

Coking, Aging, and Regeneration of Zeolites

IX. Location of Coke Formed on Hydrogen Offretite during *n*-Heptane Cracking: Mode of Deactivation

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Received June 7, 1988; revised January 23, 1989

Adsorption experiments were carried out on a series of hydrogen offretite (H-OFF) samples coked during *n*-heptane cracking at 450°C. Three adsorbates of different molecular size were chosen: nitrogen, *n*-hexane, and 3-methylpentane. The decrease, caused by coke, in the diffusion rate and in the pore volume accessible to these adsorbates allows confirmation of the location of coke deduced from its composition. At a low content (<1 wt%), coke has practically no effect on the volume of the pores (large channels) accessible to 3-methylpentane but causes a decrease in the pore volume accessible to *n*-hexane (large channels + gmelinite cages); therefore, coke is located in the gmelinite cages. With coke contents between 1 and 3.5 wt%, part of the coke is also located in the large channels since it limits or even blocks the access of *n*-hexane and, above all, of 3-methylpentane to part of the large channels. With a high content, coke blocks the access of all the adsorbates to the entire pore volume because it is deposited on the outer surface. Whatever the coke content the deactivation of H-OFF occurs through pore blockage. With a low content the small molecules located in the gmelinite cages occupy about 40% of the volume and block the access of *n*-heptane to their acid sites whereas with a high content the highly polyaromatic molecules located on the outer surface block the access of *n*-heptane to all the inner acid sites. © 1989

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INTRODUCTION

In a previous paper (1), the composition of the carbonaceous compounds ("coke") entrapped in hydrogen offretite (H-OFF) during *n*-heptane cracking was determined. The location of the main coke components was suggested by their molecular size and their volatility. Initially, small compounds such as isobutene and benzenics formed in the gmelinite cages remain blocked there. By condensation reactions with other compounds, they transform into polyaromatic molecules (with three or four rings). Because of their size, these molecules cannot be located entirely in the gmelinite cages and hence overflow into the large channels. Finally, highly polyaromatic molecules are

formed by the growth of the aromatic molecules located near the outer surface.

This location of coke will be confirmed here by adsorption experiments carried out on various samples of coked offretite. For this purpose, three adsorbates of different molecular size were used: (i) nitrogen, which can occupy the total void volume; (ii) *n*-hexane (a molecule with a kinetic diameter similar to that of the reactant, *n*-heptane), which can diffuse in the gmelinite cages and in the large channels; and (iii) 3-methylpentane, which can penetrate only the large channels (2). The amount adsorbed at equilibrium and the rate of adsorption were determined as a function of the coke content. Moreover, the comparison of the effect of coke on the adsorption properties and on the rate of *n*-heptane cracking will allow us to propose a mecha-

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nism for H-OFF deactivation as we have done for H-mordenite, H-ZSM5, and HY (3).

EXPERIMENTAL

Fresh offretite and eight coked samples (wt% equal to 0.8, 2.0, 3.5, 4.5, 6.0, 8.0, 8.6, and 10.0) were characterized by adsorption measurements. These samples were the samples used in Ref. (1) either for the kinetic study of coking or for the analysis of coke.

Adsorption isotherms of nitrogen at 77 K and of *n*-hexane and 3-methylpentane at 273 K were determined with a Sartorius 4433 electrobalance. The time constant of this balance is very short in comparison to the adsorption time. A small amount of each sample (<30 mg), hence a very small thickness of the zeolite layer, was used, which enabled us to avoid nonisothermicity and intercrystalline diffusion. Because of the relatively large volume of the apparatus, the adsorption pressure can be considered as constant. To calculate 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 in the gmelinite cages were determined at 273 K using the following equation obtained from Fick's law for a time *t* sufficiently long (4, 5),

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

where M_t and M_∞ are the masses adsorbed at times *t* and ∞ and r_0 is the equivalent radius of the crystallites. *n*-Hexane diffusion in the large channels being very rapid, this equation cannot be used for determining the diffusion coefficients. Hence the following equation proposed by Breck (6) for short times was used,

$$\frac{M_t}{M_\infty} = \frac{6}{\pi^{0.5}} \frac{1 + K}{K} \left(\frac{D}{r_0^2} \right)^{0.5} t^{0.5},$$

where *K* is the ratio of the adsorbate con-

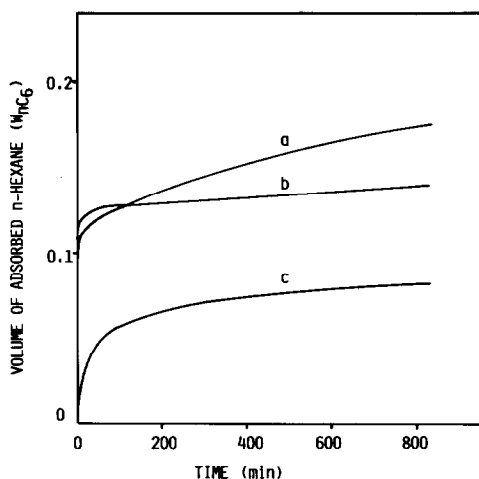


FIG. 1. Volume of *n*-hexane (nC_6) adsorbed per gram of zeolite at 273 K. W_{nC_6} (cm^3/g) at $P/P_0 = 0.1$ (P is the operating pressure and P_0 the saturation pressure) for the following percentages of coke: (a) 0%, (b) 0.8%, and (c) 3.5%.

centration in the gas phase to that in the crystals at equilibrium.

In the case of 3-methylpentane diffusion in the large channels of offretite, which occurs at an average rate, both the equations allowed the estimation of the diffusion coefficients.

RESULTS

The adsorption of nitrogen, *n*-hexane, and 3-methylpentane was studied on eight coked samples. The adsorption capacity was estimated for the three adsorbates. However, the kinetics was determined only for hydrocarbons since the rate of nitrogen diffusion is too high to be estimated.

1. Diffusion Kinetics of *n*-Hexane and of 3-Methylpentane

As examples, Figs. 1 and 2 show, for a P/P_0 value of 0.1 (P , operating pressure; P_0 , vapor pressure), the change in the pore volume W occupied by *n*-hexane and by 3-methylpentane as a function of time for the coke-free zeolite and for two coked samples. For the three samples, W increases rapidly during the first minutes and then

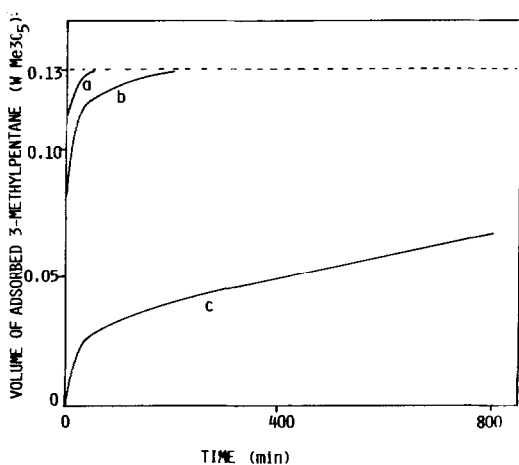


FIG. 2. Volume of 3-methylpentane (Me_3C_5) adsorbed per gram of zeolite at 273 K. $W_{\text{Me}_3\text{C}_5}$ (cm^3/g) at $P/P_0 = 0.1$ for the following percentages of coke: (a) 0%, (b) 0.8%, and (c) 3.5%.

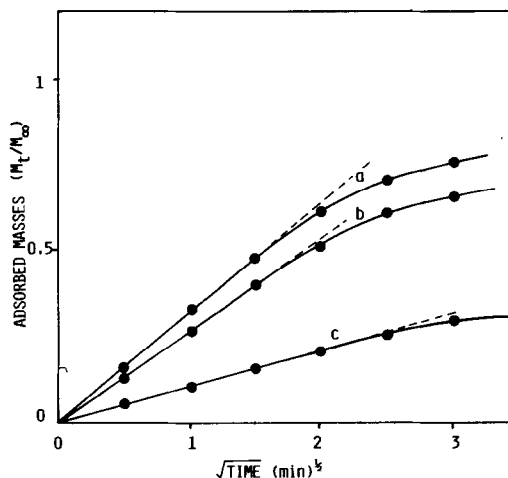


FIG. 3. Kinetics of *n*-hexane adsorption for short adsorption times at $P/P_0 = 0.1$ (P is the operating pressure and P_0 is the saturation pressure) for the following percentages of coke: (a) 0%, (b) 0.8%, and (c) 3.5%.

more slowly, a quasi-equilibrium being obtained after about 12 h. In the case of *n*-hexane adsorption (at least for the coke-free zeolite) the first part of the curves corresponds to the diffusion in the large channels and the other to the diffusion in the gmelinite cages. Figures 3 and 4 show that the experimental results are in good agreement with the equations proposed for the estimation of the diffusion coefficients D . This is also the case for 3-methylpentane diffusion whether the equation used be the one for short or for long reaction times; the

results obtained with the two equations are very similar (Table 1). Table 1 shows the decrease in the values of the diffusion coefficients when the coke content increases.

2. Adsorption Capacity for Nitrogen, *n*-Hexane, and 3-Methylpentane

Figures 5–7 show as a function of P/P_0 the change in the pore volume occupied at equilibrium (after 12 h) by the adsorbates. For all the samples the adsorption isotherms are of Type I in the Brunauer classification. The adsorption capacity W_1 was

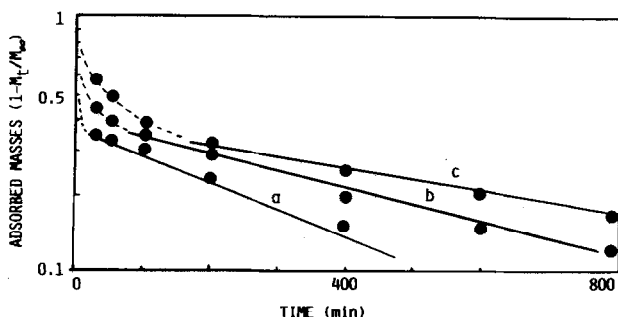


FIG. 4. Kinetics of *n*-hexane adsorption for long adsorption times at $P/P_0 = 0.1$ (P is the operating pressure and P_0 is the saturation pressure) for the following percentages of coke: (a) 0%, (b) 0.8%, and (c) 3.5%.

TABLE 1

Effect of Coke on the Diffusion Rates of *n*-Hexane and of 3-Methylpentane

Coke wt%	$D/r_0^2(10^{-6} \text{ s}^{-1})$		
	<i>n</i> -Hexane		3-Methylpentane
	Channels	Gmelinite cages	
0	150	4	85 ^a (70) ^b
0.8	100	2	50 (36)
3.5	14	1	1 (1.6)
4.5	5	<i>e</i>	<i>e</i>
8.6	1	—	—
10	<i>e</i>	—	—

Note. *a* and *b* from equations used with long and short diffusion times. *D*, diffusion coefficient; r_0 equivalent radius of the zeolite crystallites.

estimated by extrapolation at $P/P_0 = 1$ of the quasi-linear part of the isotherm. As has already been noted (7), nitrogen occupies the entire pore volume of the coke-free zeolite, *n*-hexane the large channels and the gmelinite cages, and 3-methylpentane the large channels only. The decrease of W_1

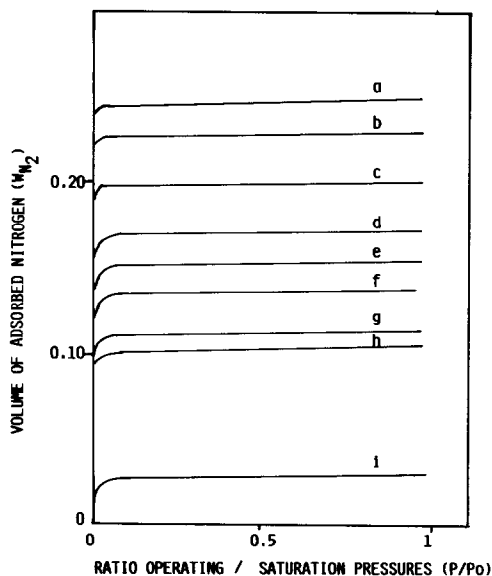


FIG. 5. Volume of nitrogen adsorbed per gram of zeolite at 77 K. W_{N_2} (cm^3/g) versus P/P_0 for the following percentages of coke: (a) 0%, (b) 0.8%, (c) 2%, (d) 3.5%, (e) 4.5%, (f) 6%, (g) 8%, (h) 8.6%, and (i) 10%.

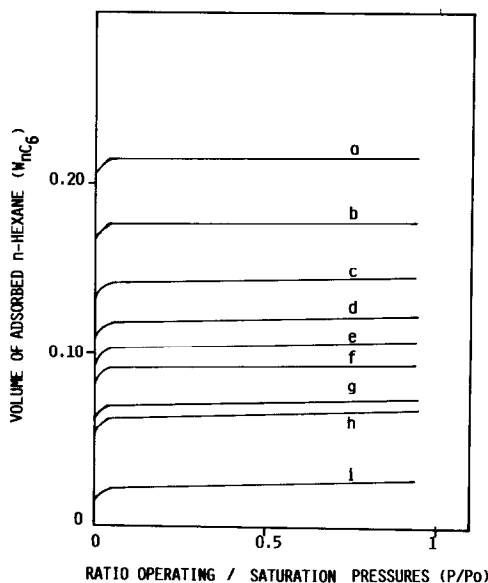


FIG. 6. Volume of *n*-hexane adsorbed per gram of zeolite at 273 K. W_{nC_6} (cm^3/g) versus P/P_0 for the following percentages of coke: (a) 0%, (b) 0.8%, (c) 2%, (d) 3.5%, (e) 4.5%, (f) 6%, (g) 8%, (h) 8.6%, and (i) 10%.

caused by coke depends on the adsorbate considered (Fig. 8). The values of W_1 for nitrogen and for *n*-hexane decrease in parallel and in a regular way until the coke content equals 8 wt%, above which the decrease is much more pronounced: the values of W_1 then are close to zero for about 10 wt% coke. With 3-methylpentane W_1 decreases very little for low coke content but then above 2 wt%, very strongly.

DISCUSSION

1. Location of the Coke Components

The change in the pore volume W_1 accessible to nitrogen, to *n*-hexane, and to 3-methylpentane confirms the hypotheses deduced from the composition of coke concerning its location (1):

—Initially the coke is located only in the gmelinite cages: indeed there is no decrease in W_1 for 3-methylpentane (i.e., the large channels) whereas with *n*-hexane (large channels + gmelinite cages) and with nitro-

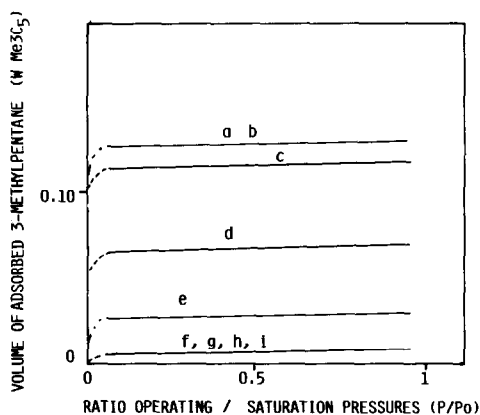


FIG. 7. Volume of 3-methylpentane adsorbed per gram of zeolite at 273 K. $W_{Me_3C_5}$ (cm^3/g) versus P/P_0 for the following percentages of coke: (a) 0%, (b) 0.8%, (c) 2%, (d) 3.5%, (e) 4.5%, (f) 6%, (g) 8%, (h) 8.6%, and (i) 10%.

gen (all the void volume) W_1 decreases significantly.

—For coke contents above 1 wt%, W_1 for 3-methylpentane begins to decrease. This shows that part of the coke is located in the large channels. Between 1 and 2 wt% this decrease is smaller than that for *n*-hexane but above 2 wt% it is much greater. Above

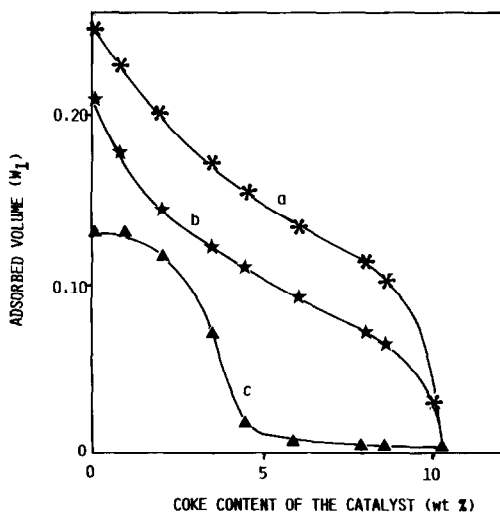


FIG. 8. Change of the volume adsorbed per gram of zeolite: W_1 (cm^3/g) as a function of the coke content for (a) N_2 at 77 K, (b) nC_6 at 273 K, and (c) Me_3C_5 at 273 K.

this coke content, *n*-hexane most probably continues to have access to part of the large channel volume which has become completely inaccessible to 3-methylpentane. This is to be expected since *n*-hexane being smaller than 3-methylpentane is able to diffuse through the large channels in spite of the partial obstruction by coke or to penetrate the large channels through the unobstructed gmelinite cages. Partial obstruction of large channels is moreover confirmed by diffusivity measurements (Table 1). While for low coke contents, the diffusivities of *n*-hexane and 3-methylpentane are similar, for coke contents equal to or greater than 3.5 wt% the diffusivity of 3-methylpentane is much lower than that of *n*-hexane (about 10 times for 3.5 wt% coke). For a coke content of about 5 wt%, W_1 for 3-methylpentane is very small (less than 10% of the large channel volume) whereas W_1 for *n*-hexane remains large (about 50% of the value found for the fresh H-OFF), i.e., slightly smaller than the large channel volume, but larger than the gmelinite volume. *n*-Hexane continues therefore to penetrate a fraction of the large channels and of the gmelinite cages.

—Above 8 wt% coke, W_1 for *n*-hexane decreases sharply close to 0 for 10 wt%. This blockage of the pore volume could be due to the formation of heavy polyaromatic compounds deposited on the outer surface of the zeolite crystallites.

2. Mode of Deactivation

Figure 9 shows that at low coke content the decrease in activity is probably due to the decrease in the pore volume accessible to the reactant *n*-heptane. Indeed 0.8 wt% coke causes a decrease of 15% both in the activity and in the W_1 for *n*-hexane (a molecule with a kinetic diameter similar to that of *n*-heptane). However, at high coke content the decrease in activity becomes more marked than the decrease in W_1 for *n*-hexane. This could be due to limitations in the diffusion rate of *n*-heptane: indeed, Table 1 shows a marked decrease of the diffusion

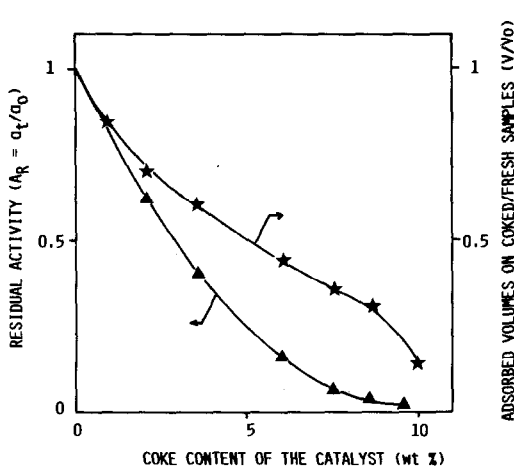


FIG. 9. Change against the coke content of the residual activity (A_R) and of the ratio of the volumes of n -hexane adsorbed on the coked sample and on the fresh sample (V/V_0).

rates of n -hexane in the large channels and in the gmelinite cages when the coke content increases.

Figure 10 gives as a function of the coke content the number of coke molecules estimated from the coke composition (I) by using the same hypotheses as previously (8). It can be noted that the total number is at a maximum (after 6 h of reaction) equal to 8% of the total number of acid sites and to about 21% of the number of the strong acid

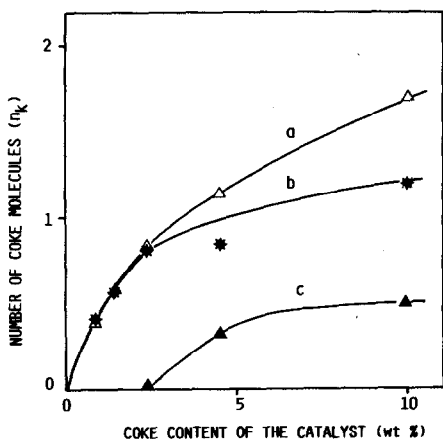


FIG. 10. Number of molecules ($n_k \times 10^{20}/g$) in the coke deposited on H-OFF zeolite: (a) total number, (b) in the soluble part, and (c) in the insoluble part.

sites (sites on which the adsorption heat of NH_3 is greater than 100 kJ mol^{-1} (I)). Since after this period of time there is practically no cracking activity, we can conclude that the deactivation is mainly due to pore blockage. This is confirmed when the relative decrease in activity ($1 - A_R$, the residual activity) is compared to the ratio n_k/n_{A2} of the number of coke molecules to the number of strong acid sites. In Fig. 11 giving $1 - A_R$ as a function of n_k/n_{A2} we have plotted the experimental values and drawn straight lines with different slopes ($(1 - A_R)/(n_k/n_{A2}) = 1, 3, \text{ or } 5$). If the experimental points are located on the straight line with the slope equal to 1, it can be concluded that one coke molecule renders one strong acid site inactive (with the slope equal to 3, three acid sites, etc.) provided, however, that the strong acid sites have the same cracking activity. Figure 11 shows that for a very low coke content (0.2 wt%) one coke molecule makes one strong acid site inactive; deactivation occurs therefore through site coverage. However for a 0.8 wt% coke content, one coke molecule makes about three strong acid sites inactive, which is characteristic of a deactiva-

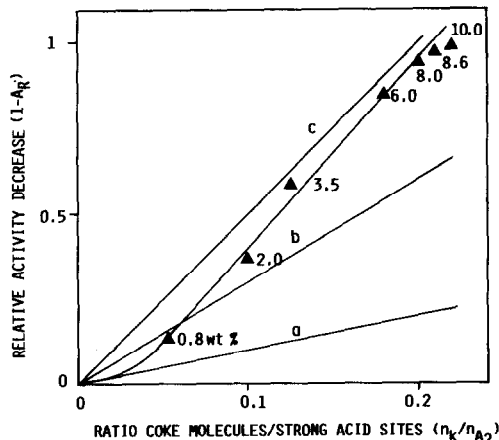


FIG. 11. Relative decrease in activity ($1 - A_R$) as a function of the ratio of the number of coke molecules to the number of strong acid sites (n_k/n_{A2}): (a) $(1 - A_R)/(n_k/n_{A2}) = 1$; (b) $(1 - A_R)/(n_k/n_{A2}) = 3$; (c) $(1 - A_R)/(n_k/n_{A2}) = 5$; experimental values (\blacktriangle) and coke content (wt%).

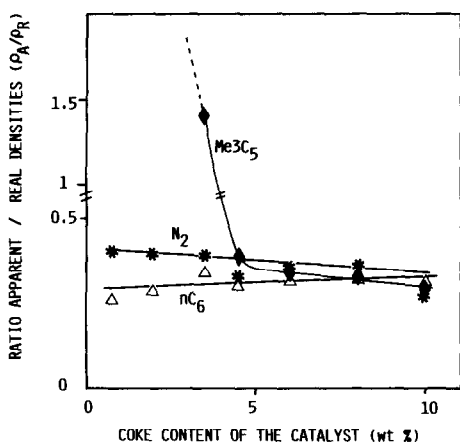


FIG. 12. Change of the ratio of the apparent (ρ_A) to the real (ρ_R) densities as a function of the coke content.

tion through pore blockage. This pore blockage is still more marked at high coke content: indeed for a 10 wt% coke content one coke molecule makes five strong acid sites inactive (Fig. 11). This is obviously due to the presence on the outer surface of the H-OFF crystallites of highly polyaromatic molecules (9).

This pore blockage is confirmed by the comparison between the apparent and the real coke densities ρ_A and ρ_R . ρ_A is the weight of coke measured per cubic centimeter of the pore volume made inaccessible to the adsorbates and ρ_R is the density of coke calculated from the densities of its components (8). Figure 12 shows that even at a 0.8 wt% coke content, only 30 to 40% of the pore volume inaccessible to nitrogen or to *n*-hexane is occupied by coke. The same applies to the pore volume inaccessible to 3-methylpentane but only for coke contents higher than 3.5 wt%. For lower coke contents ρ_A/ρ_R is greater than 1, is ∞ for 0.8 wt%, and is equal to 4 and 1.4 for 2 and 3.5 wt%. This is due to the fact that at low coke content coke is mainly located in the gmelinite cages and limits but does not block the diffusion of 3-methylpentane in the large channels (Table 1). The low value of ρ_A/ρ_R found when ρ_A is calculated from

n-hexane or nitrogen adsorption experiments means therefore that each coke molecule blocks the access to the entire volume of a gmelinite cage but occupies at the most 40% of this volume. This is compatible at least for a 0.8 wt% coke content with the average size of the coke molecules, namely 60 \AA^3 , i.e., about 40% of the volume of a gmelinite cage. For 2 and 3.5 wt% the average size of the coke molecules is equal to 85 and to 120 \AA^3 , i.e., about 60 and 80% of the volume of a gmelinite cage. These high values prove that the coke molecules overflow into the large channels. This probably explains also why apparently more than one acid site per coke molecule is made inactive (Fig. 11): a coke molecule blocks the access to the acid sites of the gmelinite cage and of the part of the large channel near the cage. It also limits the access of the reactant to the other acid sites of the large channel causing a decrease in the reaction rate.

The formation of all the coke molecules begins in the gmelinite cages and at least a part of each molecule will obviously be situated inside the cages. Therefore, it seems interesting to compare, as a function of the coke content, the number of coke molecules n_k with that of gmelinite cages n_G . Figure 13 shows that at the most (after 6 h

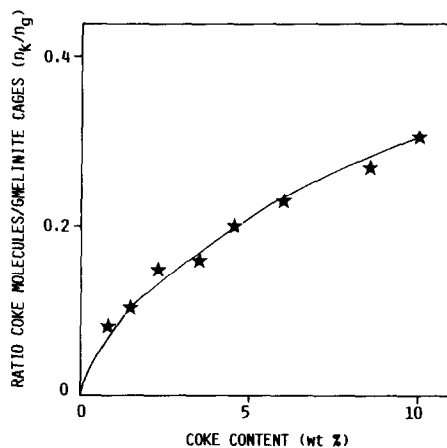


FIG. 13. Change of the ratio of the number of coke molecules to the number of gmelinite cages (n_k/n_G) as a function of the coke content.

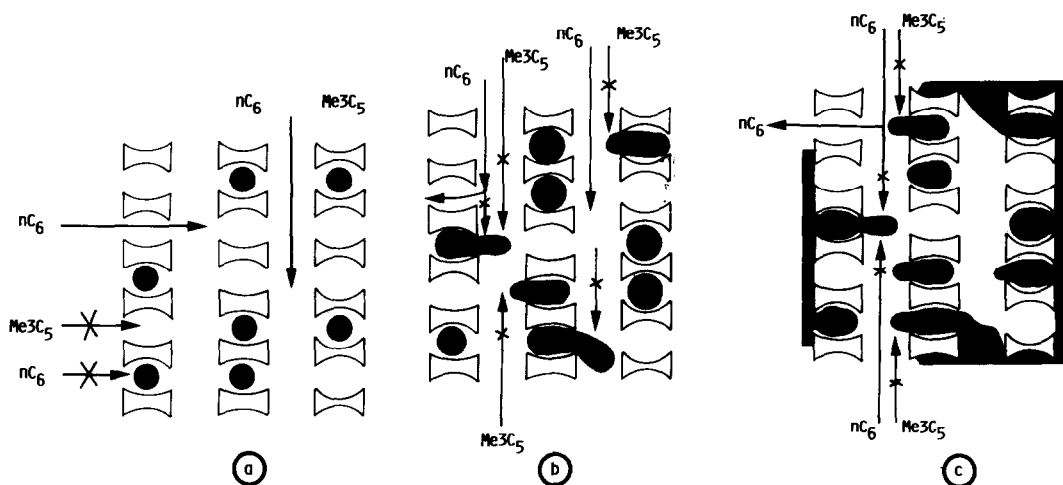


FIG. 14. Schematic representation of coke location in the H-OFF zeolite for (a) low coke content (0.2 wt%), (b) coke content between 0.2 and 4.5%, and (c) high coke content.

of reaction and complete deactivation) the n_k/n_G ratio is equal to 0.3. Only a small percentage of the gmelinite cages is therefore occupied by coke even though some coke molecules can occupy more than one gmelinite cage.

Figures 14a–14c show how the coking and the aging of H-OFF can be visualized:

—At very low coke content (Fig. 14a) small molecules (isobutene, monoaromatics) entrapped in the gmelinite cages obstruct the entry of the reactant and consequently make the strong acid sites located there inactive for *n*-heptane cracking.

—For coke contents between 0.8 and 4.5% (Fig. 14b) coke is constituted of polyaromatic molecules (with three or four rings) located in the gmelinite cages but overflowing into the large channels. These molecules limit or block the access to the large channels of the reactant and, above all, of the branched alkanes like 3-methylpentane.

—For larger coke content (Fig. 14c), highly polyaromatic molecules formed through growth of the coke molecules located in the pores near the outer surface block the access of the reactant to the acid

sites of the large channels and of the gmelinite cages.

CONCLUSION

Adsorption experiments carried out with nitrogen, *n*-hexane, and 3-methylpentane on coked offretite samples allow us to confirm the location of coke which was deduced from its composition and to propose a scheme for H-OFF deactivation. The formation of coke begins with the trapping of branched molecules formed by *n*-heptane cracking in gmelinite cages; these molecules block the access to these gmelinite cages making their strong acid sites inactive. These molecules undergo successive reactions leading to tri- or tetraaromatic compounds which overflow into the large channels. These compounds limit or block the access of the reactant to a fraction of the large channels. Finally, at high coke contents, highly polyaromatic molecules formed through growth of the coke molecules located near the outer surface cover this surface. These polyaromatic compounds block the access of the reactant to all the inner acid sites, making the zeolite completely inactive.

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