

Coking, Aging, and Regeneration of Zeolites

II. Deactivation of HY Zeolite during *n*-Heptane Cracking¹

P. MAGNOUX, P. CARTRAUD, S. MIGNARD, AND M. GUISET²

Laboratoire de Catalyse en Chimie Organique, UA CNRS 350, Université de Poitiers, 40 avenue du Recteur Pineau, 86022 Poitiers Cedex, France

Received July 21, 1986; revised January 26, 1987

Heavy carbonaceous compounds (coke) are deposited very rapidly during *n*-heptane cracking on a stabilized HY zeolite at 450°C, decreasing its activity, modifying its selectivity and its adsorption properties. Deactivation of the zeolite can be explained mainly by partial or total blocking of access to the active centers, even for low coke content. Indeed, while the decrease of the pore volume accessible to *n*-hexane (hence to the reactant *n*-heptane) is about 3 times less than the decrease of the activity, calorimetric study of NH₃ adsorption shows that the sites which no longer adsorb NH₃ are the strongest. Moreover, the diffusivity of *n*-hexane in the pore volume which remains accessible is definitely smaller than in the coke-free zeolite. Finally, the pore volume which has become inaccessible to *n*-hexane is, even at low coke content, about three times smaller than the volume really occupied by coke (estimated from its density). This deactivation through pore blockage is due to the fact that, even at low coke content, the coke molecules are sufficiently large to prevent access of the reactant to the supercages of the zeolite. © 1987 Academic Press Inc.

INTRODUCTION

Deactivation of acid zeolites is mainly due to the formation of carbonaceous products ("coke"), which occurs during all transformations of organic compounds. It has been proved that coking is a shape-selective process: indeed, the rate (1, 2) and the selectivity (2-4) are essentially determined by the zeolite pore structure. Thus the coke formation rate is from 50 (1) to 1000 (2) times lower on the small or intermediate pore-size zeolites than on those with large pores; the coke composition depends mainly on the space available for its formation (2): coke will be polyaromatic and very heavy if the reactions leading to its formation are not limited by steric constraints (e.g., in the supercages of Y zeolites), whereas it will be less aromatic and lighter in the opposite case (e.g., in ZSM-5).

The aging rate of zeolites is also determined by their pore structure (5-7). This

has been shown notably by the works of Dejaifve *et al.* (6) and of Guisnet *et al.* (2, 7). As is the case with all porous catalysts (8, 9), deactivation can occur in two ways, namely, site coverage (active sites poisoned by coke adsorption) or pore blockage (active sites inaccessible to reactants). However, with zeolites, since their pore sizes are close to those of organic molecules, pore blockage will be more likely than with amorphous catalysts. This is why the type of circulation of the molecules of the reactant is one of the most significant parameters of zeolite deactivation, the sensitivity of a reaction to coking being greater with monodimensional than with three-dimensional circulation (2, 5, 7). Indeed, with the former, blockage of a channel obstructs the access to numerous active sites, whereas with the latter the sites remain accessible by other paths.

We have recently undertaken a detailed study of coking, aging, and regeneration of protonic zeolites. The first investigations focused on the detailed analysis of carbonaceous compounds formed during *n*-heptane cracking on various zeolites at

¹ Part I of this series is Ref. (2).

² To whom correspondence should be addressed.

450°C (2, 10). The effect of coke on the activity of these zeolites is being studied with the aim of specifying the significance of the two ways of deactivation (pore blockage and site coverage). The distinction between these two ways is not easy and various techniques must be employed (5). This is the case here with HY, the effect of coke being determined not only on the rate and on the selectivity of *n*-heptane cracking but also on the adsorption of various molecules (nitrogen, *n*-hexane, and ammonia).

EXPERIMENTAL

HY (Na_{0.8}H_{47.7}Al_{48.5}Si_{143.5}O₃₈₄) was obtained by calcination at 500°C under a 10-h dry-air flow of an ultrastable NH₄ zeolite (LZY82 from Union Carbide). Coke formation was studied during the transformation of *n*-heptane carried out in a flow reactor under the following conditions: *T* = 450°C, *p*_{N₂} = 0.7 × 10⁵ Pa, *p*_{*n*-heptane} = 0.3 × 10⁵ Pa, 25.6 g of *n*-heptane injected per gram of catalyst per hour.

Adsorption isotherms of nitrogen at 77 K and of *n*-hexane at 273 K were determined by microgravimetry. For calculating the volume of the adsorbed phase its density was taken as the liquid phase density at the adsorption temperature.

The diffusion coefficients (*D*) of *n*-hexane were determined at 273 K using the following equation obtained from Fick's law for a sufficiently long time *t* (11, 12):

$$\ln \left(1 - \frac{M_t}{M_\infty} \right) = \ln \frac{6}{\pi^2} - \pi^2 \left(\frac{D}{r_0^2} \right) t$$

where *M_t* and *M_∞* are the masses adsorbed at times *t* and ∞ and *r₀* is the average size of the crystallites.

The adsorption of NH₃ was studied at 416 K, the samples having been pretreated under vacuum (10⁻⁴–10⁻³ Pa) at 723 K. NH₃ was introduced in small amounts, the amount adsorbed being measured with a pressure gauge and the amount of heat liberated with a flowmeter-type calorimeter (13).

RESULTS

1. *n*-Heptane Transformation

Cracking is practically the only reaction observed. The activity of the zeolite (*a*) decreases with *t* (reaction time) in agreement with the equation given by Voorhies (14):

$$a = At^{-n} \quad (1)$$

where *n* equals 0.6. The initial activity (*a*₀) drawn from Eq. (1) for *t* equal to 1 min or obtained by extrapolation of the curve which gives *a* against *t*, is equal to about 0.11 mol h⁻¹ g⁻¹. After a 6-h reaction, *a* is roughly 20 times smaller.

Whatever the value of *t*, the cracking products are constituted essentially by C₃ and C₄ (80–90 wt%), with a little C₁–C₂ (2–3 wt%) and C₅–C₆ (10–12 wt%). The molar ratio C₄/C₃, initially equal to 1, decreases with *t* (0.9 after 6 h). The branching degree of C₄, C₅, and C₆ also decreases with *t*; e.g., the iso-C₄/*n*-C₄ ratio varies from 2.8 at *t* = 0 to 1.4 at *t* = 6 h. On the contrary, the olefin/alkane molar ratio increases from 0.2 to 0.9.

The rate of coke formation at the start is very fast, and only 4 times smaller than the cracking rate. As with the cracking rate, it

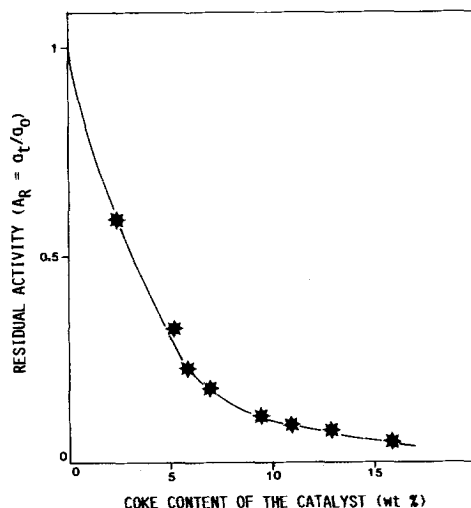


FIG. 1. Change in the residual activity *A_R* of HY zeolite vs the coke percentage.

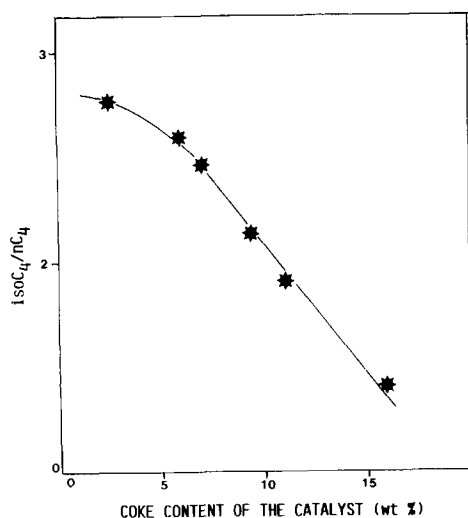


FIG. 2. Change in the ratio iso-C₄/n-C₄ versus the percentage of coke deposited on HY zeolite.

decreases with t in agreement with Voorhies' equation, the decrease being however more pronounced ($n = 1.1$).

Figure 1 shows the change, with the coke content, of the residual activity of the zeolite A_R ($A_R = a_t/a_0$, where a_t is the activity at time t and a_0 the initial activity), and Fig. 2 shows that of the molar ratio iso-C₄/n-C₄.

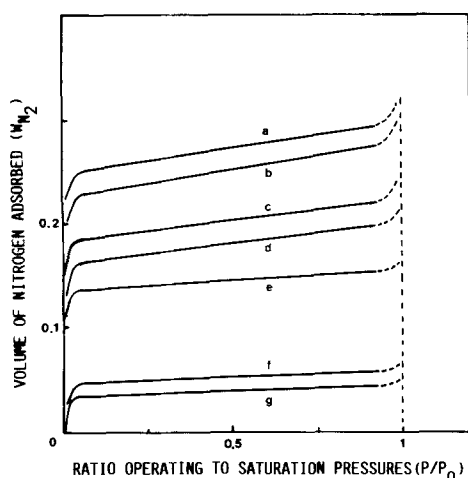


FIG. 3. Volume of nitrogen adsorbed per gram of zeolite at 77 K: W_{N_2} (cm³/g) vs the ratio of the operating pressure P to the saturation pressure P_0 for the following percentages of coke: (a) 0%, (b) 1%, (c) 5%, (d) 6.5%, (e) 9%, (f) 15.5%, (g) 16%.

2. Adsorption Capacity of the Zeolite for Nitrogen and *n*-Hexane

Figure 3 shows the change of W , the volume of nitrogen adsorbed per gram of sample at 77 K, vs P/P_0 , the operating/saturation pressure ratio. There is a very strong increase for the low P/P_0 values; then W increases very slightly (in particular for strongly coked samples) and quasilinearly. The same can be observed for *n*-hexane adsorption. The adsorption capacities of the samples were determined by extrapolation of the quasilinear part of the curves to P/P_0 equal to 1. These capacities decrease when the coke content increases, the decrease being more pronounced with *n*-hexane than with nitrogen (Fig. 4).

3. Diffusivity of *n*-Hexane

With the coke-free zeolite, *n*-hexane diffusion occurs very rapidly and its rate cannot be measured. The coke deposit strongly reduces the diffusion rate. Thus, for 6.5% coke, the ratio D/r_0^2 (D , final diffusivity; r_0 , average size of the crystallites) becomes measurable (10^{-3} s^{-1}). For 16% coke, this ratio is even 25 times lower.

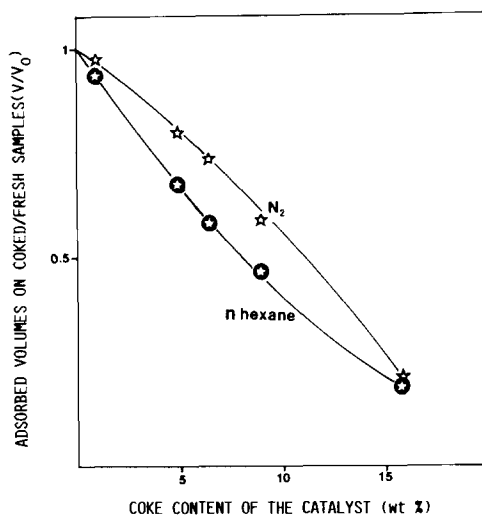


FIG. 4. Variation of the ratio of the adsorbed volumes on the coked sample and the fresh sample (V/V_0) with the coke content.

4. Ammonia Adsorption: Number and Strength of the Acid Sites

Figure 5 shows that the coke deposit reduces the number and the strength of the adsorption sites. The strongest sites are the ones which disappear first, the weak sites or those of average strength being practically unaffected; thus for 16% coke, there remain no more sites on which the adsorption heat is over 115 kJ mol^{-1} , whereas there were 1.2 to 1.5×10^{20} sites per gram (about 3/unit cell) on the coke-free zeolite; the weakest sites (23.5×10^{20} sites/g) are practically unaffected, since below 115 kJ mol^{-1} the changes of the adsorption heat against the number of NH_3 molecules adsorbed are more or less identical for the coked and the noncoked samples.

DISCUSSION

The discussion will be based on the results reported in two previous papers (2, 10) giving the detailed composition of the carbonaceous compounds ("coke") deposited on HY zeolite in the same operating conditions. Some of these compounds, mainly polyaromatic, are soluble in CH_2Cl_2 (light polyaromatics with 3 to 7 rings carrying some small alkyl groups) and some

insoluble (heavy polyaromatics with more than 7 rings). The degree of aromaticity of the coke and therefore its content in insoluble compounds increases with reaction time (or with the coke content); thus after a 2-min reaction (2.5% coke), all the coke is soluble, whereas after a 6-h reaction (16% coke) only 15% remains soluble.

It can be seen (Figs. 1 and 4) that the decrease in activity is much more pronounced than that of the adsorption capacity: a 1% coke deposit suppresses 15% of the activity but only 6% of the pore volume accessible to *n*-hexane, a compound having the same size as *n*-heptane. This could mean that deactivation occurs at least partially by site coverage. However, the calorimetric study shows that only the strongest acid sites (Lewis and Brønsted, these latter being the only active ones) no longer adsorb NH_3 (Fig. 5). The blockage of the access to the Brønsted sites, which are very strong and hence very active, can explain why the decrease in activity is greater than that of the adsorption capacity. Moreover, the more pronounced decrease of the activity is also partly due to the greater difficulty which the reactants have to reach the accessible acid sites; indeed, the diffusion rate in the pores which remain accessible is much lower than in the coke-free zeolite and therefore *n*-heptane cracking could be limited by the diffusion phenomena. In agreement with this, it can be noted that certain selectivities change from the value found for large pore-size zeolites to that found for zeolites with smaller pores (15); thus the iso- $\text{C}_4/\text{n-C}_4$ ratio decreases and the C_4/C_3 molar ratio becomes lower than 1 as a result of the difficulty of desorption of iso- C_4 formed by *n*-heptane cracking. Coke therefore affects the circulation of the reactant and of the products in the porous network in two ways: the larger molecules of coke completely prevent access to one part of the pore structure, whereas the smaller ones obstruct without preventing access to the other part. The relative significance of

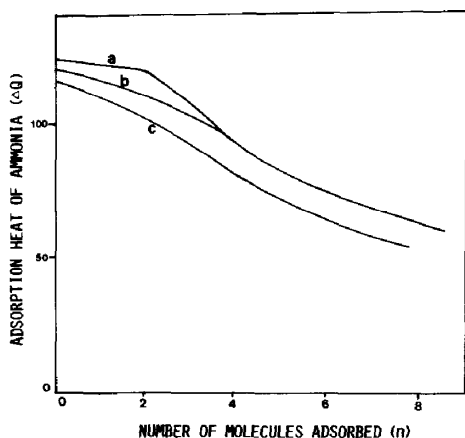


FIG. 5. Adsorption heat of ammonia (ΔQ , kJ mol^{-1}) as a function of the number of molecules adsorbed ($n \times 10^{20}/\text{g}$) on samples (a) without coke, (b) with 6.5% coke, and (c) with 16% coke.

these two parts depends on the size of the molecules used as adsorbents or as reactants: thus the coke deposit causes a decrease of the accessible pore volume which is twice greater for *n*-hexane (kinetic diameter 4.3 Å) than for nitrogen (kinetic diameter 3.6 Å).

The comparison between ρ_A and ρ_R (apparent and real densities) shows that only a small part of the pore volume inaccessible to *n*-hexane is occupied by coke (Fig. 6). ρ_A is the weight of coke measured per cm³ of the inaccessible pore volume. ρ_R is the density of coke estimated from the densities of its components. We have assumed the density of the insoluble part of the coke to be that of graphite, viz., 2.2 g/cm³, and that of the soluble part, which contains polyaromatic compounds such as pyrene ($\rho = 1.27$ g/cm³) and coronene ($\rho = 1.38$ g/cm³), to be 1.3 g/cm³. Taking into account the yields of solubilization, ρ_R of the coke increases from 1.3 g/cm³ after 2 min to 2.05 g/cm³ after 6 h.

ρ_A/ρ_R , ρ_A being determined for *n*-hexane, is much lower than 1 even for small coke contents: it equals 0.4 for 1% coke which means that only 40% of the volume inaccessible to *n*-hexane (and hence to *n*-heptane) is occupied by coke. This is not

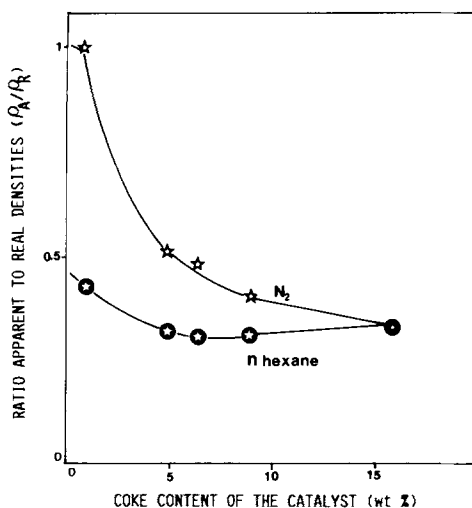


FIG. 6. Change of the ratio of the apparent (ρ_A) and real (ρ_R) densities as a function of the coke content.

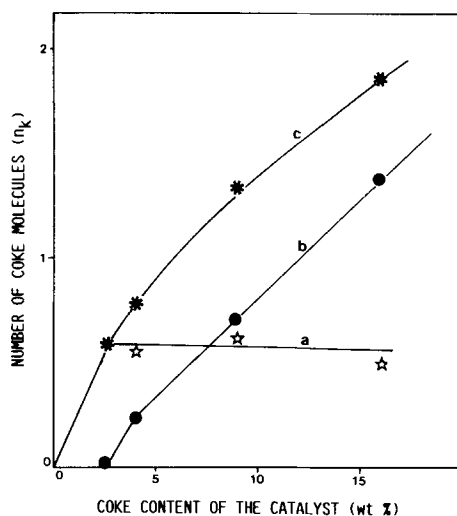


FIG. 7. Number of molecules ($n_k \times 10^{20}/g$) in the coke deposited on HY zeolite (a) in the soluble part, (b) in the insoluble part, (c) total number.

surprising since the coke molecules already have an average of 5 aromatic rings and their bulk can therefore reach about $8 \text{ \AA} \times 12 \text{ \AA} \times 3 \text{ \AA}$. ρ_A/ρ_R decreases slightly with the coke content. With nitrogen, ρ_A/ρ_R at low coke contents is close to 1 which means that all the inaccessible volume is hence occupied by coke; the value of this ratio decreases with the coke content and becomes for 16% coke equal to that found for *n*-hexane.

It is interesting to establish a comparison between the number of coke molecules and the number of zeolite supercages. The number of coke molecules can be estimated from the composition of the coke. While the estimation is relatively precise in the case of the soluble fractions, the same does not apply to the insoluble fractions. Their H/C atomic ratio is first determined from the relative significance of the soluble and insoluble fractions as well as from the H/C of all the coke and of its soluble part. The approximate number of aromatic rings which the compounds of the insoluble fractions present are then deduced and consequently the average molar weight of these compounds. The number of molecules is then obtained from the insoluble coke con-

tent. Figure 7 presents the total number of coke molecules per gram of catalyst as a function of the coke content estimated in this way. It can be noticed that the total number remains always below the number of the Y zeolite supercages ($4.2 \times 10^{20}/\text{g}$); thus for 16% coke, it is 2.5 times lower. Moreover, if the decrease of the pore volume accessible to *n*-hexane and the coke molecules/supercages ratio are compared the conclusion is that for low contents one molecule can block one supercage, whereas at high coke content it blocks two (Fig. 8). This is quite in agreement with the chemical formulas found for these molecules (2, 10): all the soluble coke molecules can be contained in one supercage, whereas those of nonsoluble coke require at least two.

There are many more coke molecules than there are sites which have become incapable of adsorbing NH_3 (Fig. 9), actually 5 times more at very low and twice more at very high coke contents. This is quite normal since the very basic NH_3 molecule is capable of replacing polyaromatic molecules. The calorimetric study therefore allows the determination of only the number and the strength of the sites

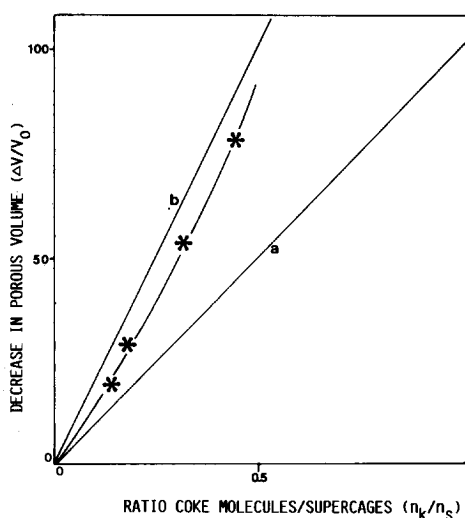


FIG. 8. Decrease in the porous volume accessible to *n*-hexane ($\Delta V/V_0$) vs ratio of number of coke molecules to number of supercages (n_k/n_s): (a) $\Delta V/V_0/n_k/n_s = 1$; (b) $\Delta V/V_0/n_k/n_s = 2$.

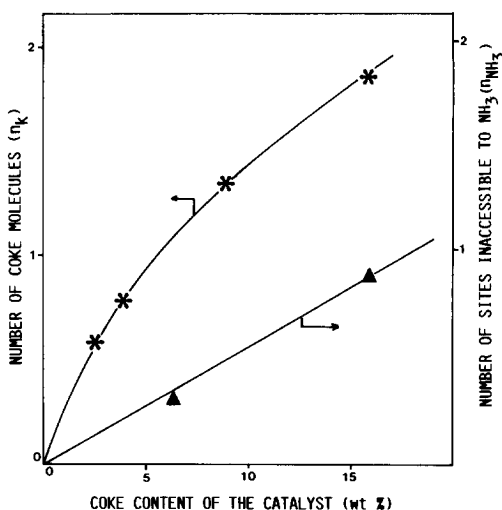


FIG. 9. Total number of coke molecules ($n_k \times 10^{20}/\text{g}$) and number of sites inaccessible to NH_3 ($n_{\text{NH}_3} \times 10^{20}/\text{g}$) as a function of the coke content.

which have become inaccessible to NH_3 . These are the strongest sites, which means that the coke molecules are situated close by and hence were probably formed on these sites. The percentage of acid sites not accessible to NH_3 is very low, namely, 1.5% of all the acid sites and 10% of the strong acid sites (on which the adsorption heat of NH_3 is greater than 100 kJ mol^{-1}) for 6.5% coke. For 16% coke the respective figures are 4 and 30%. This can be explained by the small size of the NH_3 molecule (kinetic diameter 2.6 \AA) which can penetrate the pore network where nitrogen (3.4 \AA) or *n*-hexane (4.3 \AA) cannot do so.

CONCLUSION

During the cracking of *n*-heptane on HY zeolite, polyaromatic molecules are rapidly formed near the strongest acid sites, causing their deactivation because:

(i) The small molecules limit access to acid sites without completely obstructing them.

(ii) The largest molecules (more than 4–6 aromatic rings) totally prevent access of the reactant to the acid sites. Even at low coke content (1%) the decrease of the volume

accessible to the reactant is about 3 times greater than the volume of the coke deposit. The molecules which have less than 8 aromatic rings generally occupy one supercage, whereas the larger molecules formed at high content occupy two supercages.

REFERENCES

1. Rollmann, L. D., and Walsh, D. E., *J. Catal.* **56**, 139 (1979).
2. Guisnet, M., Magnoux, P., and Canaff, C., in "Chemical Reactions in Organic and Inorganic Constrained Systems" (R. Setton, Ed.), NATO Series C 165, p. 131. Reidel, Dordrecht, 1986.
3. Rollmann, L. D., and Walsh, D. E., in "Progress in Catalyst Deactivation" (J. L. Figueiredo, Ed.), NATO ASI Series E, No. 54, p. 81. Nijhoff, The Hague, 1982.
4. Derouane, E. G., Gilson, J. P., and Nagy, J. B., *Zeolites* **2**, 42 (1982).
5. Derouane, E. G., in "Catalysis by Acids and Bases" (B. Imelik *et al.*, Eds.), Studies in Surface Science and Catalysis, Vol. 20, p. 221. Elsevier, Amsterdam, 1985.
6. Dejaifve, P., Auroux, A., Gravelle, P. C., Vedrine, J. C., Gabelica, Z., and Derouane, E. G., *J. Catal.* **70**, 123 (1981).
7. Guisnet, M., Bourdillon, G., and Gueguen, C., *Zeolites* **84** (1984).
8. Beekman, J. W., and Froment, G. F., *Ind. Eng. Chem. Fund.* **18**, 245 (1979).
9. Beekman, J. W., and Froment, G. F., *Chem. Eng. Sci.* **35**, 805 (1980).
10. Guisnet, M., Magnoux, P., and Canaff, C., in "New Developments in Zeolite Science Technology", Proceedings, 7th International Zeolite Conference (Y. Murakami, A. Iijima, and J. W. Ward, Eds.), p. 701. Kodansha Ltd., Tokyo, 1986.
11. Ruthven, D. M., and Doetch, I. H., *J. Chem. Soc., Faraday Trans. I* **72**, 1043 (1976).
12. Wu, P., Debebe, A., and Ma, Y. M., *Zeolites* **3**, 118 (1983).
13. Cartraud, P., Cointot, A., Dufour, M., Gnep, N. S., Guisnet, M., Joly, G., and Tejada, J., *Appl. Catal.* **21**, 85 (1986).
14. Voorhies, A., *Ind. Eng. Chem.* **37**, 318 (1945).
15. Mirodatos C., and Barthomeuf, D., *J. Catal.* **93**, 246 (1983).