

Shape Selective Catalysis and Reaction Mechanisms

M. GUISET and G. PEROT

ERA CNRS Catalyse Organique, Université de Poitiers
40, Avenue du Recteur Pineau, 86022 Poitiers Cedex, France

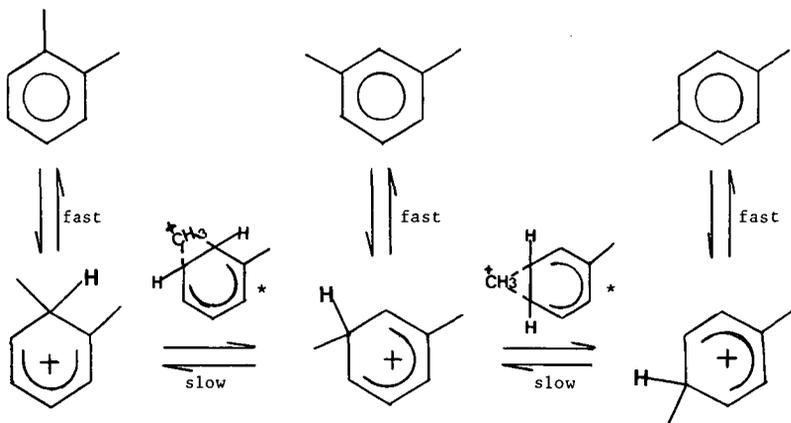
Thanks to the progress recently accomplished in the field of the synthesis and the modifications of zeolitic materials, the chemist now disposes of a large choice of acid catalysts. The problem lies in the selection, through a reliable method, of the one best suited for obtaining selectively a given reaction. The aim of this paper is to show that, by using model reactions, catalysts can be chosen on the basis of their shape selective properties. For this however the reaction mechanisms as well as the reasons for possible modifications in rate and orientation must be perfectly known.

1. Main factors governing reaction selectivity over acid zeolites

1.1. Isomerization and disproportionation of aromatic hydrocarbons over zeolites.

1.1.1. Xylene isomerization

Over amorphous catalysts (1-3) xylene isomerization involves methyl shift in benzenium ion intermediates as the rate limiting step (scheme 1).



Scheme 1 : Isomerization of xylenes on acid catalysts * Transition state according to (4).

With m-xylene as the reactant and over amorphous catalysts and Y zeolite, two parallel reactions leading to o-xylene and p-xylene can take place at similar rates. However over mordenite, offretite and ZSM5, the p-xylene formation is faster (5). This is mainly a matter of diffusion rate (6). The p-xylene molecule being smaller in size diffuses out of the porous structure more readily than o-xylene. It must be noticed that the intermediates and the transition states involved in the two reactions differ slightly in size and structure. Thus the possibility of steric effects cannot be excluded.

The isomerization of o-xylene into p-xylene involves two consecutive steps. At 350°C, the reaction is negligible over amorphous catalysts and Y zeolite but quite important over mordenite and very important over ZSM5 (5). Three factors converge to increase p-xylene selectivity from Y zeolite to mordenite and ZSM5 : i) the decrease in average pore dimension which increases residence time in the structure ; ii) the increase in acid strength which increases the rates of the two consecutive steps leading from o-xylene to p-xylene ; iii) the smaller size of p-xylene, favoring its desorption.

1.1.2. Xylene disproportionation

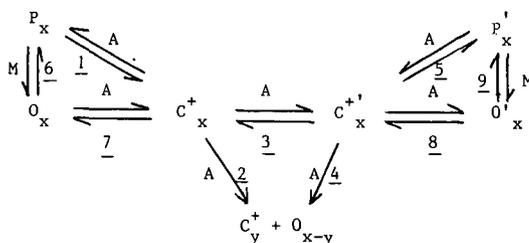
Xylenes can undergo simultaneously isomerization as well as disproportionation into toluene and trimethylbenzenes. The disproportionation mechanism involves bimolecular intermediates (1,7) much more bulky than the benzenium intermediates involved in isomerization. This is probably why the disproportionation/isomerization rate ratio (r_D/r_I) increases as more space becomes available in the porous structure of the zeolite.

However r_D/r_I also seems to depend on the acidity of the zeolite. It decreases as the degree of exchange of protons for sodium cations in H-mordenite increases (8,9). This is more a matter of site density than acid strength. Indeed poisoning experiments with pyridine show that the acid strength required for both reactions is practically the same. But disproportionation requires probably two adjacent acid sites (1,7,10) while isomerization requires only one acid site. Hence the decrease in r_D/r_I from Y zeolite to ZSM5 may partly be explained by the site density decrease.

1.2. Alkane transformation

Over acid and bifunctional catalysts, alkanes undergo three main reactions : isomerization, cracking and disproportionation. All three of them involve carbocations as intermediates and their relative importance depends both on the characteristics of the alkane (size, degree of branching) and of the catalyst (acidity, porous structure, hydrogenation activity).

Scheme 2 shows the different chemical steps involved in the isomerization and the cracking of alkanes.



Scheme 2 : Isomerization and cracking of alkanes on acid and on bifunctional catalysts. P:paraffin , O:olefin , C⁺:carbocation , x,y:number of carbon atoms, A:acid step ,M:metallic step.

1.2.1. Alkane transformation on pure zeolite catalysts

Alkane cracking on pure acid catalysts occurs through steps 1, 2, 3 and 4 of scheme 2. The carbenium ion formation certainly results from intermolecular hydride transfer between a reactant molecule and a preadsorbed cation while steps 2, 3 and 4 are considered as monomolecular reactions.

In the absence of steric constraints or of diffusional limitations, the cracking rate is related to the stability of the intermediate carbenium ions (C_x^+ and C_x^{*+}). Thus over Y zeolite at 400°C isooctane cracking is 25 to 40 times faster than n-hexane cracking and 150 to 300 times faster than n-pentane cracking. The difference in reactivity of alkanes depends on the active sites: the greater their acid strength, the smaller the difference (12).

The intracrystalline structure has also a considerable influence on the relative reactivities of alkanes. Frilette et al (11) consider as shape selective the zeolites for which the "constraint index" CI (ratio of the apparent cracking rate constants of n-hexane and 3-methylpentane) is greater than 1. Due to the higher reactivity of 3-methylpentane towards carbenium ion formation, the CI of non-shape selective materials is smaller than 1. In the case of intermediate pore size zeolites the CI value ($1 < CI < 12$) is determined by steric constraints in the bimolecular formation of the carbenium ion (step 1, scheme 2) (13,14). On the contrary for erionite which has small pore openings and large cavities the high value of CI is due only to differences in diffusional limitations for n-hexane on the one hand and 3-methylpentane on the other.

The acidity and the structure of zeolites also influence considerably the product distribution of alkane cracking (12). In the case of isooctane about 75 % of the cracking products can be considered as resulting from the successive steps 1 and 2 of scheme 2, the remaining 25 % result from one isomerization step followed by cracking of the rearranged carbocation (sequence 1,3,4). Over mordenite and ZSM5, direct cracking (sequence 1,2) is responsible respectively for 50 and 10 % of the products only, the remainder results from multiple transformations of isooctane. The differences between the three zeolites can be attributed to diffusional limitations.

In the case of pentanes and hexanes, the cracking steps (2,4) become so slow that the formation of isomers (step 5) is observed. The isomerization/cracking rate ratio depends on the zeolite. For n-pentane transformation at 400°C, it increases from almost zero over ZSM5 to about 0.7 over mordenite and 3.5 over Y zeolite (12). This may be due to the intrinsic selectivity of the catalytic sites but steric constraints to the bimolecular transition state of step 5 may also play an important role on ZSM5.

Over mordenite pentane cracking and isomerization are accompanied by some disproportionation into C_4 and C_6 products. With butanes this reaction is the only one that can be observed at low conversion (15). This is easily understandable since butane disproportionation involves secondary carbenium ions while its cracking or intramolecular isomerization necessarily involves primary cation (16). Disproportionation needing very strong acid sites (17), Y zeolite is less active than mordenite. Another explanation must be found for the inactivity of ZSM5. Probably the bimolecular C_8 intermediate cannot be formed inside the porous structure of ZSM5. On the other hand, disproportionation is certainly a "demanding reaction" (requiring several sites) so that the low density of acid sites in ZSM5 could explain its inactivity.

1.2.2. Isomerization and cracking of n-heptane over mechanical mixtures of platinum-alumina and zeolites (Y, mordenite, ZSM5).

The presence of the metallic component increases the carbocation formation ($P_x + C_x^+$) and isomer desorption ($C_x^{*+} + P_x'$) rates. On bifunctional catalysts, C_x^+ formation involves successively i) the alkane dehydrogenation on the metallic sites (reaction 6) ii) the migration of the intermediate olefins from the metallic to the acid sites and iii) the adsorption of olefins on Brönsted acid sites (step 7). The isomer desorption involves the reverse sequence.

As has been mentioned by other authors (18-20) in the case of heavier n-alkanes, cracking always follows isomerization: the cracking of linear carbocations (step 2) compared to their isomerization (step 3) and to the cracking of branched cations (step 4) is very slow. In accordance with this step-by-step pathway, it can be observed that the isomerization/cracking rate ratio (r_i/r_c) depends on the amount of platinum-alumina in the catalyst (i.e. on the residence time of the intermediate olefins on the zeolite). At low platinum-alumina contents the products result from a multistep

acid catalyzed reaction. This reaction leads to a total cracking of each individual molecule of dehydrogenated n-heptane : therefore, light products are largely predominant, r_c increases faster than r_T . At high platinum-alumina contents, the isocation cracking (step 4) now competes with its desorption to isheptanes ($C_7^+ \rightarrow P_7^+$) and r_T increases at the expense of r_c . r_T/r_c should in fact increase to a limit which would depend on the characteristics of the zeolite particles (size ; pore dimensions ; nature, strength and density of the acid sites).

Taking into consideration the above examples it can be concluded that the selectivity of the reactions on shape-selective materials depends on the frequently simultaneous influence of three well-known factors :

- a) own characteristics of the catalytic centers ;
- b) limitations to the diffusion of reactants and products ;
- c) steric constraints to the formation of transition states.

However, no evidence is found that diffusional limitations or steric constraints may lead to the formation of new intermediates.

2. Characterization of zeolites using model reactions.

The relationship between the structure of zeolites and their selectivity in a given reaction may be used to screen the best catalysts to characterize the porosity of synthetic or modified materials. The information that will be obtained will depend on the above factors. The ideal conditions for a good characterization of the porous structure are the following : i) factor a is known ; ii) the collected information concerns only one or other of factors b and c. Moreover in every case it is important that the influence of the external surface on the activity be known and if possible suppressed (21).

2.1. Diffusional limitations (factor b)

In order to limit the influence of steric constraints (factor c), reactions involving only monomolecular intermediates are recommended.

The relative reactivities of a series of organic compounds may be used. In this case the reactivity may vary according to the size of both the reactant and the products. Moreover as the reactants in one given series (alkanes, alcohols...) differ slightly, the reactivity can depend on the characteristics of the catalytic centers (factor a) which may change from one zeolite to the other.

One reactant undergoing competitive reactions can also be used. In this case, the selectivity depends only on the size of the products and a more precise determination of pore aperture can thus be obtained. Moreover, if the competitive reactions involved proceed through the same mechanism (as is the case for m-xylene isomerization) the influence of factor a can be considered as negligible.

Reactions involving consecutive steps (e.g. o-xylene isomerization) are not well adapted to the characterization of the porous structure of zeolites because their selectivity depends not only on pore size but also on the density and activity of acid centers.

2.2. Steric constraints in the neighbourhood of the active centers (factor c)

Reactions for which diffusional limitations (factor b) can be neglected must be chosen. Those involving bimolecular transition states are particularly well suited since the molecules of both the reactants and the products are generally much smaller than the transition states. However, even in this case the effect of factor b cannot always be excluded (see 1.2.1. constraint index).

In practice the inhibition to the transition state formation can be measured by comparing the rates of the bimolecular reaction and of another reaction without steric constraints.

To be free of the influence of factor a, it is convenient to choose a reactant offering the possibility of several competitive transformations through the same mechanism (e.g. formation of isomers) with one acting as the "shape sensitive" reaction and the other as reference. The disproportionation of m-xylene into 1,2,3- , 1,2,4- and 1,3,5-trimethylbenzenes offers such a possibility inasmuch as the formation of 1,3,5-trimethylbenzene suffers the intervention of a bulkier intermediate than that of 1,2,3- and 1,2,4-trimethylbenzenes (22).

However, if the mechanisms of the "shape sensitive" reaction and of the reaction taken as reference are different (e.g. disproportionation and isomerization of aromatics), factor *a* becomes decisively important since the relative rates of transformation in the two directions may depend on the density and on the strength of the acid sites.

The differences in reactivities of reactants belonging to the same class of compounds can also be used (e.g. constraint index measurement). Again attention must be drawn to the fact that different reactants entail differences in reactivity which could be dependent on the acid strength of the zeolite.

It can be noticed finally that it is possible to characterize in one experiment factors *b* and *c* if the reactant undergoes several reactions whose selectivities depend for some only on factor *b*, for others only on factor *c*. Such is the case for *m*-xylene transformation (5) : the isomerization selectivity supplies information on pore size while the disproportionation/isomerization rate ratio as well as the distribution of the trimethylbenzenes supplies information on the space disposable in the neighbourhood of the active sites.

LITERATURE CITED

- (1) Poutsma, M.L., in *Zeolite Chemistry and Catalysis*, J.A. Rabo Ed., p. 437, ACS Monograph 171, American Chemical Society, Washington 1976.
- (2) Hanson, K.L. and Engel, A.J., *A.I. ChE Journal* **13**, 260 (1967).
- (3) Cortes, A. and Corma, A., *J. Catal.* **51**, 338 (1978).
- (4) Matsumoto, H., Take J.I. and YONEDA, Y., *J. Catal.* **11**, 211 (1968), *J. Catal.* **19**, 113 (1970).
- (5) Gnep, N.S., Tejada, J., Guisnet, M., *Bull. Soc. Chim.* **5** (1982).
- (6) Young, L.B., Butter, S.A. and Kaeding, W.W., *J. Catal.* **76**, 418 (1982).
- (7) Gnep, N.S. and Guisnet, M., *Appl. Catal.* **1**, 329 (1981).
- (8) Ratnasamy, P., Sivasankar, S. and Vishnoi, S., *J. Catal.* **69**, 428 (1981).
- (9) Tejada, J., Gnep, N.S., Guisnet, M., to be published.
- (10) Pukanic, G.W. and Massoth, F.E., *J. Catal.* **28**, 304 (1973).
- (11) Frilette, V.J., Haag, W.O., Lago, R.M., *J. Catal.* **67**, 218 (1981).
- (12) Hilaireau, P., Bourdillon, G., Perot, G., Guisnet, M., to be published.
- (13) Weisz, P.B., in *Proc. 7th Intern. Congr. Catalysis, Tokyo (1980)* ; Plenary Lectures, Preprint Pl.
- (14) Haag, W.O., Lago, R.M. and Weisz, P.B., *Faraday Discussions of the Chemical Society* **72**, 317 (1981).
- (15) Guisnet, M., Gnep, N.S., Bearez, C. and Chevalier, F., in "*Catalysis by Zeolites*" (B. Imelik et al Eds) Elsevier Scientific Publishing Company, Amsterdam 77 (1980).
- (16) Hilaireau, P., Bearez, C., Chevalier, F., Perot, G. and Guisnet, M., *Zeolites* **2**, 69 (1982).
- (17) Bearez, C., Chevalier, F., Guisnet, M., to be published.
- (18) Steinjs, M., Froment, G.F., Jacobs, P.A., Uytterhoeven, J.B., Weitkamp, J., Erdöl, Kohle, Erdgas, Petrochem. **31**, 581 (1978).
- (19) Steinjs, M. and Froment, G.F., Jacobs, P. and Uytterhoeven, J.B., Weitkamp, J., *Ind. Eng. Chem. Prod. Res. Dev.* **20**, 654 (1981).
- (20) Steinjs, M. and Froment, G.F., *Ind. Eng. Chem. Prod. Res. Dev.* **20**, 660 (1981).
- (21) Kibby, C.L., Perrotta, A.J. and Massoth, F.E., *J. Catal.* **35**, 256 (1974).
- (22) Csicsery, S.M., in *Zeolite Chemistry and Catalysis*, J.A. Rabo Ed., p. 680, ACS Monograph 171, American Chemical Society, Washington 1976.