Influence of Acid Site Densities on the Mode of Alkane Cracking

Giuseppe Giannetto, Subashe Sansare, and Michel Guisnet*
Laboratoire Associé au CNRS 350, Catalyse Organique, UER Sciences, 40, Avenue du Recteur Pineau, 86022 Poitiers Cedex, France

On isolated sites of dealuminated Y zeolite the formation of carbenium ions through intermolecular hydride transfer is highly unfavoured and consequently alkane cracking occurs through a monomolecular mechanism with pentaco-ordinate carbonium ions as intermediates.

Until recently, alkane cracking on solid acid catalysts was explained by a carbenium ion chain mechanism which consisted of two steps: carbenium ion formation by bimolecular hydride transfer followed by β scission. However recent studies on zeolites have shown that several mechanisms could intervene. Haag and Dessau[1] have demonstrated that the differences in selectivities between Y and ZSM5 zeolites are due to the existence of two different cracking mechanisms the relative importance of which depends on the catalyst: the classical carbenium ion mechanism and a monomolecular mechanism with pentaco-ordinated carbonium ions as intermediates. With Y zeolite the former mechanism is favoured, while in the small pores of ZSM5 alkane cracking occurs mainly through the latter mechanism since the hydride transfer requiring a bimolecular transition state would be sterically hindered. In this communication we show that a monomolecular mechanism is also highly favoured with Y zeolites when the density of their acid centres is very low.

The transformation of n-heptane was studied at 350 °C, $p(N_2)$ 0.9 bar, p(n-heptane) 0.1 bar, in a dynamic reactor on two protonic Y zeolites with Si : Al ratios equal to 3 (HY3) or to 35 (HY35). The HY3 sample was obtained by calcination of an ultrastable NH_4 zeolite (US YNH_4 from Union Carbide) at 500 °C for 10 h in a dry air flow. The HY35 sample was prepared by a $SiCl_4$ dealumination[2] of US YNH_4 followed by 3 h treatment with HCl at 100 °C. The dealuminated sample had a greater proportion of strong acid sites than HY3: thus the ratio $n(A_1) : n(A_2)$ [where $n(A_1)$ is the theoretical total number of acid sites and $n(A_2)$ the number of acid sites for which the heat of NH_3 adsorption is greater than 100 KJ mol^{-1}] was equal to 7.5 on HY3 and to 5.2 on HY35.

The initial activity of HY3 was about 60 times higher than that of HY35. Its value per theoretical acid site (A_1) was seven times higher than that of HY35 and per strong acid site (A_2) ten times higher. The active sites of HY35 however were stronger than those of HY3; HY3 poisoned by pyridine recovered 90% of its activity after desorption treatment at

500 °C, but HY35 treated in the same way recovered less than 60%. HY3 deactivated very rapidly (after 1 h only 25% of its initial activity remained) while HY35 deactivated very slowly. This can be explained by the slower coke formation on HY35 (0.1% after 1 h) than on HY3 (4.5%).

The product distributions were dependent on the zeolite used; in the case of HY3 it also depended on the degree of the coke deactivation. On HY3 about 90% of the cracking products consisted of C_3 and C_4 species in practically equimolar amounts. The alkene : alkane ratio was very low on the fresh catalysts (0.25 : 1) and was slightly under 1 after deactivation. The C_4 species were mainly branched (branched : straight chain 4.5 : 1). On HY35, besides C_3 and C_4, C_1 and C_2 (up to 35% of the cracking products) and C_5 and C_6 species were found, C_4 species were less branched than on HY3, the alkene : alkane ratio was very high (2.5—3.0 : 1), and a significant amount of hydrogen was formed.

All these observations can be explained by invoking two different mechanisms for the cracking of n-heptane, the relative significance of each depending on the density of the acid sites. (i) One is the classical carbenium ion mechanism (mechanism A). In this mechanism the limiting step is the formation of the carbenium ion R^+ by hydride transfer from the alkane RH to a pre-existing carbenium ion R^{1+}, equation (1). This step is followed by the β scission of R^+ with formation of an alkene and of a carbenium ion. When R^+ is a linear secondary carbocation, its scission leads to a primary carbenium ion and consequently occurs very slowly. In this case isomerization of R^+ will precede its scission.[3]

On HY3, the product distribution is practically the one that can be expected with this mechanism i.e. preferential scission to give C_3 and C_4 fragments. Indeed the other scissions C_1 + C_6, C_2 + C_5 needing the intervention of primary carbenium ions, are highly unfavoured.

The alkene : alkane ratio is at best 1 : 1. Alkane scission should lead to one alkene molecule for one alkane molecule. However the alkenes are very reactive and are involved in several steps of coke formation (alkylation, hydrogen transfer etc.) and therefore are formed in smaller quantities than the alkanes.

$$RH + R^{1+} \xrightarrow{\text{H transfer}} R^+ + R^1H \qquad (1)$$
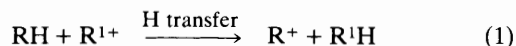
(ii) The second mechanism allows for the formation of alkenes in greater quanitities than alkanes, of hydrogen, and of C_1 and of C_2 species as observed on HY35. Formation of these could be accounted for by a radical mechanism as proposed recently by Clarke et al.[4] for the conversion of dimethyl ether on HZSM5 or by a mechanism involving non classical pentaco-ordinated carbonium ions as intermediates[1] (mechanism B). This second mechanism is the more likely since HY35 has very strong acid centres and pyridine inhibits
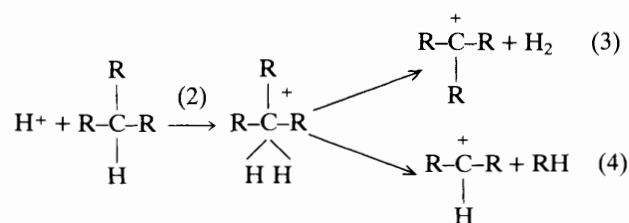
n-heptane cracking. The carbonium ions formed by alkane protonation cleave to give hydrogen or an alkane and a carbenium ion, equations (2)—(4). This process is most likely the initiation step of mechanism A. Indeed on catalysts such as HY3 the carbenium ions will react with n-heptane via reaction (1). On HY35, reaction (1) is slow compared to reactions (2) and (3) which explains the high value of the alkene : alkane ratio. This particular behaviour of HY35, similar to that of HZSM5, cannot be explained by steric constraints which would limit the formation of the bimolecular transition state of reaction (1). Nor can the low activity of HY35 for this reaction be related to the greater strength of the acid sites; indeed it is well known that the stronger the acid sites the higher their activity. The low acid site density of HY35 could explain its low activity provided it is admitted that this bimolecular reaction needs two adjacent sites for catalysis to occur. Several other bimolecular reactions (aromatic hydrocarbon dispro-portionation,[5,6] butane disproportionation[7]) apparently demand this. The lower activity of HY35 in reaction (1) could also explain the lower activity of its acid sites for n-heptane cracking and for coke formation. Indeed on HY3 which has a high density of acid sites reaction (1) becomes much faster than reactions (2) and (3) either for kinetic reasons (higher order) or because its catalysis requires weaker acid centres than reactions (2) and (3).

References

1 W. O. Haag and R. M. Dessau, Proceedings of the 8th International Congress on Catalysis, Dechema, Berlin, 1984, vol. 2, p. 305.
2 H. K. Beyer and I. Belenykaja, 'Catalysis by Zeolites,' eds. B. Imelik, C. Naccache, G. Coudurier, Y. Bentaarit, and J. C. Vedrine, Studies in Surface Science and Catalysis, Elsevier, Amsterdam, Oxford, New York, 1980, vol. 5, p. 203.
3 A. Corma, J. Planelles, and F. Thomas, J. Catal., 1985, 94, 445.
4 J. K. A. Clarke, R. Darcy, B. F. Hegarty, E. O' Donoghue, V. Amir-Ebrahimi, and J. J. Rooney, J. Chem. Soc., Chem. Commun., 1986, 425.
5 R. P. L. Absil, J. B. Butt, and J. S. Dranoff, J. Catal., 1984, 85, 415.
6 N. S. Gnep and M. Guisnet, Appl. Catal., 1981, 1, 329.
7 M. Guisnet, F. Avendano, C. Bearez, and F. Chevalier, J. Chem. Soc., Chem. Commun., 1985, 336.