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

I. Acidic and Structural Properties

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The study of the acid properties of faujasite-type zeolites, X and Y, cationated, decationated and aluminum-deficient has led to the evaluation of a number α_0 which characterizes a structural acidity parameter. It tends towards its highest value for the ultrastable forms and it drops to zero for the limit content, in a faujasite lattice, of 96 aluminum per unit cell. Its decrease with the increase in the aluminum content gives a numerical measure of a so-called "self-neutralization effect" of the aluminum atoms towards the properties studied in the supercage. This numerical value ($\approx 1.45 \times 10^{-2}$) is a specific property of the faujasite structure.

INTRODUCTION

The importance of thermally stable zeolites leads to a large development of the research in the field of ultrastable zeolites. Such solids are obtained from Y zeolites either by heating in well defined conditions (*1, 2*) or by removal of aluminum atoms with ethylenediaminetetraacetic acid (EDTA) (*3–5*). In this last case the stability of the aluminum-deficient zeolites increases according to the decrease in aluminum content. The aim of the present work is the study of the acid properties of the faujasite-type zeolites, aluminum deficient or not.

Physical (*6*) or chemical methods (*7*) may be applied to the characterization of the acid sites. Taking into account some special features peculiar to the titration with *n*-butylamine (*8*), the method may be usefully employed even in the case of zeolites. The base (pK_b close to that of piperidine) can induce migration of inaccessible protons (*9*) and steric hindrance is not the main factor which controls reactions involving organic species such as, for example, butylammonium ions (*10*).

A rapid survey of previous results (*11*) obtained with different cationated zeolites is necessary in order to deduce a general property of these zeolites and to introduce the study of the acid properties of the aluminum-deficient materials.

EXPERIMENTAL

Materials

Cationated samples. The commercial Union Carbide NaX and NaY have been used as starting materials. The preparation of partially protonated samples containing various amounts of Na, K, Ca or La ions has been described (*11*). Because of the different atomic weights of these cations, a fixed amount of zeolite (for example 1 g) does not contain the same number of units of reference (for example the number of SiO_4 tetrahedra or the number of unit cells). In order to make easier the comparison between the various samples, all the results are expressed for one unit cell. The contents in cations appear in Fig. 1 in equivalents per unit cell. The names of the samples NaHY, KHY, CaHY and LaHY describe both the protons and the cations they contain.

Aluminum-deficient and ultrastable samples. The weight of the zeolites depends

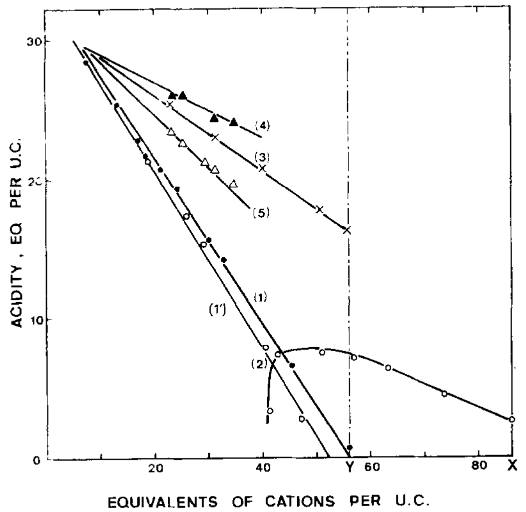

FIG. 1. Acidity in eq per unit cell (u.c.) (strength ⩾ 3 10^{-4}% H_2SO_4) versus the number of eq of cations per u.c. 1–NaHY, 1′–KHY, 2–NaHX, 3–CaHY, 4–LaHY heat treated at 300°, 5–LaHY heat treated at 550°.

on the degree of the removal of the aluminum atoms. Hence the results are expressed per unit cell assuming that, in a unit cell, the total number of SiO_4 and $(AlO_4)^-$ tetrahedra is unchanged.

Ethylenediaminetetra-acetic acid was used to prepare the $(X)_{EDTA}$ aluminum-deficient zeolites (Table 1). Their chemical composition makes possible the evaluation of the number of aluminum and sodium atoms per unit cell. There are two series of aluminum content (76.5 and 74 Al/unit cell) with two values for sodium ions.

TABLE 1
COMPOSITION OF ALUMINUM-DEFICIENT ZEOLITES

Catalysts	SiO_2 %	Al_2O_3 %	Na_2O %	Al/ u.c.	Na/ u.c.
X Zeolites					
1_a-$(X)_{EDTA}$[a]	56	31.8	12.2	76.5	49
1_b-$(X)_{EDTA}$	53.8	30.5	15.7	76.5	66
2_a-$(X)_{EDTA}$	58.9	31.5	9.6	74	37
2_b-$(X)_{EDTA}$	56.7	30.2	13.1	74	53
Y Zeolites					
3_a-$(Y)_{EDTA}$[a]	74.5	23.5	2	52	7
3_b-$(Y)_A$[b]	68.2	21.8	10	52.5	39
4_a-$(Y)_{EDTA}$	77.9	20.2	1.9	48	7
4_b-$(Y)_A$	74.2	21	4.8	48	18
5_a-$(Y)_{EDTA}$	79.9	18.4	1.7	41	6
5_b-$(Y)_{EDTA}$	74	17.1	8.9	41	34.5

[a] $(X)_{EDTA}$, $(Y)_{EDTA}$: Treated with EDTA.
[b] $(Y)_A$: Treatment with acetylacetone.

Either acetylacetone or EDTA were used to prepare the Y aluminum deficient samples. Acetylacetone was used in CCl_4 solutions at room temperature. It gave two Y aluminum-deficient zeolites referred to in Table 1 as $(Y)_A$. EDTA employed according to (*3*, *4*) led to the $(Y)_{EDTA}$ samples. The aluminum-deficient Y zeolites are distributed according to three aluminum contents (52, 48, and 41 Al/unit cell) and two sodium amounts for each of these groups (Table 1).

Acidity Measurements

The usual titration with solutions of *n*-butylamine in benzene leads to the value of the acidity expressed in equivalent per unit cell for several acid strengths defined by Hammett and arylmethanol indicators according to the studies of Drushel and Sommers (*8*).

Except for one series of LaHY zeolites, the samples were heated in dry air at 380 and 550° for 15 hr before acidity measurements. The procedure employed avoided any deep-bed effect.

RESULTS

Acidity of Partially Cationated Zeolites

NaHY zeolites. Some results obtained with NaHY zeolites were already described and discussed (*11*). Only the facts related to the present subject will be pointed out.

Figure 1 gives the total acidity of the X and Y zeolites versus their cation content.

Plotting the number of equivalent of acidity versus the number of Na^+ ions per dehydrated unit cell leads for the Y sample to a straight line (curve 1) all along the abscissa axis and the slope so calculated for a dehydrated cell is slightly different from a previous result. Its value is $\alpha_0 = 0.6$.

The X sample loses its crystalline structure for a degree of exchange greater than 50%. The nonlinear part of curve 2 is then meaningless. The slope of the straight part is $\alpha_0 = 0.16$.

The two values are obtained within a precision of ±5%.

It was already shown that for each of the two zeolites the curves related to stronger acidities are parallel to those of Fig. 1. Therefore the straight lines obtained with six very different indicators (Hammett and arylmethanol) have the same slope (Table 3). Furthermore the slope is also the same for all the degrees of exchange while the size of the cavity slightly changes. These two results indicate the lack of any steric effect of the indicators. It is noteworthy that from the results of Turkevich *et al.* (*12*) one may calculate ratios comparable to α_0, of which the values vary from 0.6 to 1.25.

KHY, CaHY, LaHY zeolites. The total acidity (in eq per unit cell) is reported in Fig. 1 versus the number of equivalents of cations K, Ca and La per unit cell.

For the Y samples the slope α of each straight line (curves 3, 4, 5 in Fig. 1) is less than α_0. The results given by multivalent ions can be explained by the known reaction (*6*) of the ions with water which leads to a partial neutralization of the aluminum sites.

According to the reaction:

$$Me^{n+}\,(OH_2)_{(n-1)} \rightleftharpoons Me(OH)^{+}{}_{(n-1)} + (n-1)\,H^{+}$$

it can be deduced that whatever be the valency of the cation Me, it would only neutralize one aluminum site and it would be associated with $(n - 1)$ protons. LaHY heated at 550°C undergoes another reaction which leads to the neutralization of two aluminum sites by one La ion (*13*).

Table 2 compares the ratios of the slopes α/α_0 with the ratios of the number of neutralized aluminum sites to the cation valency. The two series of values are very close to each other. This confirms the hypothesis of such a partial neutralization and leads us to look very carefully at the slope α_0.

Its specific property may be easily deduced from the same acidity measurements by plotting the experimental results versus the number of cations per unit cell (Fig. 2) instead of the number of equivalents of cations as in Fig. 1. The experimental points of Fig. 1 have not been drawn again for the sake of clarity and only the resulting curves are reported. For Y zeolites the limit content in bivalent ion is then 28 and 56/3 for trivalent ions.

TABLE 2

CORRELATIONS BETWEEN THE CATION VALENCY AND THE RATIO α/α_0

Catalysts	Cation valency	N^a	N/cation valency	α/α_0
NaHY	1	1	1	1
KHY	1	1	1	1.09
CaHY	2	1	1/2	0.48
LaHY (300)[b]	3	1	1/3	0.33
LaHY (550)	3	1	2/3	0.65

[a] Number of neutralized aluminum sites by one ion.

[b] Treatment temperature.

Figure 2 shows very clearly that α_0 (slope of the three lines) is not at all related to the nature of the cation in the solid. It only depends on the type of the zeolite X or Y.

Furthermore an important comment has

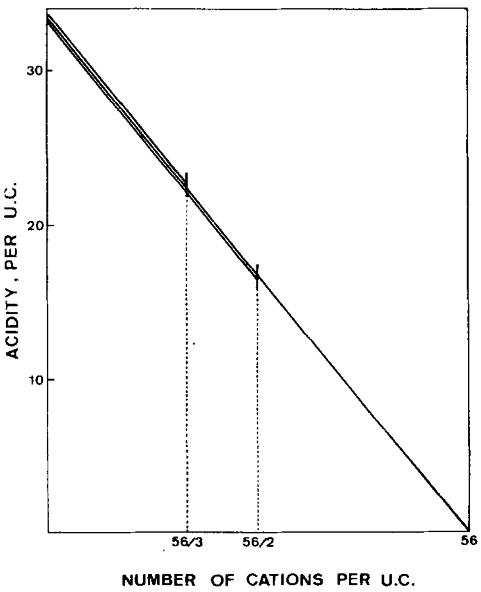

FIG. 2. Acidity in eq per unit cell (u.c.) (strength ⩾ 3 10^{-4}% H_2SO_4) versus the number of cations per u.c. Abscissas: 56/3 LaHY; 56/2 CaHY; 56 NaHY.

to be made on the linearity of the lines of Fig. 2. The slope measures the increase in acidity (expressed in eq per unit cell) corresponding to the removal of one cation. As α_0 is constant, the increase is the same whatever the number of cations in the zeolite. As, according to the ion content, the cations are localized in very defined positions it may be said that whatever be this location, the increase in acidity is the same.

This result could be explained in terms of a migration of ions towards the supercage which would keep constant the number of ions in the big cavity. However, at low cation content there would be a lack of cations and the slope would be modified. The very good linearity indicates that the location of the ions in the different sites (SI, SI′, SII, SIII . . .) does not influence the amount of butylamine which enters the supercage.

As the slope α_0 is independent of the cation (nature, valency, location and content) it is a specific parameter of the zeolite structure during its titration by *n*-butylamine.

These first results have to be completed by other experiments in order to confirm, strengthen and extend the validity of the α_0 value and then explain its significance. First of all the effects of the temperature and of the basic reagent have been studied. Secondly the acidity of the aluminum-deficient zeolites have been measured.

Effect of temperature. The acidity measurements of Y zeolites were repeated after a thermal treatment of the NaHY at 450° instead of the usual 550° temperature. The results are independent of these temperatures and the slope has the same value $\alpha_0 = 0.6$ previously found.

Effect of base. Two amines smaller than *n*-butylamine were tried. Solutions of methylamine and propylamine in benzene were employed for the titration of several NaHY samples heat treated at 550°. The results with methylamine are more imprecise but nevertheless the values obtained are very close to the other ones. With propylamine the measured acidity is the same as with butylamine. Consequently the slopes are identical. Furthermore the same slope is again obtained with the several indicators used, i.e., it does not depend on the strength of the acidity. Then the fact that the three amines give the same slope corroborates the lack of any effect of the size of the reagents.

Acidity of Aluminum-Deficient Faujasite Type Zeolites

The acidity of the X and Y aluminum-deficient zeolites described in Table 1 was measured by the titration with *n*-butylamine. The colored indicators are those previously used. The Hammett indicators are referred to as H– and the arylmethanol ones as Ar– in Table 3. As usual the different acid strengths are given by the composition of sulfuric acid solutions.

The slopes α_0 which may be calculated for each sample from the experimental values are very close for all the acid strengths. The mean values are listed in Table 3.

For Y aluminum-deficient samples the α_0 values are higher than for the initial Y and they increase as the aluminum content decreases. Such a property cannot be attributed to a change in the porosity and a consequent best accessibility of the butylamine molecule in the supercage since, in fact, Table 3 shows that the acidity (i.e., the amount of butylamine employed) is not higher for the aluminum-deficient Y samples than for the initial Y, for similar content in sodium ions. Only the slope α_0 is increased. Furthermore the removal of the aluminum atoms leads to a lattice contraction (*4, 14*) and the supercage volume is slightly reduced.

It is noteworthy that, on one hand the samples 3_a and 3_b and on the other hand the zeolites 4_a and 4_b, containing, respectively, 52 and 48 aluminum per unit cell give very significant acidity results in spite of the differences in their preparation (treatment with EDTA or acetylacetone).

The results for the samples containing less than 50% of their 56 initial aluminum per unit cell are not reported here, as the loss of the crystalline structure modifies

TABLE 3

Acidity Measurements of X, Y and Aluminum-Deficient Zeolites

Catalysts	Acidity (eq per u.c.)						α_0
	H—3 × 10^{-4}%[a]	H—72%	H—90%	Ar—50%[b]	Ar—77%	Ar—88%	
NaHX (43.5)[c]	—	4.9	3.4	—	—	2.7	
NaHX (57)	—	2.8	1.2	5.9	1.7	0.6	
NaHX (63)	6.4	1.8	—	4.9	0.7	—	0.16
NaHX (86)	2.6	—	—	0	—	—	
1_a-$(X)_{EDTA}$	9.4	—	—	8.1	—	—	
1_b-$(X)_{EDTA}$	4.2	—	—	3.2	—	—	0.30
2_a-$(X)_{EDTA}$	10.3	—	6.9	9.6	—	6.9	
2_b-$(X)_{EDTA}$	5.2	—	2.2	5.0	—	2.2	0.33
NaHY (13)[c]	25.9	23.4	16.2	24.5	22.2	16.4	
NaHY (30)	15.7	13.3	6	14.2	12	6.2	0.60
3_a-$(Y)_{EDTA}$	26	—	—	—	—	—	
3_b-$(Y)_A$	5.45	—	—	—	—	—	0.64
4_a-$(Y)_{EDTA}$	25	24.5	23.5	24.5	24.5	23.5	
4_b-$(Y)_A$	17.3	16.6	16.0	16.5	16	15.4	0.70
5_a-$(Y)_{EDTA}$	—	—	22.8	—	—	22.8	
5_b-$(Y)_{EDTA}$	—	—	1.45	—	—	1.45	0.81

[a] H— denotes Hammett indicators.

[b] Ar— denotes arylmethanol indicators. The concentrations of sulfuric acid solutions given in % determine the acid strength.

[c] Na^+ content per u.c.

the acidity results and the slope determination becomes meaningless.

The α_0 values for X aluminum-deficient samples also increases, beyond 0.16, as the lattice loses aluminum atoms. The comparison between the X starting zeolite and the one containing 74 aluminum per unit cell indicates a growth by a factor of 2 for the α_0 slope. As previously, this very high increase cannot be explained by textural changes.

It is noticeable that these last α_0 values are comprised between that of X and Y initial samples just like their aluminum content. The continuous increase from 0.16 for the more aluminated zeolite to 0.81 for the more dealuminated one suggests to plot these values versus the number of aluminum atoms per unit cell. Figure 3 is then obtained. The equation of the straight line is: $\alpha_0 = -1.45 \times 10^{-2}\, n_{Al} + 1.4$ where n_{Al} = number of Al per unit cell.

Discussion

Cationated and Decationated X and Y

The results obtained with cationated zeolites bring out the importance of the slope α_0. According to the several parameters tested, its properties may be summarized as follows.

It is independent of:

—the base which is used to determine it,
—the acid strength of the sites and of the nature of the indicator used,

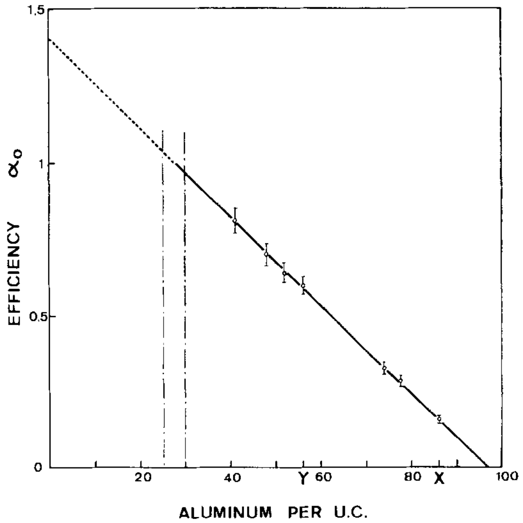

Fig. 3. Relationship between the α_0 value and the number of Al per unit cell (u.c.).

—the nature, valency, location and content of the cation,

—the dehydration temperature of the samples between 450 and 550°C.

It only depends on the type X or Y of the zeolite.

This slope α_0, better than the absolute value of the acidity which depends upon the cation content and the strength of the acid sites, can express an acidic property of the zeolite. It looks like a general property of a given zeolite.

$\alpha_0 = 0.6$ is a property of Y zeolite.

$\alpha_0 = 0.16$ is a property of X zeolite.

Up to now the values of α_0 have essentially been considered as a mathematical property of the straight lines of Fig. 1 (curve 1 and 2) and of Fig. 2. A physical meaning may be drawn out in the scope of the structural characteristics of the zeolites.

The value $\alpha_0 = 0.6$ means that for Y zeolite the exchange of one Na^+ ion by a proton increases the acidity of only 0.6 eq per unit cell. For the same situation the acidity of X zeolite varies by 0.16 eq per unit cell.

The origin of the lower value for X zeolite is certainly to be investigated in the manner described by Pickert *et al.* (*15*) and Dempsey (*16*). They found by mathematical calculations on the electrostatic fields in the faujasite-type zeolites that for the same cation at a given distance from a cationic site the field is smaller in X zeolite than in Y. As the titration by the butylamine gives α_0 values smaller for Y, the amine, which only enters the supercage, could then be sensitive to the resultant in this big cavity of the components of the various fields created by the positive charges and the negative $(AlO_4)^-$ tetrahedra. Hence, only a fraction of the theoretical charge of one $(AlO_4)^-$ tetrahedron participates in the acidity, developed in the supercage, which has to be neutralized by the amine. This fraction can then be represented by the α_0 value which only depends on the type of the zeolite, i.e., its aluminum content.

It must be kept in mind that on the contrary the chemical neutralization of individual and localized sites SI, SI′, SII, . . . , is not affected by the number of aluminum atoms in the unit cell. For instance, each of the 86 $(AlO_4)^-$ tetrahedra, in NaX zeolite, is neutralized by one monovalent ion. On the opposite the titration by the amine gives informations on the resulting effects which occur in the supercage.

These comments lead us to say that in a chemical spelling α_0 would be the efficiency in the supercage of an aluminum site.

Aluminum-Deficient Zeolites

Figure 3 and Table 3 show that α_0 increases as the aluminum content decreases. Therefore, α_0 may be defined in a more general meaning, for all the samples studied and further for all the faujasite type zeolites, as a measure in the supercage of the efficiency towards the basic reagents of the acidity linked to the $(AlO_4)^-$ tetrahedra.

Besides the fundamental interest of the α_0 values peculiar to each zeolite, it is very fruitful to look at the regular dependence of α_0 *on the aluminum content* (*Fig. 3*). It indicates firstly that all the materials described constitute a continuous range of zeolites of which the properties change regularly with the chemical composition. Secondly the origin of the material has no importance since usual or aluminum-deficient zeolites give α_0 values lying on the same curve. Thirdly the remarkable linear relationship of Fig. 3 denotes a very simple mathematical law between the efficiency of the acid sites and the aluminum content. The coefficient $\simeq 1.45 \times 10^{-2}$ of the straight line has a very precise meaning: the introduction of one aluminum more in the unit cell of a faujasite zeolite leads to a decrease of the efficiency of all the pre-existing aluminum atoms of $\simeq 1.45 \times 10^{-2}$ equivalent (or $\simeq 1.45\%$) per site. This quantitative value states precisely the influence of the space distributed aluminum on the resulting field in the supercage. Chemically, such a property may be interpreted as a "self-neutralization" or a "self-inhibition" effect of the aluminic sites. Such a "self-inhibition" coefficient may explain some differences in X and Y zeolite properties, particularly the well-known smaller catalytic activity of X compared to that of Y. It is a very important intrinsic parameter of the faujasite lattice.

The two limits of the line of Fig. 3 have also a definite physical meaning. The extrapolation of the line towards the highest aluminum content indicates that α_0 drops to zero for an abscissa very close to 96 aluminum per unit cell. Since according to an empirical rule (*17*) two $(AlO_4)^-$ tetrahedra cannot be adjacent, the upper number of 96 aluminum per unit cell is a stability limit for the faujasite structure. Therefore, $\alpha_0 = 0$ denotes that each aluminum of such a material would be wholly inhibited by its neighbors and no acid–base reaction would occur in the supercage.

On the other hand, the slope α_0 (efficiency of a site) would not be higher than one. It is very interesting to note that $\alpha_0 = 1$ would be reached for an abscissa close to 28 ± 3 aluminum per unit cell. This aluminum content is already well known in Y zeolites since it determines the limit of the structure stability (*3, 14, 18*). The α_0 measurements show that this chemical composition is not a characteristic of Y zeolites but more generally of the faujasite structure. A number of 28 ± 3 aluminum per unit cell gives the highest efficiency relatively to the acidity created by the aluminic sites. The influence in the supercage of each $(AlO_4)^-$ tetrahedron is not perturbed by its neighbors and each of them acts as a whole towards the acid–base reactions in the big cavity.

Further studies on the stability and structure of the same aluminum-deficient zeolites will point out the same number of 28 ± 3 aluminum per unit cell (*14, 19*). The question arises to understand how these aluminum atoms may be distributed in a unit cell. More detailed studies would be needed to explain clearly such a point.

Furthermore it is worth pointing out that both α_0 and thermal stability (*19*) of the materials increases when aluminum is removed.

CONCLUSIONS

The present study defines the α_0 parameter which is obtained from acidity measurements with molecules which enter only the supercage. Taking advantage of this property very important information on the resulting influence of the $(AlO_4)^-$ tetrahedra in this big cavity are found. α_0 is defined as the efficiency of an acid site or as the efficiency of an aluminum site towards the acid–base reactions in the supercage. It is related to a structural property of the faujasite type zeolite and its two limiting values (0 and 1) coincide with the two limits of the stability of the crystalline structure (96 and 28 aluminum per unit cell). Moreover it makes possible the determination of a loss in reactivity close to 1.45% for each aluminum atom when the aluminum content is increased by one per unit cell. This last value is an important specific characteristic of the faujasite structure as it could explain the known inverse relationship between the catalytic properties and the aluminum content.

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