

Coking, Aging, and Regeneration of Zeolites

VIII. Nature of Coke Formed on Hydrogen Offretite during *n*-Heptane Cracking: Mode of Formation

P. MAGNOUX, M. GUISET, ¹S. MIGNARD, AND P. CARTRAUD

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

Received June 7, 1988; revised January 23, 1989

The carbonaceous compounds (coke) responsible for the deactivation of hydrogen offretite during *n*-heptane cracking at 450°C were analyzed in detail for different reaction times. With this zeolite, which has a double pore system, *n*-heptane cracking occurs partly in the gmelinite cages and partly in the large channels, but in both cases through the carbenium ion chain mechanism. It is shown that the coke formation begins in the gmelinite cages starting from branched cracking products (e.g., isobutene) too bulky to be desorbed. These products undergo reactions leading successively to monoaromatic, biaromatic, and polyaromatic products. The polyaromatic products, because of their size, cannot be located entirely in the gmelinite cages and hence overflow into the large channels. With long reaction times, highly condensed polyaromatics are formed by the growth of the coke molecules in the pores near the outer surface which they cover. © 1989 Academic Press, Inc.

INTRODUCTION

A new method for the characterization of the carbonaceous compounds ("coke") responsible for the deactivation of zeolites during the transformation of organic molecules has previously been developed (1). Thanks to this method, it was possible to show how the operating conditions (reaction time (2, 3), temperature (1, 4)) and the zeolite pore structure (1-4) influence the composition of coke. Moreover, by coupling coke analysis and adsorption measurements on the coked samples, the deactivation mode could be specified in the case of *n*-heptane cracking on HY, H-mordenite, and H-ZSM5 (5, 6). These techniques are applied here to H-offretite (H-OFF), a zeolite with a particular pore structure. Indeed, contrarily to the three zeolites previously studied, H-OFF presents two types of pores both accessible to *n*-heptane used here as a reactant: rectilinear, cylindrical channels (12-membered ox-

xygen-ring apertures, diameter = 6.3 Å) interconnecting through gmelinite cages (8-membered oxygen-ring apertures, diameter = 4.5-5 Å) (7, 8). While the gmelinite cages are accessible only to nonbulky molecules such as those of linear alkanes, the channel diameter is sufficiently large to allow the diffusion of relatively bulky molecules (branched alkanes or olefins, aromatics).

In this paper, the composition of the carbonaceous compounds formed during *n*-heptane cracking is examined as a function of reaction time. Their size and their volatility will enable us to determine their location either within the zeolite (gmelinite cages or large channels) or on the outer surface. The adsorption results used in the second paper allow us to confirm this location and to propose a mode for H-OFF deactivation.

EXPERIMENTAL

H-Offretite ($K_{0.4}H_{3.7}Al_{4.1}Si_{13.9}O_{36}$) was supplied by Grace Davison. The values obtained for its adsorption capacity for nitro-

¹ To whom correspondence should be addressed.

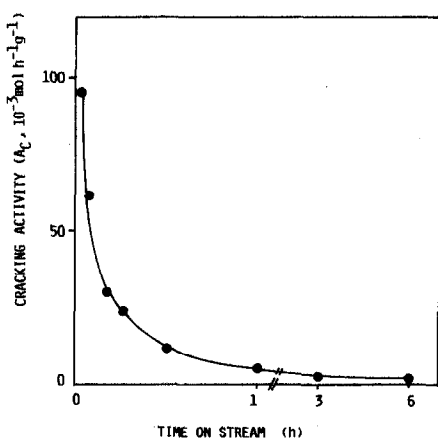


FIG. 1. Cracking activity A_c (10^{-3} mol of n -heptane transformed $\text{h}^{-1} \text{g}^{-1}$) as a function of reaction time t (h).

gen ($0.251 \text{ cm}^3 \text{ g}^{-1}$), for n -hexane ($0.217 \text{ cm}^3 \text{ g}^{-1}$), and for o -xylene ($0.14 \text{ cm}^3 \text{ g}^{-1}$) were consistent with the offretite structure (9): nitrogen occupies the total void volume, n -hexane the main channels and the gmelinite cages, and o -xylene the main channels only. Ultrastable HY zeolite, USHY ($\text{Na}_{0.8} \text{H}_{47.7} \text{Al}_{48.5} \text{Si}_{143.5} \text{O}_{384}$), was obtained by calcination at 520°C under a dry air flow of a sample of USNH_4Y from Union Carbide. The acidity of the zeolites was characterized by NH_3 adsorption followed by calorimetry (10). The number of strong acid sites (sites for which the NH_3 adsorption heat was greater than 100 kJ mol^{-1}) is $3.4 \times 10^{20} \text{ g}^{-1}$ for USHY and 6.8×10^{20} for H-OFF. On the average the heat of adsorption on these sites is equal to 120 kJ mol^{-1} on USHY as against 130 kJ mol^{-1} on H-OFF.

Coke formation was studied during the transformation of n -heptane carried out in a flow reactor at 450°C , $p(\text{N}_2) = 0.7 \times 10^5 \text{ Pa}$, $p(n\text{-heptane}) = 0.3 \times 10^5 \text{ Pa}$. A WWH value of 25.6 h^{-1} was used for the determination of the cracking and coking rates and a value of 2.6 h^{-1} for the preparation of coked samples for coke analysis.

The experimental methods used to determine the H/C ratio of the carbonaceous deposits as well as those used to recover and

to analyze the coke components have already been described (1, 2).

RESULTS

1. n -Heptane Cracking, Coking, and Deactivation

Figure 1 shows that the cracking activity of H-OFF decreases very rapidly with time on stream: equal to about $100 \times 10^{-3} \text{ mol h}^{-1} \text{ g}^{-1}$ after 2 min of reaction, it is three times lower after 10 min and 80 times lower after 6 h. Whatever the reaction time the cracking products are constituted mainly of $\text{C}_3 + \text{C}_4$ (80–85 molar%), the other products being C_1 and C_2 (5–10%) and C_5 and C_6 (5–10%). The C_3/C_4 molar ratio equal to 2 during the first 15 min decreases subsequently to become close to 1 after 2 h of reaction. $\text{C}_4\text{--C}_6$ cracking products are mainly linear; thus, $\text{isoC}_4/n\text{C}_4$ is equal to 0.45 after 2 min of reaction and to 0.30 after 15 min. The molar ratio olefins/alkanes in the cracking products, which is initially equal to 0.45, increases with reaction time becoming close to 1 after 1 h of reaction. The value of this ratio depends on the number of carbon atoms of the cracking products (Table 1).

The rate of coking during the first 2 min is $6 \times 10^{-3} \text{ mol}$ of n -heptane transformed into coke per hour and per gram, and therefore is about 5 times lower than the cracking rate. It decreases rapidly with reaction time (Fig. 2).

2. Coke Composition

2.1. Atomic H/C ratio and yield of solubilization in methylene chloride (R). The atomic H/C ratio decreases when the coke

TABLE 1

Catalyst	Initial Values (after 2 min of Reaction) of the Olefin/Alkane Ratio in the Cracking Products				
	C_2^-/C_2	C_3^-/C_3	$n\text{C}_4^-/n\text{C}_4$	$i\text{C}_4^-/i\text{C}_4$	o/s
H-OFF	4	0.32	0.39	0.62	0.45
USHY	1.4	0.25	0.18	0.05	0.2

Note. o/s, Olefin/alkane overall ratio.

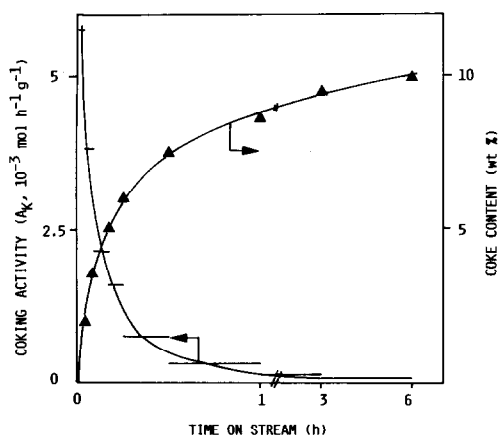


FIG. 2. Coking activity A_K (10^{-3} mol of *n*-heptane transformed $\text{h}^{-1} \text{g}^{-1}$) and coke content of the catalysts (wt%) against reaction time t (h).

content (therefore, the time on stream) increases. Its value is greater than 1 (nonpolyaromatic coke) for low coke contents and close to 0.5 (polyaromatic coke) for contents greater than 5 wt% (Fig. 3).

Figure 3 shows that the yield of coke recovered in methylene chloride (R) is always lower than 100%. This is due, in the case of coke contents greater than 5%, to the presence of polyaromatic compounds insoluble in methylene chloride. These compounds are found in the form of small black particles having an atomic H/C ratio lower than

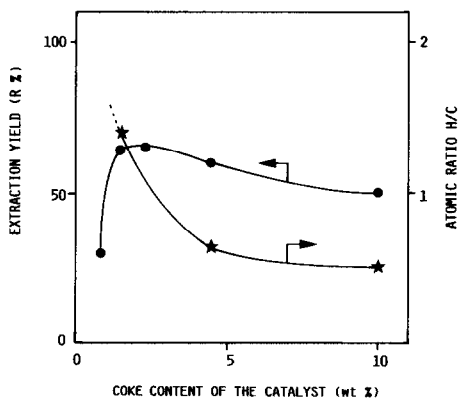


FIG. 3. Yield of coke recovered in methylene chloride (R) and atomic H/C ratio as functions of the coke content (wt%).

0.5. For contents below or equal to 2.3%, black particles are not observed and the yield of coke recovered is lower than 100% because of the presence of volatile compounds. The more volatile are eliminated during the treatment of the coke zeolite by the hydrofluoric acid solution. Chromatographic analyses show that these are mainly isobutene, methylcyclopentane, benzene, and xylenes in proportions depending on the coke content. The evaporation of methylene chloride is accompanied by the elimination of less volatile compounds (mainly benzenic).

Figure 4 shows the change of the amounts of insoluble coke and of light coke as a function of the coke content. It must be noted that for low coke contents ($\leq 2.3\%$) the light coke was considered the sum of the soluble and of the volatile parts while for high coke contents it was considered equal to the soluble part. This probably explains why for a 4.5 wt% coke content the value found for light coke is smaller than what was expected (Fig. 4).

2.2. Analysis of soluble coke by GC, HPLC, MS, and ^1H NMR. All these analyses were carried out after evaporation of methylene chloride, and therefore, also of the more volatile coke components. GC analysis shows that the soluble cokes are always very complex mixtures, whose compositions depend on the coke content,

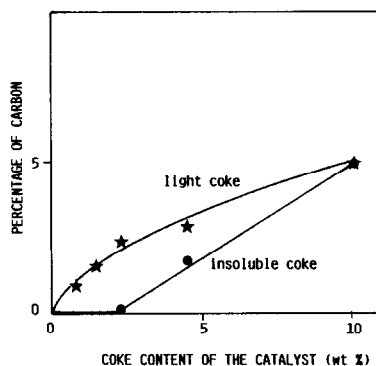


FIG. 4. Percentages of light coke and of insoluble coke as functions of the coke content (wt%).

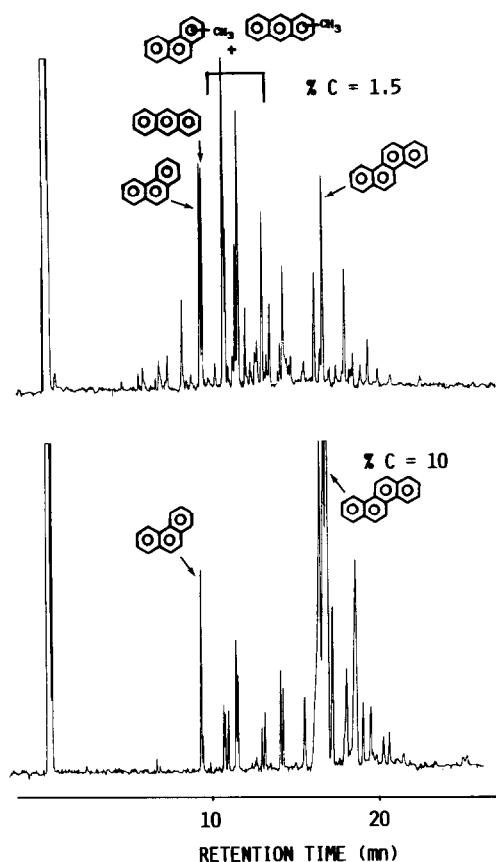


FIG. 5. Gas phase chromatograms of solvent extracts obtained after dissolution of the zeolite by hydrofluoric acid. The formulas of the main components are indicated.

the higher the content the less the number of components (Fig. 5). A great number of the components are identified by comparison with reference compounds. HPLC shows that the products have two to three aromatic rings at low coke contents and three to four at higher coke contents. ^1H NMR shows that the aromaticity increases with the coke content (Fig. 6). The percentage of aromatic protons increases at the expense of the percentage of aliphatic protons; the percentage of alkylaromatic protons (from groups carried by aromatic rings) passes through a maximum for a 2.3 wt% coke content. The MS analysis carried out at a low ionization energy (10 eV) in order to avoid fragmentation confirms that

the higher the coke content the less the number of components. The formulas of the main components deduced from their molecular weight are given in Table 2. These formulas are in good agreement with the mass spectra obtained through GC-MS coupling.

DISCUSSION

We shall compare first the activity and the selectivity of H-OFF for *n*-heptane cracking to those of USHY, a zeolite in which configurational limitations and steric constraints are less pronounced. Cracking mechanisms will be discussed. Coking and deactivation rates on H-OFF and on USHY will also be compared. Finally the location of coke molecules in the H-OFF pores will be specified.

1. Activity and Selectivity of H-OFF for *n*-Heptane Cracking: Cracking Mechanisms

H-OFF has an initial activity about 1.6 times greater than USHY: $0.1 \text{ mol h}^{-1} \text{ g}^{-1}$ after 2 min of reaction compared to $0.066 \text{ mol h}^{-1} \text{ g}^{-1}$. This greater activity may be due to the greater number of strong acid sites: H-OFF has a number of strong acid sites (sites on which the heat of ammonia adsorption is greater than 100 kJ mol^{-1}) two times greater than that of USHY. The ac-

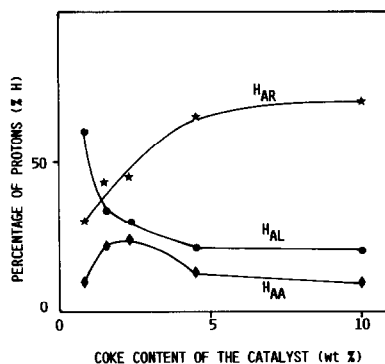
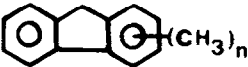



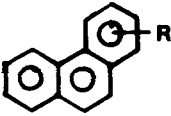
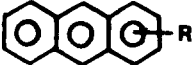
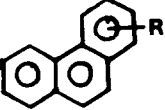
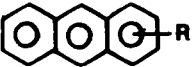
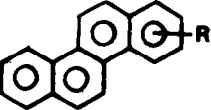
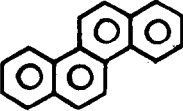


FIG. 6. Analysis of the soluble coke by ^1H NMR. Change in the percentages of aromatic protons (H_{AR}), of alkylaromatic protons (H_{AA}), and of aliphatic protons (H_{AL}) as a function of coke content (wt%).

TABLE 2

Formulas of the Main Components of the Coke Soluble in Methylene Chloride

Coke (wt%)	Main families	Main components				
		Formula	bp at 760 Torr	Size ^a (Å)		
0.8		$C_{14}H_{12}(n = 1)$	290	6×9.5		
		$C_{15}H_{14}(n = 2)$				
		$C_{12}H_8$	270	7×7		
	C_nH_{2n-8}		$C_{10}H_{12}(R=CH_3)$	190	6×7	
	C_nH_{2n-12}		$C_{10}H_8(R=H)$	218	6×7	
	(a)				6.5×8.5	
	C_nH_{2n-18}	(b)		$C_{14}H_{10}(R=H)$	340	6×9.5
1.5	(a)				6.5×8.5	
2.3	C_nH_{2n-18}	(b)			6×9.5	
4.5				$C_{15}H_{12}(R=CH_3)$	320	
	C_nH_{2n-24}		$C_{19}H_{14}(R=CH_3)$	448	6.5×12	
			$C_{18}H_{12}(R=H)$			
10	C_nH_{2n-24}		$C_{18}H_{12}$	448	6.5×12	

^a Minimal size estimated from the lengths of the aromatic C-C and C-H bonds (1.4 and 1.1 Å, respectively).

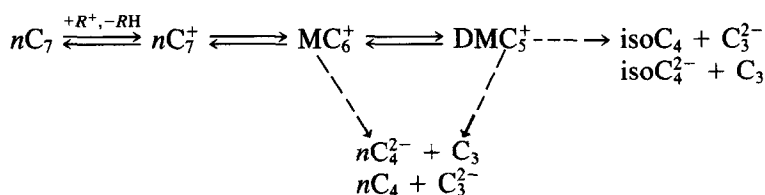
tivity of a strong acid site is therefore slightly smaller on H-OFF than on USHY despite the fact that its acid sites are stronger: on the average the heat of ammonia adsorption on the strong sites of H-OFF is equal to 130 kJ mol⁻¹ compared to 120 kJ mol⁻¹ on USHY. Steric constraints in the narrower pore structure of H-OFF are probably responsible for this lower activity.

The selectivities of H-OFF and USHY are also quite different, as already mentioned (11). However, on both zeolites, C₃ and C₄ are the main products but on H-OFF the C₃/C₄ molar ratio is initially equal to 2 compared to 1 on USHY and the iso/nC₄ ratio is equal to 0.45 on H-OFF compared to 2.8 on USHY. However, the main part of the cracking products on H-OFF probably result, as is the case for USHY, from the scission of carbenium ions since the formation of C₂ and, above all, of C₁ is very slow. Protolytic scission could be responsible for this formation of C₁, C₂ (12). The coexistence on zeolites of these two modes of cracking is well-known, their significance depending on the characteristics of the acid sites and of the zeolite porosity (11–13) as well as on the operating conditions (12).

On the other hand the olefin/alkane ratio

of the cracking products is initially lower than 1 (0.45 after 2 min of reaction) indicating secondary reactions (such as hydrogen transfer) of olefinic products. However, this ratio is higher than that on USHY (0.2 after 2 min of reaction). This difference between the two zeolites can be related to the existence of steric constraints in the narrow pore structure of H-OFF which limit the bimolecular hydrogen transfer reactions. Table 1 shows moreover that the difference between the olefin/alkane ratio found on USHY and on H-OFF is greater with branched molecules than with linear ones: *i*C₄²⁻/*i*C₄ is about 12 times higher on H-OFF than on USHY, whereas C₂²⁻/C₂, C₃²⁻/C₃, and *n*C₄²⁻/*n*C₄ are only 2.8, 1.3, and 2.2 times higher, respectively. This could be due to the more significant steric constraints on hydrogen transfer toward isobutene than toward the less bulky olefins.

The cracking product distribution found on H-OFF can be explained by the possibility of *n*-heptane reacting both in the gmelinite cages and in the large channels (14). On the acid sites of the large channels *n*-heptane undergoes the same reactions as on the acid sites of USHY with formation of C₃ + mainly branched C₄:



Olefinic products which are highly reactive undergo bimolecular reactions (alkylation, hydrogen transfer, etc.) with the consequence of an olefin/alkane ratio in the cracking products below 1. In the gmelinite cages the same process occurs but the branched C₄ hydrocarbons remain entrapped with, consequently, a low C₄/C₃ ratio. IsoC₄ hydrocarbons can react with the compounds entering the gmelinite cages.

With *n*-heptane, C₁₁ intermediates, which crack into C₃–C₆ products, could be formed. The low amount of C₅–C₆ cracking products shows that this type of reaction has little significance. Cyclization and aromatization via hydrogen transfer leading to the coke molecules (volatile or not) can also occur. The low values of the iso/nC₄ and C₄/C₃ ratios lead to the conclusion that cracking occurs essentially in the gmelinite

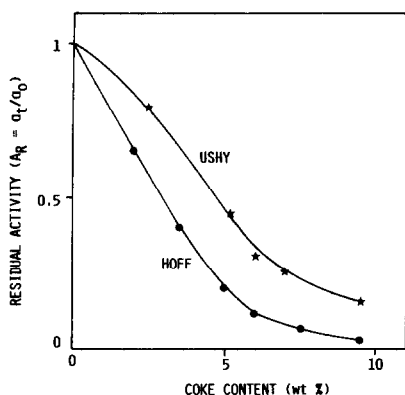


FIG. 7. Residual activity ($A_R = a_t/a_0$; a_t , activity for t ; and a_0 , initial activity) of the zeolites USHY and H-OFF versus their coke contents (wt%).

cages. According to certain authors (11), the low C_4/C_3 ratio could also result from high field gradients in H-OFF.

2. Coking and Deactivation Rates

On H-OFF the initial coking rate is lower than that on USHY, viz., $6.6 \times 10^{-3} \text{ mol h}^{-1} \text{ g}^{-1}$ during the first 2 min of reaction compared to $8.7 \times 10^{-3} \text{ mol h}^{-1} \text{ g}^{-1}$. Therefore, the cracking/coking rate ratio is higher on H-OFF (about 15) than on USHY (about 8), which can be explained by steric constraints inhibiting the formation of coke molecules in the offretite pores. Obviously, these steric constraints would be particularly marked in the gmelinite cages.

While the coking rate is lower on H-OFF than on USHY, the deactivating effect of coke is more significant on H-OFF (Fig. 7). This can be explained by an earlier inhibition of the reactant diffusion in the narrower H-OFF pores: indeed small molecules like isoC_4 retained in the gmelinite cages limit the access of the reactant to the acid sites of these cages; as the large channels of H-OFF are narrower than the pores of USHY they can be more easily blocked. Moreover, while the n -heptane diffusion can occur three-dimensionally this is not so for branched products. They can only dif-

fuse through the large channels with the consequence of a highly significant effect of pore blockage (15, 16).

3. Location of the Coke Components

The identification of the coke components makes it possible to discuss their location. At low coke content, all the components have boiling points much lower than the reaction temperatures (Table 2) and consequently would diffuse into the gas phase if they were not entrapped in the zeolite pores. The adsorption on the acid sites of these weakly basic molecules cannot alone explain this blockage. The reason for their retention is therefore steric. Their size being generally smaller or similar to that of the large channels (about 6.5 \AA), most of the coke molecules soluble in methylene chloride (even at high coke contents) could probably diffuse in these large channels. Indeed, it is generally assumed that at a high temperature the pore structure of zeolites is not rigid and can accommodate molecules larger by about 1 \AA than the pore size. Therefore, it is probable that these molecules are entrapped in the gmelinite cages. Figure 8 shows that even for high coke content all the molecules soluble in methylene chloride can be located in these cages. However, most of them are too large, and therefore they overflow into the large channels. The change of the $\text{isoC}_4/n\text{C}_4$ ratio with coke content can thus be explained. Indeed, if only the gmelinite cages were

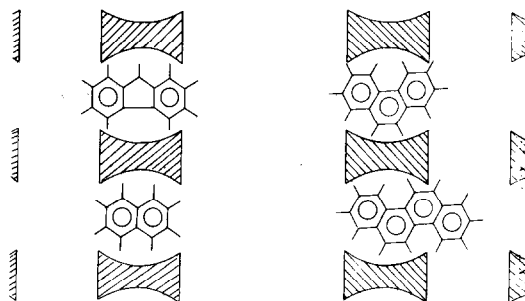


FIG. 8. Mode of formation of coke on H-OFF. Main components formed inside the gmelinite cages.

blocked by coke, this ratio would increase, while in fact it decreases slightly.

We can thus conclude that all the coke molecules soluble in methylene chloride are formed and located in the gmelinite cages, most of them, however, overflowing into the large channels. This preferential formation of coke in these cages can be related to the easy trapping of relatively small molecules: isobutene and benzenic compounds. These molecules can undergo numerous secondary transformations leading to polyaromatic molecules such as phenanthrenes, anthracenes, or chrysenes. This preferential formation of coke can be related also to the fact that, as is shown by the low values of C_4/C_3 and of $isoC_4/nC_4$ ratios, cracking occurs mainly in the gmelinite cages. The large molecules insoluble in methylene chloride formed at high coke contents seem to be located on the external surface of the offretite crystallites (17). They can be formed directly on the external acid sites or by growth of the polyaromatic molecules located in gmelinite cages near the outer surface. The change in the coke content of the amounts of soluble and insoluble coke seems to be in favor of this latter hypothesis (Fig. 4).

The following successive stages can be quoted to explain the coke formation of H-OFF:

1. Formation and trapping of small molecules in gmelinite cages: iC_4^{2-} , monoaromatic, biaromatic.

2. Formation through transformations of mono- and biaromatic compounds formed in stage 1 (alkylation, cyclization, aromatization) of tri- and tetraaromatic molecules entrapped in the gmelinite cages and overflowing into the large channels.

3. Formation of highly polyaromatic compounds through growth of the molecules formed in stage 2 in the pores near the outer surface.

CONCLUSION

n-Heptane cracking on H-OFF occurs partly in the gmelinite cages, partly in the large channels, and in both cases through

the carbenium ion chain mechanism. The branched products blocked in the gmelinite cages lead through the reaction with other molecules to polyaromatic compounds with three to four rings. These compounds overflow into the large channels. Moreover, their growth leads to highly polyaromatic molecules covering the outer surface of the crystallites.

REFERENCES

1. Magnoux, P., Roger, P., Canaff, C., Fouché, V., Gnep, N. S., and Guisnet, M., in "Catalyst Deactivation" (B. Delmon and G. F. Froment, Eds.), Studies in Surface Science and Catalysis, Vol. 34, p. 317. Elsevier, Amsterdam, 1987.
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. Guisnet, M., Magnoux, P., and Canaff, C., in "New Developments in Zeolite Science Technology, Proceedings 7th International Zeolite Conference" (Y. Murakami *et al.*, Eds.), p. 701. Kodansha Ltd., Tokyo, 1986.
4. Magnoux, P., Fouché, V., and Guisnet, M., *Bull. Soc. Chim. Fr.* **6**, 969 (1987).
5. Magnoux, P., Cartraud, P., Mignard, S., and Guisnet, M., *J. Catal.* **106**, 235 (1987).
6. Magnoux, P., Cartraud, P., Mignard, S., and Guisnet, M., *J. Catal.* **106**, 242 (1987).
7. Whyte, T. E., Jr., Wu, E. L., Ken, G. T., and Venuto, P. B., *J. Catal.* **20**, 88 (1971).
8. Chen, N. Y., in "Proceedings, 5th International Congress on Catalysis, Palm Beach, 1972" (J. W. Hightower, Ed.), p. 1343. North-Holland, Amsterdam, 1973.
9. Breck, W. C., and Grose, R. W., *Adv. Chem. Ser.* **121**, 319 (1973).
10. Cartraud, P., to be published.
11. Mirodatos, C., and Barthomeuf, D., *J. Catal.* **93**, 246 (1985); **114**, 121 (1988).
12. Haag, W. O., and Dessau, R. M., in "Proceedings, 8th International Congress on Catalysis, Berlin, 1984," Vol. 2, p. 305. Dechema, Frankfurt-am-Main, 1984.
13. Corma, A., Planelles, J., and Tomas, F., *J. Catal.* **94**, 445 (1985).
14. Bourdillon, G., Guisnet, M., and Gueguen, C., *Zeolites* **6**, 221 (1986).
15. 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.
16. Gnep, N. S., Tejada, J., and Guisnet, M., *Bull. Soc. Chim. Fr.* **45** (1987).
17. Gallezot, P., Leclercq, C., Guisnet, M., and Magnoux, P., *J. Catal.* **114**, 100 (1988).