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The Role of Different Types of Acid Site in the Cracking of Alkanes on Zeolite Catalysts

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The cracking of *n*-heptane on a rare-earth (RE)HY zeolite has been studied in the temperature range 400–470°C. By measuring the initial selectivities with respect to the various reaction products, and carrying out molecular orbital calculations it has been found that cracking can initially take place on Brønsted acid sites via protolytic cracking, or on Lewis acid sites via a classical β-scission mechanism. The activation energy for protolytic cracking is lower than for β-scission both for *n*-heptane and for the iso-heptanes. From energetic considerations, a scheme of cracking can be suggested where the cracking proceeds by hydride transfer and β-scission mainly via branched heptanes. © 1985 Academic Press, Inc.

INTRODUCTION

It is generally accepted that the catalytic cracking of alkanes takes place by a carbenium ion-type mechanism. A matter of discussion is the first step of the reaction, i.e., the formation of the carbenium ion. In the case of cracking with superacids in the liquid phase, it has been shown that the initiating step occurs by protonation of the alkane to give a carbonium ion (*1–5*). In the case of heterogeneous catalysis with solid superacids, Hattori *et al.* (*6, 7*) have proposed that an initial carbenium ion is formed by abstraction of a hydride ion from the alkane by a Lewis acid site of the catalyst. When zeolites have been used as cracking catalysts several hypotheses for the initiation step have been reported:

A carbenium ion is formed via abstraction of a hydride ion by a Lewis site (tricoordinated aluminum and/or AlO^+-type species) (*8–12*).

A carbenium ion is formed via abstraction of a hydride ion by a strong Brønsted site (*13–16*).

A pentacoordinated carbocation is formed via protonation of the alkane by a strong Brønsted site (*13*).

The initial carbenium ion is formed via protonation of an olefin generated by thermal cracking or present as an impurity in the feed (*17–19*).

The electric fields associated with the cations can be responsible for the polarization of the reactant molecules (*20*).

Several studies have produced partial proofs for one or another mechanism for the initiation of the cracking of alkanes. Thus, it has been observed that the OH groups localized in the supercage of a HY zeolite are consumed during the catalytic cracking of alkanes (*21, 22*). Anufriev *et al.* (*23*) have seen an increase in the rate of cracking of alkanes when olefins were introduced into the feed. This result agrees with the observations of Aldridge *et al.* (*22*). These authors have shown that there is an induction period for the cracking of *n*-hexane on a LaY zeolite, and that the induction period is inversely proportional to the reaction rate.

López Agudo *et al.* (*24*) have studied the cracking of *n*-heptane on a CrHNaY zeolite

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and obtained the initial selectivities with respect to the various reaction products in the absence of decay. Under these conditions they observed that the paraffin/olefin (P/O) ratio is higher than one, while aromatics and coke were found as secondary products. Therefore, a source of hydrogen is needed to explain their results.

In the present work the mechanism for the initiation and development of paraffin cracking has been studied by investigating the cracking of *n*-heptane on a (RE)HY ultrastable zeolite and by carrying out molecular orbital calculations to simulate the reactions postulated on the basis of the experimental results.

EXPERIMENTAL

Materials. The catalyst was prepared by repeated exchange of a NaY zeolite (SK-40, Si/Al = 2.25), obtained from Linde Company, with a solution containing La^{3+} and Ce^{3+} ions in a ratio of 3 to 1, and subsequently with a solution containing NH_4^+ ions. The Na^+ form was stirred in a La^{3+} + Ce^{3+} solution for 6 h, and then filtered and washed. The filtrate was dried at 110°C for 12 h and calcined at 550°C for 2 h. This procedure was repeated until 80% of the original Na^+ content was exchanged. Subsequently, the remaining Na^+ was exchanged by NH_4^+ as above. Thereafter the zeolite was pelletized, crushed, and steamed at 500°C for 3 h.

The *n*-heptane used was a Carlo Erba 99.9% purity reactant.

Procedure. The experiments were carried out in a fixed-bed tubular reactor. The reactant was charged at the top of the reactor by means of a pump, feeding at a constant rate. To minimize the thermal effects of the cracking reaction the catalyst was diluted to a constant volume using ground glass of the same mesh size as the catalyst. Condensed liquid products from the reaction were trapped in a pot, after passing through a condenser located below the reactor, while the gaseous products were trapped in gas burettes. The closed system allowed mass balances to be made, and only experiments with mass balances of 100 ± 5% were considered.

In a typical run, the reactor was initially purged with N_2 for 20 min. An amount of 10.0 ml of *n*-heptane (6.88 g) was pumped through the reactor at a constant rate, over a given weight of catalyst (given cat/oil ratio (P)), for a total time $t_f = 2.5$ min. Additional data up to $t_f = 50.0$ min were obtained at a constant P value by changing the rate at which the same quantity of reactant was pumped through the same packing. Various cat/oil curves at different values of P were obtained by repeating the process with different weights of catalyst in the reactor. At the end of each run, the reactor was purged with N_2 and all liquid and gaseous products were analyzed by gas chromatography on a SE-30 silicone on Chromosorb P column and a Porapak Q-silica gel column, respectively, using a HP-5840A chromatograph. In our conditions and with the gas mixtures analyzed, hydrogen could be detected in concentrations of 100 ppm. The analysis of the coke deposited on the surface of the catalyst was carried out using air as the oxidant and measuring the amount of H_2O and CO_2 formed.

MO Calculations. A semiempirical approach to the MO formalism has been adopted to deal with the size of the molecule studied. The MINDO/3 method (*25*) has been selected because of its usefulness for the study of various properties of organic ions, both *classical* and *nonclassical*, in the gas phase, mainly those concerned with calculations of energies of reactions involving fragmentations (*26*). MINDO/3 calculations have proved useful in a great variety of cases in giving the correct order of magnitude of the energies of alternative transition states and hence they can be helpful in determining reaction mechanism (*27*). All the geometrical optimizations were performed using the variable metric method described by Murtagh and Sargent (*28*) and adapted by Rinaldi (*29*) for semiempirical energy calculations.

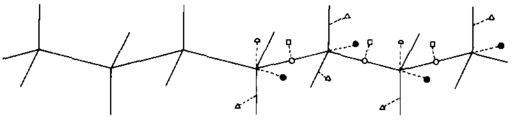


FIG. 1. Starting points adopted for the search of the possible minima of protonated *n*-heptane. See text for details.

The stationary points on the MINDO/3 energy hypersurface of the protonated *n*-heptane have been studied. The *n*-heptane molecule was arranged in a symmetrical conformation in order to reduce the number of starting points to be considered. Three main protonation schemes were adopted: (1) protonation in the middle of a C–C bond, (2) protonation in the middle of a C–H bond (△ in Fig. 1), and (3) protonation over a C atom to yield a pentacoordinated structure. Two classes of starting point were taken for protonation over the C–C bond, viz. (i) placing the H^+ just over the bond (○ in Fig. 1), or (ii) placing it to form a bent-bridged structure (□ in Fig. 1). Similarly, two types of attack of a C atom were considered, viz. (i) over the H–C–H face (● in Fig. 1), or (ii) on top of the H–C–C face (⌓ in Fig. 1). The complexes with a linear C–H–H structure have been shown to be less stable than other structures (*30*) and will not be considered here. All starting points which have been considered are presented in Fig. 1.

The two-dimensional cross section of the cracking hypersurface was obtained by independently scanning the distances d_1 (C–C) and d_2 (C–H) (see Fig. 2), starting from protonated *n*-heptane structures of the linear bridge type (C–H–C). The molecular orbital study corresponds to the transformation of an isolated protonated hydrocarbon into different cracking products. A better understanding of the process would be obtained if the interaction energy between the protonated hydrocarbon and catalyst could be calculated. However, MO calculations on such an interacting model are not feasible at the MINDO/3 level, because of the large number of atoms needed to represent a significant fragment of the surface of the catalyst. In any case, the energies involved in intermolecular interactions are much smaller than those involved in the breaking of chemical bonds. We think, therefore, that these interaction energies would only introduce small quantitative modifications in our results.

RESULTS AND DISCUSSION

A classical β-cracking mechanism taking place over an acid site gives a P/O (paraffin/olefin) ratio of unity in the reaction products. In the case where the initiation of cracking occurs via olefins, that ratio would also be unity. The behavior of the P/O ratio may be observed experimentally by merely looking at the values of the initial selectivities with respect to the various reaction products, since under these conditions the results are not disguised by consecutive reactions such as, for instance, hydrogen transfer. We have obtained here the selectivity curves for the several groups of products formed, in the absence of decay and thermal cracking (Fig. 3). From these curves the values of the initial selectivities have been calculated at different levels of conversion. In Fig. 3g one sees that the P/O ratio is significantly greater than unity for low conversion levels (<2%), and it decreases as the level of conversion increases. Obviously, the high P/O ratio found cannot be explained only in terms of a cracking mechanism through Lewis acid sites, since some kind of hydrogen supplier would be needed. Possible hydrogen donors are cycloalkanes, while producing aro-

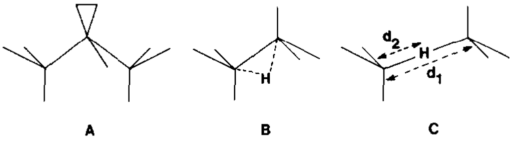


FIG. 2. Minima found in the hypersurface corresponding to $n\text{-}C_7H_{17}^+$. Only that part of the *n*-heptane skeleton related with protonation is depicted.

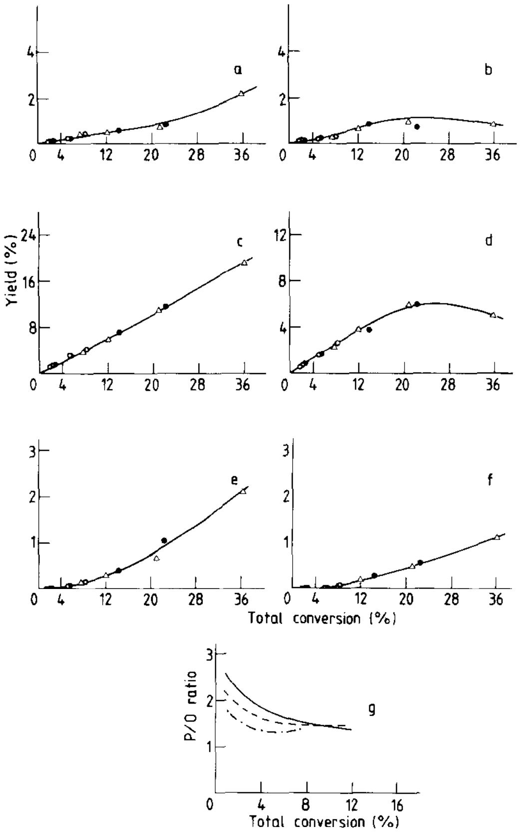


FIG. 3. Selectivity curves to the different groups of products at 400°C: (a) $C_2 + C_5$; (b) $C_2^{2-} + C_5^{2-}$; (c) $C_3 + C_4$; (d) $C_3^{2-} + C_4^{2-}$; (e) aromatics; (f) coke; (g) P/O ratio of the reaction products at: (—) 400°C; (---) 430°C; (-·-·-) 470°C; (○) 0.07, (●) 0.146, (△) 0.29 cat/oil (g/g).

matics, and coke. However, under our experimental conditions (Fig. 3) both aromatics and coke appear as secondary products, and therefore they cannot be considered responsible for the high P/O ratio found in the cracked products at very low levels of conversion. The other possible sources of hydrogen are the OH groups of the catalyst. If this were so, then it would be necessary to postulate, for the first step of the cracking reaction, an interaction between the n-heptane and the Brønsted acid centers of the catalyst. We have simulated that interaction, and three types of minima have been found in the MINDO/3 surface of protonated *n*-heptane, labeled as A, B, C (see Fig. 2). The A type can be described as a strong molecular complex between H_2 and a heptyl carbenium ion. The structures B and C represent a hydrogen atom bridged between two carbon atoms, forming a linear C–H–C bridge or a bent-bridge structure. Such structures are similar to those reported for small carbonium ions on the basis of accurate ab initio calculations (*31*). The eight stationary energy structures have been obtained and are summarized in Fig. 4.

The first possibility of interaction is the attack of one proton from the catalyst on a C–H bond. It produces species which have been postulated during the isomerization and cracking of alkanes in superacid media (complex A) (*1–5*). It is reasonable to expect that such an intermediate complex will lead to the formation of H_2 leaving a carbenium ion. Indeed, Olah *et al.* (*1–5*) have reported the formation of molecular hydrogen during the cracking of alkanes in the presence of superacids in the liquid phase.

In the case of zeolites, the formation of hydrogen via the abstraction of a hydride ion from the hydrocarbon by means of a Brønsted acid site has been postulated by Minachev *et al.* (*32*) to explain the effect of H_2 partial pressure on the rate of the isomerization of alkanes in the presence of a zeolite. However, in our work, we have not

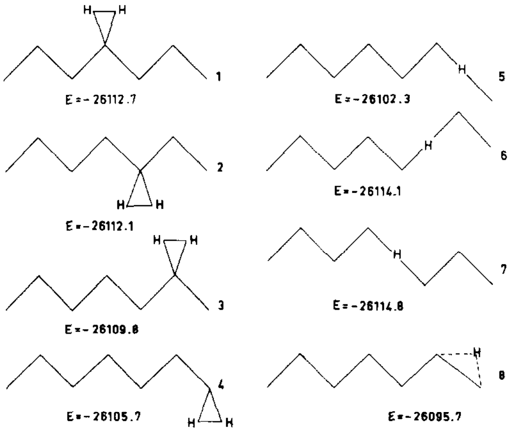


FIG. 4. Structures and energies in kcal · mol^{-1} associated with the various minima in the hypersurface of protonated *n*-heptane.

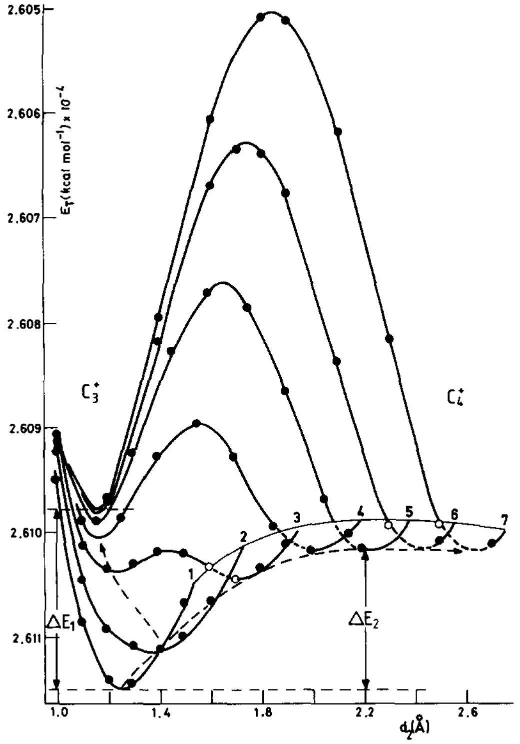


FIG. 5. Two-dimensional cross section of the energy surface for the cracking process of structure 7 (Fig. 4) leading to C_3 and C_4. Each curve from 1 to 7 corresponds to a one-dimensional cross section associated with a fixed value of d_1 in the range from 2.5 to 3.7 Å, with a scanning step of 0.2 Å. Dashed lines indicate the minimum energy reaction path. E_T is the molecular energy. ΔE = 17.5 kcal · mol^{-1} is the energy barrier for cracking to C_3^+ + C_4; ΔE_2 = 13.5 kcal · mol^{-1} is the energy barrier for cracking to C_3 + C_4^+.

seen hydrogen as a reaction product during the cracking of n-heptane, and in those cases where hydrogen has been reported as a product (*33, 34*) the results were obscured by thermal cracking (*35*). In any case a mechanism involving Brønsted acid sites as hydride ion abstracting agents will produce a carbenium ion which, by cracking, will yield a theoretical P/O ratio of unity, which we did not observe in our experiments.

The other possibility for the interaction of a Brønsted acid with an alkane molecule is the attack of a proton on a C–C bond of the alkane to give structures of the type B and C bridge (see Fig. 2). The more stable structures (see Fig. 4) correspond to linear bridge C-like structures where the hydrogen atom is placed between two secondary carbons. Other structures such as those labeled 1 and 2 (Fig. 4) show calculated MINDO/3 energies that are similar to those of the more stable bridged structures 6 and 7. However, Hiraoka and Kebarle (*36–38*) have shown experimentally from the study of the reaction surface of $C_3H_9^+$ that the C–C breaking process starts from structures type B or C, i.e., bridge-like structures, while MINDO/3 calculations lead to the same conclusion (*39*). Thus we have performed our cracking surface study starting from the more stable linear bridged structure. In Figs. 5 and 6 are shown the two-dimensional cross sections of the energy hypersurfaces corresponding to the structures labeled as 6 and 7 in Fig. 4. The two

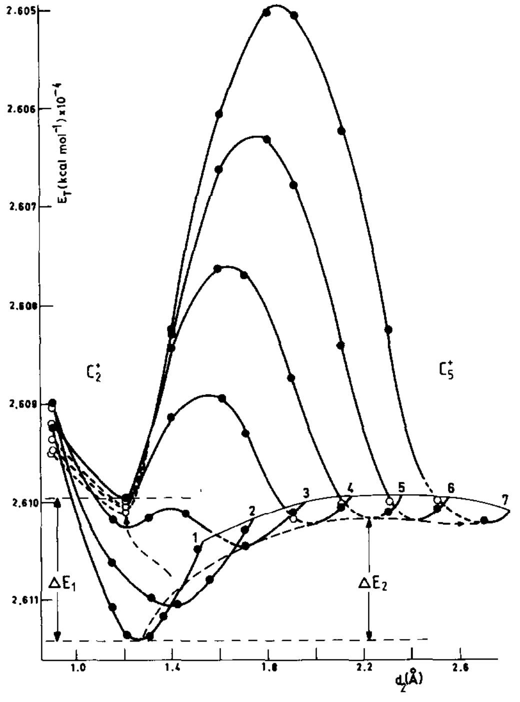


FIG. 6. Two-dimensional cross section for the cracking process of structure 6 (Fig. 4), leading to C_2 and C_5. E_T is the molecular energy. ΔE_1 = 15 kcal · mol^{-1}, is the energy barrier for cracking *n*-heptane into C_2^+ + C_5; ΔE_2 = 12.5 kcal · mol^{-1} is the energy barrier for cracking into C_2 + C_5^+.

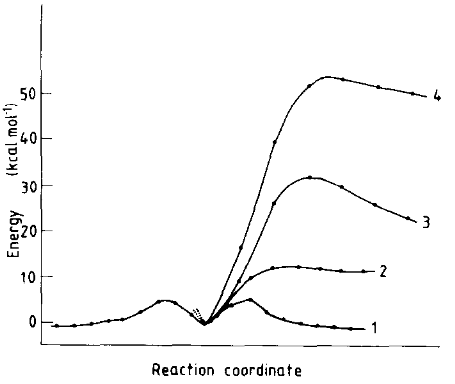


FIG. 7. Energetic profiles associated with the following processes: (1) H^- transfer from $(CH_3)_2CH$ and $(CH_3)_3C^+$ (Ref. (*40*)). (2) Protolytic cracking to give C_3 + C_4. (3) β-Cracking of i-heptane to give $C–C^+–C$ + nC_4 (Ref. (*40*)). (4) β-Cracking of *n*-heptane to give $C^+–C–C$ + nC_4 (Ref. (*40*)).

parameters d_1 and d_2 have been taken as independent. From those figures, one sees that the energy barrier for the protolytic cracking process is in the range of 12 to 18 kcal · mol^{-1}. Moreover, when the bridged complex is formed it is much easier to crack than to interconvert from minima of the bridged species to those of complex ones, since the latter process shows an energetic barrier higher than either the protolytic cracking or dehydrogenation (*36–39*). Therefore, in this second case a carbonium ion is formed that can crack to produce a paraffin, which desorbs into the gaseous stream, and an adsorbed carbenium ion. Thus, a surface covered with carbenium ions is generated. The carbenium ions will keep the reaction going by creating new C_7^+ carbenium ions through a hydride transfer reaction

$$C^+_{n(n<7)} + C_7 \rightarrow C_n + C_7^+$$

The heptyl carbenium ions produce, by β-scission, one olefin and a new adsorbed carbenium ion. This mechanism may explain not only the high P/O ratio found at low conversion levels, but also its decrease (for still lower levels of conversion) when increasing the level of conversion. The overall mechanism can be expressed in a simplified way by the equations

$$ZH + C_j \rightarrow C_jH^+ \;.\;.\;.\; Z^-$$

$$C_jH^+ \;.\;.\;.\; Z^- \rightarrow C_m + C_n^+ \;.\;.\;.\; Z^-$$

$(j = m + n)$ Protolytic cracking

$$C_n^+ \;.\;.\;.\; Z^- + C_j \rightarrow C_n + C_j^+ \;.\;.\;.\; Z^-$$

Hydride transfer

$$C_j^+ \;.\;.\;.\; Z^- \rightarrow C_l^{2-} + C_s^+ \;.\;.\;.\; Z^-$$

$(j = l + s)$ β-cleavage

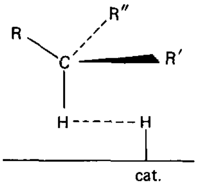
In the scheme ZH represents an acid zeolite and C_j is a paraffin, where j is the number of carbon atoms; C_n and C_l^{2-} are alkanes and olefines, respectively.

It is clear that with the proposed mechanism it is not necessary to invoke the formation of H_2 as a reaction product. Furthermore, by looking at Fig. 7, one sees that the process which involves the lowest activation energy is the hydride transfer between an adsorbed carbenium ion and a paraffin, followed by the protolytic cracking which requires a lower activation energy than the β-cracking via carbenium ions, either directly from *n*-heptane or through the iso forms.

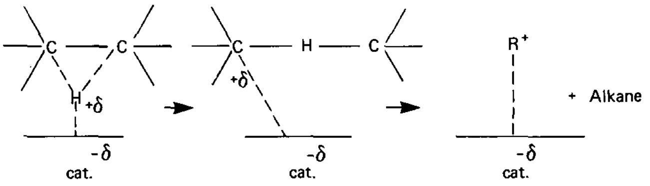
These results indicate that from an energy point of view the protolytic cracking, together with β-cracking through *n*-heptane isomers, should be the process responsible for the first cracking events and the formation of the surface covered with carbenium ions. When such a surface is formed, the reaction will proceed by β-cracking, mainly via the branched isomers of heptane.

It should be noted that Olah *et al.* (*1–5*) have reported the formation of H_2 when superacids are used as catalysts in homogenous liquid phase, where there are hydrogen atoms providing a very low electron density. On the other hand, Hattori *et al.* (*6, 7*) have reported that in the presence of heterogeneous superacids no evolution of H_2 was observed. These authors interpreted that feature on the basis of the lower acidity of the Brønsted acid sites on heterogeneous catalysts compared with homogeneous superacid catalysts. Hence it can be considered that in the heterogeneous case the Brønsted sites provide an electronic density considerably larger than in the homogeneous case.

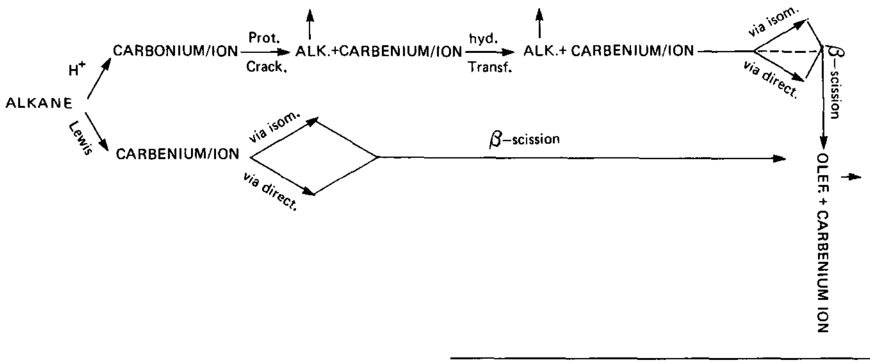
In the case of zeolites, the acid strength of the Brønsted sites is lower than that of superacids (*41*), and as indicated before, we have not detected H_2 in the products. Thus, in the case of our zeolite catalyst the electronic charge transfer from the C–H bond to the H–H bond, which is being formed, will be less important than for the case of superacid catalysts. In other words, in the case of zeolites the C–H bond remains stronger than for superacid homogeneous catalysts, and consequently the new H–H bond being formed will be weaker than in the first case, i.e., the H_2 structure will not be clearly established in the case of zeolite catalysts. If this is true, the formation of A-like structures cannot be considered to be likely; we propose for this case, complexes of the type



The strength of the acid sites in zeolites would be able to produce B- or C-like structures which can give protolytic cracking in consecutive steps:



In conclusion it can be said that cracking takes place through two parallel pathways:



It is obvious that in the first stages of the reaction the product distribution should be dependent on the ratio carbonium ions/carbenium ions or, similarly, on the Brønsted/Lewis site ratio.

Following the reaction scheme presented above, and taking into account the values of the activation energies for the different processes, it is obvious that an increase in the reaction temperature would produce a decrease in the P/O ratio obtained at short contact time and times on stream. Indeed, such behavior is observed in Fig. 3g.

Note added in proof: While this paper was in press, Haag and Dessau (W. D. Haag, R. M. Dessau, "Proceedings 8th International Congress on Catalysis, Berlin, July 1984." II-305) also proposed the possibility of protolytic cracking of 3-Methylpentane on zeolite catalysts.

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