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Activation of Hydrogen on Zeolites: Kinetics and Mechanism of *n*-Heptane Cracking on H-ZSM-5 Zeolites under High Hydrogen Pressure

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The cracking of *n*-heptane on H-ZSM-5 zeolite was studied using a tubular reactor at 543 K, 2.4 MPa total pressure and varying hydrogen and *n*-heptane partial pressures. The rate of reaction was determined at times on stream ranging from 0.5 to 62 min. Under the above experimental conditions H-ZSM-5 deactivates rapidly during the first 10 min of reaction time. The initial rate of *n*-heptane cracking is independent of the *n*-heptane partial pressure between 0.25 and 0.47 MPa, while it increases linearly with increasing hydrogen partial pressure. This is interpreted with the assumption that under these reaction conditions the desorption of adsorbed intermediates is the rate determining step and that the rate of desorption can be increased by hydrogen via hydride transfer from molecular hydrogen, producing a high paraffin/olefin ratio in the reaction products. In addition to this effect, hydrogen diminishes the rate of catalyst coking. © 1995 Academic Press, Inc.

INTRODUCTION

Cracking of *n*-heptane is generally used as a test reaction to investigate the acidic and geometric properties of zeolites (1). Carbocations are assumed to be the reactive intermediates during cracking. A general picture has been developed for explaining varying product distributions with temperature (2), structure of the catalyst (2), partial pressure of the feed (3) and level of conversion (4, 5) by assuming that the cracking reaction can occur through a monomolecular and a bimolecular reaction mechanism. The former mechanism is based on the protolytic cracking of an initially formed carboninium ion, while the latter involves carbenium ions as intermediates (3). A connection between both mechanisms is the attack of a Brønsted acid site on a carbon–hydrogen bond to form a carbonium ion, which loses H_2 and leaves a carbenium ion on the surface (6). It has been demonstrated theoretically that the reverse process can also take place (7). This was taken into account to explain the hydrogenation of olefins catalyzed by acid solids (8, 9). Indeed, it has been proposed (7) that molecular hydrogen can also interact with adsorbed carbenium ions. However, contradictory results on the effect of hydrogen on acid-catalyzed reactions have been reported (7, 10, 11). For example, Zhao and Wojciechowski (10) found that cracking of 2-methylpentane on HY at 673 K at a total pressure of 0.1 MPa gave similar activities and selectivities in nitrogen and hydrogen atmospheres. On the other hand, Corma et al. (11) confirmed that the cracking of *n*-heptane on fluorinated γ-Al_2O_3 and LaHY zeolite at 723 K and 2.4 MPa total pressure was inhibited in the presence of hydrogen. Similar results were found (7) during conversion of methycyclohexane at 723 K over NaHY zeolite. Garin *et al.* (12) found that the isomerization of butane was catalyzed by solid super-acids and the initial activity was lower in a hydrogen than in a nitrogen atmosphere. In these cases the authors proposed that hydrogen diminishes the average lifetime of intermediate carbenium ions by hydrogenating them. However, it has also been demonstrated that hydrogen can increase the rate of *n*-heptane cracking (13). In this case, the positive influence of hydrogen was partly attributed to the hydrogenation of olefins, which by remaining strongly adsorbed on Brønsted acid sites block the active centers. Hydrogen was also found to decrease the rate of the undesired reactions which lead to the deactivation of the catalyst. The latter effect was found to be evident in a series of papers dealing with conversion of hydrocarbons in hydrogen atmosphere (14–16). However, in order to discuss unambiguously the influence of hydrogen on reactions occurring on fast decaying acid catalysts, data should be obtained at short reaction times.

From the above literature review it appears that there are many indications that hydrogen intervenes in acid catalyzed cracking. Furthermore, the chosen reaction conditions seem to play a key role in the way hydrogen influences hydrocarbon conversion. In this work we have carried out a full kinetic study of *n*-heptane cracking on

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H-ZSM-5 catalyst at 543 K and 2.4 MPa total pressure, both in nitrogen and hydrogen. A model has been developed which can reconcile the different results presented in the literature concerning the effect of hydrogen on carbenium ion reactions on metal-free zeolites.

EXPERIMENTAL

Catalyst Preparation

Template-free synthesis of H-ZSM-5 was followed by ammonium exchange and calcination (17). An Si/Al ratio of 15 was determined by chemical analysis. By means of IR spectroscopy of adsorbed pyridine it was confirmed that only traces of Lewis acid sites were present in the sample.

Methods and Procedures

Cracking of *n*-heptane was carried out in a computer-controlled reaction system equipped with a stainless steel tubular reactor. The inner surface of the reaction system was passivated by coating with graphite. Blank experiments were done with *n*-heptane (cracking) and *n*-butene (hydrogenation). The *n*-heptane was introduced by means of a pump (M.P.L. Pumps Brixworth, U.K.), and after vaporization of the hydrocarbon in a preheater, it was mixed with the carrier gas stream. The flows of hydrogen and nitrogen were regulated with massflow controllers (Brooks). The total pressure of the experiments was 2.4 MPa, and it was adjusted by means of a needle valve. The reaction temperature (543 K) was measured with a thermocoupled mounted inside a stainless steel capillary which ended within the catalyst bed. The catalyst was used with a mesh size of 0.25–0.4 mm and it was diluted with SiO_2. No control by external or intraparticle diffusion was observed for the flows and particle size used in this work.

The outlet of the reactor was connected with a capillary gaschromatograph (Varian 3400) via a multiloop valve (Valco), which was operated automatically. For separation of the reaction products, a 50-m capillary column (Al_2O_3/KCl) was used.

Determination of reaction time zero. In order to determine the activity of the zeolites at short times on stream it was necessary to define the starting time of sampling. Under the applied reaction conditions using 450 mg SiO_2 in the catalyst bed as a blank, the system was fed with *n*-heptane, and samples were taken at different times after switching from the reactor bypass to the reactor. The evaluation of the area of the chromatographic peak corresponding to the *n*-heptane was analyzed at different times. The derivative of the measured area and time was calculated and the starting point for sampling was defined as that time after starting the feeding when the value of the derivative was lower than 5% of its maximum value.

Determination of the reaction kinetics. The partial pressure of *n*-heptane was varied by mixing the *n*-heptane with different amounts of the diluting gas. The partial pressure of hydrogen was adjusted by diluting it with nitrogen, while keeping the molar ratio of gases to *n*-heptane constant. During these experiments the conversion was lower than 10%.

The rate of cracking on H-ZSM-5 was calculated from the rates of formation of hydrocarbons consisting of one to six carbon atoms, i.e.,

$$\text{rate}_{\text{cracking}} = (1/7) \cdot (r_{C_1} + 2 \cdot r_{C_2} + 3 \cdot r_{C_3} + 4 \cdot r_{C_4} + 5 \cdot r_{C_5} + 6 \cdot r_{C_6}), \quad [1]$$

where the values of r_{C_i} represent the rate of formation of a hydrocarbon with *i* carbon atoms. The isomerization rate was defined as the rate of formation of branched C_7-alkanes, the dimensions of the rate being mol g^{-1} min^{-1}.

RESULTS AND DISCUSSION

Kinetics of Cracking at High Pressure on Metal-Free Zeolites

The catalytic cracking of *n*-paraffins can occur via a protolytic or a β-scission mechanism. In the case of protolytic cracking, when the rate-controlling step of the reaction is either the proton attack or the carbon–carbon bond cleavage, it can be expected that the rate of the reaction will increase with increasing partial pressure of the paraffin. Similarly, the rate of cracking via β-scission will also depend on the partial pressure of the *n*-alkane when the rate-controlling step is the carbon–carbon bond rupture: Since the reaction follows a bimolecular reaction mechanism, a sequence of different steps has to be taken into account. The adsorption (AD) of a *n*-heptane molecule (A) on a Brønsted acid site (H^+) is assumed to be the initial event. Simultaneously, dissociation occurs and a carbenium ion ($O1H^+$) and a saturated molecule (P1) are formed:

$$A + H^+ \xrightleftharpoons{k_{AD}} O1H^+ + P1 \qquad K_{AD}. \quad [2]$$

The adsorbed species $O1H^+$ is able to abstract a hydride from another reactant molecule in a surface reaction (SR1):

$$O1H^+ + A \xrightleftharpoons{k_{SR1}} P2 + AH^+ \qquad K_{SR1}. \quad [3]$$

Thus, a paraffin P2 is produced and a C_7-carbenium ion AH^+ remains on the catalyst surface. The latter can be evolved by β-cracking (SR2)

$$\mathrm{AH^+} \overset{k_{\mathrm{SR2}}}{\rightleftharpoons} \mathrm{O1} + \mathrm{O2H^+} \qquad K_{\mathrm{SR2}} \qquad [4]$$

producing an olefin O1 and a carbenium ion $\mathrm{O2H^+}$. The sequence of reaction steps ends with the desorption (D) of the olefin O2 and restoration of the Brønsted acid site:

$$\mathrm{O2H^+} \overset{k_{\mathrm{D}}}{\rightleftharpoons} \mathrm{O2} + \mathrm{H^+} \qquad K_{\mathrm{D}}. \qquad [5a]$$

Now the overall (total) reaction (t1) can be written as

$$2\mathrm{A} \rightleftharpoons \mathrm{P1} + \mathrm{P2} + \mathrm{O1} + \mathrm{O2} \qquad K_{\mathrm{t1}}. \qquad [6]$$

Furthermore, one can assume either the surface reaction (SR1) or the desorption (D) to be the rate determining step and the corresponding rate equations can then be developed. If the hydride abstraction is the slowest reaction step, one will obtain (c_t being the total concentration of the acid sites, K signifying equilibrium constants and k signifying rate constants) the rate equation depending on the partial pressures (p) given in equation [7]. However, if the desorption is rate determining, then the expression for the rate changes as given in equation [8] (using the same notation as above).

$$\text{rate} = k_{\mathrm{SR1}} \cdot c_t \cdot \frac{K_{\mathrm{AD}} \cdot \dfrac{p_{\mathrm{A}}^2}{p_{\mathrm{P1}}} - \dfrac{K_{\mathrm{D}}}{K_{\mathrm{SR2}}} \cdot p_{\mathrm{P2}} \cdot p_{\mathrm{O1}} \cdot p_{\mathrm{O2}}}{1 + \dfrac{K_{\mathrm{D}}}{K_{\mathrm{SR2}}} \cdot p_{\mathrm{O1}} \cdot p_{\mathrm{O2}} + K_{\mathrm{AD}} \cdot \dfrac{p_{\mathrm{A}}}{p_{\mathrm{P1}}} + K_{\mathrm{D}} \cdot p_{\mathrm{O2}}}. \qquad [7]$$

$$\text{rate} = k_{\mathrm{D}} \cdot c_t \cdot \frac{K_{\mathrm{t1}} \cdot \dfrac{p_{\mathrm{A}}}{p_{\mathrm{O1}} \cdot p_{\mathrm{P2}} \cdot p_{\mathrm{P1}}} - p_{\mathrm{O2}}}{1 + K_{\mathrm{SR1}} \cdot K_{\mathrm{AD}} \cdot \dfrac{p_{\mathrm{A}}^2}{p_{\mathrm{P1}} \cdot p_{\mathrm{P2}}} + K_{\mathrm{AD}} \cdot \dfrac{p_{\mathrm{A}}}{p_{\mathrm{P1}}} + \dfrac{K_{\mathrm{t1}}}{K_{\mathrm{D}}} \cdot \dfrac{p_{\mathrm{A}}}{p_{\mathrm{O1}} \cdot p_{\mathrm{P2}} \cdot p_{\mathrm{P1}}}} \qquad [8]$$

The resulting changes in the rate with regard to partial pressures derived from these equations are schematically represented in Fig. 1. In each case two distinct solutions of the equations are visualized according to two distinctive side conditions: the first one describes a situation in which the protonation of the C–C bond of the reactant molecule has to occur and a hydrocarbon is formed ($\mathrm{P1} = \mathrm{C_1} \ldots \mathrm{C_6}$). The second solution represents the protonation of the C–H bond followed by hydrogen abstraction ($\mathrm{P1} = \mathrm{H_2}$).

Assuming that the molecule (P1) formed during the initiation step is hydrogen, the presence of hydrogen should have an influence on the relationships between the rate and the partial pressures derived from Eqs. [7] and [8]. In order to simulate these behaviors, the partial pressure of P1 (p_{P1}) was replaced by $p_{\mathrm{H_2}}$ within the above given rate

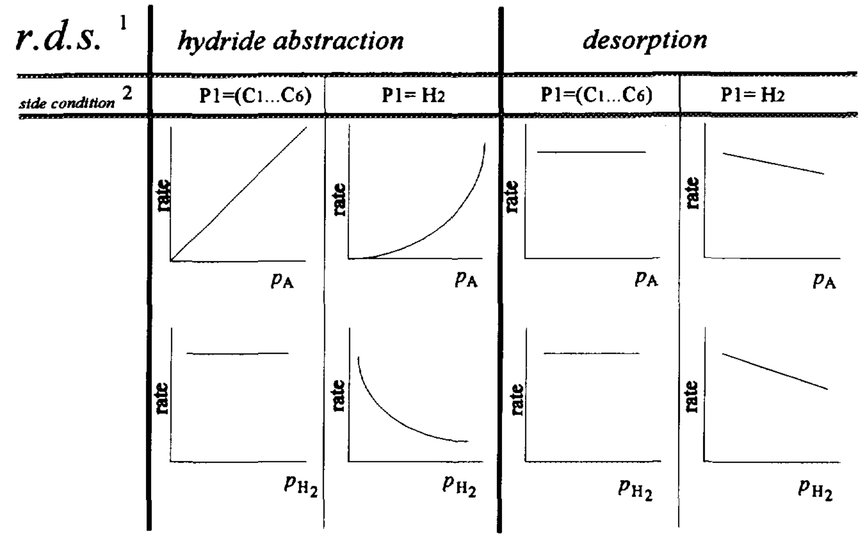

FIG. 1. Evolution of the cracking rate with varying partial pressures. [1]r.d.s.: rate determining step; [2]side condition: refers to adsorption step (AD) according to Eq. [2].

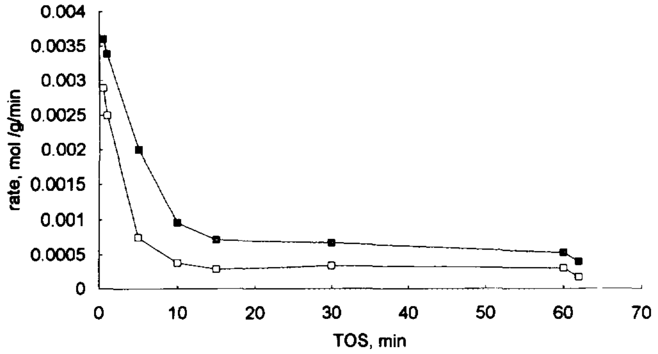

FIG. 2. Rate of *n*-heptane cracking in nitrogen and hydrogen atmosphere as a function of time on stream (TOS). (□) nitrogen, (■) hydrogen. $T = 543$ K, $p_{\text{total}} = 2.4$ MPa, $p_{C_7} = 0.4$ MPa.

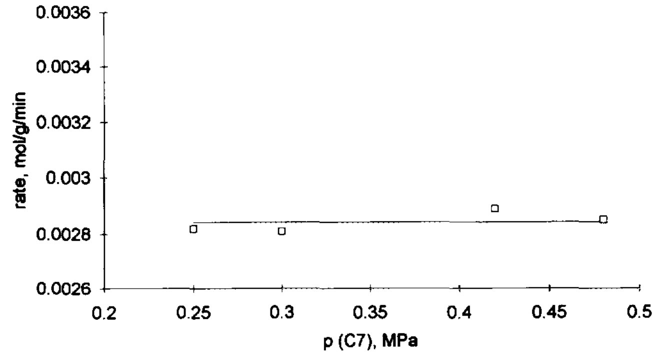

FIG. 3. Initial rate of *n*-heptane cracking in nitrogen atmosphere as a function of *n*-heptane partial pressure. $T = 543$ K, $p_{\text{total}} = 2.4$ MPa.

equations. Consequently, the increase of rate with increasing partial pressure of the educt (p_A) shows an induction period; and with increasing hydrogen partial pressure (p_{H_2}), the rate decreases, assuming that hydride abstraction is rate determining. In the case of slow olefin desorption the rate of cracking is inversely proportional to the partial pressures of the alkane and hydrogen (p_{PA} and p_{H_2}). These results indicate schematically the action of hydrogen during cracking according to the monomolecular pathway, where pentacoordinated carbocations are assumed to be intermediates.

There is one situation, i.e., when the controlling step is the desorption of products and no remarkable amounts of hydrogen are formed in reaction (2), for which the rate of cracking does not depend on the partial pressure of the *n*-alkane. Indeed, under these circumstances the order of the reaction tends to zero, the surface is saturated, and the reaction is insensitive to changes in the partial pressure of the reactant. This situation is more likely to occur when the process is carried out at low temperatures and/or high reactant partial pressures.

In the case of *n*-heptane cracking, we have followed the reaction at different times on stream (TOS). The example given in Fig. 2 demonstrates that the rate of reaction is strongly affected by the TOS, both in nitrogen and in hydrogen atmosphere. Therefore, conversions close to zero TOS have been used for carrying out the kinetic study. For this study the catalyst should be nearly fully active, diminishing spurious effects due to catalyst deactivation. By working at levels of conversion below 10%, the initial reaction rates were calculated at different partial pressures of *n*-heptane. While the total pressure was always kept constant at 2.4 MPa, the partial pressure of the hydrocarbon was changed by diluting it with nitrogen, since it has been shown (10) that this is really an inert gas for the reaction studied.

The results obtained are plotted in Fig. 3, and demonstrate that in the range studied here no influence of the partial pressure of *n*-heptane on the initial rate of cracking exists. It can therefore be assumed that under the given reaction conditions the desorption of products is the rate controlling step.

Influence of Hydrogen on the Kinetics

The initial rates of cracking were obtained keeping constant the total pressure as well as the *n*-heptane partial pressure, while changing the partial pressure of hydrogen. This was achieved by simultaneously introducing nitrogen to keep the pressure of $N_2 + H_2$ constant. In Fig. 4, it can be seen that the initial rate of cracking increases linearly when increasing the hydrogen partial pressure, and therefore there is no doubt that, under these circumstances, a role of hydrogen in the cracking mechanism can be claimed.

It has been proposed (18) that when hydrogen interacts at 77 K with a metal-free zeolite, it becomes polarized and a band at 4105 cm^{-1} appears in the IR spectrum, which has been related to hydrogen polarized by structural bridging OH-groups (19). Furthermore, H_2–D_2 ex-

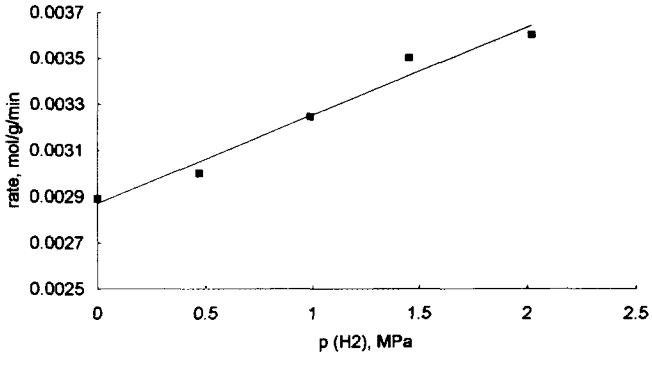

FIG. 4. Initial rate of *n*-heptane cracking in dependence on hydrogen partial pressure. $T = 543$ K, $p_{\text{total}} = 2.4$ MPa, $p_{C_7} = 0.4$ MPa.

change occurs at moderate temperatures on metal-free zeolites (20), indicating that hydrogen can be dissociated on purely acid zeolites. The fact that hydrogen can be activated on metal-free zeolites makes it possible to hydrogenate aromatics and olefins (8, 9, 21, 22). Hence, it becomes probable that hydrogen could be activated and interact with intermediate carbenium ions (or adsorbed olefins, $O2H^+$), saturating them and restoring the original Brønsted acid site. Thus, it seems to be useful to take hydride abstraction from a hydrogen molecule by an adsorbed olefin into account if the supply of hydrogen is large enough. Therefore, the equation for the desorption step should be modified as follows:

$$O2H^+ + H_2 \overset{k_D}{\rightleftharpoons} P3 + H^+ \qquad K_D \qquad [5b]$$

The balance of the overall reaction t2 has to be written:

$$2A \rightleftharpoons P1 + P2 + O1 + O2 \qquad K_{t2} \qquad [9]$$

This event represents the desorption of an adsorbed olefin combined with a hydrogenation or, in other words, the inverse of protolytic cracking of an alkane. In order to arrive at the expressions for rate in dependence on partial pressures, reaction [5a] should be replaced by reaction [5b] in cases where excess hydrogen is present:

$$\text{rate} = k_{SR1} \cdot c_t \cdot \frac{K_{AD} \cdot \dfrac{p_A^2}{p_{P1}} + \dfrac{K_{AD}}{K_{t2}} \cdot p_{O1} \cdot p_{P3} \cdot \dfrac{p_{P2}}{p_{H_2}}}{1 + K_A \cdot \dfrac{p_A}{p_{P1}} + K_D \cdot \dfrac{p_{P3}}{p_{H_2}} + K_D \cdot K_{SR2} \cdot p_{O1} \cdot \dfrac{p_{P3}}{p_{H_2}}} \qquad [10]$$

$$\text{rate} = k_D \cdot c_t \cdot \frac{K_{t2} \cdot \dfrac{p_{H_2} \cdot p_A^2}{p_{P2} \cdot p_{O1}} - p_{P3}}{1 + K_{AD} \cdot \dfrac{p_A}{p_{P1}} + K_{t2} \cdot K_D \cdot \dfrac{p_A^2}{p_{P2} \cdot p_{O1}} + K_{SR1} \cdot K_{AD} \cdot \dfrac{p_A^2}{p_{P1} \cdot p_{P2}}} \qquad [11]$$

Equation [10] presupposes hydride abstraction and Eq. [11] presupposes desorption to be rate determining.

The resulting evolutions of rate with regard to partial pressure are given in Fig. 5. If surface reaction is rate determining, the results are similar to the previously discussed case. This is not the case, however, if olefin desorption is assumed to be the slowest step and if no significant hydrogen abstraction has occurred according to reaction [2]. Under these conditions, the increase of hydrogen partial pressure (p_{H_2}) forces the reaction and, simultaneously, changes in alkane partial pressure (p_A) do not show an effect on reaction rate.

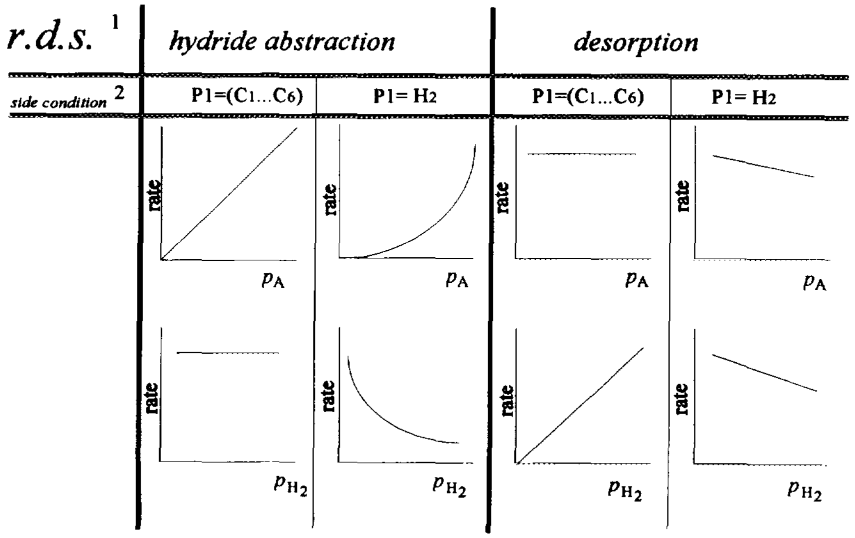

FIG. 5. Evolution of the cracking rate in the presence of hydrogen with varying partial pressures. [1]r.d.s.: rate determining step; [2]side condition: refers to adsorption step (AD) according to Eq. [2].

Comparing the results predicted by the different models, it becomes clear that, depending on the reaction conditions and the acid properties of the catalyst, one can obtain completely different experimental results with respect to the presence of hydrogen. We believe that all the apparently contradictory observations on the effect of hydrogen in carbenium ion reactions on metal-free acid zeolites can be reconciled on the basis of the results given in Figs. 1 and 5. Indeed, if the surface is fully covered and desorption of products becomes the rate determining step, a beneficial effect of hydrogen on the global initial cracking rate can be expected from Eq. [5b]. Thus, it can be expected that under reaction conditions which support desorption as the rate determining step (high partial pressure of the alkane, low temperature) the hydrogen can increase the rate of cracking reactions. However, the situation changes when the controlling step is not the desorption of products but is either the protonation, cracking, or hydride transfer. In these cases reaction [5b] would produce a decrease in the number of surface carbenium ions which would lead to a decrease in the reaction rate. This should be the case when cracking is carried out at low partial pressures of the alkane and/or higher temperatures.

Both possibilities mentioned above are only valid provided that hydrogen can react with adsorbed olefins. Whether the activation of the hydrogen molecule is carried out by the acid sites of the zeolite or by the carbocation on the zeolitic surface is not yet clear and is the object of further investigations. The former possibility has been supported by Kazansky and co-workers (18, 19) and Kasztelan and Guillaume (23). However, the second possibility cannot be ruled out a priori since hydrogen transfer from hydrocarbons is a well documented and easy reaction occurring on acid catalysts, and theoretical work has shown that this can also occur from molecular H_2 (7).

In conclusion, it can be said that either a positive or a negative effect of hydrogen in carbenium ion reactions on metal-free zeolites may be observed depending on whether the rate determining step under the particular reaction conditions used is the product desorption, or any of the previous chemical reaction steps.

Influence of Hydrogen on Selectivity and Catalyst Decay

Nevertheless, and if the proposed hydrogenation reaction [5b] is valid, hydrogen should also have an influence on the observed selectivity, as well as on catalyst decay. Taking into account the above reaction, hydrogen would become a "hydrogen transferring" molecule, which would lead to saturation of olefins. This in turn would result in an increase in the paraffin to olefin ratio in the reaction products. The results presented in Fig. 6 clearly show that a larger saturation of olefins occurs, i.e. more paraffins are produced when hydrogen is introduced during the reaction. This effect cannot be due to olefin saturation by hydrogen transfer from coke, since the effect is observed at short times on stream and low conversions where hydrogen transfer from coke is less substantial. Moreover, it has been shown recently (13) that larger amounts of coke are formed in the presence of nitrogen, yet the observed paraffin/olefin ratio is lower than in the presence of hydrogen.

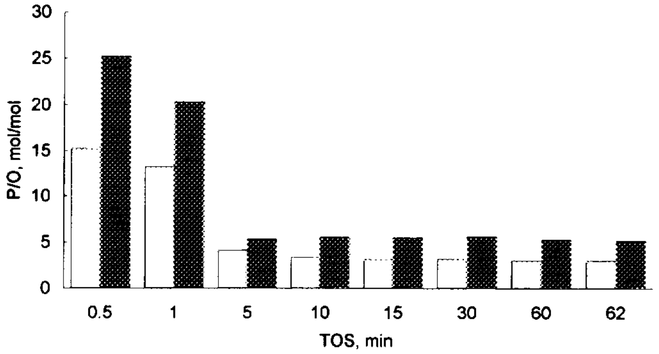

FIG. 6. Molar ratio of paraffins to olefins (P/O) in dependence on TOS. (□) nitrogen, (■) hydrogen. $T = 543$ K, $p_{\text{total}} = 2.4$ MPa, $p_{C_7} = 0.4$ MPa.

In the case of branched C_7-products, it is well known (24–26) that they are readily formed from *n*-heptane, and that the branched intermediates crack at a faster rate than the linear isomers. This implies that under cracking conditions the average lifetime of branched carbenium ions on the zeolite surface is long enough to crack before desorption occurs, and therefore, a low selectivity to branched C_7-products is found. However, since hydrogen diminishes the average lifetime of surface carbenium ions, it could be expected that the selectivity to branched C_7 products should be higher in the presence of hydrogen. The influence of hydrogen partial pressure on the initial selectivity for *n*-heptane isomerization is demonstrated in Fig. 7. The results show that the selectivity for formation of branched C_7 paraffins increases with hydrogen partial pressure, again in agreement with the proposed model.

Concerning catalyst decay, the first remarkable result is the rapid decay observed for H-ZSM-5, which is much faster than that observed under normal cracking conditions (27). This is probably a consequence of the reaction conditions used here, i.e., high pressure and lower temperature, which favor the polymerization of olefins. Indeed, it has been suggested (28–30) that the larger the extent of product oligomerization occurring during cracking of *n*-heptane in a zeolite, the larger should be the C_4/

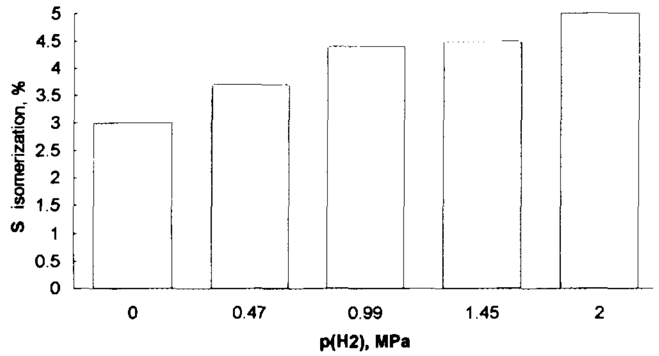

FIG. 7. Initial selectivity for isomerization during *n*-heptane conversion in dependence on hydrogen partial pressure. $T = 543$ K, $p_{\mathrm{total}} = 2.4$ MPa, $p_{C_7} = 0.4$ MPa.

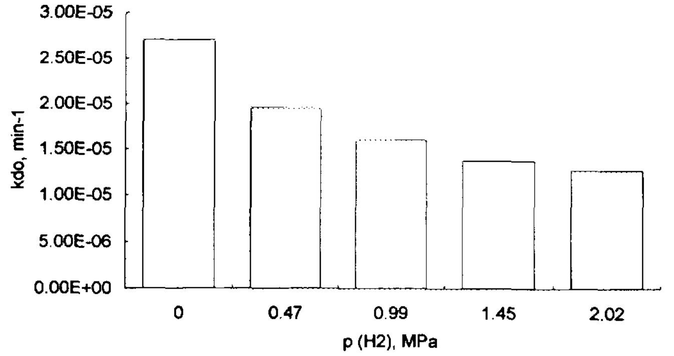

FIG. 9. Kinetic decay constants (k_{d0}) for H-ZSM-5 zeolite during *n*-heptane conversion as a function of hydrogen partial pressure.

C_3 and C_5/C_2 ratio in the cracked products. Results from Table 1 show that under our reaction conditions these ratios are much higher than those observed during cracking of *n*-heptane on a ZSM-5 zeolite under normal cracking conditions.

Moreover, and owing to the positive effect of hydrogen on olefin desorption, the formation of coke is lower when hydrogen is present (13, 14), and one should expect a slower rate of catalyst decay. In order to study this, the activity (a) of the catalyst at different hydrogen partial pressures and at short reaction times (t) was fitted to the following decay model proposed by Das and Wojciechowski (31):

$$a = \frac{\int_0^1 n_\lambda \exp(\gamma_k \lambda/RT) \exp(-k_{d0}t) \exp[(-\gamma_d \lambda/R)[1/T - 1/T_0]]\, d\lambda}{\int_0^1 n_\lambda \lambda \exp(\lambda_k \lambda/RT)\, d\lambda} \qquad [12]$$

with

$$n_\lambda = \exp\left[-1/2\left(\frac{\lambda - 1/2}{\xi}\right)^2\right] \qquad [13]$$

The activity of the catalyst was defined as the ratio of cracking rate at a given reaction time and time zero.

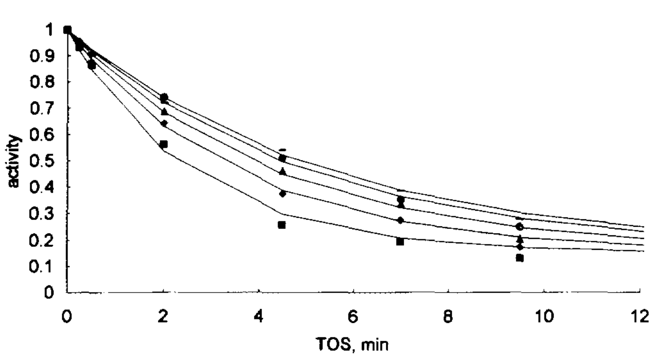

FIG. 8. Activity of H-ZSM-5 zeolite during *n*-heptane conversion at short reaction times. $T = 543$ K, $p_{\mathrm{total}} = 2.4$ MPa, $p_{C_7} = 0.4$ MPa, $p_{H_2} =$: (■) 0 MPa, (◆) 0.47 MPa, (▲) 0.99 MPa, (●) 1.45 MPa, (–) 2.00 MPa lines: calculated activity according to Eq. [12].

These values are shown in Fig. 8 for different hydrogen partial pressures applied during the reaction. The fitting of the activity curves was done by using only the parameter k_{d0} and fixing the remaining parameters as follows: $\xi = 0.029$; $\gamma_k = 30$ kJ mol^{-1} $\gamma_d = 150$ kJ mol^{-1}; $T_0 = 370$ K. The lines in Fig. 8 correspond to the calculated values of the relative activity of the catalyst as a function of the partial pressure of hydrogen and reaction time. The decay parameters k_{d0} obtained using Eqs. [12] and [13] are given in Fig. 9, and they show that the higher the partial pressure of hydrogen, the lower the decay of the metal-free H-ZSM-5 zeolite.

CONCLUSIONS

It has been shown that hydrogen becomes activated and intervenes in carbenium ion reactions on metal-free zeolites. The effect on the rate of reaction can be positive or negative depending on the rate controlling step. In the case of *n*-heptane cracking, if the controlling step is the desorption of products, the presence of H_2 increases the

TABLE 1

Product Distribution, Paraffin/Olefin Ratio (P/O) and Selectivities for the Cracking of *n*-Heptane on H-ZSM-5, T = 543 K, p_{total} = 2.4 MPa, p_{C_7} = 0.4 MPa

p_{H_2}, MPa: TOS, min:	0 0.5	0 62	2.0 0.5	2.0 62	Data from Ref. (29)[a] 0
C_1, mol%	0	0	0	0	0.72
C_2, mol%	0.13	0.27	0.33	0	9.15
C_3, mol%	23.51	22.11	24.42	28.82	53.13
C_4, mol%	43.16	37.22	41.25	41.39	31.58
C_5, mol%	22.51	23.77	22.92	20.43	4.28
C_6, mol%	10.68	16.62	10.94	9.34	1.12
P/O, mol/mol	15	2.98	25.18	5.16	1.08
S_{cracking}, %[b]	95.8	71.5	94.1	82.5	
$S_{\text{isomerization}}$, %[c]	4.2	28.5	5.9	17.5	

[a] Values are taken from Table 2 in Ref. (29). Reaction conditions: T = 743 K, p_{total} = 0.1 MPa.

[b] $$S_{\text{cracking}} = \frac{\text{rate}_{\text{cracking}}}{\text{rate}_{\text{cracking}} + \text{rate}_{\text{isomerization}}} \cdot 100\%.$$

[c] $$S_{\text{isomerization}} = \frac{\text{rate}_{\text{isomerization}}}{\text{rate}_{\text{cracking}} + \text{rate}_{\text{isomerization}}} \cdot 100\%.$$

reaction rate. However, when the controlling step is any of the previous steps, a negative effect of H_2 on the rate of cracking can be expected. This is due to the interaction of adsorbed carbenium ions (or adsorbed olefins) with hydrogen, producing the corresponding paraffin and regenerating the initial Brønsted acid site. This reaction also produces an increase in the paraffin/olefin ratio, an increase in the amount of branched (i.e. isomerized) products, as well as a decrease in coke formation and catalyst decay. The effect of H_2 during cracking of alkanes on monofunctional acid catalysts, and the interpretation given here can be relevant to explain the mechanism and effect of H_2 in hydroisomerization and hydrocracking of alkanes. Indeed, during hydroisomerization of *n*-alkanes a much larger ratio of isomerization to cracking, and lower catalyst deactivation is obtained on bifunctional metal/acid catalysts in the presence of hydrogen, than in the presence of monofunctional acid catalysts. On the basis of the present study one could expect that, owing to the presence of the metal function, a much larger surface concentration of activated hydrogen should exist in the case of the bifunctional catalyst. This could decrease the average lifetime of the adsorbed tertiary carbocations by increasing their rate of desorption. Furthermore, a more effective hydrogenation of intermediate olefinic products will also lead to a lower deactivation rate.

APPENDIX: NOMENCLATURE

p	pressure
T	temperature
TOS	time on stream
k	rate constants
K	equilibrium constants
c_t	total concentration of acid sites
a	activity
Species	
A	educt
P1, P2, P3	product paraffin
O1, O2	product olefin
$O1H^+$, $O2H^+$	carbenium ion
C_i	hydrocarbon
Indices	
AD	adsorption
SR1	surface reaction 1
SR2	surface reaction 2
D	desorption
t	overall reaction
d0	deactivation

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