Correlations between Selectivity in n-Decane Cracking, Si/Al Ratio and Field Gradient in Faujasites

C. Mirodatos,[a] A. Biloul,[a] and D. Barthomeuf[b]

[a] *Institut de Recherches sur la Catalyse, Laboratoire Propre du C.N.R.S., conventionné à l'Université Claude Bernard, Lyon I, 2 avenue Albert Einstein, 69626 Villeurbanne Cédex, France*

[b] *Laboratoire de Réactivité de Surface et Structure, U.A. 1106 C.N.R.S., Université Paris VI, France*

The increase, at low Al content, in the formation of light products up to C_3 is related to the disturbing effect of increased field gradients which would favour the cracking of a hydrocarbon near the end of the molecule.

It has been shown previously that the C_2/C_4 and C_3/C_4 ratios of the products found in the cracking of n-alkanes can be ranked for a series of different zeolite structures.[1] High ratios were related to the existence of a heterogeneous environment in the cages or channels where the molecules move, resulting from the presence of pores with a small size and a high tortuosity. High field gradients experienced by the molecules would affect the path by which the cracking reactions proceed. Such a hypothesis implies that other ways of changing the field gradient should also modify the selectivity ratios. For a given

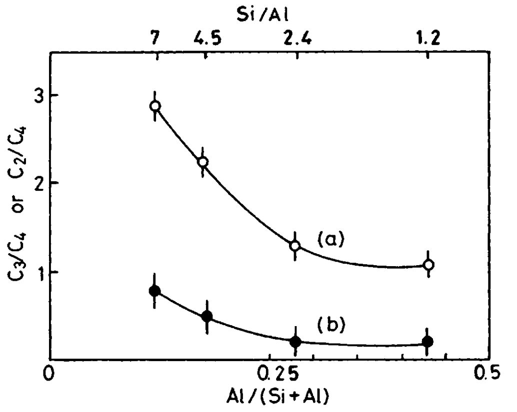

Figure 1. Dependence of selectivities (a) C_3/C_4 and (b) C_2/C_4 on the Al content in faujasites (n-decane cracking at 793 K).

zeolite structure, it is possible to vary the density of charges, *i.e.* the Al content. A decrease in the number of AlO_4^- tetrahedra should increase the field gradient which is a mathematical function of the potential created by the charges. One would then expect an increase in the selectivity ratios.

Four samples with the faujasite structure were used. A $H_{35}Na_{51}$ X-type and a $H_{47}Na_5$ Y-type zeolite were obtained from the commercial sodium forms. Two dealuminated Y-type zeolites were prepared, one with Si/Al = 4.5 by Al extraction with ethylenediaminetetra-acetic acid and the other with Si/Al = 7 by Al extraction with ammonium hexafluorosilicate. The extent of Na exchange was 84% for the two last samples. The cracking of n-decane was performed at 793 K in a microreactor with H_2 as carrier gas. The conversion was <10%.

Figure 1 shows an increase in the C_2/C_4 and C_3/C_4 ratios for low Al contents. It is well known that the acid strength of zeolites increases as the Al level decreases. One would be tempted to correlate the two properties. Nevertheless a detailed study, for faujasites and other zeolites, of the influence of the acid strength in itself on the changes in the selectivity ratios shows no direct correlation.[2] Since decreasing the Al content in zeolites modifies concomitantly the density of charges and the acid strength one has to conclude that the changes in C_2/C_4 and C_3/C_4 values arise from their dependence on density of charges only. The dispersion of a small number of charges on the walls of the pores the molecules are moving along will increase the field gradient and favour a greater polarization of the molecules. It is thus quite plausible that a hydrocarbon molecule which experiences the inner field gradient of the zeolite will be activated and cracked in a way directly related to its degree of disturbance.

Two schemes have been proposed for the catalytic cracking of alkanes in zeolites. The classical mechanism involves several reactions, β-scission being the C–C splitting step.[3] Small amounts of C_1 and C_2 products are formed, C_3—C_6 hydrocarbons being the major products. By analogy with solution studies in the presence of superacids[4,5] a non-classical mechanism has also been proposed. It involves the formation of pentaco-ordinated carbonium ions and gives, in contrast with the classical mechanism, H_2 and a large proportion of light products C_1, C_2 · · ·.[6,7]

It is suggested that the changes in the C_2/C_4 and C_3/C_4 values reflect the relative contribution of the two mechanisms for the cracking of n-alkanes in zeolites. High values, associated with high field gradients in the cavities, would indicate that the non-classical mechanism plays an important role: proton attack on the hydrocarbon near the end of the molecule would be favoured when the molecule is disturbed by high field-heterogeneity.

Received, 28th July 1986; Com. 1074

References

1 C. Mirodatos and D. Barthomeuf, *J. Catal.*, 1985, **93**, 246.

2 C. Mirodatos and D. Barthomeuf, AIChE national meeting, New Orleans, 1986, paper 46b.

3 H. H. Voge, in 'Catalysis,' vol. 6, ed. P. H. Emmett, Reinhold, New York, 1958, ch. 5, p. 407.

4 G. Olah, *J. Am. Chem. Soc.*, 1972, **94**, 808.

5 D. M. Brouwer and H. Hogeveen, *Prog. Phys. Org. Chem.*, 1972, **9**, 179.

6 W. O. Haag and R. M. Dessau, Proc. 8th Int. Congr. Catalysis, Verlag Chemie, 1984, vol. 2, 305.

7 A. Corma, J. B. Monton, and A. V. Orchilles, *Ind. Eng. Chem., Prod. Res. Dev.*, 1984, **23**, 404; *Appl. Catal.*, 1985, **16**, 59.