

# X, Y, Aluminum-Deficient, and Ultrastable Faujasite-Type Zeolites

## III. Catalytic Activity

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The catalytic properties of faujasite-type zeolites have been studied in the cracking of iso-octane. The selectivity of the reaction depends mainly on the sodium ion content.

The catalytic activity decreases with the number of strong acid sites. The active sites are linked to the aluminum sites which are related to strong acidity. They are removed only if the aluminum extraction exceeds 30% of the total aluminum content. Inactive and weak acid sites are related to the more easily removable fraction of the aluminum atoms.

This distinction of aluminum atoms into two types correlates very well with the results obtained for zeolites subjected to deep-bed calcination or heated at 870°C. The results point out the importance of  $AlO_4^-$  lattice aluminum with regard to the ultrastability.

### INTRODUCTION

The interest in faujasite-type zeolites as catalysts has led to the study of their active sites, in particular the aluminum sites. In recent years, the location of the aluminum atoms has emerged as an important parameter. Al atoms are either in anionic positions as  $AlO_4^-$  or in cationic positions as  $Al^{3+}$ . Various treatments of the faujasite-type zeolites X and Y lead to changes (1-9).

Three main classes of "modified" zeolites have been obtained and studied. First of all, the introduction of up to 16 aluminum cations in a Y zeolite containing initially 60 framework aluminum atoms per unit cell gives very active catalysts, but they are not especially stable (7, 8). Secondly, some particular treatments [heating at high temperature (2) or in deep-bed conditions (3, 6)] are found to change the initial anionic aluminum atoms of a Y zeolite in the following way: nearly two-thirds of them still occupy anionic positions, while a third has migrated towards cationic sites.

Such catalysts are very thermally stable. Lastly, a fraction of the 56 aluminum of the initial zeolite can be removed by chemical extraction (1, 4, 5, 9, 11), and this gives aluminum-deficient catalysts with high stability (1, 5, 10, 12). In a previous paper (9), it was suggested that the remaining aluminum atoms are in anionic locations. A deep-bed zeolite from which cationic aluminum have been chemically extracted could be placed in this class of "modified" faujasite (9).

In order to have a better understanding of the catalytic properties attributed to the several kinds of aluminum atoms, the aluminum-deficient zeolites have been studied in catalysis with regard to their aluminum content, which is correlated with changes in their properties. Previous results on the acidic properties have shown that only 70% of the aluminum atoms of X or Y zeolites give rise to strong acidity. The other ones are those which are easily removable and which are related to the weakest acidity

(9). IR studies of adsorbed pyridine have shown that these weakly acidic sites are related to Lewis sites and that the Brønsted sites become stronger when the degree of dealumination increases (13). Furthermore, a band at ca. 3600  $\text{cm}^{-1}$ , which was proposed as the characteristic band for ultra-stable Y zeolites by Jacobs and Uytterhoeven (6), Ward (14), and Peri (15), is also observed for aluminum-deficient samples. Finally, the sorption capacity of these catalysts has been studied (16). It has been shown that dealumination increases thermal stability as long as the aluminum content is higher than 17.4 per unit cell.

The present paper deals with changes in activity and selectivity due to decationation and aluminum removal. These studies enable us to compare some of the properties of the various forms of "modified" faujasite-type zeolites.

#### EXPERIMENTAL

**Materials.** X and Y Union Carbide zeolites were used as starting materials.

**NaH catalysts.** The sodium forms of the

TABLE 1  
NaHY AND NaHX CATALYSTS

	Na(%)	Na per unit cell	Exchange (%)	Crystallinity
<i>Y zeolites</i>	9.7	56	0	good
	7.8	45.4	19.6	good
	6.3	36.4	35.0	good
	5.7	33.1	41.2	good
	5.25	30.3	45.9	good
	4.2	24.4	56.7	good
	3.6	21.3	62.9	good
	3.2	18.7	67.0	good
	2.95	17.2	69.6	good
	2.3	13.3	76.3	good
	1.25	7.4	87.2	good
<i>X zeolites</i>	14.1	86	0	good
	10.3	63	16.7	good
	9.3	57	33.7	good
	8.4	51	40.5	nearly good
	7.0	43.3	49.5	nearly amorphous

X and Y materials were treated with aqueous  $\text{NH}_4\text{CH}_3\text{CO}_2$  solutions. The exchanged samples were first heated for 15 hr at 380°C in a stream of dry air to eliminate  $\text{NH}_3$ , and then at 550°C for 15 hr. Under such conditions, any deep-bed effect was avoided, since the flow of air carried out water and ammonia evolved from the catalyst. Furthermore, those samples do not show any properties of deep-bed products. The chemical composition and crystallinity are given in Table 1.

**Aluminum-deficient catalysts.** The first series of catalysts was obtained by treating NaY zeolites with acetylacetone in  $\text{CCl}_4$ , at room temperature, as described for zeolites or amorphous silica-aluminas (9, 17). Aluminum and sodium are removed together. The chemical composition and crystallinity of the catalysts are given in Table 2.

In the second series, the aluminum atoms were extracted from a 90% decationated  $\text{NaNH}_4\text{Y}$  sample by refluxing (4) with three organic acids, namely, ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), and diaminocyclohexane  $N,N,N',N'$ -tetraacetic acid (DCTA). The characteristics of the samples obtained are given in Table 3. The samples were heated in a stream of dry air first at 380°C for 15 hr and then at 550°C for the same time in such conditions to avoid the deep-bed effect.

The crystal stability was determined by X ray powder diffraction.

**Catalytic activity measurements.** The

TABLE 2  
ACETYLACETONE-TREATED Y ZEOLITES

	$\text{Al}_2\text{O}_3$ (%)	Al per unit cell	Al loss	Na (%)	Na per unit cell	Crystallinity
NaY	23.5	56	0	9.7	56	good
NaHY series	19.4	46.2	17.5	1.2	6.9	good
	16.9	40.3	28.2	3.4	19.6	good
	16.7	39.8	29	3.0	17.6	good
	16.2	38.7	31.2	1.8	10.5	good
	16.0	38.1	32.0	5.1	29.6	good
	16.0	38.1	32.0	2.7	15.5	good

TABLE 3  
 ORGANIC ACID-TREATED Y ZEOLITES

Extracting agent	Al <sub>2</sub> O <sub>3</sub> (%)	Al per unit cell	Al loss	Si loss	Na (%)	Na per unit cell	Crystallinity
EDTA	19.4	46.1	17.6	0	1.2	7.0	good
EDTA	18.7	44.5	20.5	0	1.26	7.3	good
DCTA	17.8	42.2	24.7	0	1.16	6.7	good
DTPA	16.5	39.3	29.8	0	1.16	6.7	good
EDTA	15.7	37.5	33	0	1.0	5.6	good
EDTA	12.8	30.5	45.5	0	0.55	3.1	good
EDTA	11.1	26.5	52.7	0	0.73	4.2	good
EDTA	7.3	17.4	69	6.3	0.44	2.5	not good
EDTA	6.4	15.0	73.2	14.7	0.34	1.9	not good

cracking of isooctane studied by the micro-catalytic method has been used to compare the catalytic properties of the zeolites. The cracking activity was determined either at 465°C or at 300°C, by passing isooctane-hydrogen or isooctane-helium mixtures over 10 mg of catalysts free from any adsorbed species by a previous heating in situ at 465°C for 15 hr under hydrogen gas flow. The partial pressure of isooctane was 100 Torr. Its conversion was less than 5%. The reaction products were analysed by gas chromatography. The column used was Chromosorb 80 mesh impregnated with TCP. Its temperature was 50°C. The flow rate was 1.8 liters/hr. The activity is expressed either by the initial rate  $r_0$  of formation of isobutene in mole  $\text{sec}^{-1}\text{g}^{-1}$  or by the amount (in percent) of the other products of reaction obtained in steady state conditions. The thermal stability of the samples was checked by catalytic measurements after a heating in a stream of dry air for 15 hr at 900°C.

**Acidity.** The titration with solutions of *n*-butylamine in benzene leads to the values of acidity expressed in equivalent per unit cell for several acid strengths defined by colored indicators according to the studies of Drushel and Sommers (18). The accuracy of results is about 5% (11, 22).

## RESULTS

### Acidity

Figure 1 shows the variation of acidity of X and Y zeolites as a function of the

degree of exchange of sodium ion for two ranges of acid strengths. The curves a and a' give the acidities for strengths higher than 88% H<sub>2</sub>SO<sub>4</sub> and the curves b and b' report strengths between 88% and  $3 \times 10^{-4}\%$  H<sub>2</sub>SO<sub>4</sub>. For the two types of zeolites, the strong acidity appears only when the degree of exchange is higher than 30%.

### Catalytic Activity

The catalytic cracking of isooctane gives methane, propane, propene, isobutene, isobutane, *cis*- and *trans*-2-butenes. The relative amounts of these products depend on the catalyst. Hence, the materials have

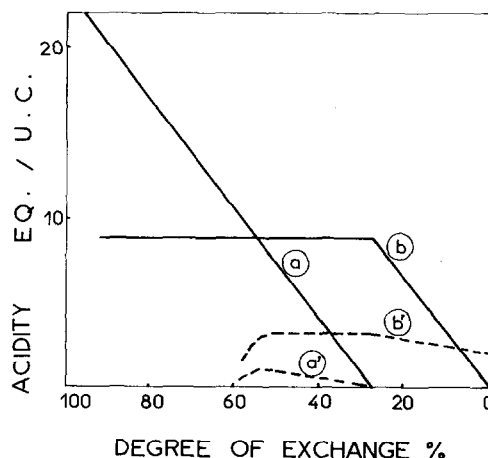
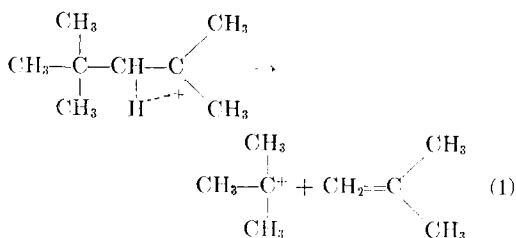


FIG. 1. Acidity as a function of the degree of exchange. (—) Y zeolite, (---) X zeolite. Curves a, a', acid strength > 88% H<sub>2</sub>SO<sub>4</sub>; curves b, b',  $3 \times 10^{-4}\%$  H<sub>2</sub>SO<sub>4</sub>, < acid strength < 88% H<sub>2</sub>SO<sub>4</sub>.

been characterized by the distribution range of the cracked products.

Preliminary experiments have shown that some of the hydrocarbon products are obtained via an intermediate involving isobutene. In order to elucidate this point, the experiments have been carried out on NaHY catalysts with the different products as successive reagents. With propene and isobutane, no reaction was observed. However, isobutene was transformed into methane with small amounts of propane, propene, isobutane and *cis*- and *trans*-2-butenes. The ratio of isobutene transformed increases as the sodium content decreases in the catalyst. These results suggested that isobutene was a primary product from which all the other ones were formed. A mechanism consistent with these results can be proposed.

In the first step the iso-octyl carbonium ion is formed from iso-octane either by adsorption on a Lewis site (19) or by reaction with a Brønsted center (20). The cracking of the carbonium ion gives isobutene and the isobutyl carbonium ion according to Eq. (1):



*Cis*- and *trans*-2-butenes are formed by isomerization reactions of butene. Propene and methane may be formed from the isobutyl carbonium ion produced in reaction (1) or by the reaction of the isobutene with a Brønsted site.

Isobutane was obtained in the presence of hydrogen, as well as when helium was used as the flowing gas (21). It can be produced from the reaction of another molecule of iso-octane with the carbonium ion isobutyl produced in reaction (1). Furthermore, some particular catalysts with well-defined sodium contents give higher isobutane production when hydrogen is employed instead of helium (21). In

these cases, some surface hydrogenating sites may be involved in the hydrogenation of isobutene to isobutane.

According to these results, the activity can be estimated either by an initial formation rate  $r_0$  in the case of isobutene or by the amounts (in percent) obtained for the other products in steady state conditions.

### *Y* zeolites

**Dependence on cation content—hydrogen atmosphere.** The catalytic activities at 465°C of several NaHY samples as a function of the number of sodium ions per unit cell are shown in Fig. 2.

Due to the great range of activities, a semilogarithmic graph was used. All the curves have a similar shape. At high sodium content, the activity is very small. It increases sharply when the degree of ex-

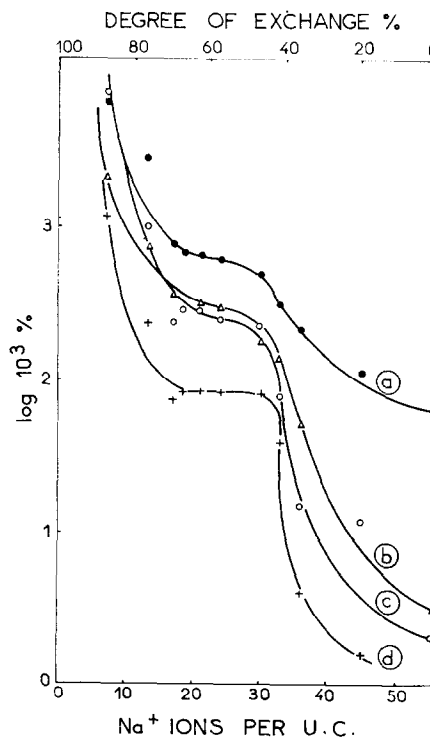


Fig. 2. Dependence of catalytic activity (log of the production in percent) on the sodium content of NaHY. (a) Isobutene, (b) propene + propane, (c) isobutane, (d) *trans* + *cis*-2-butenes.

change is higher than 30–35%. Samples containing small amounts of cations have activities which are  $10^3$  or  $10^4$  higher than the NaY starting materials. Nevertheless, the very important increase in activity cannot be due to a deep-bed effect during the treatment, since it has been verified that these samples are not more thermally stable than NaY catalysts, and furthermore they do not give an ir band at  $3600\text{ cm}^{-1}$  characteristic of ultrastable catalyst (6, 14).

From the product amounts reported in Fig. 2, one can calculate the distribution of the products for each catalyst. The results are shown in Table 4 for some of them. This table demonstrates clearly the changes in selectivity with cation content. Thus, at high cation content, the main product is isobutene, while at low cation level, isobutane is the main product.

**Dependence on cation content—helium atmosphere.** Table 4 reports the distribution range of the products obtained at  $465^\circ\text{C}$  with flowing helium as carrier gas. Table 5 gives the value of  $R$ , which is defined as the ratio of the activity relative to each product formed under hydrogen or under helium. It deviates from unity in the middle range of sodium content, particularly for the catalyst containing 30.3 ions per unit cell. It is noteworthy that the  $R$  values are the highest for isobutane and 2-butenes (by-products of isobutene formation). Hence, as reported previously, for

TABLE 5  
COMPARED CATALYTIC ACTIVITY OF NaY AND NaHY ZEOLITES UNDER FLOWING  $\text{H}_2$  OR He (AT  $465^\circ\text{C}$ )

Na <sup>+</sup> content per unit cell	Ratio $R$ of $\text{H}_2$ activity/He activity			
	Iso-butene	Iso-butane	Propene + propane	Trans-2-butene
56	1	1	1	1
30.3	2.7	14	4	20
18.7	2.1	6	3.1	4
7.4	1	1	1	1

intermediate sodium contents, the zeolite in a hydrogen atmosphere acts like a bi-functional catalyst. Such a property increases the whole catalytic activity (22) and modifies the distribution of the products.

As to the changes of  $R$  with sodium content, previous results have shown that, for isobutene formation, a degree of exchange higher than 30–35% was needed to obtain different results under hydrogen or under helium (22). The same value of 30–35% is again pointed out in the present experiments for all the reaction products.

**Dependence on sodium and aluminum content.** The acetylacetonate-treated materials give a range of samples containing various amounts of sodium and aluminum atoms (Table 2). Note that, in this case, the aluminum loss is less than 33%. Ac-

TABLE 4  
DISTRIBUTION OF THE PRODUCTS AFTER CRACKING OVER NaY AND NaHY ZEOLITES ( $465^\circ\text{C}$ , He OR  $\text{H}_2$  ATMOSPHERE)

Na <sup>+</sup> content per unit cell	Distribution of products <sup>a</sup>									
	Isobutene		Isobutane		Propene + propane		Trans-2-butene		Cis-2-butene	
	H <sub>2</sub>	He	H <sub>2</sub>	He	H <sub>2</sub>	He	H <sub>2</sub>	He	H <sub>2</sub>	He
56	0.95	0.95	0.02	0.02	0.03	0.03	0	0	0	0
36.4	0.65		0.10		0.25		0		0	
30.3	0.46	0.70	0.18	0.05	0.21	0.21	0.08	0.01	0.08	0.01
18.7	0.45	0.60	0.19	0.09	0.26	0.23	0.05	0.07	0.05	0
7.4	0.36	0.36	0.40	0.40	0.11	0.11	0.06	0.06	0.07	0.07

<sup>a</sup> Fraction in the reaction products.

ording to acidity studies on the same catalysts, this prevents the elimination of the aluminum sites which give rise to strong acidity (9).

Figure 3 shows that the catalytic activity at 465°C in hydrogen atmosphere is similar for both the aluminum-deficient and the starting NaHY zeolites. Hence the catalytic activity is independent of aluminum atoms removed, and furthermore the distribution range of the products (not given here) is exactly the same as that for non-dealuminated materials with various sodium contents (Table 4).

**Dependence on aluminum content.** Higher percentages of aluminum removal were obtained with organic acids. In this case, the activity studies have been carried out for the very low sodium content given in Table 3. Referring to Fig. 2, it can be seen that, for low cation levels, the activities are very high. Consequently, a reaction temperature of 300°C was chosen to make experimental measurements feasible. The experiments were performed in hydrogen

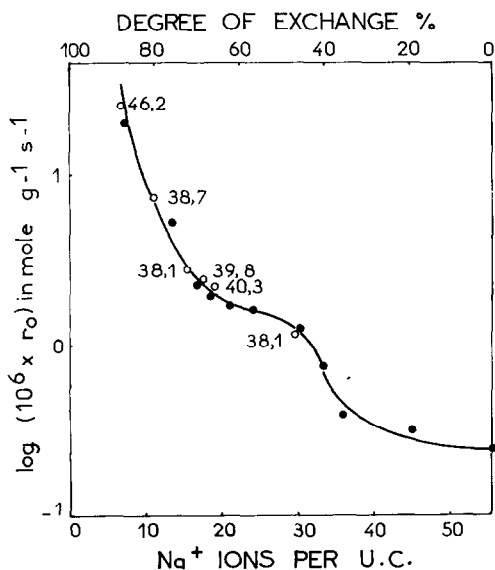


FIG. 3. Dependence of catalytic activity ( $\log r_0$ , where  $r_0$  is the initial rate of isobutene formation) on the sodium content. (●) NaHY, (○) NaHY dealuminated with acetylacetone (between brackets the number of aluminum atoms per unit cell).

TABLE 6  
CATALYTIC ACTIVITY OF ALUMINUM-DEFICIENT NaHY ZEOLITES (300°C, H<sub>2</sub> ATMOSPHERE)

Catalysts		10 <sup>6</sup> $r_0^a$ (mole sec <sup>-1</sup> g <sup>-1</sup> )	Distribution of products <sup>b</sup>		
Al per unit cell	Al loss (%)		Iso- butene	Iso- butane	Trans-2- butene
56	0	1.96	0.468	0.52	0.012
46.2	17.5	2.18	0.465	0.522	0.013
46.1	17.6	1.9	0.458	0.533	0.009
44.5	20.5	2.15	0.47	0.522	0.008
42.2	24.7	2.00	0.467	0.521	0.012
39.3	29.8	2.00	0.455	0.53	0.015
37.5	33	2.06	0.45	0.537	0.013
30.5	45.5	1.27	0.47	0.522	0.008
26.5	52.7	1.06	0.467	0.526	0.007
17.4	69	0.97	0.464	0.526	0.01
15	73.2	0.68	0.468	0.525	0.007

<sup>a</sup> Initial rate of isobutene formation.

<sup>b</sup> Fraction in the reaction products.

atmosphere. Except for the fact that the amounts of propane-propene produced are negligible at 300°C, the mechanism of the reaction is the same as that at 465°C. The rates of isobutene formation and the distribution range of the products are given in Table 6.

Up to an aluminum loss of nearly 33%, there were no significant changes in the amount of isobutene formed. Since the amount of the other products also did not show any significant variations, it is concluded that the catalytic activity is not altered in this range of aluminum depletion. Above this limit, i.e., greater than 33% loss, the activity decreases progressively with decreasing aluminum content (23). However, practically no changes in the distribution of the products was observed throughout the range of aluminum content studied.

It is worthwhile pointing out that the various extracting agents (acetylacetone, EDTA, DCTA, DTPA) give nearly the same activities for comparable aluminum losses and also similar distributions of the products. Thus, there is no dependence on the nature of the extracting agents.

The changes in activity which occur at the 33% aluminum loss cannot be related to textural modifications, since nitrogen adsorption shows no change for this aluminum content (16). Only the more dealuminated sample (15 Al/unit cell) has a nitrogen adsorption capacity lower than that of the starting zeolite.

The thermal stabilities of the non-dealuminated and dealuminated NaHY zeolites were tested by heating the samples at 900°C in dry air for 15 hr, followed by catalytic measurements at 300°C. The results showed that the non-dealuminated zeolites were rendered inactive by this treatment, whereas the dealuminated sample containing nearly 37 aluminum atoms per unit cell (corresponding to an aluminum loss of 33%) showed a high activity, comparable to those given in Table 6.

#### X zeolites

It was not possible to obtain several X aluminum-deficient zeolites with the same sodium content. In the case of acidity measurements, it was easy to interpolate the results in order to allow comparison of samples (9), but here the great changes in catalytic activity with cation content prevents such an evaluation. Hence, only decationized X zeolites were investigated.

**Dependence on sodium content.** The activity of NaHX zeolites was measured at 465°C in hydrogen atmosphere. Figure 4

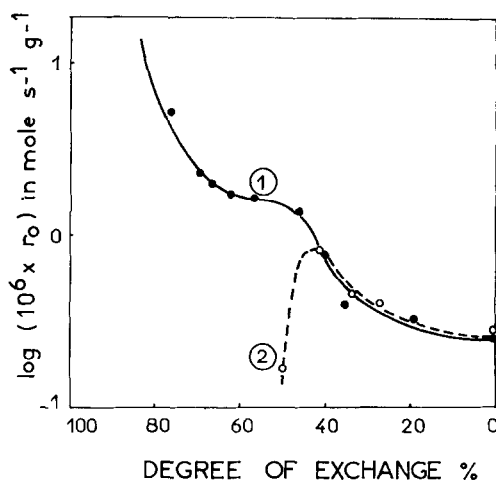


FIG. 4. Dependence of catalytic activity ( $\log r_0$ , where  $r_0$  is the initial rate of isobutene formation) on the degree of exchange. (●) NaHY, (○) NaHX.

depicts the logarithm of the initial rate of isobutene formation for decationized NaHY (curve 1) and NaHX (curve 2) as a function of the degree of exchange. The decrease in activity of NaHX samples is related to the loss of crystal structure of the highly decationized X zeolites. It is very surprising that, for low degree of exchange, the two curves are superimposed. Table 7 compares the distribution ranges of the products obtained with X and Y samples. The main product was always isobutene for X zeolites, while Y zeolites gave rise to greater amounts of by-products.

TABLE 7  
COMPARED CATALYTIC ACTIVITY OF NaHX AND NaHY ZEOLITES (465°C, H<sub>2</sub> ATMOSPHERE)

Degree of ex- change of Na <sup>+</sup> ions (%)	Distribution of products <sup>a</sup>							
	Isobutene		Isobutane		Propene + propane		Trans- + cis- 2-butene	
	X	Y	X	Y	X	Y	X	Y
0	0.90	0.95	0.04	0.02	0.06	0.03	0	0
35	0.88	0.65	0.05	0.25	0.06	0.10	0	0
40	0.82	0.56	0.11	0.19	0.04	0.17	0.07	0.02
50 <sup>b</sup>	0.76	0.46	0.16	0.21	0.07	0.18	0	0.08

<sup>a</sup> Fraction in the reaction products.

<sup>b</sup> Partial loss of the crystalline structure for the NaHX sample.

## DISCUSSION

*Active Sites*

(i) **Strength of Sites.** The catalytic activity increases sharply when more than 30% of sodium ions are exchanged (Figs. 2, 3, and 4). This particular limit also characterises the appearance of strong acid sites (Fig. 1). Hence, the catalytic properties of faujasite-type zeolites seem to be directly related to strong acid sites.

Furthermore, the activity does not change if only 30% aluminum atoms are eliminated, but starts to decrease as soon as the removal of aluminum exceeds 30%. It has also been shown that the strong acidity decreased at the same value (9).

So these results confirm the importance of strong acid sites in catalytic activity.

(ii) **Nature of sites.** It is generally considered that the cracking activity of zeolites is related to Brønsted acidity (24). Infrared studies of our samples have shown the large number of Brønsted acid sites in the active cracking catalysts (13). With regard to the origin of the protons, some successful correlations have been obtained between catalytic results and OH-band changes (25, 26) but, in other cases, it is difficult to find good correlations (27). Richardson (28) proposed a model in which the cations exert an influence via the intervening crystal structure. This may explain correlations between the acidity of OH groups and the ionic potential of the cations.

On the other hand, it has been shown that the reactivity or efficiency of acid sites decreases linearly as the aluminum content increases (11). Hence, the reactivity of active sites may be linked as well to a long-range influence of aluminum atoms, since Y zeolites are more active than X materials. In addition to this fact, the large scale of acid strengths in initial Y and X zeolites strongly suggests that each kind of aluminum atoms giving rise to a determined acid strength might have a different environment to the others. So the several acid strengths could be involved by a short range influence of the nearest atoms. This effect induces different catalytic properties of each kind of sites.

(iii) **Selectivity.** A comparison of Fig. 1

and Tables 4, 6, and 7 shows that isobutene is the main product of the reaction when the catalysts contain only weak and medium acid sites (low decationated NaHY samples) and/or a high amount of sodium (NaHX type zeolites). The product distribution is quite different for the highly decationated Y or aluminum-deficient zeolites containing strong acid sites: isobutane is then formed in great proportion. Hence, it seems that the strength of acid sites and the total number of sodium ions are important parameters on which the selectivity depends. A high extraction of aluminum atoms involving a decrease in the number of strong sites (9) causes only an activity drop without change of selectivity (Table 6). This substantiates the results of Topchieva *et al.* (29) who found that the activation energy of cumene cracking does not vary for materials having the same cation level (nearly one Na<sup>+</sup> per unit cell) and four different aluminum contents.

*Properties of Faujasite Deduced by Aluminum Removal*

(i) **Y zeolites.** The results of Table 6 and Fig. 3 show that the reagents which have been used to effect aluminum removal have no specific influence on the properties of the solids obtained. Changes in aluminum content only vary the catalytic activity if the extraction exceeds 33% of total aluminum content. Hence, it seems very probable that the aluminum atoms which are extracted up to 33% were not at all related to the active cracking sites of the initial zeolite. Moreover, the acidity results reported on the same catalysts show that the first 33% of aluminum atoms removed are only associated with weak and medium acid sites (9). On the other hand, it has been noted for decationated zeolites that the exchange exceeding 30% cations involves the liberation of strong acid sites and also active catalytic sites (Figs. 1 and 2). This suggests that the first cationic sites exchangeable are associated with the first aluminum sites removable. Neither are involved in properties such as strong acidity and catalytic activity, both studied after heating the materials at 550°C. Only the remaining aluminum and the related



acidic centers are associated with cracking activity. Hence, two main kinds of aluminum sites characterized by different properties may be determined in faujasite Y while crystallographically all aluminum atoms are identical. The first type which can be easily removed by chemical reagents is related to the cationic sites easily exchangeable. These sites which are weakly acidic, are not involved in the cracking reaction. The second type is responsible for the catalytic properties and strong acidity in zeolites.

(ii) **X zeolites.** Insufficient data on the activity of aluminum deficient X zeolites do not make possible the same comparative remarks with acid properties. Nevertheless, two facts can be pointed out. First, a degree of exchange of 30% is related to a sharp change in isobutene formation (Fig. 4) and to the appearance of strong acidity (Fig. 1) (22). Secondly, the existence of two types of aluminum atoms was previously noted in the X zeolites as regard to acidity results (9). From these considerations, it can be postulated that very probably the two classes of aluminum atoms in X zeolites would also be differentiated by their catalytic properties.

*Relation Between the Properties of  
Aluminum-Deficient and Deep-Bed,  
Ultrastable, AIHY Zeolites*

Early, Kerr (4) pointed out that the aluminum-deficient zeolites have many similarities to those obtained by McDaniel *et al.* (2) or by deep-bed heating. It has been found that the infrared spectra show the hydroxyl group band near  $3600\text{ cm}^{-1}$  typical of ultrastable zeolites (13). The present work shows that the aluminum-deficient samples are as catalytically stable as the ultrastable zeolites of McDaniel *et al.*, while their catalytic activity is not increased.

The similar properties can be explained by looking at the aluminum number affected by the several treatments. In fact, the aluminum migration towards cationic positions due to heating leaves a number of aluminum in anionic positions. Jacobs *et al.* (6), Kerr (3), and McDaniel *et al.* (2)

reported 39.6, near 38, and 38, respectively. Furthermore, Maher *et al.* (30) have shown by X ray studies that, in a commercial Y zeolite, 32 to 38 aluminum atoms are different from the other aluminum atoms. The present work shows that only 65–70% of aluminum, i.e., 36–39 atoms, are associated with active sites in catalysis. The agreement between these values suggests that the aluminum atoms which can easily migrate by heating could be those which are extractable without changing the catalytic properties. Hence, those aluminum atoms may be associated with sites which are inactive in iso-octane cracking and to the weak and medium acid sites. Their removal from the anionic framework either by extraction or by migration gives catalysts with similar properties, in particular a high thermal stability.

Lunsford *et al.* (8) have noted that, in a type Y zeolite with 60 anionic and 48 equivalents of cationic aluminum per unit cell, there is no ultrastability due to the cationic aluminum. Moreover, no hydroxyl group band at  $3600\text{ cm}^{-1}$  has been found in this zeolite AIHY. However, such a zeolite has a catalytic activity as high as zeolite catalysts containing trivalent ions such as  $\text{La}^{3+}$ .

The findings on the heterogeneity of aluminum sites may be applied to X zeolites. In fact, nearly 30% of the sites are weakly acidic and inactive for cracking.

It is interesting that the aluminum-deficient X materials can be much more decationized than the ordinary X zeolites without losing their crystalline structure. For instance, two aluminum-deficient X samples were obtained containing 77 Al–25 Na and 59 Al–32 Na (nearly a Y zeolite) per unit cell. This finding is consistent with the work of Ambis and Flank on ultrastable Y materials (31).

#### CONCLUSION

All the results suggest clearly that the ultrastability can be associated with  $\text{AlO}_4^-$  lattice aluminum. Moreover, it has been shown that the locations of aluminum atoms in anionic or cationic positions are important parameters on which the cata-

lytic activity depends. The aluminum atoms which can be removed or can migrate most readily would be linked to the least acidic and least active sites in catalysis. According to this, the active sites are associated with aluminum atoms which are strongly bonded to the framework, their nature and properties being already characterized in the starting solids.

The zeolite results are consistent with studies on amorphous silica-aluminas. Chemical extraction with acids or acetylacetone has demonstrated the existence of two main kinds of aluminum atoms in these catalysts. The silica-aluminas with reduced aluminum contents were also found to be more stable and to have special properties (17, 32). However, the very well defined crystalline arrangement of faujasite zeolites allows more specific conclusions. With both classes of catalysts, chemical removal of aluminum is a valuable means of investigating the aluminum sites, since it extracts selectively the first inactive type before removing the second kind of aluminum sites. This procedure eliminates any disturbing effect due to deposition of aluminum compounds in the zeolite framework.

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