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Model Reaction for the *in Situ* Characterization of the Hydrogenating and Acid Properties of Industrial Hydrocracking Catalysts

M. Guisnet,* C. Thomazeau,* J. L. Lemberton,* and S. Mignard†

*Laboratoire de Catalyse en Chimie Organique, URA CNRS 350, UFR Sciences, 40 Avenue du Recteur Pineau, 86022 Poitiers Cedex, France; and †Institut Francais du Pétrole, 1 et 4 Avenue de Bois-Préau, BP 311, 92506 Rueil-Malmaison Cedex, France

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A kinetic study of *o*-xylene transformation was carried out on a sulfided NiMo on Y zeolite catalyst during the hydrocracking of a model compound (*n*-heptane) under the following conditions of the process: high hydrogen pressure (5.7 MPa), presence of nitrogen and sulfur-containing compounds. *o*-Xylene inhibits *n*-heptane transformation, which can be explained by a competition for the adsorption on the acid sites between *o*-xylene and the olefinic intermediates of hydrocracking. The products of *o*-xylene transformation are the following: *p*- and *m*-xylenes (isomerization), toluene and trimethylbenzenes (disproportionation), and saturated C_8 naphthenes (dimethylcyclohexanes and trimethylcyclopentanes). It is shown that 1,3- and 1,4- dimethylcyclohexanes (and trimethylcyclopentanes) result from the isomerization of 1,2-dimethylcyclohexane and not from the hydrogenation of *m*- and *p*-xylenes. Therefore, the hydrogenating activity of hydrocracking catalysts can be characterized by the formation of dimethylcyclohexanes and trimethylcyclopentanes. Furthermore, the isomerization of xylenes, which occurs through an acid mechanism, can be used for characterizing the acid activity of hydrocracking catalysts. This is not the case for disproportionation whose rate depends on hydrogen pressure. The validity of *o*-xylene transformation for characterizing the acid and hydrogenating activities of bifunctional hydrocracking catalysts was confirmed by the use of a series of catalysts having either the same content of NiMo and different contents of zeolite or the same content of zeolite and different contents of NiMo. While the isomerization activity is strictly proportional to the zeolite content and independent of the NiMo content, the hydrogenating activity is proportional to the NiMo content and independent of the zeolite content. © 1995 Academic Press, Inc.

INTRODUCTION

In a modern refinery, hydrocracking is complementary to catalytic cracking: polyaromatic compounds can be transformed through hydrocracking, but not through catalytic cracking (1, 2). Another major interest of hydrocracking, particularly in the United States, is its great versatility, since it is possible to equilibrate supply (gasoline, gasoils, etc.) and demand. Hydrocracking catalysts are bifunctional, associating a hydro-dehydrogenating function (noble metals, sulfides of Groups VI and VIII metals) with an acidic one (silica-alumina, zeolite) (1–3). On these catalysts, the transformation of hydrocarbons involves reaction steps both on hydrogenating sites (hydrogenation and dehydrogenation) and on acid sites (rearrangement, cracking, etc.), plus diffusion steps (migration of the reaction intermediates from the hydrogenating sites to the acid sites, and vice versa). As an example, the transformation of *n*-heptane is presented in Scheme 1.

With such a reaction scheme, one can expect that the activity and the selectivity of bifunctional catalysts will be determined by the characteristics of the hydrogenating sites and of the acid sites, particularly by their relative activities, as well as by the path of diffusion between the two types of sites. This has been demonstrated by a study of *n*-alkane hydrocracking on bifunctional Pt/H zeolite catalysts (3). A relationship was found between the activity per acid site, the selectivity and the stability of Pt/HY catalysts, and the ratio of the number of active metallic sites to the number of active acid sites. Furthermore, the results obtained with Pt on shape-selective catalysts, e.g., Pt/H-ZSM-5, showed that the pore structure also plays a significant role, owing to the mode of circulation it imposes on the reactant molecules and to the steric constraints it exerts on the migration, on the formation, and on the reactivity of the intermediates (3, 4).

Therefore, the characteristics of the acid sites and of the hydrogenating sites must be known very precisely to be able to optimize hydrocracking catalysts. The adsorption of probe molecules followed by a physical technique (IR spectroscopy in particular) is generally used for characterizing the hydrogenating (5–7) and the acid sites (8–11). Unfortunately, these methods present the major inconvenience of being carried out under conditions very different from those of the industrial procedure, which makes it difficult to exploit the information obtained. This is particularly the case for complex processes, such

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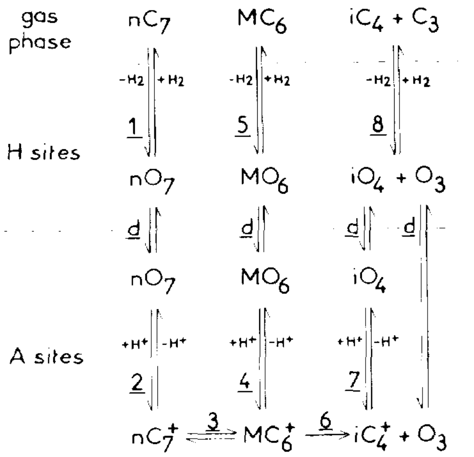


SCHEME 1. *n*-Heptane hydrocracking on bifunctional catalysts. H sites, hydrogenating sites; A sites, acid sites; d, diffusion steps; nC_7, *n*-heptane; nO_7, *n*-heptenes; MC_6, methylhexanes; MO_6, methylhexenes; iO_4, *i*-butene; iC_4, *i*-butane; C_3, propane; nC_7^+, MC_6^+, carbenium ions.

as hydrocracking, which are carried out under hydrogen pressure, and in which certain feed components (e.g., nitrogen and sulfide-containing compounds) can modify the catalytic properties of the hydrogenating sites and of the acid sites (12, 13). In such a case, the only way to characterize the active sites is to use a model reaction under the operating conditions of the process.

The aim of this work was to design a model reaction which allows one to measure the hydrogenating activity and the acid activity of hydrocracking catalysts (Ni and Mo sulfides deposited on an alumina–Y zeolite support) under industrial conditions (high hydrogen pressure, presence of N- and S-containing compounds). For reasons of simplicity, we chose the transformation of just one reactant, namely *o*-xylene, because this molecule can transform through parallel reactions catalyzed either by acid sites (isomerization) or by sulfide sites (hydrogenation). *n*-Heptane was chosen as the model reactant for the hydrocracking reaction.

EXPERIMENTAL

Hydrocracking of *n*-heptane was carried out in a flow reactor at 380°C under 6 MPa total pressure. Dimethyl disulfide and aniline were added to *n*-heptane in order to generate H_2S and NH_3, respectively. The standard reaction conditions were as follows: catalyst weight = 1.75 g, *n*-heptane contact time = 0.18 min, hydrogen/*n*-heptane molar ratio = 20, $p(nC_7) = 0.285$ MPa, $p(H_2) = 5.7$ MPa, $p(NH_3) = 5$ kPa, $p(H_2S) = 6.1$ kPa. The catalyst was first sulfided under the same flow rates and the same pressures as those used for the *n*-heptane hydrocracking reaction. The feed was injected starting at 150°C, then the temperature was raised at 285°C (1-h stage), 325°C (1-h stage), 350°C (2-h stage), and finally 380°C (reaction temperature). At steady state (after about 2 h), all the catalysts used exhibited a stable activity for *n*-heptane hydrocracking. To characterize the acid and hydrogenating properties of the catalysts, various amounts of *o*-xylene (5, 10, and 20 mol% with respect to *n*-heptane) were simply added to the previous feed (*n*-heptane + dimethyldisulfide + aniline) so as to obtain various partial pressures of *o*-xylene (0.014, 0.029, and 0.057 MPa, respectively).

All the reaction products were analyzed on-line by gas–liquid chromatography (Varian 3400) on a 50-m CP-Sil5 capillary column (Chrompack) with a temperature programming from 40 to 70°C (5°C min^{-1}).

Seven catalysts containing different amounts of Y zeolite and/or of NiMo on alumina were prepared by the Institut Français du Pétrole (Table 1). Catalysts A, B, C, D, and E contained from 0 to 14 wt.% of Y zeolite and about the same amounts of Ni and Mo, whereas catalysts D′ and E′ contain the same amount of zeolite as catalysts D and E, but half of the Ni and Mo. Catalyst E was used as the reference catalyst.

RESULTS AND DISCUSSION

1. n-Heptane and o-Xylene Transformation Schemes

n-Heptane reaction products are mainly propane and butanes (iso and *n*-) in equimolar amounts (cracking C) and *n*-heptane isomers (isomerization I). Isomerization products can be classified into monobranched isomers M (methylhexanes and ethylpentane) and multibranched isomers B (dimethylpentanes and traces of trimethylbutane). Figure 1 shows the distribution of M, B, and C as a function of *n*-heptane conversion on catalyst E under the standard reaction conditions of 380°C, $p(H_2) = 5.7$ MPa, $p(NH_3) = 5$ kPa, $p(H_2S) = 6.1$ kPa, $p(nC_7) = 0.285$ MPa. It can be seen that, under these conditions, M and B are primary products, whereas C results from the secondary transformation of M and B.

Table 2 indicates that the main products of transformation of *o*-xylene added to *n*-heptane (partial pressures of *o*-xylene ranging from 0.014 to 0.057 MPa) are *p*- and *m*-xylenes, toluene, trimethylbenzenes, and various saturated naphthenes (methylcyclohexane, dimethylcyclohexanes, and trimethylcyclopentanes); traces of

TABLE 1

Composition of the Catalysts

Catalyst	A	B	C	D	E	D′	E′
Y Zeolite (wt.%)	0	1.0	3.9	7.5	14.0	7.5	14.0
NiO + MoO_3 (wt.%)	19.4	14.3	16.4	16.8	16.2	7.5	7.8

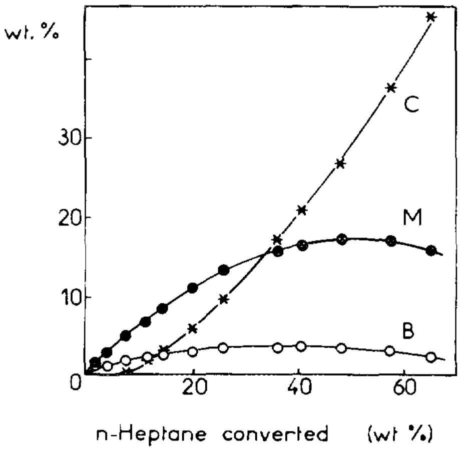
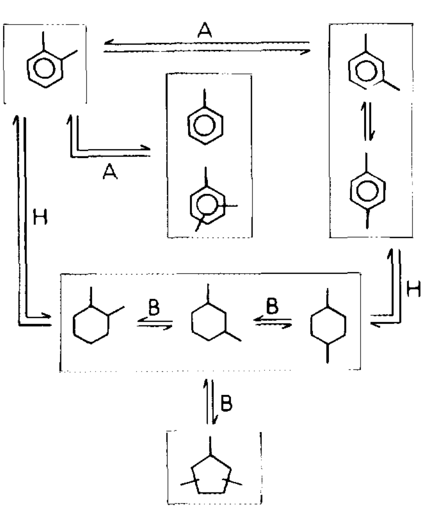


FIG. 1. Transformation of *n*-heptane on the reference NiMoS/HY catalyst. M, monobranched isomers; B, multibranched isomers; C, cracking products.



SCHEME 2. *o*-Xylene transformation. A, acid mechanism; H, hydrogenation; B, bifunctional mechanism.

ethylbenzene can also be observed. As shown by Scheme 2, these products probably result from three types of reaction catalyzed by acid sites, hydrogenating sites, or both types of sites (bifunctional catalysis):

(i) Isomerization of *o*-xylene into *m*- and *p*-xylene could occur either through an acid mechanism or through a bifunctional mechanism, the latter giving also ethylbenzene (14). Since only traces of ethylbenzene can be observed, it can be concluded that *o*-xylene isomerization occurs mainly through an acid mechanism, the bifunctional mechanism being negligible. At the high temperatures used for hydrocracking, this acid mechanism proceeds through intramolecular methyl shifts (15).

(ii) Formation of toluene and trimethylbenzenes, which are formed in quasi-equimolar amounts, results from *o*-xylene disproportionation, a typically acid reaction (16).

(iii) Production of dimethylcyclohexanes results from the hydrogenation of xylenes. They isomerize rapidly into trimethylcyclopentanes through bifunctional catalysis (17).

TABLE 2

Effect of the Pressure of *o*-Xylene and of the Contact Time on the Conversion of *o*-Xylene into Various Products

	$P_{o\text{-xylene}}$ (MPa)					
	0.014 Contact time (min)		0.029 Contact time (min)			0.057 Contact time (min)
	6.7	1.9	1.8	0.91	0.6	0.91
Total Conversion	53.0	34.5	53.0	28.0	18.5	42.5
Conversion to products (%)						
MCH	2.0	1.1	1.9	0.9	0.5	1.2
12DMCH	2.7	1.4	2.5	1.5	1.1	2.0
13 + 14DMCH	7.0	4.7	7.5	3.0	2.3	5.1
TMCP	25.2	14.5	23.1	12.6	9.1	20.1
(*m* + *p*) Xylenes	14.8	11.9	16.3	8.2	4.5	12.6
EtBZ	—	—	—	0.1	0.1	0.1
TOL	0.6	0.4	0.8	0.8	0.4	0.6
TMB	0.7	0.5	0.9	0.9	0.5	0.8

Note. MCH, methylcyclohexane; DMCH, dimethylcyclohexanes; TMCP, trimethylcyclopentanes; EtBZ, ethylbenzene; TOL, toluene; TMB, trimethylbenzenes.

Under the standard reaction conditions of *n*-heptane hydrocracking, all these products appear as primary ones (Fig. 2). Moreover, a change in the contact time (hence in the conversion of *o*-xylene) has practically no effect on the selectivity of the reaction: the hydrogenated products correspond to about 65% of the *o*-xylene converted, the isomerization products to 30%, and the disproportionation products to 5% (Fig. 2).

2. *Kinetic Study of the Transformation of n-Heptane and of n-Heptane/o-Xylene Mixture*

The effect of the pressures of hydrogen and of *n*-heptane ($p(H_2)$ and $p(nC_7)$) on the *n*-heptane transformation rate on catalyst E was determined for low *n*-heptane conversion values (< 10%), under the standard conditions of temperature and of the pressures of NH_3 and of H_2S. The effect of $p(H_2)$ was determined using the following pressures of hydrogen: 3.0, 4.5, 5.7, and 6.5 MPa, *n*-heptane pressure being always 0.285 MPa. The effect of $p(nC_7)$ was determined using *n*-heptane pressures of 0.15, 0.285 and 0.575 MPa, $p(H_2)$ being equal to 5.7 MPa. Whatever the pressures of hydrogen and of *n*-heptane, no deactivation of the catalyst was observed. The reaction order with respect to *n*-heptane was 0.4, whereas with respect to hydrogen it was −0.4. These effects of the pressures of hydrogen and of *n*-heptane on the reaction rate (r) are in good agreement with the rate equation

$$r = \frac{k_3 C_m K_1 K_2 p(nC_7)}{p(H_2) + K_1 K_2\, p(nC_7)}, \qquad [1]$$

where k_3 is the rate constant of step 3 in Scheme 1, C_m the concentration of the Brønsted acid sites in the zeolite, K_1 the equilibrium constant of *n*-heptane dehydrogenation (step 1), and K_2 the equilibrium constant of the carbenium ion formation (step 2).

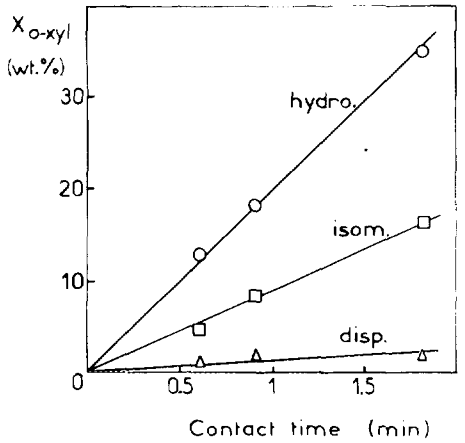


FIG. 2. Effect of the contact time on the transformation of *o*-xylene into hydrogenation, isomerization, and disproportionation products.

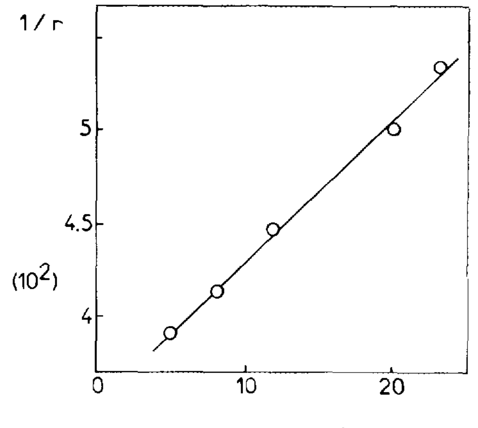


FIG. 3. Relationship between the rate of transformation of *n*-heptane (r) and the hydrogen pressure/*n*-heptane pressure ratio. (r in 10^{-3} mol h^{-1} g^{-1}.)

This equation was established (18) at low *n*-heptane conversion, so as to be able to neglect the reverse reactions and the adsorption of the products. It was also assumed that the reaction occurred through the bifunctional mechanism presented in Scheme 1, and that the rate-limiting step was the transformation of the olefinic intermediates, hence the rearrangement of the carbenium ion intermediates (step 3). Figure 3 shows that the experimental results verify equation 1, since plotting $1/r$ as function of $p(H_2)/p(nC_7)$ gives a straight line.

To determine the effect of the partial pressure of *o*-xylene on the rates of transformation of *o*-xylene and of *n*-heptane, catalyst E was first stabilized using pure *n*-heptane (Fig. 4a), which was then replaced by a mixture of *o*-xylene and *n*-heptane. *n*-Heptane pressure was kept constant, while the pressure of *o*-xylene was equal to 0.0145, 0.029, and 0.057 MPa (Figs. 4b, 4c, and 4d, respectively); several *o*-xylene contact times were used. Finally, pure *n*-heptane was injected again (Fig. 4e) under the same conditions as in Fig. 4a.

Figure 4 shows that, whatever the *o*-xylene pressure, the activity of the catalyst is perfectly stable after a short time. On the other hand, the presence of *o*-xylene provokes a decrease in *n*-heptane conversion (Figs. 4b–4d), but this decrease is totally reversible (Figs. 4a and 4e). This inhibiting effect of aromatics on the hydroisomerization and the hydrocracking of alkanes has already been observed (19–21) and explained by a competition for adsorption between the aromatics and the olefinic intermediates formed from the alkane. Aromatics being more basic than olefins, the equilibrium constant for the adsorption of the aromatic on an acid site (Scheme 3) is

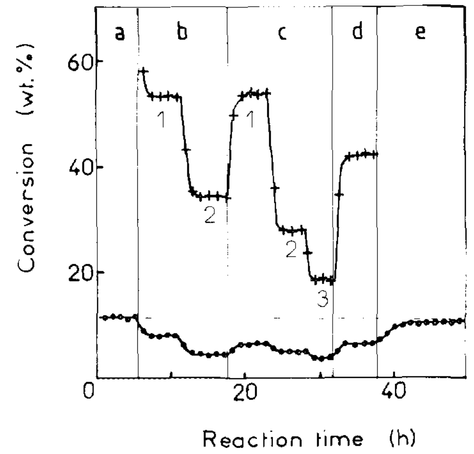


FIG. 4. Conversions of *n*-heptane and of *o*-xylene: effect of the pressure of *o*-xylene. (●) *n*-heptane conversion; (+) *o*-xylene conversion. (a, e) Pure *n*-heptane; (b) *o*-xylene pressure 0.014 MPa, contact time 6.7 min (1) or 1.9 min (2); (c) *o*-xylene pressure 0.029 MPa, contact time 1.8 min (1), 0.91 min (2) or 0.6 min (3); (d) *o*-xylene pressure 0.057 MPa, contact time 0.91 min.

much greater than that for the adsorption of olefins (Scheme 4).

Taking into account the adsorption of *o*-xylene on the acid sites, the equation found for pure *n*-heptane transformation (Eq. [1]) becomes

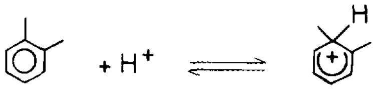
$$r = \frac{k_3 C_m K_1 K_2 p(nC_7)}{p(H_2) + K_1\, K_2\, p(nC_7) + K_5\, p(H_2)\, p(X)} \quad [2]$$

where K_5 is the equilibrium constant for *o*-xylene adsorption, and $p(X)$ the *o*-xylene pressure. At constant $p(H_2)$ and $p(nC_7)$ values, the equation can be written as

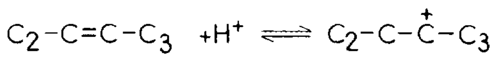
$$r = \frac{a}{b + c\, p(X)} \quad [3]$$

where a, b, and c are positive constants. Figure 5 shows that Eq. [3] is verified: $1/r$ versus $p(X)$ is a straight line with a positive slope and a positive coordinate from the origin.

Other observations are in agreement with this competition of *o*-xylene with olefinic intermediates for the adsorption on the acid sites. First, the degree of the decrease in the *n*-heptane transformation rate does not depend on the contact time, as demonstrated by Fig. 6. Furthermore, the presence of *o*-xylene causes an increase in the isomerization/cracking ratio (I/C, Fig. 7), which can be related with a decrease in the acid activity of the catalyst, hence to an increase in A_H/A_A (ratio between the hydrogenating activity A_H and the acid activity A_A). Indeed, it was demonstrated during a study of *n*-heptane transformation on a series of Pt/HY catalysts (3) that the higher the A_H/A_A ratio, the higher the I/C ratio.



SCHEME 3



$$C_2\text{-}C{=}C\text{-}C_3 \ + H^+ \rightleftharpoons C_2\text{-}C\text{-}\overset{+}{C}\text{-}C_3$$

SCHEME 4

Table 2 shows the amounts of *o*-xylene conversion products obtained for various pressures of *o*-xylene and for various contact times. For the same contact time, the greater the pressure of *o*-xylene, the higher the *o*-xylene conversion. On the other hand, the effect of the pressure of *o*-xylene depends on the reaction considered: the reaction order with respect to *o*-xylene is about 0.75 for hydrogenation (formation of dimethylcyclohexanes and trimethylcyclopentanes), 0.55 for isomerization (formation of *p*- and *m*-xylenes), and 1.15 for disproportionation (formation of toluene and trimethylbenzenes). The intermediate partial pressure of *o*-xylene (0.029 MPa) was chosen for further experiments. Indeed, at the lowest pressure (0.014 MPa), *o*-xylene and its reaction products represent only 5% of *n*-heptane and its reaction products, which reduces the accuracy of the results. On the other hand, at the highest pressure (0.057 MPa), the conversion of *o*-xylene is always high (> 40%), even for short contact times.

3. *Characterization of the Acid Activity and the Hydrogenating Activity*

The formation of C_8 naphthenes (dimethylcyclohexanes and trimethylcyclopentanes) from *o*-xylene under

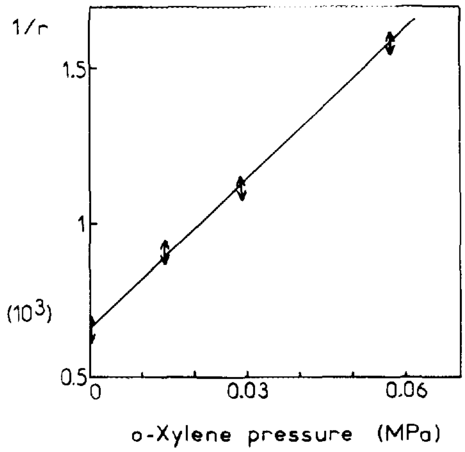


FIG. 5. Relationship between the rate of transformation of *n*-heptane (r) and the pressure of *o*-xylene. (r in 10^{-3} mol h^{-1} g^{-1}.)

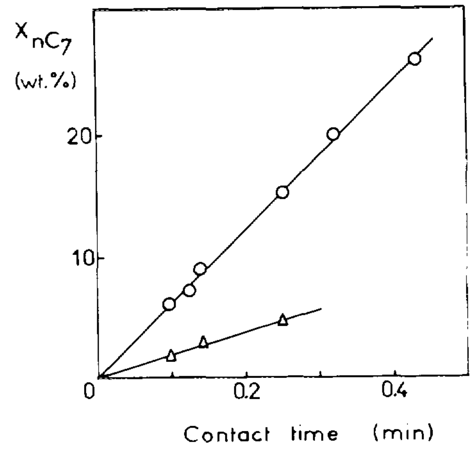


FIG. 6. Effect of *o*-xylene on the total conversion of *n*-heptane (X_nC_7). (○) *n*-heptane alone; (△) *n*-heptane in the presence of *o*-xylene.

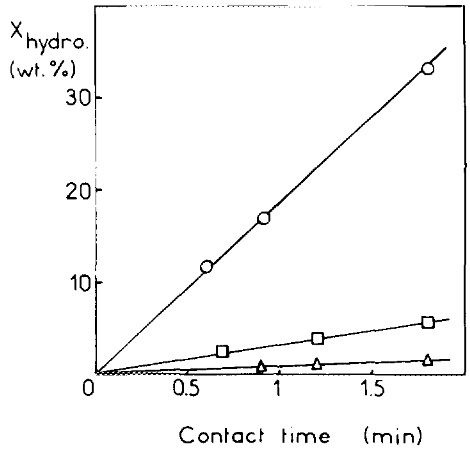


FIG. 8. Effect of the hydrogen pressure on the transformation of *o*-xylene into hydrogenation products (X_{hydro}). (○) 5.7 MPa; (□) 2 MPa; (△) 1 MPa.

the standard conditions of hydrocracking can be considered as representative of the hydrogenating activity of the catalyst. Under the operating conditions, the thermodynamic equilibrium between *o*-xylene and the C_8 naphthenes strongly favors the latter (22). Furthermore, the transformation of *o*-xylene into hydrogenated products is proportional to the contact time (Fig. 8), which allows an accurate determination of the activity of the catalyst for this reaction.

Most of the C_8 naphthenes result either from the direct hydrogenation of *o*-xylene into 1,2-dimethylcyclohexane or from the rapid isomerization of the latter into 1,3- and 1,4-dimethylcyclohexanes and into trimethylcyclopentanes. Only a very small amount of these products result from the transformation of *p*- and *m*-xylenes. Indeed, the three xylene isomers hydrogenate at similar rates (23) and the concentration of *o*-xylene is much higher than that of its isomers. Assuming a reaction order with respect to *o*-xylene equal to 1, the amount of hydrogenated products issuing from *p*- and *m*-xylenes can be estimated to about 5% for the shorter contact time (0.6 min, Table 2).

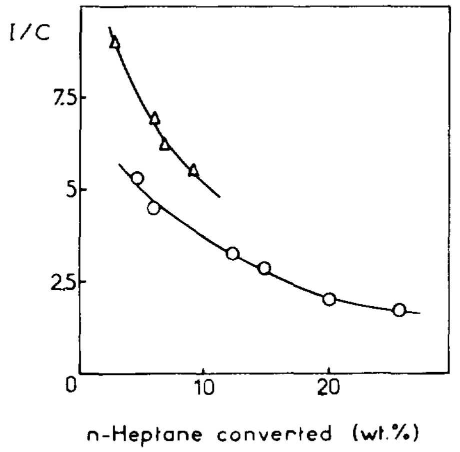
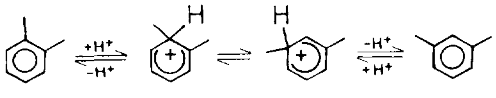


FIG. 7. Effect of *o*-xylene on the isomerization/cracking selectivity of *n*-heptane hydrocracking (I/C). (○) *n*-heptane alone; (△) *n*-heptane in the presence of *o*-xylene.

On the other hand, the activity for the isomerization of *o*-xylene can be considered as representative of the acid activity of the catalyst. Indeed, this reaction can occur only through acid catalysis: only traces of ethylbenzene are formed, which excludes the possibility of a bifunctional isomerization of *o*-xylene. Furthermore, as indicated above, it is probable that only a small amount of the isomers formed are hydrogenated. Finally, the conversion measured during the experiments is much smaller than the one calculated at the thermodynamic equilibrium (22). For the same reasons, the activity for the disproportion of *o*-xylene could also be considered as representative of the acid activity. However, this reaction occurs through a bimolecular mechanism and therefore is also affected by the density of the acid sites (24, 25). Consequently, *o*-xylene isomerization is probably better adapted than disproportionation for the characterization of acidity.

It was also very important to make sure that the formation rates of *p*-xylene and of *m*-xylene were not affected by the hydrogenating activity (secondary hydrogenation of the xylene isomers). This was possible by operating under different pressures of hydrogen. Indeed, xylene isomerization occurs through methyl shift in the benzenium ion intermediates (Scheme 5) and consequently must not be affected by hydrogen pressure (26, 27), while the higher this pressure, the faster the hydrogenation of xylenes.



SCHEME 5

The transformation of the *n*-heptane/*o*-xylene mixture was then studied under the standard operating conditions, except for the hydrogen pressure which was lowered to 1 or 2 MPa. After operating under a 1-MPa hydrogen pressure, the catalyst did not recover its initial activity for pure *n*-heptane hydrocracking under a 5.7-MPa hydrogen pressure. This indicated an irreversible deactivation of the catalyst in the presence of *o*-xylene, very probably through coke formation, owing to a too low pressure of hydrogen. This deactivation did not exist when the transformation of the *n*-heptane/*o*-xylene mixture was carried out under a 2-MPa hydrogen pressure (Fig. 9). As expected, the higher the hydrogen pressure, the faster the *o*-xylene hydrogenation (Fig. 8), with a reaction order with respect to hydrogen of about 1.7. On the contrary, the rate of formation of *m*- and *p*-xylenes was the same under a 2-MPa hydrogen pressure as under 5.7 MPa (Fig. 10). The slower rate measured under the 1-MPa hydrogen pressure can be related to the deactivation of the catalyst observed under these conditions. Hence, these results confirm that the formation of the xylene isomers is not influenced by the hydrogenating activity of the catalyst, and that the hydrogenation of these isomers can be neglected. Therefore, the acid activity of hydrocracking catalysts can be estimated from their activity for *o*-xylene isomerization.

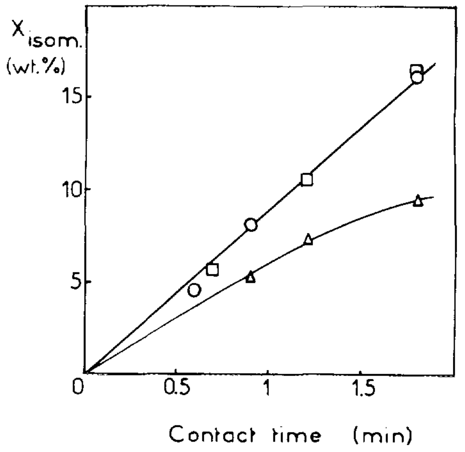


FIG. 10. Effect of the hydrogen pressure on the transformation of *o*-xylene into isomerization products (X_{isom}). (○) 5.7 MPa; (□) 2 MPa; (△) 1 MPa.

On the other hand, the rate of xylene disproportionation depends on hydrogen pressure: the greater the hydrogen pressure, the lower the disproportionation rate (Fig. 11). This inhibiting effect of hydrogen on the disproportionation of methylaromatics was previously observed (26, 27) and explained by a reaction between hydrogen and the benzylic carbocations intermediates (Scheme 6).

Since this reaction is the reverse reaction of the formation of benzylic carbocations from methyl aromatics, it decreases the concentration of benzylic carbocations and hence the disproportionation rate. This reaction would be favored when hydrogen is activated on redox sites (27). Consequently, the disproportionation of xylene depends not only on the acid activity but also on the hydrogenating activity and therefore cannot be used for characterizing the acidity of hydrocracking catalysts.

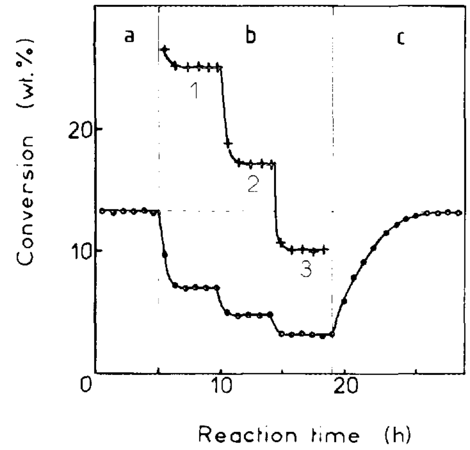


FIG. 9. Conversions of *n*-heptane and *o*-xylene: effect of the hydrogen pressure. (●) *n*-heptane conversion; (+) *o*-xylene conversion. (a, c) Hydrogen pressure 5.7 MPa; (b) hydrogen pressure 2 MPa, *o*-xylene contact time 1.8 min (1), 1.2 min (2), or 0.7 min (3).

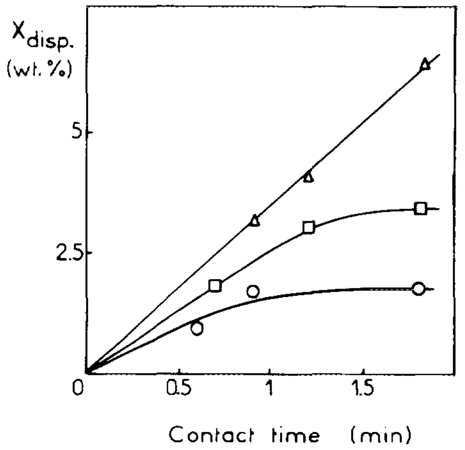
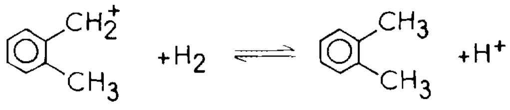


FIG. 11. Effect of the hydrogen pressure on the transformation of *o*-xylene into disproportionation products (X_{disp}). (○) 5.7 MPa; (□) 2 MPa; (△) 1 MPa.



SCHEME 6

From this study, it can be concluded that the hydrogenating activity and the acid activity of hydrocracking catalysts can be determined by *o*-xylene transformation under the conditions of hydrocracking. The hydrogenating activity will be characterized by the activity for the transformation of *o*-xylene into dimethylcyclohexanes and trimethylcyclopentanes (A_H), and the acid activity by the activity for the isomerization of *o*-xylene into *p*- and *m*-xylenes (A_I).

4. *Validity of the Model Reaction*

In order to confirm the interest of *o*-xylene transformation for the characterization of hydrocracking catalysts, a series of catalysts with known acid and hydrogenating properties was prepared and tested in the *n*-heptane/*o*-xylene reaction. Four catalysts (A, B, C, and D in Table 1) contained the same amount of Ni and Mo as the reference catalyst E, but less Y zeolite (from 0 to 7.5 wt.%). Since the zeolite used was always the same, these catalysts would differ in the number but not in the strength of the acid sites. Consequently, their activity for the transformation of *o*-xylene into *p*- and *m*-xylenes (A_I) would be proportional to the zeolite content, whereas their hydrogenating activity A_H would be the same. Two other catalysts (D′ and E′ in Table 1) were prepared, containing the same amount of zeolite as catalysts D and E, but with half the amount of Ni and Mo, and with the same Ni/(Ni + Mo) atomic ratio. In this case, catalysts D′ and E′ would have the same acid activity A_I at catalysts D and E, respectively, but their hydrogenating activity A_H would be proportional to the NiMo content.

On these catalysts, we investigated successively:

(a) the transformation of pure *n*-heptane under the standard reaction conditions (hydrogen pressure = 5.7 MPa);

(b) the transformation of the *n*-heptane/*o*-xylene mixture under the same conditions as in (a), at various contact times;

(c) the transformation of pure *n*-heptane as in (a);

(d) the transformation of the *n*-heptane/*o*-xylene mixture under a 2-MPa hydrogen pressure, the other conditions being as in (b);

(e) the transformation of pure *n*-heptane as in (a).

The aim of experiment(e) was to check that there was no deactivation of the catalysts, which is true for all the catalysts tested.

TABLE 3

Hydrogenating Activities A_H and Isomerization Activities A_I of the Catalysts (10^{-4}mol h^{-1} g^{-1})

Catalyst	A	B	C	D	E	D′	E′
A_H (5.7 MPa H_2)	4.8	4.5	4.7	4.5	4.7	1.8	1.7
A_I (2.0 MPa H_2)	0.2	0.4	0.7	1.3	2.0	1.5	2.1
A_I (5.7 MPa H_2)	0.3	0.5	0.8	1.6	1.9	1.7	2.3

For all the catalysts, the isomerization activity A_I does not depend on the hydrogen pressure (Table 3), which indicates that, in order to save time, the model reaction could be limited to experiments a, b, and c. Moreover, Table 3 also indicates that catalysts A, B, C, D, and E, which have similar Ni and Mo contents, exhibit very similar hydrogenating activities whereas their isomerization activity increases when the content of zeolite in the catalyst increases. This increase in isomerization activity is proportional to the zeolite content (Fig. 12). On the contrary, similar isomerization activities are measured for the catalysts containing the same amount of zeolite (i.e., D and D′ on one hand, E and E′ on the other), whereas the hydrogenating activity is higher with catalysts containing the greater amount of Ni and Mo (D > D′, E > E′). For both pairs of catalysts, the hydrogenating activity is proportional to the Ni and Mo content (Fig. 13).

All these results are those which can be expected from the changes in the contents of zeolite and of Ni and Mo. Consequently, it can be concluded that the model reaction elaborated in the present work allows one to characterize the hydrogenating and the acid functions of hydrocracking catalysts under industrial conditions.

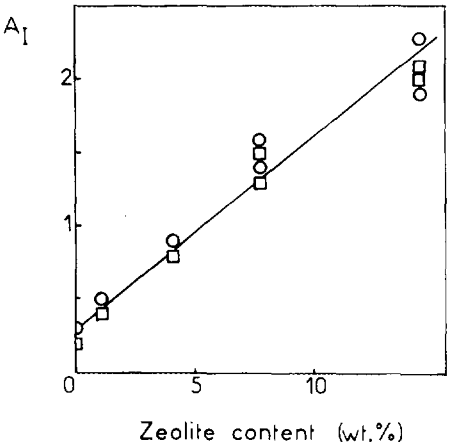


FIG. 12. Effect of the zeolite content on the isomerization activity A_I of the catalysts (activities in 10^{-4} mol h^{-1} g^{-1}). Hydrogen pressure: 5.7 MPa (○); 2 MPa (□).

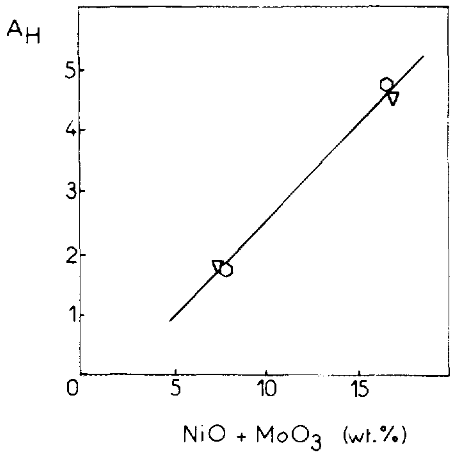


FIG. 13. Effect of the NiMo content on the hydrogenating activity A_H of the catalysts (activities in 10^{-4} mol h^{-1} g^{-1}). Zeolite content: 7.5 wt.% (▽); 14 wt.% (○).

CONCLUSION

The transformation of *o*-xylene allows one to characterize simultaneously the hydrogenating and the acid functions of hydrocracking catalysts under industrial conditions. The acid activity can be estimated from the formation rate of the *m* and *p*-isomers of *o*-xylene. This activity is strictly proportional to the content of zeolite of the catalyst, and does not depend on the content of Ni and Mo or on the hydrogen pressure. The hydrogenating activity can be defined as the formation rate of all the C_8 naphthenic compounds, which is proportional to the content of Ni and Mo of the catalyst and independent of the zeolite content.

This reaction can therefore be used to characterize industrial catalysts. Furthermore, from a fundamental point of view, it permits one to quantify the effect on the selectivity of the catalysts of the balance between the hydrogenating and the acid functions. Finally, this reaction could also be of great interest in determining the effect on both functions of various reaction parameters, such as the partial pressures of ammonia and of hydrogen sulfide or the effect of coke deposition.

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