

## Coking, Aging, and Regeneration of Zeolites

### III. Comparison of the Deactivation Modes of H-Mordenite, HZSM-5, and HY during *n*-Heptane Cracking

P. MAGNOUX, P. CARTRAUD, S. MIGNARD, AND M. GUISET<sup>1</sup>

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

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The rates of deactivation by carbonaceous residues (coke) of HY, H-mordenite, and HZSM-5, which have similar initial activities in *n*-heptane cracking are quite different: HZSM-5 forms very little coke and is very stable, while HM deactivates much faster than HY. The deactivation mechanisms of these zeolites could be specified by comparing as a function of the coke content: (i) the cracking activity of these zeolites and their capacity for adsorption of *n*-hexane, (ii) the volume apparently and really occupied by coke, and (iii) the number of coke molecules and of sites on which NH<sub>3</sub> can no longer be adsorbed. On HY, polyaromatic molecules are very rapidly formed on the strongest acid sites, these molecules obstructing partially or completely the access of the reactant to the acid sites. On HZSM-5 deactivation is initially due to the "coverage" of the acid sites, located at channel intersections, by alkylaromatics with 1 or 2 rings; later on (above 3% coke content) polyaromatic molecules, formed on the external surface, block access to a part of the pore volume. On HM deactivation is due to pore blockage: even at very low coke contents (1% coke), coke can block the access of *n*-heptane to a pore volume 10 times greater than the volume really occupied by the coke. © 1987 Academic Press, Inc.

#### INTRODUCTION

We specified in part II (1) the mechanism of deactivation of HY zeolite caused by the coke deposited during *n*-heptane cracking at 450°C by comparing the changes of its activity and of its adsorption properties as functions of the amount and the composition of the coke. We study here the deactivation of proton-containing mordenite (HM), another large pore-size zeolite but with a monodimensional network, and of HZSM-5, an intermediate pore-size zeolite with a three-dimensional network. The results are compared with those obtained on HY.

#### EXPERIMENTAL

HY (Na<sub>0.8</sub>H<sub>47.7</sub>Al<sub>48.5</sub>Si<sub>143.5</sub>O<sub>384</sub>) and HM (Na<sub>0.5</sub>H<sub>5.2</sub>Al<sub>5.7</sub>Si<sub>42.3</sub>O<sub>96</sub>) were supplied by Union Carbide and by Norton, respectively. HZSM-5 (Na<sub>0.001</sub>H<sub>2.1</sub>Al<sub>2.1</sub>Si<sub>93.9</sub>O<sub>192</sub>)

was synthesized following Mobil patents (2). Before usage the samples were pretreated at 500°C under a dry air flow for 10 h.

The kinetic study of the coke formation was carried out in a dynamic fixed-bed reactor in the following conditions:  $T = 450^\circ\text{C}$ ,  $P_{\text{N}_2} = 0.7 \times 10^5 \text{ Pa}$ ,  $P_{n\text{-heptane}} = 0.3 \times 10^5 \text{ Pa}$ , 25.6 g *n*-heptane injected per gram of catalyst per hour.

The adsorption methods have been described previously (1). The samples used for the studies were coked either during the kinetic study or during the preparation of the samples used for the coke analysis (3).

#### RESULTS

##### 1. *n*-Heptane Transformation

On the three zeolites, cracking is the only reaction. The activity of HM decreases rapidly with the time *t* and becomes almost equal to zero after 30 min; the activity of HY decreases more slowly and that of

<sup>1</sup> To whom correspondence should be addressed.

TABLE 1

Initial Activities:  $a_0$  ( $10^{-3}$  mol *n*-Heptane Transformed into Cracking Products or into Coke  $\text{h}^{-1} \text{g}^{-1}$ ) of Various Zeolites and Deactivation Coefficients  $n$

Zeolite:	HY	HM	HZSM-5
Cracking			
$a_0$	110	165	55
$n$	0.6	1.4	0.05
Coke formation			
$a_0$	30	160	0.065
$n$	1.1	2.5	0.4

HZSM-5 extremely slowly. The values of  $a_0$  (activity  $a$  for  $t = 1$  min) and  $n$  obtained from the Voorhies equation (4),  $a = At^{-n}$ , are given in Table 1.

On all the zeolites, the cracking products are constituted essentially by  $C_3$  and  $C_4$ : 80–90% on HY and on HM, and 70–75% on HZSM-5. These hydrocarbons are accompanied by  $C_1$ – $C_2$  (2–3% on HY, 3–5% on HM, and 5–7% on HZSM-5) and by  $C_5$ – $C_6$  (10–12% on HY, 10–15% on HM, and 15–20% on HZSM-5). Whatever the value of  $t$ , the molar ratio  $C_4/C_3$  equals about 0.6 on HZSM-5 and 1 on HM. On HY, it is equal to 1 at the start and to 0.9 after 6 h. On HZSM-5,  $i$ - $C_4/n$ - $C_4$  is always equal to 0.55, whereas on HM and on HY it is greater, but decreases with  $t$  (from 2 to 1.5 for HM and from 2.8 to 1.4 for HY). On all the zeolites the molar ratio olefin/alkane, after deactivation, is close to one, the initial value being 0.2 on HY, 0.25 on HM, and 0.8 on HZSM-5.

Coke formation, initially very rapid on HY and on HM, is very slow on HZSM-5. On all the zeolites, it decreases with  $t$  in agreement with the Voorhies equation.  $a_0$  ( $a$  for  $t = 1$  min) and  $n$  are given in Table 1. The deactivation is faster with coke formation than with cracking ( $n$  greater). Initially on HM the rate of coke formation is close to that of cracking; on HY, it is 4 times slower and on HZSM-5 nearly 1000 times slower.

Figure 1 shows the change of the residual activity of the zeolites ( $A_R = a_t/a_0$ , where  $a_t$  is the activity at time  $t$  and  $a_0$  the initial activity) as a function of the coke content. It can be noticed that on HY and on HM the poisoning effect of the coke decreases with coke content in contrast to what can be observed on HZSM-5: for this zeolite, at least up to 7% coke, the higher the coke content the more pronounced the decrease in activity.

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

Figure 2 gives the values of the adsorption capacities of the three zeolites. The values for coke-free HY and HZSM-5 are the same for nitrogen and for *n*-hexane, namely,  $0.29 \text{ cm}^3 \text{ g}^{-1}$  for HY and  $0.175 \text{ cm}^3 \text{ g}^{-1}$  for HZSM-5; in the case of HM, nitrogen occupies the whole of the pore volume (small and large channels,  $0.18 \text{ cm}^3 \text{ g}^{-1}$ ), *n*-hexane only penetrating the large channels ( $0.12 \text{ cm}^3 \text{ g}^{-1}$ ). For HZSM-5, coke reduces the pore volume accessible to nitrogen and that accessible to *n*-heptane in the same proportions; the effect of coke is more pronounced above 3–4% content. For HY the reduction of the pore volume is slightly more pronounced for *n*-hexane than for nitrogen. Lastly, with HM, the pore volume accessible to nitrogen decreases very little at first (up to 1.5% coke) then becomes more pronounced. For *n*-hexane,

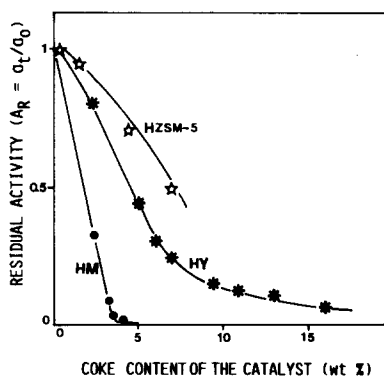


FIG. 1. Change in the residual activity ( $A_R$ ) of the zeolites vs their coke content.

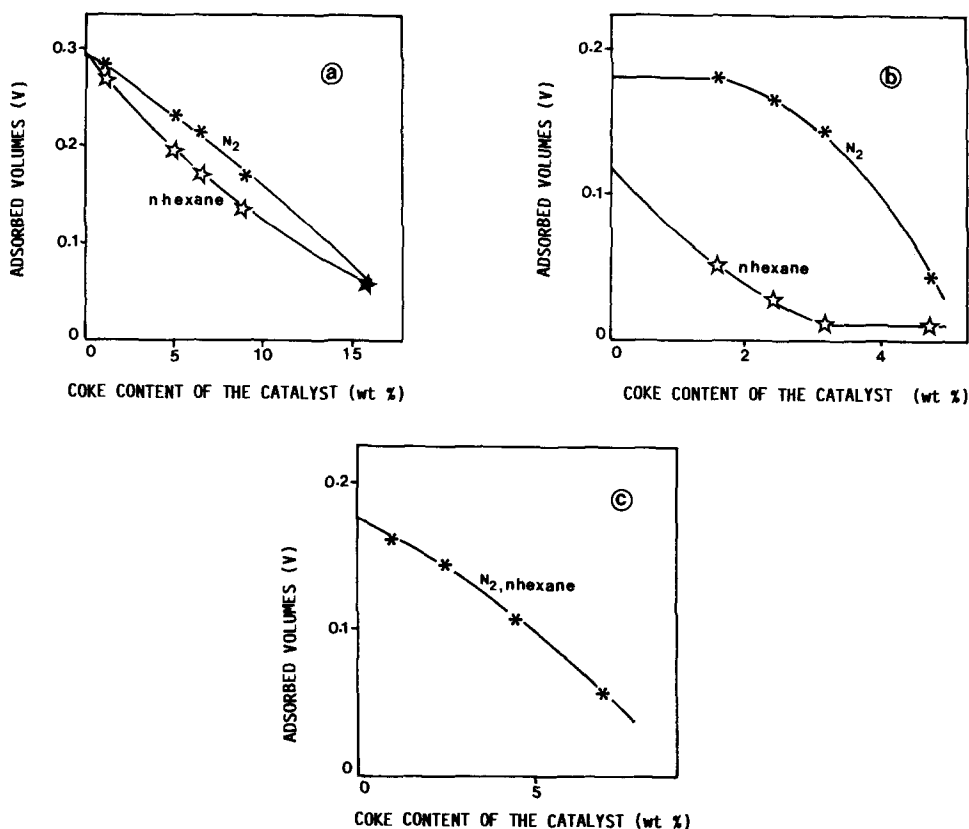


FIG. 2. Change of the adsorbed volumes ( $V$ ) against the coke content on (a) HY, (b) HM, and (c) HZSM-5.

the decrease is initially very pronounced but above 3% coke, the volume accessible remains practically constant (about 10% of the adsorption capacity of the coke-free zeolite).

### 3. Diffusivity of *n*-Hexane

Up to 2.5% coke the rate of *n*-hexane diffusion in HZSM-5 is not affected; beyond 2.5%, it decreases slightly: it is 4 times lower on the sample with 4.5% coke than on the coke-free zeolite. However with HM, the rate of *n*-hexane diffusion decreases greatly, even for low coke contents (10 times for 1.5% coke, 20 for 2.3% coke); above 3% coke, *n*-hexane diffuses very slowly in this zeolite. With HY (1), the effect of coke on the diffusion is between those found on the other two zeolites.

### 4. $NH_3$ Adsorption: Number and Strength of Acid Sites

With HY (1) and HM (Fig. 3) the coke deposit prevents ammonia from reaching the strongest acid sites: thus for HY a 10% coke deposit eliminates all those sites ( $1.2$  to  $1.5 \times 10^{20} \text{ g}^{-1}$ ) on which the adsorption heat is greater than  $115 \text{ kJ mol}^{-1}$ , the weaker sites being practically unaffected (1). On HM, 3% coke prevents ammonia adsorption on  $3 \times 10^{20}$  very strong sites  $\text{g}^{-1}$  (adsorption heat about  $140 \text{ kJ mol}^{-1}$ ) and 4.5% coke eliminates all those sites on which the adsorption heat is greater than  $130 \text{ kJ mol}^{-1}$  ( $4$  to  $6 \times 10^{20}$  sites  $\text{g}^{-1}$ ). In the case of HZSM-5, coke seems to have little effect up to 2.5% coke; for 4.5% coke a great part of the strong acid sites is eliminated:  $0.6 \times 10^{20}$  out of the  $0.9 \times 10^{20}$  sites

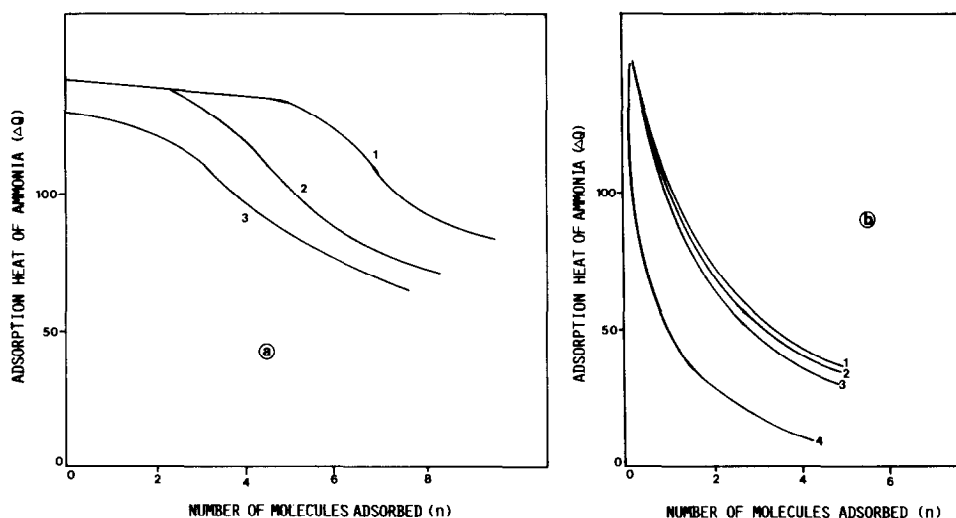


FIG. 3. Adsorption heat of ammonia ( $\Delta Q$ ,  $\text{kJ mol}^{-1}$ ) as a function of the number of molecules adsorbed ( $n \times 10^{20}/\text{g}$ ) on the samples. (a) HM, (1) without coke, (2) with 3% coke, (3) with 4.5% coke. (b) HZSM-5, (1) without coke, (2) with 1% coke, (3) with 2.5% coke, (4) with 4.5% coke.

$\text{g}^{-1}$  on which the adsorption heat is greater than  $100 \text{ kJ mol}^{-1}$ .

## DISCUSSION

### 1. Activity, Selectivity, and Acidity of the Three Zeolites

Initially, the cracking activity of HM is 1.5 times greater than that of HY and 3 times than that of HZSM-5. The same order is found for the formation of coke but the differences are more pronounced: HM is 5 times more active than HY and 2500 than HZSM-5. The differences in the cracking activities can be well explained by the differences in acidity: HM has  $7.5 \times 10^{20}$  sites  $\text{g}^{-1}$  on which the adsorption heat is greater than  $100 \text{ kJ mol}^{-1}$ , HY about twice less and HZSM-5 about 6 times less. On the average, these sites are stronger on HZSM-5 (average adsorption heat about  $145 \text{ kJ mol}^{-1}$ ) than on HM ( $135 \text{ kJ mol}^{-1}$ ) and on HY ( $120 \text{ kJ mol}^{-1}$ ). As far as the formation of coke is concerned, the greater strength and the higher number of HM acid sites can probably explain why it is more active than HY. On the other hand, the very low activity of HZSM-5 cannot be due entirely to

its acidity. Indeed, while the lower density of its acid sites is partly responsible for its reduced coking activity (5, 6), the steric constraints exerted by its porous network on the formation of the bulky intermediates of coking also play a significant role: the coking activity of a strongly dealuminated HY zeolite which presents a site density even lower is 10 times greater than that of HZSM-5 (7).

The product distributions on the three zeolites can be explained for the most part by the classical mechanism: formation of an  $n\text{-C}_7$  carbenium ion, isomerization, then scission into  $\text{C}_3$  and  $\text{C}_4$  fragments, secondary transformations of the olefinic products by alkylation, by hydrogen transfer, and so on (8, 9). However, the formation of  $\text{C}_1$  and  $\text{C}_2$  (very limited, except on HZSM-5) cannot be explained by this mechanism and most probably result from the scission of carbonium ions (10). On the two large-pore zeolites, the secondary transformations of olefins are very rapid and the olefin/alkane ratios are initially much smaller than 1, which is not the case on HZSM-5; this different behavior of HZSM-5 could be due to the steric constraints

exerted by its porous network on the formation of the very bulky (because bimolecular) intermediates involved in the olefin transformations. Moreover, on this zeolite, iso-C<sub>4</sub>/n-C<sub>4</sub> is lower and C<sub>4</sub>/C<sub>3</sub> is much lower than 1, which is most probably due to diffusional limitations affecting the transport of iso-C<sub>4</sub> (11). Since these compounds remain longer in the porous network of the zeolite the probability of their transformation will be greater than that of other molecules C<sub>3</sub> or C<sub>4</sub> (1).

## 2. Mode of Deactivation of the Zeolites

The aging rates of the zeolites are very different: for cracking HZSM-5 deactivates very slowly ( $n \approx 0.05$ ), whereas on the contrary HM loses rapidly nearly all its activity ( $n \approx 1.4$ ); HY shows an interme-

diante behavior. These differences are due partly to differences in the rates of coke formation but also to differences in the effect of coke on the cracking rate. Thus, at the start, the poisoning effect of coke is about 1.5 times greater on HY and 5–6 times on HM than on HZSM-5 (Fig. 1).

In order to specify the mode of deactivation (pore blockage or site coverage) we shall compare more particularly the following as a function of the coke content of the zeolites:

(a) their cracking activity and their capacity for adsorption of *n*-hexane, a molecule with a kinetic diameter similar to that of the reactant (Fig. 4);

(b) the volumes apparently and really occupied by coke (Fig. 5 and Ref. (1));

(c) the numbers of coke molecules and of

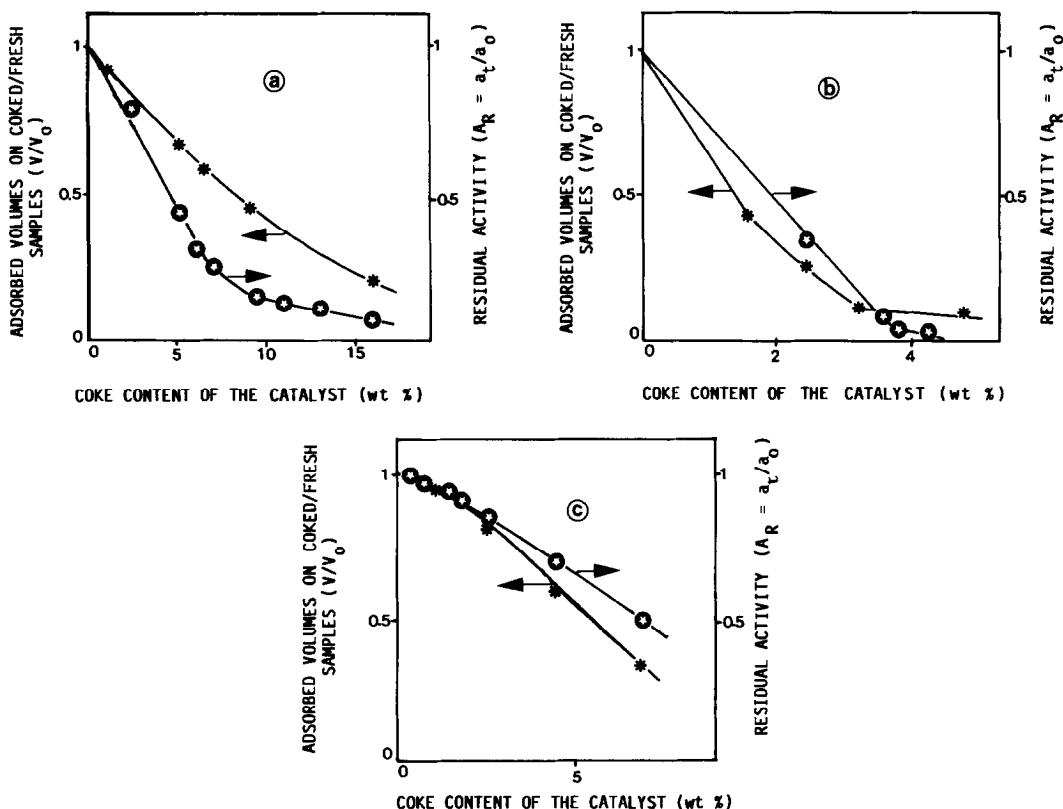


FIG. 4. Change against the coke content of the ratio of the adsorbed *n*-hexane volumes on the coked sample to the fresh sample ( $V/V_0$ ) and of the residual activity ( $A_R$ ). (a) HY, (b) H-mordenite, and (c) HZSM-5.

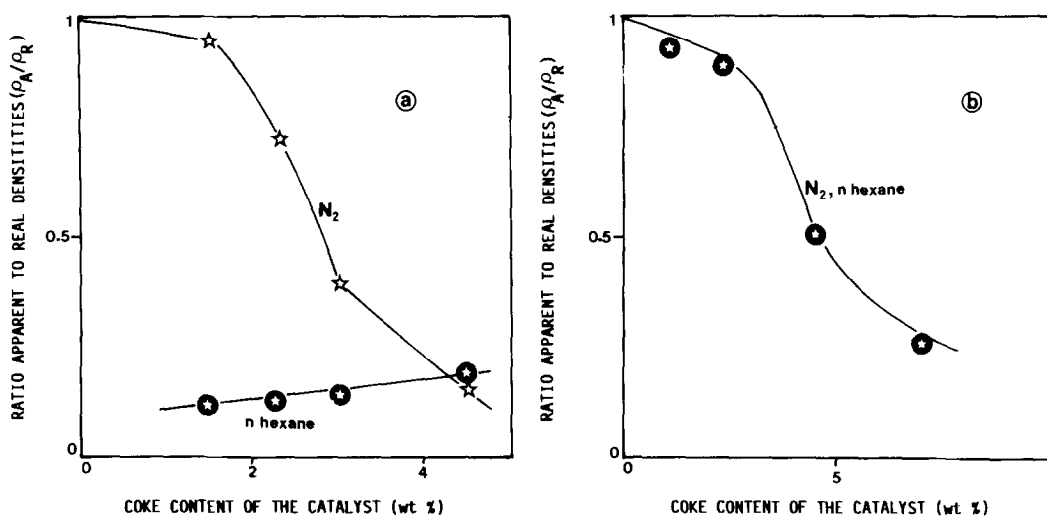


FIG. 5. Change of the ratio of the apparent ( $\rho_A$ ) and real ( $\rho_R$ ) densities as a function of the coke content.  $\rho_A/\rho_R$  is equal to the ratio of the volumes apparently and really occupied by coke. (a) H-mordenite and (b) HZSM-5.

sites on which  $NH_3$  can no longer be adsorbed (Fig. 6 and Ref. (1)).

For the estimation of the volume really occupied by coke and of the number of coke molecules, reference is made to part I of this series (3) giving the composition of coke deposited under the same conditions as above.

For HY it was possible to conclude previously (1) that (i) deactivation was due to a total obstruction of the access to part of the pores and a partial obstruction to the re-

mainder, (ii) the coke molecules are formed rapidly on the very strong acid sites. Figure 7 shows how the formation of the coke molecules and their deactivating effect could be conceived:

(a) Initially polyaromatics with alkyl groups are very rapidly formed on the strongest acid sites; as soon as they attain a certain size (more than 3 aromatic rings) their migration becomes very slow and these molecules obstruct the pore entry ( $\approx 8 \text{ \AA}$ ) of the supercages, limiting, or preven-

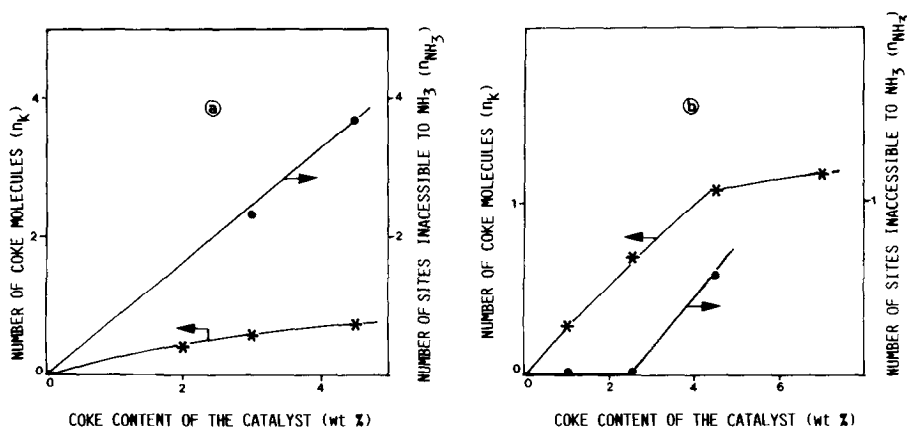


FIG. 6. Total number of coke molecules ( $n_k \times 10^{20}/g$ ) and number of sites inaccessible to  $NH_3$  ( $n_{NH_3} \times 10^{20}/g$ ) as a function of the coke content. (a) H-mordenite and (b) HZSM-5.

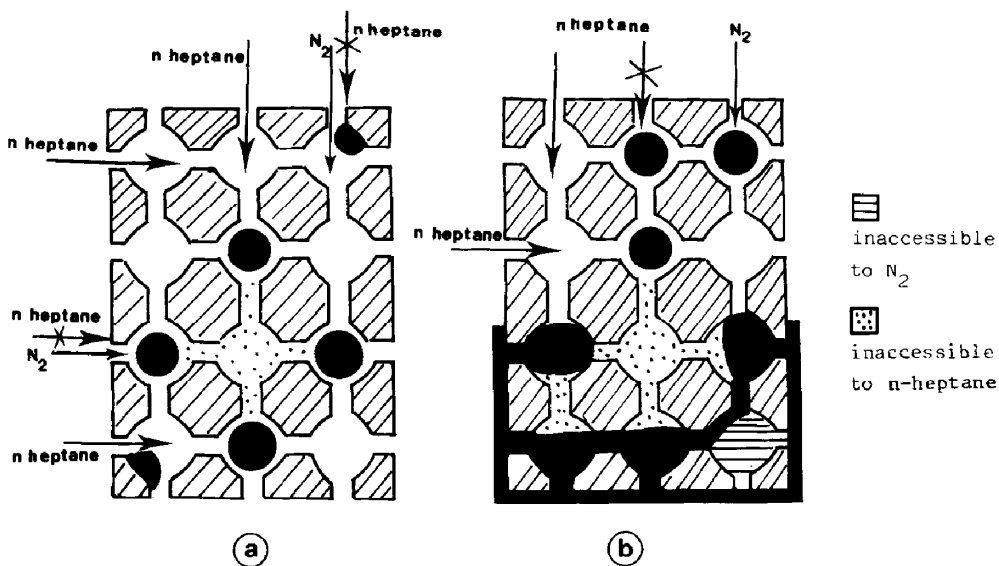


FIG. 7. Schematic representation of coke distribution in the HY zeolite for (a) low coke content and (b) high coke content.

ting the penetration of *n*-heptane (4.3 Å). The degree of obstruction depends not only on the size of the molecules but also on their location in the supercages (the actual location will depend on whether the molecule is adsorbed or not).

(b) Then the coke content increases very slowly. This increase is due not only to the formation of new coke molecules but also to the growth in size of the molecules already formed. Certain molecules can oc-

cupy several supercages and even spread over the outer surface; they obstruct the access to a great part of the pore volume not only of *n*-heptane but also of smaller molecules such as nitrogen or ammonia.

For HZSM-5 (Fig. 8) deactivation is initially due the "coverage" of acid sites located at channel intersections by alkylaromatics with 1 or 2 rings; later on, bulkier molecules (insoluble polyaromatics) formed extremely slowly either on the ex-

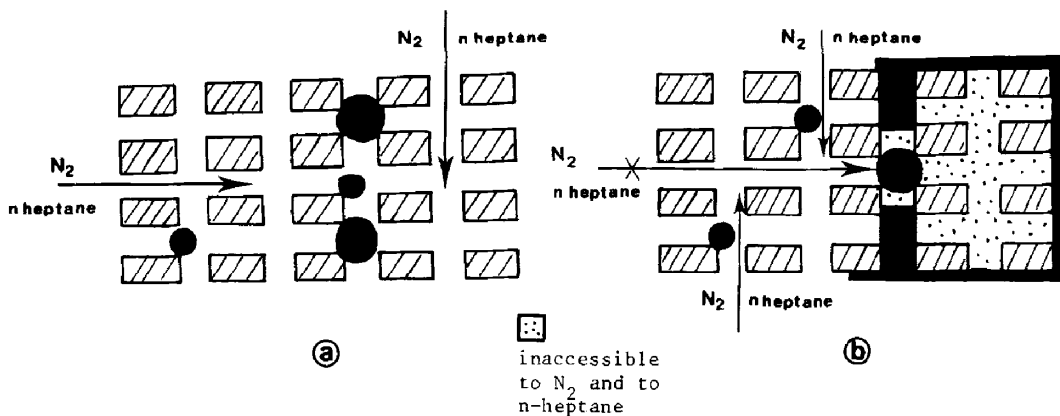


FIG. 8. Schematic representation of coke distribution in the HZSM-5 zeolite for (a) low content and (b) high coke content.

ternal acid sites or more likely by growth of the coke molecules located on the acid sites near the external surface, can obstruct the porosity (pore blockage). This formation of coke on the external surface has already been observed during the conversion of methanol into hydrocarbons (12–14). The change in the mode of deactivation is shown by the shape of the curves of adsorption capacity for *n*-hexane or activity as a function of coke content (Fig. 4c). By the first mode (site coverage) about 16% coke would be necessary to suppress the activity and the adsorption capacity, whereas by pore blockage (which becomes significant above 4% coke) 8% would be enough for all the volume to become inaccessible to *n*-hexane. At low coke contents the decrease in the adsorption capacities and in the activity are identical; the acid sites occupied by coke showed therefore the same activity and hence were probably of the same strength. This is easily understood if, as proposed elsewhere (15, 16), all the acid sites of HZSM-5 are equivalent. Beyond 3% coke, i.e., at the start of pore blockage, the activity decreases more slowly than the adsorption capacity; this can be explained if it is assumed that the coke molecules have a certain mobility at reaction temperature allowing the *n*-heptane to circulate more easily than at the temperature at which the *n*-hexane adsorption was studied.

$\rho_A/\rho_R$ , the ratio of apparent and real densities of coke, is between 0.8 and 0.9 for coke contents lower than 3%,  $\rho_A$  being the density of coke measured per cm<sup>3</sup> of the inaccessible pore volume and  $\rho_R$  the density estimated from its composition. Below 3% the volume occupied by coke is therefore only slightly lower than the volume made inaccessible to nitrogen or to *n*-hexane (Fig. 5b). This is quite in agreement with the location of the coke molecules at channel intersections. However, at higher coke contents,  $\rho_A/\rho_R$  is much lower than 1, which means that a significant part of the pore volume (until 70% for 7% coke) which is

not occupied by coke has become inaccessible to the adsorbates. The hypothesis of a pore blockage by coke deposit on the external surface of the crystallites is thus confirmed.

The information given by the calorimetric study of NH<sub>3</sub> adsorption agrees with the scheme of coking and aging of the ZSM-5 zeolite. It should be pointed out that this technique allows one to determine only the number and the strength of the acid sites which have become inaccessible to NH<sub>3</sub>. At low coke contents no change in the number and in the strength of sites adsorbing NH<sub>3</sub> can be observed (Figs. 3 and 6b). This small basic molecule continues therefore to be adsorbed on all the sites as could be predicted from the nature and the size of the coke molecules (3). However, at high coke contents a significant number of acid sites become inaccessible to NH<sub>3</sub> (Figs. 3 and 6b); thus from 2 to 4.5% coke, the number of sites which can no longer adsorb NH<sub>3</sub> is at least twice greater than the increase in the number of coke molecules, which proves the pore blockage.

With HM (Fig. 9) deactivation, as already noted by other authors (12, 13), is essentially due to pore blockage:

The decrease of the adsorption capacity is very pronounced: 3.5% coke is sufficient to eliminate 90% of the volume accessible to *n*-hexane and to suppress almost all the activity. Even at low coke contents the diffusivity of *n*-hexane is very much reduced. Whatever the coke content the number of sites made inaccessible to NH<sub>3</sub> is definitely greater (3–5 times) than the number of coke molecules (Fig. 6a).

$\rho_A/\rho_R$ ,  $\rho_A$  being determined for *n*-hexane, is always very small, namely, 0.12–0.20. This means that only 12–20% of the pore volume which has become inaccessible to *n*-hexane (hence to *n*-heptane) is occupied by coke, which is quite characteristic of a channel blockage. With nitrogen,  $\rho_A/\rho_R$  close to 1 at low coke contents decreases very rapidly and at 4.5% coke becomes



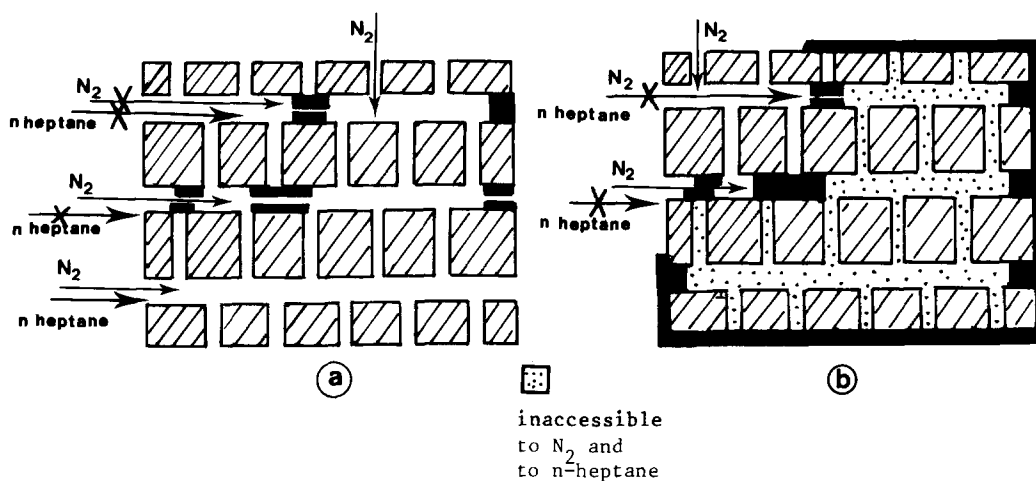


FIG. 9. Schematic representation of coke distribution in the H-mordenite zeolite for (a) low coke content and (b) high coke content.

equal to the value found for *n*-hexane (Fig. 5a). This can be easily understood since in the coke-free zeolite, the circulation of nitrogen occurs in all directions, whereas that of *n*-hexane is monodimensional; at low coke contents, nitrogen can pass through the narrow channels and attain all the volume which is not occupied by coke, in particular, the volume which has become inaccessible to *n*-hexane (Fig. 2b); at high contents part of the coke deposited on the external surface or at the entry to the narrow channels prevents the circulation of nitrogen through these channels.

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