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

II. Acid Strength and Aluminum Site Reactivity

R. BEAUMONT AND D. BARTHOMEUF

Institut de Recherches sur la Catalyse, 69-Villeurbanne; and Université Claude Bernard, Lyon L. France

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The removal of aluminum atoms from faujasite-type zeolites has been studied with regard to acidity changes in the catalysts. On the one hand, dealumination gives rise to zeolites of which the acidity can be predetermined by choosing the aluminum content. Some of them have only strong acid centers. On the other hand the results show a heterogeneity attributable to structural requirements in the chemical properties of the aluminum atoms of the normal X or Y zeolites. As the acidity originates from the aluminum sites, the differences in the aluminum reactivity are reflected in parallel changes in the reactivity of the acid sites towards cation exchange and in the existence of several acid strengths. Furthermore, the dealumination increases the stability of X zeolites.

INTRODUCTION

Some properties of zeolites X and Y, either aluminum deficient or not, have been reported in a previous paper (*1*). The systematic study of their acidic properties as a function of cation content leads to the determination of a structural acidity parameter, α_0, which is defined as the acid site efficiency in the supercage. It is not at all related to the ion-exchange capacity. It depends on the aluminum content of the zeolite. Its lower limit ($\alpha_0 = 0$) characterizes a faujasite-type zeolite with a maximum aluminum content of 96/unit cell (uc), while the upper limit ($\alpha_0 = 1$) is obtained for the ultrastable form containing approximately 28 aluminum atoms/uc. With a lower aluminum content the crystalline structure is destroyed and therefore the acidity measurements are meaningless. Moreover the acidity measured by butylamine titration decreases linearly with the increase in the sodium content. The straight lines obtained resemble acidity results with OH groups (*2*) and atomic hydrogen (*3*) versus the same variable.

The present paper reports values for acidity and information on the acid strength distribution in a number of aluminum-deficient X and Y type zeolites.

EXPERIMENTAL METHODS

Materials

The X and Y Union Carbide faujasite-type zeolites are the starting materials. The general formula of the sodium form (NaX or NaY) is

$$(\mathrm{Na})_x(\mathrm{AlO}_2)_x(\mathrm{SiO}_2)_y, n\mathrm{H_2O}$$

with $x = 86$ and $y = 106$ for X samples; and $x = 56$ and $y = 136$ for Y samples.

A decrease in the aluminum atom content is obtained by dealumination with organic reagents. The aluminum-deficient zeolites contain $\mathrm{Na^+}$ and protons. They are referred to as NaH[X] or NaH[Y] with a symbol characterizing the extracting agent.

Y Samples

Four organic compounds were used to prepare dealuminated Y zeolites. First of

TABLE 1
Chemical Composition of Acetylacetone-Treated Y Zeolites (NaH[Y]$_A$)

Al_2O_3 %	Al per uc	Na %	Na per uc
19.4	46.2	1.2	6.9
16.9	40.3	3.4	19.6
16.7	39.8	3.0	17.6
16.0	38.1	5.1	29.6
16.0	38.1	2.7	15.5

all, solutions of acetylacetone (25 ml) in carbon tetrachloride (240 ml) were in contact, for 90 min at room temperature, with 5 g zeolite $NaNH_4Y$ with varying sodium content. The samples were then washed with acetone and water. The chemical composition of the NaH[Y]$_A$ zeolites are given in Table 1. Aqueous solutions of ethylenediaminetetraacetic acid (EDTA) were used according to (*4*), to extract aluminum atoms from Y zeolites which were nearly 90% decationized. Table 2 gives the chemical compositions of some of the prepared samples NaH[Y]$_{EDTA}$. Using the same treatment, two other organic acids were used instead of EDTA. From diethylenetriaminepentaacetic acid (DTPA) and diaminocyclohexane-N,N,N',N'-tetraacetic acid (DCTA) the samples NaH[Y]$_{DTPA}$ and NaH[Y]$_{DCTA}$ were derived. They are listed in Table 3 with the number x moles of acid per atom of aluminum contained in the weight of zeolite used for an experiment.

TABLE 2
Chemical Composition of EDTA-Treated Y Zeolites (NaH[Y]$_{EDTA}$)

Al_2O_3 %	Al per uc	Al_2O_3 loss %	Na %	Na per uc	SiO_2 loss %
19.4	46.2	17.6	1.2	7.0	0
18.7	44.5	20.5	1.26	7.3	0
15.7	37.5	33.0	1.0	5.6	0
14.6	34.9	37.7	1.0	5.6	0
12.3	29.4	47.5	0.56	3.2	0
11.1	26.5	52.7	0.73	4.2	0
7.3	17.4	69.0	0.44	2.5	6.3
6.4	15.0	73.2	0.34	1.9	14.7

X Samples

NaX samples treated in the same way with aqueous solutions of EDTA gave the NaH[X]$_{EDTA}$ zeolites listed in Table 4.

Crystallinity

X-Ray studies show that Y aluminum-deficient zeolites have a good crystallinity if less than 50% of the aluminum atoms (28 Al) are removed. Normal X zeolite loses its crystallinity with less than 43 sodium ions/unit cell. Only X aluminum-deficient zeolites with a good crystallinity were studied.

Acidity Measurements

Before the measurements the zeolites were heat treated in dry air at 380°C for 15 hr and then at 550°C for a similar period in conditions which avoid the deep-bed effect.

Titration with n-butylamine and colored indicators chosen according to the studies of Drushel and Sommers (*5*), gives acidity in equivalents per unit cell. It has already been shown that the arylmethanol and Hammett indicators give similar results (*1, 7*); therefore the results obtained with the Hammett indicator (strength: 3.10^{-4}% H_2SO_4) are described here together with those from the arylmethanol series (strength: 77% and 88% H_2SO_4).

TABLE 3
Chemical Composition of Y Zeolites Treated with Organic Acids

Catalyst	x moles of acid per Al atom	Al_2O_3 %	Al per uc	Na %	Na per uc
NaH[Y]$_{EDTA}$	0.3	16.5	39.3	1.16	6.7
NaH[Y]$_{DTPA}$	0.3	16.5	39.3	1.16	6.7
NaH[Y]$_{DCTA}$	0.3	17.8	42.1	1.16	6.7

TABLE 4
CHEMICAL COMPOSITION OF EDTA-TREATED X ZEOLITES ($NaH[X]_{EDTA}$)

Al_2O_3 %	Al per uc	Na %	Na per uc
27	69.3	7.7	46.9
27	69.3	39.2	24
25.5	65.5	57.5	35.1

Unit of Reference for Zeolites

As previously stated (*1*), results must be expressed by a unit of reference which does not depend on the aluminum and sodium content. Results per unit cell allow an easy comparison of the samples. The more usual way to consider the composition of a unit cell is according to structural findings (*1*, *5*), keeping the total number of SiO_4 and $(AlO_4)^-$ tetrahedra constant even in the case of dealumination. Nevertheless another calculation is applied in the present case in order to simplify the description of the acidity results. The X and Y aluminum-deficient zeolites are characterized by the respective unit cells of initial sieves X and Y with regard to the number of SiO_4 and $(AlO_4)^-$ tetrahedra.

RESULTS

Y Zeolites

Influence of aluminum and sodium content. The acetylacetone aluminum-deficient samples give an interesting series of zeolites in which both the number of aluminum atoms and of sodium cations is varied. Previous results with zeolites (*1*, *7*) showed that acidity was dependent on the sodium content. Figure 1 compares these results with the curve obtained from the acetylacetone aluminum-deficient samples. Only two acid strengths are reported. The results of the strong acidity (curve 1) are very similar for the normal material and the aluminum-deficient samples; all the experimental points are very close to the same straight line. The total acidity however, depends on the aluminum content, since the aluminum-deficient samples (curve 2′) give lower results than the initial Y zeolite (curve 2). The acidity decay is higher for the low sodium ion samples.

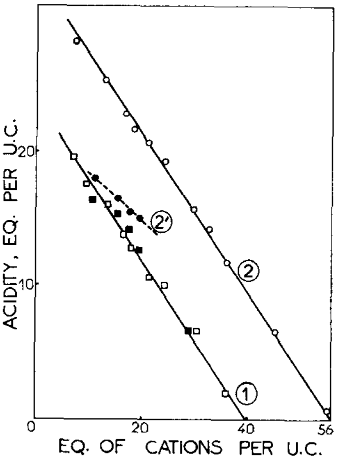

FIG. 1. The dependence of acidity on Na content for Y type zeolites: (1) strong acidity (88% H_2SO_4), NaHY (□) and $NaH[Y]_A$ (■); (2) total acidity (3×10^{-4}% H_2SO_4) NaHY, (○); (2′) total acidity (3×10^{-4}% H_2SO_4), $NaH[Y]_A$ (●).

It is interesting to note in Fig. 1, the lowest number of sodium ions ($56 - 40 = 16$) which must be exchanged by protons to give a Y zeolite with a strong acidity. Therefore 30% of the total number of sodium cations neutralizes the weakest acidity and 70% interacts with the stronger one.

Influence of aluminum content. The linearity of the acidity results plotted against the sodium content makes the comparison of samples (Tables 2 and 3) containing various amounts of aluminum and sodium atoms possible. A simple extrapolation with 5–6 sodium atoms/unit cell gives the corresponding acidity. The curves in Fig. 2 show, for three acid strengths, the dependence of the acidity calculated in this way (*8*). Acidity values lie on the same curves regardless of the extracting agent. Zeolites containing less than 35 aluminum atoms/unit cell are only strongly acid and the three curves become superimposed.

X Zeolites

Influence of aluminum and sodium content. The strong acidity of the samples

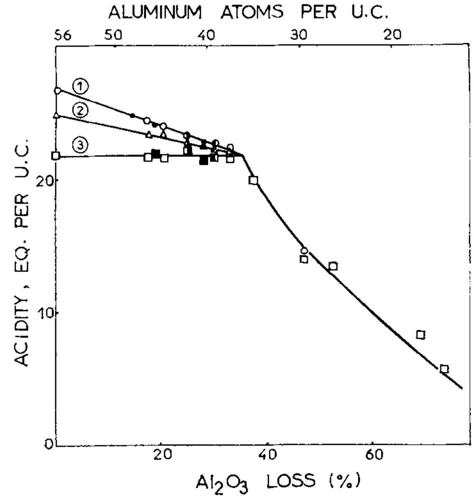

FIG. 2. The dependence of acidity on Al content for Y type zeolites:

	$NaH[Y]_{EDTA}$	$NaH[Y]_A$	$NaH[Y]_{DTPA}$	$NaH[Y]_{DCTA}$
(1) total acidity (3 × 10^{-4}% H_2SO_4)	○	●	◐	◑
(2) intermediate acidity (77% H_2SO_4)	△	▲	◭	◮
(3) strong acidity (88% H_2SO_4)	□	■	◧	◨

listed in Table 4 are shown in Fig. 3. They are compared to the results from the X normal zeolites. For this initial sieve the loss of structural stability leads to an important decrease in the acidity when the sodium content per unit cell is lower than about 43 cations (strong acidity, curve 1) or 50 cations (total acidity, curve 2). That aluminum-deficient samples have a meaningful strong acidity far beyond this stability limit is apparent from curve 1 in Fig. 3. The total acidity decay (curve 2′) may be attributed either to the beginning of the loss of structure stability or to the dealumination.

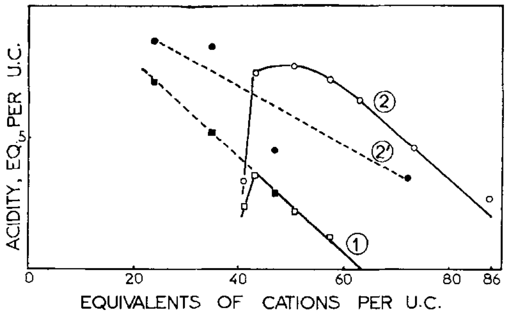

FIG. 3. The dependence of acidity on Na content for X type zeolites: (1) strong acidity (88% H_2SO_4), NaHX (□) and $NaH[X]_{EDTA}$ (■); (2) total acidity (3 × 10^{-4}% H_2SO_4), NaHX (○); (2′) total acidity (3 × 10^{-4}% H_2SO_4), $NaH[X]_{EDTA}$ (●).

Influence of aluminum content. The small number of X dealuminated samples does not allow acidity versus the aluminum content to be plotted. Nevertheless, taking account of the linearity of acidity versus sodium content, it is possible to extrapolate some acidity values for two samples in order to keep the number of sodium ions per unit cell constant. Hence for 53 sodium ions/unit cell, the total acidity of the normal X is 7.6 equiv/uc and that of an X containing 66 aluminum atoms (aluminum removal close to 23%) is decreased to 6 equiv/uc. The strong acidity does not depend on the aluminum content and is 1.8 equiv/uc. A more dealuminated X zeolite (about 40%) containing 46 sodium ions/unit cell has no more weak acid sites and its strong acidity is at least four times smaller than might be expected from Fig. 3.

DISCUSSION

Chemical Treatments

Results in Table 1 show that the more dealuminated samples using acetylacetone still contain 38 aluminum atoms/unit cell. That is, no more than about 30% of the aluminum atoms are removed. Even hot solutions of acetylacetone cannot pass this limit. In this way only the most easily removable part of the aluminum is extracted. The three other reagents, which are organic acids, can remove a greater proportion of the aluminum atoms or even remove them entirely (*4*). Table 3 shows few differences between the three acids. Under identical experimental conditions EDTA and DTPA extract the same amount while DCTA is only slightly less reactive. Thus the enolic function gives acetylacetone a smaller extracting power than the acid character does for the three other reagents. This property is particularly interesting since it makes possible the detection of different reactivities of the aluminum in the faujasite structure while the acid extraction does not bring out any easily detectable differences between the aluminum atoms.

Acidity and Aluminum Site Reactivity

The acid properties of the aluminum-deficient zeolites depicted in Figs. 1 to 3 show that in every case (X or Y zeolite) the total acidity decreases at the beginning of aluminum removal while the strong acidity is constant.

Figure 2 enables a detailed comment on these changes in the Y zeolites to be made. First of all, with reference to the properties of aluminum-deficient zeolites, catalysts containing less than about 35 aluminum atoms/unit cell are characterized by a single, strong acidity. More pronounced dealuminations preserve this property even when the structure begins to be destroyed ($Al < 28/uc$) or when silica is removed from the material ($Al < 15/uc$). A second conclusion can be drawn with regard to the initial zeolite. The extraction begins to remove the aluminum atoms selectively giving the lowest acidities (about 35% of the total aluminum content). The aluminum atoms associated with the strong acidity (65%) are extracted only after there is no more aluminum of the first type. These results demonstrate that the chemical properties of the aluminum of the faujasite lattice are not homogeneous and that furthermore they characterize two major types of aluminum sites and evaluate their number. Such heterogeneity in the chemical reactivity with the extracting agents confirms the fact that acetylacetone, a gentle reagent, can only extract aluminum atoms of the first type.

Besides this, Fig. 1 shows that the exchange of sodium ions by protons begins to eliminate the cations associated with the weakest sites. The strong acid sites are exchanged only when there are no more sodium ions linked to acid centers of the first type, i.e., when 30% of the total sodium ions have been eliminated. Hence only the weakest acid centers are selectively concerned in the beginning of the aluminum removal or in the exchange of sodium by protons. After 30–35% of the total number of sites have been involved the strong acid centers start to react. Neither diffusion phenomena nor changes in the accessibility of the several extracting agents and indicators can explain why the strong acid sites are selectively involved only after the removal of 30–35% of the aluminum or sodium cations.

As the acidic properties originate from the aluminum sites, the correlation between the two series of results strengthens, and gives a more general significance to, the differences in chemical reactivity of the two main types of aluminum atoms. Apart from this, such results show that the scattering of the acid strength of the Y zeolites is linked to some property of the aluminum sites, i.e., to a fundamental property of their structure.

These results are in excellent agreement with those of other authors regarding Y-type zeolites. Kerr (*9*) showed that deep-bed calcination of Y zeolites moves some of the aluminum atoms from anionic to cationic positions. A further treatment with 0.1 *N* NaOH solutions extracts these aluminum atoms and gives zeolites containing 39.6 aluminum atoms/unit cell. Jacobs and Uytterhoeven (*10*) obtained a value of 38 after the same treatment. Maher, Hunter and Scherzer (*11*) showed by X-ray studies that the so-called ultrastable Y material has 38 framework aluminum atoms; furthermore, they showed that the decationated (or "sodium–aluminum") form also has the same number of framework aluminum.

Since the present work reports a number of aluminum sites associated with strong acidity (close to 35–40), all these results are consistent with the idea that the various methods detect a general property of the Y zeolites, independent of the kind of treatment (heating or chemical extraction). Furthermore the results of Maher, Hunter and Scherzer (*11*) show that these aluminum atoms are already distinguished in a Y zeolite containing a small amount of sodium ions (9 Na^+/uc). The present paper characterizes them in Y samples of various sodium content, since for example acetylacetone extraction from different NaHY zeolites (Table 1) always gives the same limit of 38 aluminum atoms remaining/unit cell.

All the results suggest that 35 to 40 aluminum atoms are strongly linked in the lattice. The other aluminum atoms, up to 56, consist of differently and more weakly bonded atoms. Their removal from the framework, either by chemical extraction or by heating at 800°C or in deep-bed conditions, gives rise to new material.

On the other hand, it is noteworthy that some results on the more stable zeolites (Al-deficient) are very specific. These catalysts contain between 25 and 30 aluminum atoms/unit cell. It was shown that the efficiency of the acid sites tends towards unity for these chemical compositions (*1*). As such zeolites have only strong acidity it can be deduced that each aluminum atom of an ultrastable zeolite gives rise in the supercage to one strong acid center. None of the other faujasite type zeolites has this property.

The acidity results available for X zeolites do not allow a quantitative evaluation of the several aluminum types. Figure 3 shows, however, that 27 to 30% of the sodium ions must be removed before the strong acidity is involved in the exchange. Results given by 23% and 40% X aluminum-deficient materials show that strong acidity decreases for aluminum removal between these two percentages. The two series of numerical values are in a similar range. It may be concluded that, as with Y zeolites, aluminic sites of various reactivities exist and correlate with the several acid strengths detected in X zeolites. Also, the dealumination of the two zeolites increases the ratio of strong acidity.

Other important results can be drawn from Fig. 3. The X normal zeolite, heat treated at 550°C before the acidity measurements, loses its structure when it contains less than 43 aluminum atoms/unit cell. Aluminum-deficient samples keep their structure well and give very significant acidity results after the same heating, even for a sodium content as low as 25 sodium ions/unit cell. Thus the structure stability of X zeolites with decationation is greatly enhanced by dealumination. This result is very similar to the known increase in the thermal stability of Y dealuminated zeolites.

CONCLUSIONS

The study of the dealumination and of the acid properties of faujasite-type zeolites reveals a heterogeneity in the chemical properties of the aluminum sites. This could be consistent with some specific arrangements in the stable commercial forms of faujasite-type zeolites. Other zeolites derived from the parent X and Y forms, for example by extraction of the aluminum atoms as in the present work, can have different structural requirements since they are more homogeneous with regard to the strength of the acidity.

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