Also, the catalytic sequence can be described by elementary reactions as shown in Scheme 1.

Some kinetic models showed that the hydrogenation of toluene started by the addition of hydride on the molecule adsorbed on a metallic vacancy and followed by the addition of proton [33–35]. The rate-determining step should be the addition of proton in agreement with numerous authors [12,23,33–35]. The adsorption

and desorption steps were equilibrated and the number of active sites was supposed constant. The computation is made according to the classical Langmuir–Hinshelwood kinetics except that a surface charge conservation equation was added [33,34].

The rate of the reaction is given by the following equation, according to step (d):

$$r_A = k_4[\star-AH^-][\bullet-S^{2-}H^+] \quad (3)$$

where r_A is the rate of the reaction, k_4 is the rate constant and $[\star-AH^-]$ and $[\bullet-S^{2-}H^+]$ are the concentrations of adsorbed species.

According to step (b) and step (c) respectively, the concentrations $[\bullet-S^{2-}H^+]$ and $[\star-AH^-]$ are:

$$[\bullet-S^{2-}H^+] = \frac{K_{H_2}P_{H_2}[\star-V][\bullet-S^{2-}]}{[\star-H^-]} \quad (4)$$

$$[\star-AH^-] = \frac{K_3[\star-A][\star-H^-]}{[\star-V]} \quad (5)$$

According to step (a), the concentration $[\star-A]$ is:

$$[\star-A] = K_A P_A [\star-V] \quad (6)$$

Eq. (5) becomes:

$$[\star-AH^-] = K_3 K_A P_A [\star-H^-] \quad (7)$$

and Eq. (3) can be written as:

$$r_A = k_4 K_3 K_A P_A K_{H_2} P_{H_2} [\star-V][\bullet-S^{2-}] \quad (8)$$

For the two types of sites, two conservation equations are written:

$$[\star-V]_0 = [\star-A] + [\star-H^-] + [\star-AH^-] + [\star-V] \quad (9)$$

$$[\bullet-S^{2-}]_0 = [\bullet-S^{2-}H^+] + [\bullet-S^{2-}] \quad (10)$$

At low partial pressure of H_2S , therefore in absence of H_2S the surface coverage by proton and hydride species is very low [35]. Then,

$$[\star-H^-] \ll [\star-A] + [\star-AH^-] + [\star-V] \text{ and } [\bullet-S^{2-}H^+] \ll [\bullet-S^{2-}]$$

As $[\star-AH^-]$ is proportional to $[\star-H^-]$, Eq. (7), we suppose that $[\star-AH^-] < [\star-A] + [\star-V]$.

Eq. (9) becomes:

$$[\star-V]_0 = [\star-V] + [\star-A] \quad (11)$$

and by Eq. (6) $[\star-V] = [\star-V]_0 - K_A P_A [\star-V]$ or $[\star-V] = [\star-V]_0 / (1 + K_A P_A)$.

Thus Eq. (8) becomes:

$$r_A = \frac{k_4 K_3 K_A P_A K_{H_2} P_{H_2} [\bullet-S^{2-}]_0 [\star-V]_0}{(1 + K_A P_A)} \quad (12)$$

As k_4 , K_3 , K_{H_2} , $[\star-V]_0$ and $[\bullet-S^{2-}]_0$ are constant and $k_4 K_3 K_{H_2} [\bullet-S^{2-}]_0 [\star-V]_0$ considered to be equal to k_A then:

$$r_A = \frac{k_A K_A P_A P_{H_2}}{1 + K_A P_A} \quad (13)$$

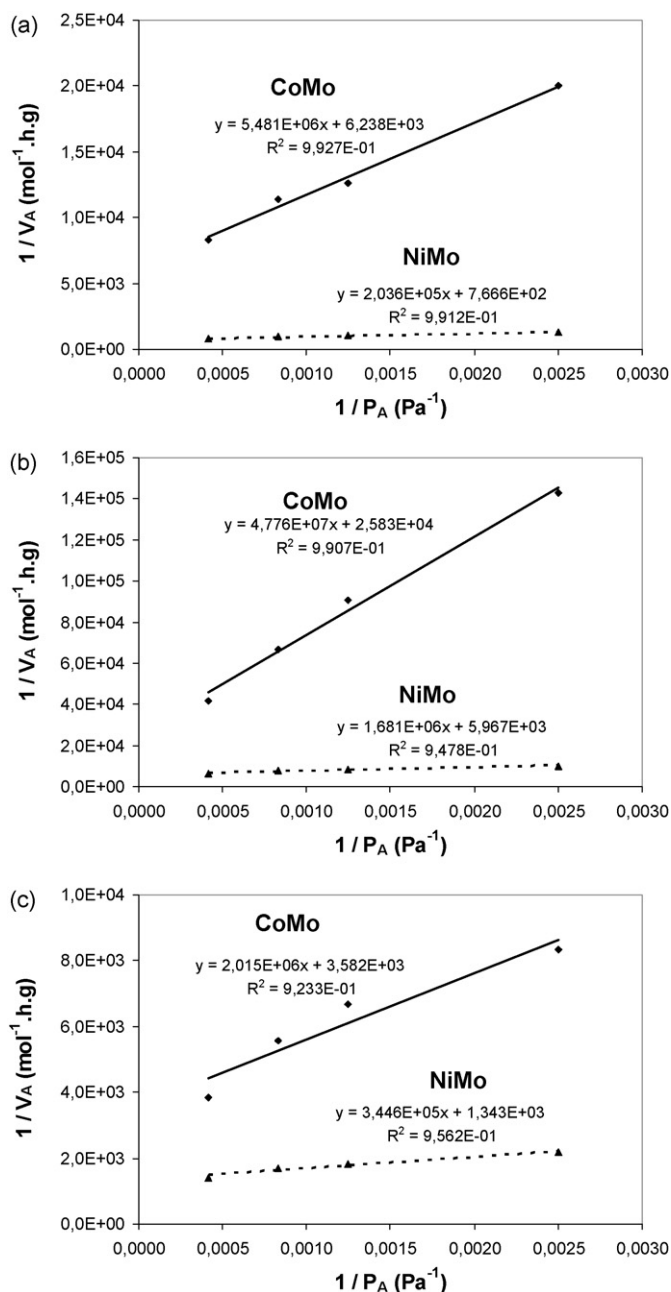


Fig. 1. Hydrogenation rate of olefin A as a function of its partial pressure over sulfide NiMo/Al₂O₃ (dotted line) and CoMo/Al₂O₃ (solid line) catalysts with $P_{H_2} = 85$ kPa – linearization according to Eq. (14). (a) Cyclopentene, (b) 1-methylcyclopentene, (c) 3,3-dimethylbut-1-ene.

Eq. (13) is quite similar to a kinetic equation derived from an Eley–Rideal mechanism and is coherent with a first-order kinetics with respect to dihydrogen (Table 2). This equation can be linearized as a function of the partial pressure of olefin A:

$$\frac{1}{r_A} = \frac{1}{k_A K_A P_{H_2}} \frac{1}{P_A} + \frac{1}{k_A P_{H_2}} \quad (14)$$

When $1/r_A$ is plotted vs $1/P_A$ straight lines are always obtained (Fig. 1). The rate constant k_A can be deduced from the origin and the adsorption constant K_A from the slope (Table 3).

From the data reported in Table 3, theoretical rates can be calculated by Eq. (13) and compared to the experimental values (Figs. 2 and 3). These curves show that the kinetic equation derived from the Langmuir–Hinshelwood model and the

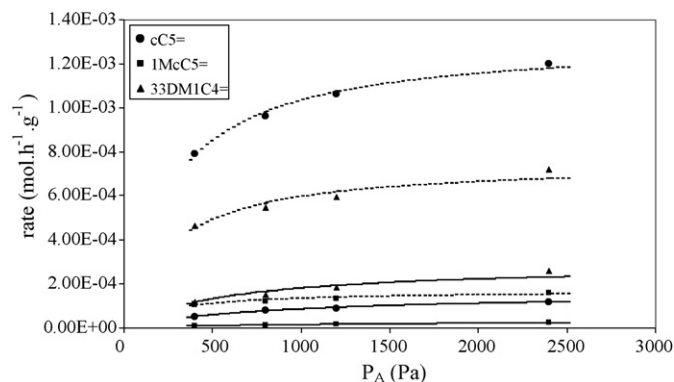


Fig. 2. Influence of the partial pressure of olefin A on the hydrogenation rate. Lines represent the calculated rates on NiMo (dotted line) and on CoMo catalysts (solid line). Points are the experimental data.

assumptions made in Eqs. (4)–(11) fit well with the experimental results.

4. Discussion

4.1. Olefin hydrogenation rate

Whatever the olefin, the apparent rate constants of olefin hydrogenation on NiMo catalysts are greater than over CoMo catalysts (Table 3). This result is consistent with previous results [15,17,21] which indicated that the promotion effect of Ni on the hydrogenation of olefins was more significant than that of Co.

Taking 1-methylcyclopentene as reference over each catalyst, the following ranking can be given for the three olefins:

$$\text{CoMo: } 1\text{McC}_5^= (1) < c\text{C}_5^= (4.1) < 33\text{DM1C}_4^= (7.2);$$

$$\text{NiMo: } 1\text{McC}_5^= (1) < 33\text{DM1C}_4^= (4.4) < c\text{C}_5^= (7.7).$$

In our previous study [21], the relative hydrogenation reactivity scales were determined by varying the residence time, the partial pressures keeping fixed with $P_{H_2} = 85$ kPa and $P_{\text{olefin}} = 2400$ Pa.

$$\text{CoMo: } 1\text{McC}_5^= (1) < c\text{C}_5^= (4.6) < 33\text{DM1C}_4^= (11.2);$$

$$\text{NiMo: } 1\text{McC}_5^= (1) < 33\text{DM1C}_4^= (4.1) < c\text{C}_5^= (6.9).$$

The two sequences are the same despite slightly different experimental conditions. We can notice the reverse positions of $c\text{C}_5^=$ and $33\text{DM1C}_4^=$ on these scales. Taking into account our mechanistic assumptions, this confirms our choice of the rate-determining step.

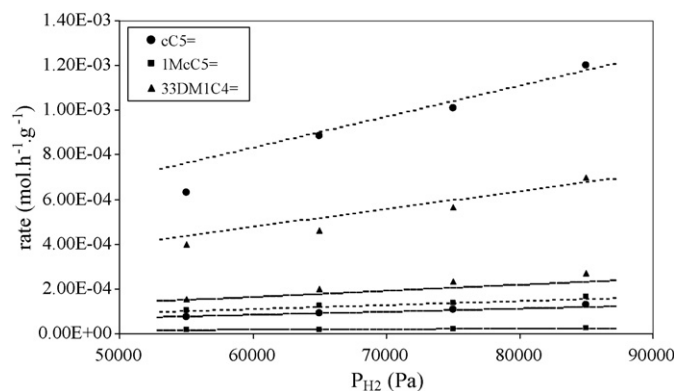


Fig. 3. Influence of the partial pressure of dihydrogen on the hydrogenation rate. Lines represent the calculated rates on NiMo (dotted line) and on CoMo catalysts (solid line). Points are the experimental data.

Table 3
Hydrogenation of olefin A at 150 °C on sulfide NiMo/Al₂O₃ and CoMo/Al₂O₃ catalysts – apparent rate constant k_A and adsorption constant K_A .

Olefin A	Apparent rate constant k_A (10^{-9} mol h ⁻¹ g ⁻¹ Pa ⁻¹)		Adsorption constant K_A (10^{-3} Pa ⁻¹)	
	NiMo	CoMo	NiMo	CoMo
cC ₅ =	15.4	1.9	3.8	1.1
1McC ₅ =	2.0	0.46	3.6	0.54
33DM1C ₄ =	8.8	3.3	3.9	1.8

4.2. Olefin adsorption

On NiMo catalyst, the apparent partial orders with respect to olefin are always close to 0.25 (Table 2) and their adsorption constants are close to 3.8×10^{-3} Pa⁻¹, whatever the olefin (Table 3).

On CoMo catalyst, the apparent partial orders with respect to olefin are higher and between 0.43 and 0.69 (Table 2) while the adsorption constants of olefins on CoMo catalysts are lower than on NiMo catalysts (Table 3). These results are coherent: an apparent order with respect to olefins close to zero means that the olefin is strongly adsorbed and recovers the surface.

From the data reported in Table 3, the adsorption constants of olefins can be classed as:

1McC₅=/CoMo (0.54) < cC₅=/CoMo (1.1) < 33DM1C₄=/CoMo (1.8) < 1McC₅=/NiMo (3.6) ≈ cC₅=/NiMo (3.8) ≈ 33DM1C₄=/NiMo (3.9)

On CoMo catalyst, the olefin with the highest steric hindrance is less adsorbed than the others. On NiMo catalyst, the olefins are more strongly adsorbed and there is no influence of the structure. Therefore the structure of olefins will have a greater impact on their reactivity on CoMo catalysts than NiMo ones. This explains quite well why CoMo catalysts are more efficient in the selective hydrodesulfurization of FCC gasoline than NiMo catalysts [7].

It was shown in our previous study [21] that the CoMo catalyst appears as more acidic than the NiMo one. It was also shown that the maximal acidity of CoMo/Al₂O₃ catalysts could be observed for a Co/Co+Mo atomic ratio of 0.30, which corresponds to the cobalt content in the present catalyst [39,40]. Therefore, it seems that the basic olefins would adsorb on the vacancy more strongly on the CoMo catalyst than the NiMo one. Elsewhere, DFT calculations and STM experiments [41–43] showed that presence of nickel induces the formation of bigger vacancies with multi-unsaturation of metallic atoms. Consequently, olefins will be better adsorbed over NiMo catalysts despite their lower acidity. To summarize, adsorption of olefins appears to depend mainly on the structure of the active phase and one could wonder if catalyst acidity moderate this effect.

4.3. A new simple kinetic model to describe hydrogenation reactions over hydrotreating catalysts

We have shown that a quite simple pseudo Eley–Rideal law obtained after approximations made on the Langmuir–Hinshelwood model describes very well our experimental results. According to the Eley–Rideal model, dihydrogen reacts as if it was not adsorbed on the surface. This result is apparently inconsistent with mechanism of heterolytic dissociation of dihydrogen proposed in the literature [17,23,31,34–36]. However, if we look at in details, both theories are quite compatible. First, we have calculated that the apparent partial orders with respect to dihydrogen are always higher than 1, whatever the olefin (Table 2), which is characteristic of weakly bonded hydrogen to the surface. Some DFT studies [44–47] have also shown that hydrogen activation is likely over sulfide phases as MoS₂, CoMoS and NiMoS. Despite heterolytic adsorption of dihydrogen, it has been established that hydrogen species are very mobile on the surface. So, these hydrogen species on the surface could be assimilated to gaseous dihydrogen in a kinetic model. An Eley–Rideal type model in respect with hydrogen

would therefore be quite satisfactory. This simple model could be used to calculate kinetic constants for hydrotreating reactions of complex fractions (or real feeds).

5. Conclusion

Kinetic investigation of the hydrogenation of several olefins over CoMo/Al₂O₃ and NiMo/Al₂O₃ sulfided catalysts was conducted in order to understand both promoter and structure effects. A pseudo Eley–Rideal model, obtained after approximations made on the Langmuir–Hinshelwood theory, is very consistent with our experimental results.

It was shown that the rate-determining step of the reaction is the addition of a proton on the olefin. Moreover, hydrogenation of olefins was depending on two key parameters:

- (1) Apparent hydrogenation rate constants: they were consistent with the olefin reactivities previously determined over both catalysts. Except on the NiMo catalyst where cyclopentene was the most reactive, the rates in hydrogenation of the olefins decreased with increasing substitution of their double bond, which means in the order of reactivity:

3, 3-dimethylbut-1-ene > cyclopentene > 1-methylcyclopentene

- (2) Adsorption constants of olefins: on CoMo catalyst, the olefin with the highest steric hindrance is less adsorbed than the others. On NiMo catalyst, the olefins are better adsorbed and there is no influence of the structure.

Therefore the structure of olefins will have a greater impact on their reactivity on CoMo catalysts than NiMo ones. Hence, CoMo catalysts are good candidates for the selective HDS of FCC gasoline.

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