

## Dealumination of Zeolites

### III. Effect of Extra-Framework Aluminum Species on the Activity, Selectivity, and Stability of Y Zeolites in *n*-Heptane Cracking

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A series of dealuminated Y samples with between 12 and 48 framework aluminum species per unit cell ( $N_{Al}$ ) were prepared by steaming of a  $NH_4NaY$  zeolite. A treatment with dilute HCl solution was applied to the samples in order to eliminate, without modifying the framework composition, the extra-framework aluminum species (EFAL) created by steaming. The activity, stability, and the selectivity in *n*-heptane cracking at 350°C of the two series of samples were compared. For high values of  $N_{Al}$ , EFAL species have a promoting effect on the rates of isomerization, cracking, hydrogen transfer, and coking but increase the deactivating effect of coke. An inductive influence of their Lewis acid sites on the protonic sites of the zeolite ("superacid sites") would be responsible for these effects. For  $N_{Al} < 15$  the reaction rates do not depend on the EFAL species probably because they are too far from the protonic sites. With all the reactions the activities of the dealuminated samples pass through a maximum for  $N_{Al}$  between 35 and 40. The cracking activity of the highly dealuminated samples of the series containing few EFAL species is proportional to the number of the framework acid sites whereas for hydrogen transfer and for coking the activity depends also on the acid site density. This is attributed to the fact that these two reactions require many bimolecular steps and therefore demand the participation of several acid sites in their catalysis. © 1991 Academic Press, Inc.

#### INTRODUCTION

It is the remarkable thermal and catalytic stability of high silica zeolites which make them interesting for numerous industrial processes. Depending on the pore structure, these zeolites can be directly synthesized (e.g., MFI) or obtained through dealumination of low silica zeolites (e.g., faujasite). The methods of preparation of aluminum-deficient Y and mordenite zeolites were recently reviewed by Scherzer (1). The most used methods for industrial purposes consist of the calcination of the ammonium (or protonic) form of the zeolite at high temperature in the presence of steam. The alumi-

num species extracted from the framework remain in the zeolites; the defect sites created by dealumination are filled in to a large extent by silicon, which leads to a high silicon framework. Different types of non-framework aluminum species (EFAL), neutral or cationic, can be formed depending on the conditions of the hydrothermal treatment and on the characteristics of the starting zeolite (1–5). EFAL species are responsible for the appearance of Lewis acidity (6, 7) and also for the presence of IR hydroxyl bands at 3700 and 3610  $cm^{-1}$  generally considered as non-acidic (7–9). However, a part of the hydroxyl groups vibrating at 3610  $cm^{-1}$  could be superacid (10).

It is well demonstrated that EFAL species formed during mild steaming of ZSM-5 are responsible for an enhancement of the activity of this zeolite. All investigators (11–15)

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explain this enhancement by an interaction of Brønsted acid sites of H-ZSM-5 and of Lewis sites of EFAL. The possibility of an inductive influence of Lewis sites on the protonic acidity of zeolites was mentioned a long time ago (16, 17). According to Mirodatos and Barthomeuf (18), this influence could explain why during toluene disproportionation steamed mordenite samples could activate hydrogen and thus reduce coke formation (19). However, with Y zeolites, the situation is more complex. Certain authors (20–22) claim that EFAL species have a negative effect on the activity of steamed zeolites while others authors (2, 23–25) found the contrary. Several proposals can be made for explaining these differences, as follows.

(i) The steaming conditions are not identical and consequently the nature (neutral or cationic), the size, and the location of the EFAL species could be different.

(ii) The conditions of the acid treatment generally used for eliminating EFAL species of the zeolite are often different. This acid treatment cannot only dissolve the EFAL species but can also eliminate residual sodium atoms and even, in certain cases, can provoke a supplementary dealumination of the zeolite framework. Moreover, the change in acidity with the elimination of the EFAL species from the zeolite depends on their nature; thus protonic sites are formed only by elimination of cationic EFAL species.

(iii) The sites active in the model reactions used to characterize the zeolites can be different. Thus while it seems clear that the isomerization and disproportionation of alkylaromatics and the cracking of various alkanes (26, 27) are catalyzed by protonic sites, Lewis acid sites (such as these of EFAL species) could participate in other reactions, e.g., oligomerization of ethylene (25).

(iv) EFAL species deposited on the outer surface of the crystallites or on the walls of the mesopores created by dealumination (28) could limit the diffusion of bulky reactants to the active sites. This is probably

the case during the cracking of vacuum gas oil (29).

(v) The initial deactivation of the Y zeolites is generally very rapid. There is therefore a great imprecision in the comparison of the initial activities of the samples with and without EFAL species, all the more so since the rates of deactivation are not identical (22).

The objective of this work is to specify the effect of EFAL species on the catalytic properties of Y zeolites dealuminated by hydrothermal treatment. *n*-Heptane cracking at 350°C was chosen as a model reaction and the activity, stability, and selectivity of steamed zeolites were compared before and after elimination of EFAL species by acid treatment. The conditions of steaming were varied so as to obtain samples with different values of  $N_{Al}$  (number of framework aluminum atoms per unit cell) and hence it was possible to specify the effect of  $N_{Al}$  on the catalytic properties.

#### EXPERIMENTAL

The dealuminated samples were prepared by hydrothermal treatment in a flow reactor of a  $NH_4NaY$  zeolite ( $(NH_4)_{48}Na_{14}Al_{62}Si_{130}O_{384}$ ). The procedure used for this dealumination was described in Part II (30) and the operating conditions are specified in Table 1. The acid treatment used for eliminating extra-framework species formed during hydrothermal treatment was carried out under the following conditions: temperature 25°C and addition of a dilute solution of hydrochloric acid (0.01 to 0.1 *N*) to a stirred mixture of water and of zeolite. To avoid supplementary dealumination of the framework the addition of hydrochloric acid was stopped when the pH became equal to 2.7 (8). The amount of hydrochloric acid used depended on the number of EFAL species in the samples. This amount varied from  $1.7 \times 10^{-3} \text{ mol h}^{-1}\text{g}^{-1}$  zeolite for sample 1a to  $8.0 \times 10^{-3}$  for sample 8a. This amount corresponded to 1–1.3 molecules of hydrochloric acid per extra-framework Al atom (16). In order to obtain samples with differ-

TABLE 1  
Conditions of Preparation and Physicochemical Characteristics of the Samples

Series	Steaming conditions			Samples	Chemical analysis		X-ray diffraction		
	$T$ (°C)	$P_{\text{water}}$ (kPa)	$t$ (h)		% Na	Si/Al	$a_0$	Si/Al	$C_{\text{RX}}^a$
1	500	93.3	1	a	0.38	2.1	24.605	3.03	89
				b	0.21	2.65	24.605	3.04	90
2	500	93.3	13	a	0.30	2.1	24.543	3.73	89
				b	0.19	3.04	24.538	3.80	88
3	600	93.3	4	a	0.38	2.1	24.498	4.43	87
				b	0.21	3.68	24.498	4.43	87
4	650	93.3	8	a	0.29	2.1	24.455	5.31	83
				b	0.24	2.84	24.455	5.31	84
				c	0.24	4.11	24.457	5.28	83
5	760	0 <sup>b</sup>	3	a	0.40	2.1	24.433	5.90	81
				b	0.39	2.50	24.432	5.91	82
				c	0.35	2.88	24.433	5.91	82
				d	0.37	2.92	24.433	5.90	79
				e	0.36	2.98	24.433	5.90	81
				f	0.40	4.58	24.431	5.94	80
6	550,700	93.3	3	a	0.21	2.1	24.401	6.94	85
				b	0.1	5.74	24.4006	6.95	86
7	540,750	93.3	3	a	0.30	2.1	24.322	11.7	83
				b	0.16	9.80	24.324	11.5	82
8	540,820	0 <sup>b</sup>	3	a	0.23	2.1	24.291	15.7	69
				b	0.1	9.33	24.291	15.7	69

Note. Samples a have undergone steaming, two exchanges with  $\text{NH}_4^+$ , and calcination under dry nitrogen flow at 500°C. Samples b–f have undergone acid treatment after steaming and calcination under dry nitrogen flow at 500°C.

<sup>a</sup> Reference untreated  $\text{NH}_4\text{NaY}$

<sup>b</sup>  $P_{\text{water}} = 0$ , self-steaming

ent amounts of extra-framework species (series 4 and 5, Table 1) smaller quantities of hydrochloric acid were added to the zeolite. The duration of the acid treatment was 3 h, after which the samples were thoroughly washed with water until no  $\text{Cl}^-$  was detected.

The *n*-heptane transformation was carried out at 350°C in a flow reactor under normal pressure with a nitrogen/*n*-heptane ratio of 9. The reaction products were analyzed by on-line gas chromatography, using a 50-m fused silica PLOT  $\text{Al}_2\text{O}_3$  capillary column. The temperature was programmed as follows: 6 min at 80°C, 20°C/min increase to 200°C, then 30 min at 200°C. The percentage of coke was determined by CNRS Solaize:

the coked sample was treated at 1050°C under an excess of oxygen, the gases formed flowed through a CuO bed so as to complete the combustion, and  $\text{CO}_2$  was determined by coulometry.

## RESULTS

### 1. Physicochemical Characteristics of the Zeolites

Table 1 gives the conditions of steaming used to prepare the samples and the information obtained from their chemical analysis (wt% Na, atomic Si/Al ratio) and from X-ray diffraction (unit cell parameter  $a_0$  and crystallinity  $C_{\text{RX}}$  estimated by ASTM methods). The number of aluminum atoms per unit cell  $N_{\text{Al}}$  (and therefore the atomic

TABLE 2  
Unit Cell Formula and Catalytic Properties of the Dealuminated Samples

Series	Samples	Unit cell formula	$N_{\text{EFAL}}$	$A_0/C_{\text{RX}}$ (mmol · h <sup>-1</sup> g <sup>-1</sup> )	Af/A0	Coke (%)	(s/o) <sub>0</sub>	(iC <sub>4</sub> /nC <sub>4</sub> ) <sup>a</sup>
1	a	Na <sub>2</sub> Al <sub>47.7</sub> Si <sub>144.3</sub> O <sub>384</sub>	21.1	46.9	0.06	4.36	12.2	4.0
	b	Na <sub>1</sub> Al <sub>47.7</sub> Si <sub>144.3</sub> O <sub>384</sub>	6.8	31.7	0.13	3.70	9.1	4.0
2	a	Na <sub>2</sub> Al <sub>40.6</sub> Si <sub>151.4</sub> O <sub>384</sub>	31.6	56.3	0.05	6.53	18.5	5.1
	b	Na <sub>1</sub> Al <sub>40.6</sub> Si <sub>152</sub> O <sub>384</sub>	9.2	38.6	0.06	5.39	13.0	4.2
3	a	Na <sub>2</sub> Al <sub>35.4</sub> Si <sub>156.6</sub> O <sub>384</sub>	39.3	67.2	0.06	5.60	19.6	5.2
	b	Na <sub>1</sub> Al <sub>35.4</sub> Si <sub>156.6</sub> O <sub>384</sub>	7.2	33.7	0.11	—	9.1	4.5
4	a	Na <sub>1.5</sub> Al <sub>30.4</sub> Si <sub>161.6</sub> O <sub>384</sub>	46.6	47.1	0.033	4.24	27.0	6.4
	b	Na <sub>1.3</sub> Al <sub>30.4</sub> Si <sub>161.6</sub> O <sub>384</sub>	25.5	30.4	0.041	3.35	16.7	6.0
5	c	Na <sub>1.3</sub> Al <sub>30.4</sub> Si <sub>161.6</sub> O <sub>384</sub>	8.9	27.6	0.063	3.10	7.7	5.1
	a	Na <sub>2</sub> Al <sub>27.8</sub> Si <sub>164.2</sub> O <sub>384</sub>	50.5	32.9	0.044	4.10	17.8	6.9
5	b	Na <sub>2</sub> Al <sub>27.8</sub> Si <sub>164.2</sub> O <sub>384</sub>	37.9	27.3	0.040	3.05	13.3	7.0
	c	Na <sub>1.8</sub> Al <sub>27.8</sub> Si <sub>164.2</sub> O <sub>384</sub>	29.2	24.6	0.052	2.87	11.8	6.5
5	d	Na <sub>2</sub> Al <sub>27.8</sub> Si <sub>164.2</sub> O <sub>384</sub>	28.4	25.8	0.071	—	7.7	4.8
	e	Na <sub>1.8</sub> Al <sub>27.8</sub> Si <sub>164.2</sub> O <sub>384</sub>	27.3	25.9	0.088	2.81	6.7	4.6
5	f	Na <sub>2</sub> Al <sub>27.6</sub> Si <sub>164.2</sub> O <sub>384</sub>	8.1	24.1	0.0083	2.60	7.7	4.0
	a	Na <sub>1</sub> Al <sub>24.2</sub> Si <sub>167.8</sub> O <sub>384</sub>	55.8	25.5	0.061	2.41	7.7	4.8
6	b	Na <sub>0.5</sub> Al <sub>24.1</sub> Si <sub>167.9</sub> O <sub>384</sub>	5.0	21.2	0.066	1.88	5.3	4.0
	a	Na <sub>1.6</sub> Al <sub>15.1</sub> Si <sub>176.9</sub> O <sub>384</sub>	69.2	12.6	0.11	1.57	5	4.3
7	b	Na <sub>0.8</sub> Al <sub>15.3</sub> Si <sub>176.7</sub> O <sub>384</sub>	2.9	11.9	0.10	1.47	4.2	3.8
	a	Na <sub>1</sub> Al <sub>11.5</sub> Si <sub>180.5</sub> O <sub>384</sub>	74.6	9.81	0.15	0.47	3.5	4.0
8	b	Na <sub>0.5</sub> Al <sub>11.5</sub> Si <sub>180.5</sub> O <sub>384</sub>	7.8	10.3	0.12	0.49	3.5	3.9

<sup>a</sup> At 10% conversion.

framework Si/Al ratio) was calculated from  $a_0$  by using the equation proposed by Breck and Flanigen (31). The unit cell formula and the number of extra-framework species  $N_{\text{EFAL}}$  (Table 2) were determined from the chemical composition of the samples (percentage Al, Si, Na) and from  $N_{\text{Al}}$ . For this determination it was supposed that the extra-framework deposits were mainly composed of aluminum species and contained practically no silicon or sodium atoms.

Table 2 shows that a large part of the EFAL species can be eliminated through treatment with hydrochloric acid solutions without supplementary framework dealumination. However, the elimination of these species was accompanied by a partial exchange of the sodium ions (Table 1).

## 2. Activity, Stability, and Selectivity of the Zeolites

On all the zeolite samples *n*-heptane was transformed into isomers and cracking prod-

ucts. Figures 1a and 1b show as examples how the activities of the zeolites of series 1 and 2 change with time on stream. Whatever the sample, the activity decreases very rapidly during the first 20 min and then more slowly. For the samples of series 4 and 5, the higher  $N_{\text{EFAL}}$  the higher  $A_0$ , the activity after 2 min (Fig. 2). However, Fig. 3 shows that  $A_0$  is higher for samples with a large amount of EFAL species at least for high values of  $N_{\text{Al}}$  (>20). Whatever the samples (with high or low  $N_{\text{EFAL}}$ )  $A_0$  passes through a maximum for a high value of  $N_{\text{Al}}$  (35 and 40). In order to obtain the real activity per gram of zeolite,  $A_0$  was divided by the crystallinity  $C_{\text{RX}}$ .

The deactivation of the samples increases when  $N_{\text{EFAL}}$  increases. Table 2 shows that for most of the series of samples  $A_f/A_0$ , the ratio of the activities after 70 min and after 2 min is greater for samples with a low amount of EFAL species. This has as a consequence that  $A_f$  is greater for samples with

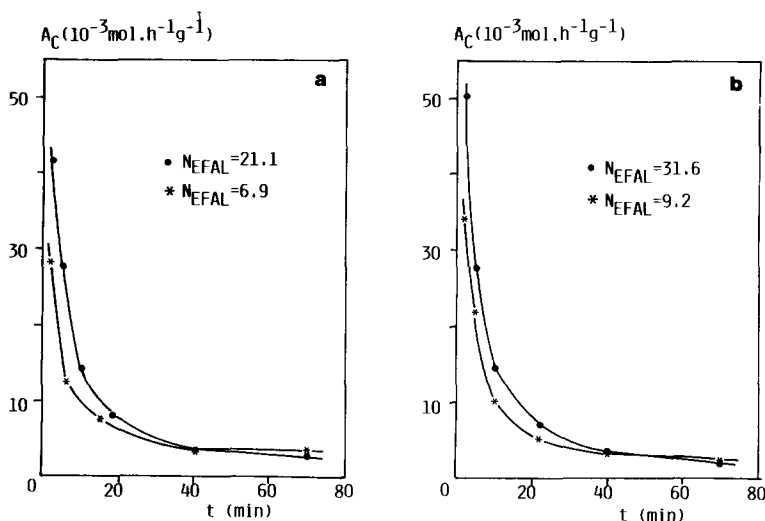


FIG. 1. Cracking activity  $A_c$  ( $10^{-3} \text{ mol} \cdot \text{h}^{-1} \text{ g}^{-1}$ ) as a function of time on stream  $t$  (min) · (a) series 1, (b) series 2.

few EFAL species while  $A_0$  is smaller (Table 2).

Figure 4 shows that the percentage of coke formed after 70 min is, at least for  $N_{\text{Al}} > 20$ , greater on samples with a large amount of EFAL species. This promoting effect of EFAL on coking was confirmed by a kinetic study of the coke formation on the samples of series 4 (Fig. 5). The ratio  $mk/$

$mc$  between the amounts of  $n$ -heptane transformed into coke and into desorbed products (isomers + cracking products) increases also with  $N_{\text{EFAL}}$  (Fig. 6). For  $N_{\text{Al}} > 20$ ,  $mk/mc$  during 70 min of reaction is greater on the samples with a large amount of EFAL species. If for samples with high or low  $N_{\text{EFAL}}$ ,  $mk/mc$  (Fig. 7) and the percentage of coke (Fig. 4) pass through a maximum for a high value of  $N_{\text{Al}}$ .

On all the samples, the isomerization/cracking rate ratio  $I/C$  increases with time on stream, the deactivation apparently affecting the cracking more than the isomerization. This can be related to the fact that cracking is consecutive to isomerization and therefore is more favored for high conversions (Fig. 8). For the same value of conversion (e.g., 10%, Fig. 9)  $I/C$  is higher on the samples with many EFAL species than on the samples with few. It passes through a maximum for a number of aluminum per unit cell of about 35 (Fig. 9). In the cracking products  $C_3$  and  $C_4$  are always the main compounds (>80%). The  $\text{iso}/nC_4$  ratio is always high (between 4 and 7 at 2 min). This ratio decreases with the conversion (with increasing time on stream). For the same value

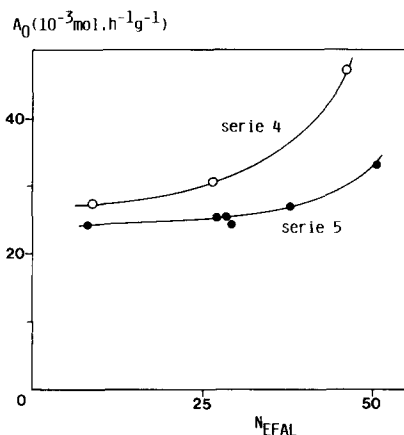


FIG. 2. Initial activity  $A_0$  ( $10^{-3} \text{ mol} \cdot \text{h}^{-1} \text{ g}^{-1}$ ) as a function of  $N_{\text{EFAL}}$ , the number of extra-framework aluminum species, for the samples of series 4 and 5.

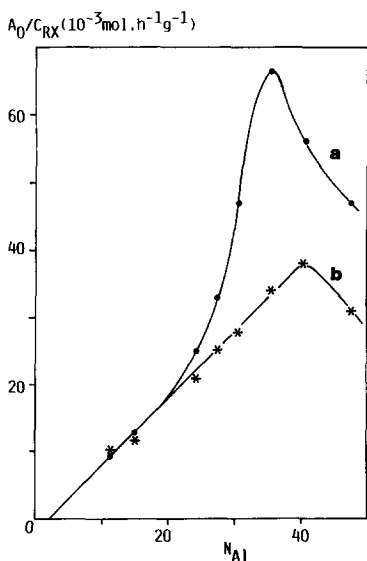


FIG. 3. Initial activity after correction of the crystallinity ( $A_0/C_{RX}$ ,  $10^{-3} \text{ mol} \cdot \text{h}^{-1} \text{g}^{-1}$ ) as a function of  $N_{Al}$ , the number of framework aluminum atoms per unit cell. (a) Samples with a large amount of extra-framework aluminum species, (b) samples with a small amount.

of conversion,  $iso/nC_4$  is higher on samples with many EFAL species; it passes through a maximum for  $N_{Al}$  equal to about 35. The alkane/olefin ratio in the cracking products ( $s/o$ ), initially much higher than 1 (Table 2) increases rapidly with time on stream (Fig. 10). At least for  $N_{Al} > 12$  the value of  $s/o$  obtained initially (after 2 min reaction),  $(s/o)_0$  is smaller for samples with many EFAL species than for those with few species. For both types of samples  $(s/o)_0$  passes through a maximum for a high value of  $N_{Al}$ .

#### DISCUSSION

We discuss successively the effect of  $N_{EFAL}$  and  $N_{Al}$  (number of extra-framework species and framework aluminum atoms per unit cell) on the activity, stability, and selectivity of the dealuminated samples.

##### 1. Activity

The initial activity of the samples ( $A_0$ ) depends on  $N_{Al}$  and on  $N_{EFAL}$  (Fig. 3). For  $N_{Al}$

$> 15$  the activity of the samples with many EFAL species (20 to 55 per unit cell) is greater than that of the samples treated by hydrochloric acid and therefore have few EFAL species. For  $N_{Al} < 15$  the activity of the samples with many and with few EFAL species are identical. The acid treatment can have effects other than the simple elimination of EFAL species. In particular, there is a partial exchange of sodium cations (Table 1) and also of cationic extra-framework species with formation of protonic sites. It is obvious that this increase in the number of protonic sites cannot explain the decrease in activity provoked by the acid treatment of the samples with  $N_{Al} > 15$ . The acid treatment could also cause a supplementary dealumination of the zeolite, consequently decreasing the number of acid sites and possibly the activity. However, Table 1 shows that the dealumination caused by the acid treatment is quite negligible. EFAL species could limit the rate of diffusion of the reactant and thus the rate of *n*-heptane cracking. If this were the case, the elimination of EFAL species would cause an increase in activity. Inaccuracies, due to deactivation, in the determination of  $A_0$  (activity

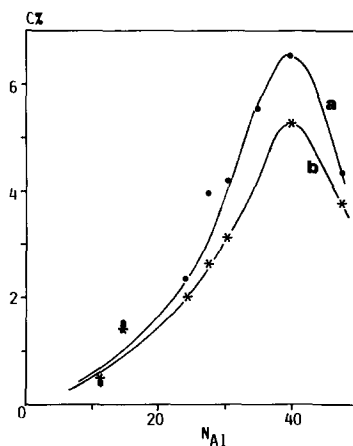


FIG. 4. Percentage of coke formed after 70-min reaction as a function of  $N_{Al}$ , the number of framework aluminum atoms per unit cell. (a) Samples with a large amount of EFAL species, (b) samples with a small amount.

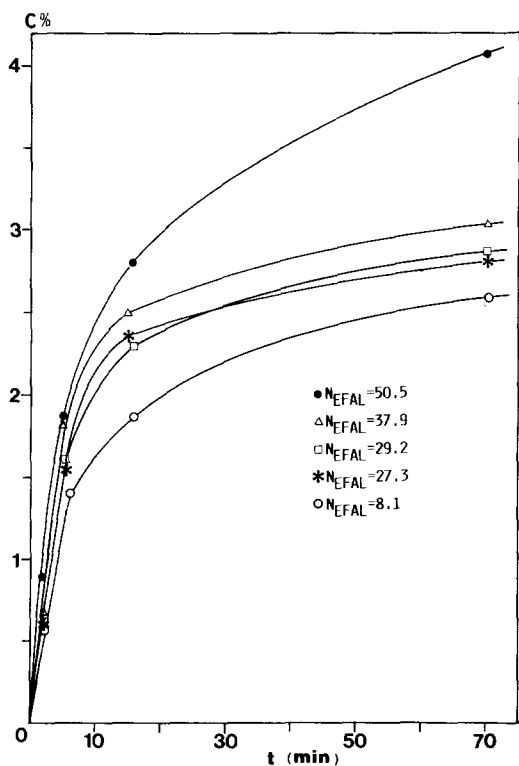


FIG. 5. Change with time on stream  $t$  (min) of the percentage of coke formed on the samples of series 5.

after 2 min reaction) cannot explain the differences between the values of  $A_0$  of the samples rich in EFAL species and poor in EFAL species. Indeed, the deactivation of the samples rich in EFAL species is the more rapid and therefore the difference between the initial activities of the samples (at time zero) is greater than that between the  $A_0$  values.

The greater activity of the samples rich in EFAL species is therefore due to a direct or indirect participation of EFAL species in  $n$ -heptane cracking; the acid sites of EFAL species are mainly Lewis sites (6) which are often considered as inactive for cracking of alkanes such as  $n$ -heptane. If it were really the case, the positive effect of EFAL species on the cracking activity would be due to an inductive influence of the Lewis sites of EFAL species on the protonic sites of the

zeolite (superacid sites). The fact that the effect of EFAL species depends on  $N_{Al}$  (hence on  $N_{EFAL}$  (Table 2)) can be explained by a change in the nature of EFAL and/or in their location as a function of the conditions of the hydrothermal treatment. According to various authors (3, 32), EFAL species formed at low temperatures would be located as small particles in the supercages of the zeolite. Samples with  $N_{Al} > 15$  for which EFAL species play a significant role were obtained by hydrothermal treatment at relatively low temperatures. Probable interactions between small particles of EFAL species located in the cavities and the hydroxyl groups of the zeolite could explain the positive effect of EFAL species on the activity. At high temperatures of hydrothermal treatment, EFAL species migrate out of the micropore system toward the zeolite surface or to the mesopores created by steaming forming clusters by condensation (5). There is no possible interaction between the Lewis acid sites of these clusters and the

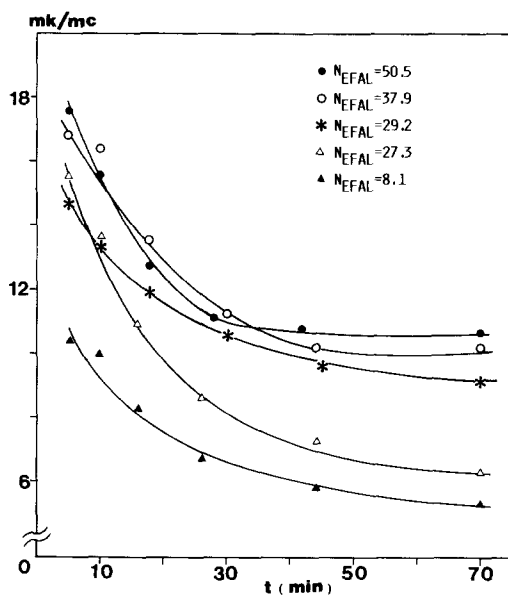


FIG. 6. Change with time on stream  $t$  (min) of  $mk/mc$ , the ratio of the amounts of  $n$ -heptane transformed into coke and into desorbed products, on the samples of series 5.

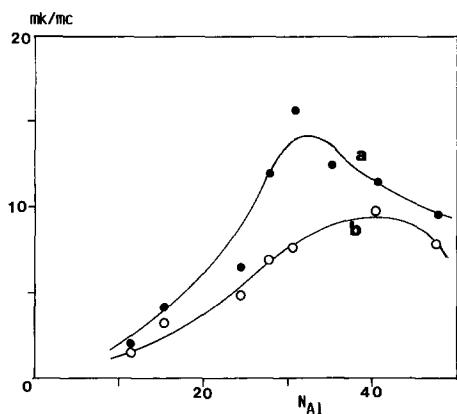


FIG. 7. Ratio ( $mk/mc$ ) of the amounts of  $n$ -heptane transformed into coke and into desorbed products for 70-min reaction as a function of  $N_{Al}$ , the number of framework aluminum atoms per unit cell. (a) Samples with a large amount of EFAL species, (b) samples with a small amount.

hydroxyl groups of the zeolite and hence no positive effect of EFAL species.

For samples rich or poor in EFAL species the activity passes through a maximum for  $N_{Al}$  between 35 and 40. Below this value the activity of the samples with few EFAL species is quasi-proportional to  $N_{Al}$  and therefore to the number of acid sites

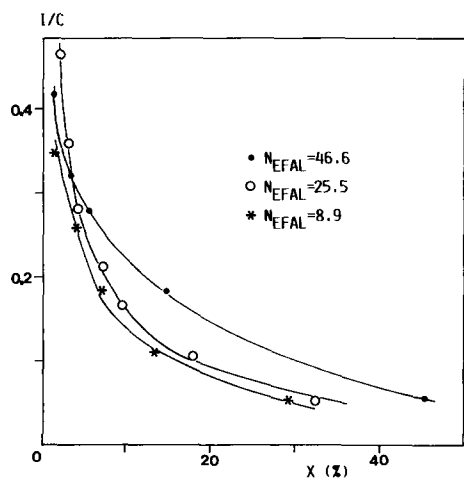


FIG. 8. Ratio ( $I/C$ ) of the cracking and isomerization rates on the samples of series 4 as a function of the conversion  $X$  (%).

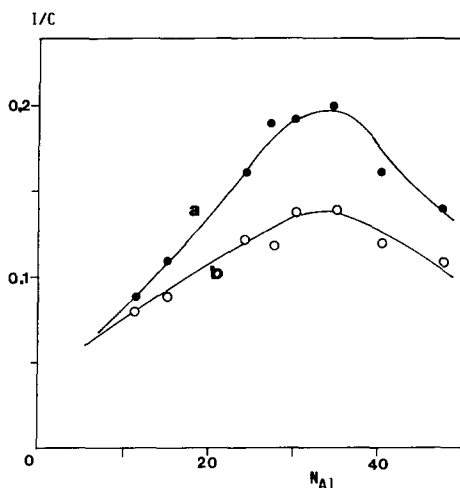


FIG. 9. Ratio ( $I/C$ ) of the cracking and isomerization rates for 10% of  $n$ -heptane conversion as a function of  $N_{Al}$ , the number of framework aluminum atoms per unit cell. (a) Samples with a large amount of EFAL species, (b) samples with a small amount.

(( $N_{Al} - N_{Na}$ )). The activity becomes equal to zero for  $N_{Al}$  equal to about 2, i.e., for  $N_{Al} - N_{Na}$  equal to zero. This change in activity with  $N_{Al}$  is the one expected from the topological model proposed by D. Barthomeuf (33, 34). The maximum corresponds to the value of  $N_{Al}$  below which none of the  $AlO_4^-$  is in a next-nearest neighborhood situation. Below this  $N_{Al}$  value the strength of each acid site is maximum. Therefore the activity per acid site must be the same for all the zeolites (see Fig. 6). The value of  $N_{Al}$  corresponding to the maximum (35–40) is slightly higher than the value estimated by Barthomeuf (33) from the topological model.

## 2. Coke Formation and Zeolite Stability

The change with  $N_{EFAL}$  and  $N_{Al}$  of the coking activity is practically the same as the one found for the cracking activity (Fig. 4): EFAL species increase the coke formation at least for high values of  $N_{Al}$ . For samples rich or poor in EFAL species the coking activity passes through a maximum for  $N_{Al}$  equal to about 40. However, below this  $N_{Al}$



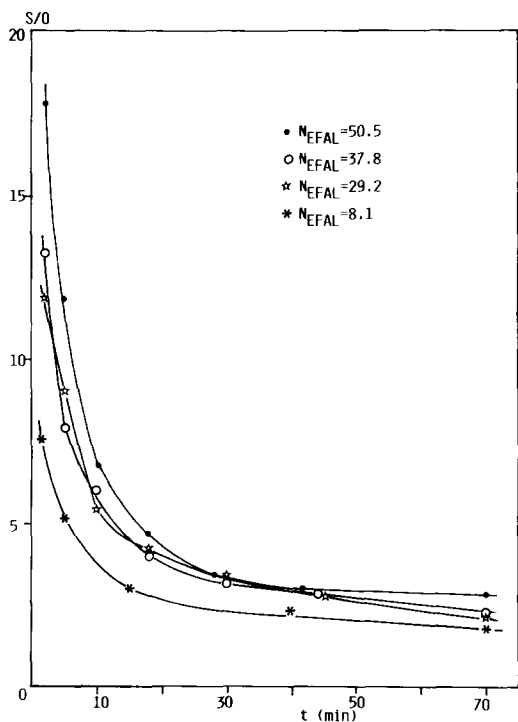


FIG. 10. Change with time on stream  $t$  (min) of the alkane/olefin ratio ( $s/o$ ) in the cracking products on the samples of series 5.

value the coking activity of the samples with few EFAL species is not proportional to the number of acid sites ( $N_{Al}-N_{Na}$ ) as was the case for the cracking activity. Figure 11 shows that the greater the density of the acid sites in the zeolite the greater their coking activity. This is what is generally found and attributed to the fact that the formation of a coke molecule requires numerous steps which are often bimolecular and therefore requires the participation of numerous acid sites (35, 36).

EFAL species play a negative role in the zeolite stability. The ratio of the final to the initial activities  $A_t/A_0$  generally increases when the EFAL species are eliminated from the zeolite (Table 2). Moreover, the higher  $N_{Al}$  the lower the stability. The changes in stability with  $N_{EFAL}$  are to a large extent due to the promoting effect EFAL species have on coking. However, it is also partly due to

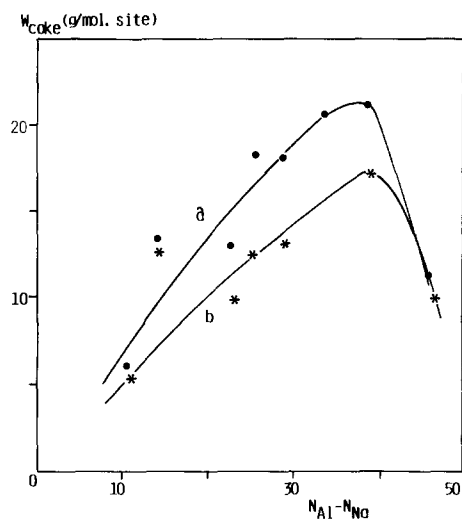


FIG. 11. Weight of coke formed per mol of framework acid site after 70-min reaction ( $W_{coke}$ , g/mol site) as a function of the number of framework acid sites per unit cell ( $N_{Al}-N_{Na}$ ). (a) Samples with many EFAL species; (b) samples with few EFAL species.

difference in the deactivating effects of coke for samples with many and with few EFAL species. This is shown clearly in Fig. 12 for the series 5 samples: the deactivating effect of coke decreases when  $N_{EFAL}$  decreases.

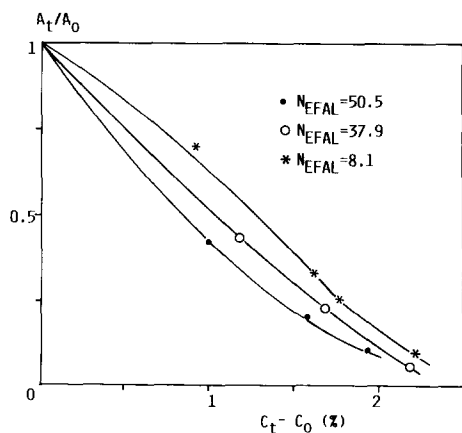


FIG. 12. Change of  $A_t/A_0$  the ratio of the activities after a certain time of reaction  $t$  and after 2 min reaction as a function of  $C_t-C_0$  (%), the difference between the percentages of coke deposited at time  $t$  and at 2 min, respectively.

The deactivation of Y zeolites occurs through blockage of the access of the reactants to the supercages in which coke is deposited (37), which means that EFAL species participate with coke in the blockage. Coking (and cracking) occurs consequently to a significant extent in the cavities containing EFAL species. This is in good agreement with the hypothesis of superacid sites created by an inductive effect of Lewis acid sites of EFAL species on the framework protonic sites. Again this effect of EFAL species on the coking rate and on the stability (Table 2, series 7 and 8) does not exist for the samples with low  $N_{Al}$  values in which EFAL species are mainly located on the outer surface or in mesopores.

### 3. Selectivities

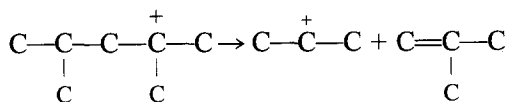
*n*-Heptane cracking probably occurs through the following steps (38):

(1) Formation of a  $nC_7^+$  carbenium ion through hydride transfer from *n*-heptane to a preexisting carbenium ion;

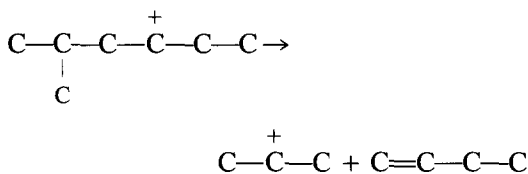
(2) isomerization of the  $nC_7^+$  carbenium ion into an  $iC_7^+$  carbenium ion through protonated cyclopropane intermediates (30);

(3)  $\beta$ -scission of mono- or bibranch  $iC_7^+$  carbenium ions.

Step 1 is generally considered the limiting step. Moreover, as the *iso/nC<sub>4</sub>* ratio is high the main scissions are those occurring from carbenium ions with a 2,2- or 2,4-dimethylpentane skeleton which can lead to *isoC<sub>4</sub>*, e.g.,



This type of scission which involves one tertiary and one secondary carbenium ion (type B (40)) is faster than the scission of carbenium ions with methylhexane skeleton which involves two secondary carbenium ions (type A), e.g.,



The olefins resulting from cracking undergo numerous secondary reactions, with the result that the alkane/olefin ratio (*s/o*) is always greater than 1 (ratio which would be obtained without secondary reactions). These secondary reactions, namely oligomerization, alkylation, and hydrogen transfer, lead to the formation of coke. Hydrogen transfer (from naphthenes compounds to olefins) is the reaction which consumes the largest amount of olefins and *s/o* can therefore be considered in a first approximation as representative of the ratio of the hydrogen transfer to cracking rates; the higher *s/o* the greater this ratio (41, 42).

The elimination of EFAL species by acid treatment causes some changes in selectivity: decrease in the alkane/olefin ratio (*s/o*), decrease in the ratio isomerization to cracking rate (*I/C*) and in the *iso/nC<sub>4</sub>* ratio. As already shown for the activity and for coking/cracking rate ratio the effect of EFAL species is less pronounced for highly dealuminated samples. Changes in the nature and/or in the location of the EFAL species with the dealumination level probably explain these observations.

**3.1 Alkane/olefin ratio (*s/o*).** EFAL species have a positive effect on this ratio (Fig. 13) and therefore on the ratio of the hydrogen transfer to cracking rates. Since they have also a positive effect on the cracking rate (Figure 3), we can conclude that EFAL species have a more pronounced positive effect on hydrogen transfer than on cracking. This was the case for coking compared to cracking (Fig. 6). The change with  $N_{Al}$  of *s/o* and therefore of the hydrogen transfer to cracking rate ratio (Fig. 13) is quite similar to the change of the coking to cracking rate ratio *mk/mc* (Fig. 6): *s/o*, like *mk/mc*, passes through a maximum for  $N_{Al}$  equal to 35 for the samples with many EFAL species and

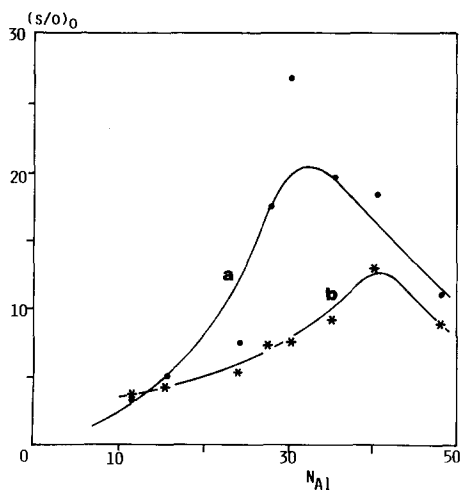


FIG. 13. Initial alkane/olefin ratio  $(s/o)_0$  in the cracking products as a function of  $N_{Al}$ , the number of aluminum atoms per unit cell. (a) Samples with a large amount of EFAL species, (b) samples with a small amount.

to 40 for the samples with few such species. There is therefore definitely a relationship between hydrogen transfer and coking, which is quite normal since hydrogen transfer is a significant step of coking. The hypotheses we have proposed to explain the change of the coking rate with  $N_{EFAL}$  and with  $N_{Al}$  could thus explain that of the rate of hydrogen transfer.

**3.2. Isomerization/cracking rate ratio ( $I/C$ ) and  $iso/nC_4$  ratios.** EFAL species have a positive effect on the values of these ratios. Both ratios pass through a maximum for  $N_{Al}$  of about 35 whether it be for the samples with few or with many EFAL species. The similar change of the two ratios with  $N_{Al}$  and with  $N_{EFAL}$  is quite normal: indeed, the higher the isomerization rate compared to the cracking rate the more significant the amount of carbenium ions with a dimethylpentane skeleton which lead by cracking to  $isoC_4$  products. However, it is more difficult to explain why EFAL species increase the isomerization rate more significantly than the cracking rate. An increase in acid strength (such as that caused by the inductive effect of EFAL species on

the protonic acidity) should favor the most difficult reaction, i.e., the cracking of carbenium ions with a methylhexane skeleton (type A scissions) which leads to  $nC_4$  products. Moreover, the elimination of EFAL species could allow a faster diffusion of the reactant and of the product molecules in the zeolite but should favor the formation of branched products (isomers,  $isoC_4$ ), i.e., the contrary of what was observed. The change with  $N_{Al}$  of  $I/C$  is similar to the change observed for the coking/cracking rate ratio (Fig. 6) and for the hydrogen transfer/cracking rate ratio (Fig. 13). Modifications with  $N_{Al}$  of the characteristics of the acid sites (in particular strength and density) could therefore be responsible for this  $I/C$  change.

## CONCLUSION

The activity, stability, and selectivity for  $n$ -heptane cracking of dealuminated samples are strongly influenced by the numbers of framework aluminum atoms ( $N_{Al}$ ) and of extra-framework aluminum species ( $N_{EFAL}$ ). For high values of  $N_{Al}$ , EFAL species have a promoting effect on the rates of isomerization of cracking, of hydrogen transfer, and of coking. This can be explained by an inductive influence of the Lewis acid sites of these species on the protonic sites of the zeolite. However, EFAL species increase the deactivating effect of coke. For  $N_{Al} < 15$ , EFAL species have practically no effect on the reaction rates, probably because they are too far from the protonic sites. For all the reactions, the activities of the dealuminated samples pass through a maximum for  $N_{Al}$  between 35 and 40, i.e., for a value slightly higher than that estimated from a topological model (33). In agreement with this model the cracking activity of the highly dealuminated samples which have few EFAL species is proportional to their number of acid sites. This is not the case for reactions such as hydrogen transfer and coking which require several acid sites for their catalysis. For these latter

reactions the density of acid sites has also a pronounced positive effect on the activity.

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