JOURNAL OF CATALYSIS 73, 205–215 (1982)

Electronegativity and Catalytic Properties of Zeolites

STANKO HOČEVAR AND BOJAN DRŽAJ

Boris Kidrič Institute of Chemistry, Hajdrihova 19, 61000 Ljubljana, Yugoslavia

Received March 2, 1981; revised August 20, 1981

The theorem of protonic acidity and catalytic activity of zeolites in acid-catalyzed reactions was evaluated. This theorem enables one to calculate from the known chemical composition of a zeolite its protonic activity, and to evaluate quantitatively the average acidity strength through the use of the average partial hydrogen charge. In general acid-catalyzed reactions the average partial hydrogen charges on zeolites are linearly correlated with their catalytic activities.

I. INTRODUCTION

One may prepare an unlimited number of homologues with only one structural type of zeolite, for instance, faujasite (FAU), by varying the number of Al atoms in the elementary cell, the degree of ion exchange, and the type of exchange cation. The experimental limits of the Al content in the elementary cell of faujasite have presently reached the point that is predicted by theory (*1*), namely, the Si:Al ratio of 1:1 on the one hand (*2*) and on the other practically pure SiO_2 having the structure of faujasite and obtained by dealumination (*3*, *4*). The reaction of cation exchange in zeolites is controllable (*5*), and almost all metals in the periodic system can be built into the zeolite as cations. Therefore, we have at our disposal an unlimited number of homologues, which fundamentally facilitates our study and determination of the laws concerning the physicochemical properties of the zeolite of a given structural type.

The acidity of zeolites rightly belongs among the most extensively investigated properties of zeolites (*6*). Three researchers stand out from the others on account of their thorough treatment of the problems relating to the acidity and correlation between acidity and catalytic activity of zeolites, namely, Ward (*7*), Topchieva (*8*), and Barthomeuf (*9*). The work of Barthomeuf on the acidic properties of faujasite-type zeolites and the derivation of the "structural parameter of acidity" (α_0) (*10*) is especially important for the development of concepts concerning the physicochemical properties of zeolites in general.

II. THEORETICAL ANALYSIS

1. Quantum-Chemical Bases of the Activity Coefficient of Protons in the Homologous Series of Faujasites

Sanderson's model of electronegativity (*11–15*) at the moment represents the only quantum-chemical method whereby it is possible to investigate quantitatively and to interpret a considerable number of physicochemical properties of zeolites including their acidity (*16*, *17*). According to this model the intermediate electronegativity of a compound is defined as a geometrical mean of the atomic electronegativities of elements. For the compound with an overall formula

$$(E_1)p_1(E_2)p_2(E_3)p_3 \ . \ . \ . \ (E_i)p_i,$$

where E_i is a gramme-atom of the element E_i and p_i is its stoichiometric coefficient, the intermediate electronegativity would be

$$S_{\text{int}} = \left(\prod_i S_i^{p_i}\right)^{\frac{1}{\sum_i p_i}} \qquad (1)$$

where S_i is the atomic electronegativity of the element E_i. The average partial charge on atoms of an element E_i in the compound

TABLE 1

Atomic Electronegativities of Elements

Element	Electronegativity
H	3.55[a]
Na	0.70[a]
Mg	1.56[a]
Al	2.22[a]
Si	2.84[a]
Ca	1.22[a]
Sc	1.88[b]
Ti	2.27[b]
Zn	2.98[a]
Sr	1.06[a]
Y	1.75[b]
La	1.90[b]

[a] From Ref. (*15*).
[b] From Ref. (*14*).

is defined as

$$\sigma_i = \frac{S_{\text{int}} - S_i}{2.08(S_i)^{1/2}}. \tag{2}$$

We will now attempt to evaluate the *changes* of the intermediate electronegativity and the *changes* of the average partial atomic charges as functions of isomorphous exchange of Si for Al in a faujasite structure whose chemical formula is

$$\text{Na}_x(\text{Al}_x\text{Si}_{192-x}\text{O}_{384})$$

for the values $0 \leq x \leq 96$.

Using atomic electronegativity values given in Table 1 we calculated the intermediate electronegativities $S_{\text{int}}(N_{\text{Al}})$ which are given in Table 2. The function $S_{\text{int}}(N_{\text{Al}})$ is *nonlinear* even though we can fit it by linear regression and obtain a determination coefficient $r^2 = 0.994$.

Experimental values of the number of Al atoms in the elementary cell of the faujasite type usually range in the interval between $N_{\text{Al}} = 86$ (for the Na–X, FAU type of zeolite) and $N_{\text{Al}} = 28$ (for the dealuminized Na–Y, FAU type of zeolite) (*10*). Linear regression of intermediate electronegativities in this interval yields

$$S_{\text{int}}(N_{\text{Al}}) = -0.01041 \times N_{\text{Al}} + 4.1445. \tag{3}$$

Inserting this regression into Eq. (2) the regressions for average partial charges are obtained:

$$\begin{aligned} \sigma_{\text{Al}}(N_{\text{Al}}) &= -0.00336 \times N_{\text{Al}} + 0.62097, \\ \sigma_{\text{Si}}(N_{\text{Al}}) &= -0.00297 \times N_{\text{Al}} + 0.37215, \\ \sigma_{\text{O}}(N_{\text{Al}}) &= -0.00219 \times N_{\text{Si}} - 0.22443, \\ \sigma_{\text{Na}}(N_{\text{Al}}) &= -0.00598 \times N_{\text{Al}} + 1.97931. \end{aligned} \tag{4}$$

At this point we must emphasize that we are not interested in *the absolute values* of the partial charges on different atoms in the zeolite structure but in the tendency of the sum of regressions for the average partial charges of the elements that constitute the zeolite as a function of N_{Al} which illustrates best the tendency of changes occurring in the interaction of the atoms of zeolite-forming elements:

$$\sum_i \sigma_i(N_{\text{Al}}) = -0.01450 \times N_{\text{Al}} + 2.748 \quad (i = \text{Al, Si, O, Na}). \tag{5}$$

According to Loewenstein's rule (*1*) the isomorphous exchange of Si for Al can be carried out only up to the ratio Si : Al = 1 : 1. Thus for the homologous series of faujasites, the maximum number of Al atoms in the elementary cell N_{Al} equals 96. If we use this number as a reference state (*2, 9*), we can write the tendency of the sum of

TABLE 2

Intermediate Electronegativities as a Function of the Number of Al Atoms (N_{Al}) in the Elementary Cell of Faujasite

N_{Al}	96	88	78	68	58	48	38	28	18	8	0
S_{int}	3.175	3.243	3.333	3.427	3.528	3.635	3.748	3.869	3.999	4.137	4.256

regressions for average partial charges of faujasite-forming elements as a function of N_{Al} as

$$\sum_i \sigma_i(N_{\mathrm{Al}}) - \left(\sum_i \sigma_i(N_{\mathrm{Al}})\right)_{N_{\mathrm{Al}}=96} = -1.45 \times 10^{-2} \times N_{\mathrm{Al}} + 1.4. \qquad (6)$$

Equations (4) reveal the fact that the ionic character of individual chemical bonds in the zeolite decreases with each new Al atom in the elementary cell of faujasite series homologues. In other words, delocalization of electron density increases, and this brings about a diminution in the effectiveness of inductive influence upon the O–H bond of all Al atoms in the elementary cell of faujasite. All the O–H bonds gain in strength with each new Al atom in the elementary cell of faujasite, while the protonic acidity decreases.

These conclusions are in concordance with conclusions derived on the basis of other semiempirical quantum-chemical calculations on model zeolite clusters (*18–21*).

Equation (6) represents a quantum-chemical elucidation of the "structural parameter of acidity" (α_0) that Barthomeuf has established experimentally and for which she has supplied the equation (*10*):

$$\alpha_0 = -1.45 \times 10^{-2} \times N_{\mathrm{Al}} + 1.4. \qquad (7)$$

It follows from Eqs. (6) and (7) that

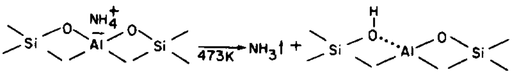
$$\alpha_0 = \sum_i \sigma_i(N_{\mathrm{Al}}) - \left(\sum_i \sigma_i(N_{\mathrm{Al}})\right)_{N_{\mathrm{Al}}=96} \quad (i = \mathrm{Al, Si, O, Na}). \qquad (8)$$

The "structural parameter of acidity" (α_0) has been given a quantum-chemical elucidation and can be termed now "the activity coefficient of the proton in faujasite-type zeolites."

Weak nonlinearity of the intermediate zeolite electronegativity as a function of the number of Al atoms in the elementary cell of faujasite (N_{Al}) has been neglected for the sake of an easier comparison with the experimental results reported by Barthomeuf in which case such nonlinearity simply could not be ascertained owing to the measurement errors.

2. *Theorem of Protonic Acidity and Catalytic Activity of Zeolites in Acid-Catalyzed Reactions*

Protons can be built into the structure of a zeolite by means of ion exchange, thermal decomposition of the NH_4^+-exchanged form, hydrolysis of hydration water in the exchange cations, or the reduction of cations into a lower-valence state (*6*). Most often, we use for the preparation of proton-acidic forms of zeolites the reactions of thermal decomposition of the NH_4^+-exchanged form of the zeolite and of hydrolysis of hydration water at the exchange cations (*22*). The two reactions may be expressed in the following form:



(9)

$$\mathrm{Me}^{n+}(\mathrm{OH}_2)_{(n-1)} \xrightarrow{T_1} \mathrm{Me(OH)}^{+}_{(n-1)} + (n-1)\mathrm{H}^+ \xrightarrow{T_2} \mathrm{Me(OH)}^{2+}_{(n-2)} + (n-2)\mathrm{H}^+ + \mathrm{H_2O}; \qquad (T_1 < T_2). \qquad (10)$$

The number of protonic centers produced will depend, in addition to the stoichiometry of reactions (9) and (10), upon the theoretical cation exchange capacity, the stoichiometry of the ion-exchange reactions, the degree of ion exchange, and the structure of the zeolitic framework (spatial obstacles to the diffusion of exchange cations on the exchange sites in zeolite).

Axiom 1. Provided that

(a) ion exchange has occurred in an equilibrated and stoichiometric manner,

(b) the degree of ion exchange has reached $\alpha = 1.0$, and

(c) the stoichiometry of hydrolysis of hydration water in exchange cations is in agreement with Eq. (10), we can derive the following conclusions from Eq. (10):

1. In the process of heating, monoionic

TABLE 3

Theoretical Values of the Activity of Protons of Monoionic Forms of Y-Type Faujasite ($N_{Al} = 56$)

Ionic form	A (mol/el.c.)	$\frac{\text{Number of Al atoms neutralized with one cation}}{\text{Valence of cation}}$
HY(T_2)	32.93	1
LaY(T_2)	10.98	2/3
LaY(T_1)	21.95	1/3
CaY(T_2)	16.46	1/2

Note. $T_2 > T_1$.

forms of zeolites of univalent exchange cations (e.g., alkali metals) ($n = 1$) will not generate any protons and will thus show no protonic acidity.

2. Monoionic forms of zeolites of divalent metals (e.g., alkaline-earth metals) ($n = 2$) will have one optimum temperature point (each type of cation a different one!), at which one proton is generated on each exchanged cation and the concentration of protons equals one-half of the theoretical cation exchange capacity of a given zeolite.

3. Monoionic forms of zeolites of trivalent metals (e.g., rare earth) ($n = 3$) will have two optimum temperature points, at one of which (namely, the lower temperature T_1), two protons are generated on each exchanged cation and the concentration of protons equals two-thirds of the concentration of protons of the monoionic H^+ zeolite form. At the other temperature point (namely, the higher temperature T_2) one proton is generated on each exchanged cation and the concentration of protons equals one-third of the concentration of protons of the monoionic H^+ zeolite form.

The concentration of protons which have been formed, given as the number of protons in the elementary cell of the zeolite, can then be computed from

$$[H^+] = n_{H^+}\alpha N_{Al}/Z_{cat}, \qquad (11)$$

where n_{H^+} is the number of protons generated per exchanged cation, Z_{cat} is the valence of the exchange cation, α is the degree of ion exchange, and N_{Al} stands for the number of Al atoms in the elementary cell of the zeolite.

Axiom 2. The concentration of protons can be calculated for various structural types of zeolites as the molar concentrations of protons. We will establish that mo-

TABLE 4

Theoretical Values of the Activity of Protons of Ionic Forms of Y-Type Faujasite ($N_{Al} = 56$) as a Function of the Degree of Ion Exchange (α)

α	n''	A (mol/el.c.)			
		NaY → HY(T_2)	LaY → HY(T_2)	LaY → HY(T_1)	CaY → HY(T_2)
0.0	0.0	0.00	10.98	21.95	16.46
0.2	11.2	6.59	15.37	24.15	19.76
0.4	22.4	13.17	19.76	26.34	23.05
0.6	33.6	19.76	24.15	28.54	26.34
0.8	44.8	26.34	28.54	30.73	29.63
1.0	56.0	32.93	32.93	32.93	32.93
Slope of the straight line β		0.588	0.394	0.196	0.294
$\beta/\alpha_0^{(\text{theo})}$		1.00	0.67	0.33	0.50

Note. n'' is the number of exchanged moles per elementary cell, and β is the slope of the straight line $A = \varphi(n)$.

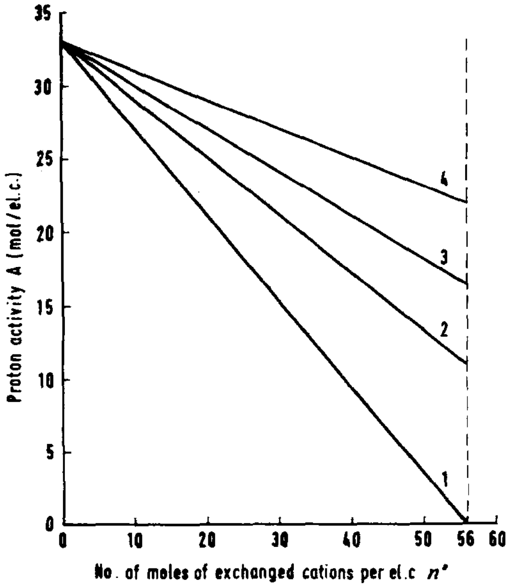


FIG. 1. Activity of protons as a function of the number of exchanged moles of cations per elementary cell. 1—NaY → HY(T_2); 2—LaY → HY(T_2); 3—CaY → HY(T_2); 4—LaY → HY(T_1).

lar concentrations are very high, ranging from 4.76 mol/liter for the L-type zeolite to 9.5 mol/liter for the X-type zeolite (*23*). In the theory of solutions, we employ at such concentrations of protons only the activity ("effective concentration") (*24*). It has been observed that within a given homologous series acidity decreases in the zeolites that have a larger number of Al atoms in the elementary cell. For example, the faujasite X-type zeolite is less acidic than the faujasite Y-type zeolite (*10*). Hence it is possible to assume also for zeolites that the activity of protons equals

$$a_{H^+} = [H^+] \cdot f_{H^+}, \qquad (12)$$

where a_{H^+} is the activity of protons, and f_{H^+} the activity coefficient of protons contained in zeolite.

In the general hypothesis concerning the physicochemical properties of zeolites given by Barthomeuf (*9*), the author suggests that the properties of zeolites be determined by the changes in the chemical potential of framework ions and framework atoms, much in a similar way as in the treatment of solutions. The importance of zeolite interactions calls for the definition of the activity coefficients of framework ions or framework atoms not only with respect to the investigation of ion-exchange properties, but also with regard to the study of other properties of framework ions or framework atoms. High concentration of protons in zeolites results from the content of the $[AlO_4]^-$ tetrahedra in them. The latter entails high density of charges, and thereby strong electrostatic interactions which diminish the effectiveness of protons. We can take these very interactions into consideration when dealing with the activity coefficients, just as they are treated by the Debye–Hückel theory of solutions of electrolytes. What we presently lack is a thermodynamic definition of the activity coefficients of framework ions and framework atoms in zeolites. We have indicated earlier (Section II.1) how it is possible to define the activity coefficient of protons on a nonthermodynamic basis for the homologous series of faujasites. In this particular homologous series, we may equalize f_{H^+} with α_0.

Axiom 3. The catalytic activity of zeolites in acid-catalyzed reactions correlates either with the number of acidic centers or with their strength depending on the type of catalyzed reaction (*8, 25*). Both properties are structurally sensitive and cannot be treated separately whenever the correlation with

TABLE 5

Acidity of Monoionic Forms of Y-Type Faujasite ($N_{Al} = 56$)

Cation	Brønsted acidity in arbitrary units[a]	Activity of protons in arbitrary units[b]
Na	0.0	0.0
Mg	6.9	8.2
La	11.3	11.0
H	15.8	16.5

[a] Ref. (*7*)
[b] Theoretical.

the catalytic activity of a certain type of catalyzed reaction is involved (*26*). The available literature of an experimental nature enables us to assume (*8*) that strong acidic centers catalyze also the reactions which occur on weaker acidic centers, whereas the reverse is not true.

The catalytic activity of zeolites in acid-catalyzed reactions is subordinated either to the laws of general acidity catalysis (when the catalytic activity depends on the acidity strength), in which case it is subject to the linear free energy relationships (LFER), or to the laws of specific acidity catalysis (when the catalytic activity depends on the proton activity). In the former case, the Brønsted–Polanyi relation and compensation rule (*26, 27*) are applied to the catalytic activity of zeolites in acid-catalyzed reactions.

III. APPLICATIONS

The theorem enables us to calculate from the known chemical composition of a zeolite its protonic activity, and to evaluate quantitatively the average acidity strength by the agency of the average partial hydrogen charge. Let us now examine the practical applicability of our theorem in the case of the homologous series of faujasites.

1. The Dependence of the Activity of Protons upon the Type of Exchange Cation and upon the Degree of Ion Exchange

On the basis of Axioms 1 and 2 (Eqs. (11) and (12)), we can calculate from the known chemical composition of any homologue in the series of faujasites the activity of protons, that is, the effective number of acidic sites per elementary cell in a homologue. Let us compute the activity of protons with various ionic forms and with a varying degree of ion exchange (α) for the Y-type faujasite having the composition of a dehydrated elementary cell:

$$\mathrm{Na_{56}Al_{56}Si_{136}O_{384}}.$$

We will employ linear regression for the calculation of the activity coefficient of protons (α_0):

$$\alpha_0^{(\mathrm{theo})} = -1.45 \times 10^{-2} \times N_{\mathrm{Al}} + 1.4.$$

At $N_{\mathrm{Al}} = 56$, $\alpha_0^{(\mathrm{theo})}$ equals 0.588.

Table 3 gives the calculated values of the activity of protons in various monoionic forms of the Y-type zeolite, and the proportion of the number of neutralized $(\mathrm{AlO_4})^-$ tetrahedra in the framework with one exchange cation to the valence of that exchange cation.

Table 4 presents the values of the activity of protons, calculated from Eqs. (11) and (12), as a function of the degree of ion exchange (α) for the systems

$$\mathrm{NaY} \rightarrow \mathrm{HY}, \tag{i}$$

$$\mathrm{LaY} \rightarrow \mathrm{HY}, \tag{ii}$$

$$\mathrm{LaY}(T_2) \rightarrow \mathrm{HY}, \tag{iii}$$

$$\mathrm{CaY} \rightarrow \mathrm{HY}. \tag{iv}$$

TABLE 6

Intermediate Electronegativity and Hydrogen Charge as a Function of the Degree of Ion Exchange (α)

α	NaY → HY(T_2)		LaY → HY(T_2)		LaY → HY(T_1)		CaY → HY(T_2)	
	S_{int}	σ_{H}	S_{int}	σ_{H}	S_{int}	σ_{H}	S_{int}	σ_{H}
0.0	3.548	0.001	4.038	0.125	4.023	0.121	3.908	0.091
0.2	3.651	0.026	4.050	0.128	4.037	0.124	3.945	0.101
0.4	3.759	0.053	4.062	0.131	4.053	0.128	3.982	0.110
0.6	3.868	0.081	4.074	0.134	4.067	0.132	4.021	0.120
0.8	3.982	0.110	4.086	0.137	4.083	0.136	4.059	0.130
1.0	4.098	0.140	4.098	0.140	4.098	0.140	4.098	0.140

The data from Table 4 are shown graphically in Fig. 1. The comparison between the theoretical values of the activity of protons as presented in Tables 3 and 4 and indicated in Fig. 1, and the experimental results reported by Beaumont and Barthomeuf (*10*), which were obtained for the zeolite of the same type (type Y, $N_{Al} = 56$), yields a very good agreement.

The calculated activity of protons of monoionic forms of Y-type zeolite ($N_{Al} = 56$), expressed in arbitrary units, is in very good agreement with the acidity which has been determined experimentally by ir absorption spectra of pyridine on the zeolite and expressed in arbitrary units (*7*). The comparison is given in Table 5.

2. *The Dependence of Acidity Strength (of Hydrogen Charge) upon the Type of Exchange Cation and upon the Degree of Ion Exchange*

The notion of "the activity of protons" in a zeolite is not directly related to the notion of "the acid strength." "Brønsted acidity is a dynamic concept and depends mainly upon the rate at which energy and matter can be exchanged between *in casu* the zeolite and a molecule with lower electronegativity" (*16*). The acid strength is a relative notion in terms of the comparative proton-acceptor molecule used. The strength of Brønsted acidity can be comparatively described by means of any physicochemical quantity that relates to the strength of the O–H bond, for instance, protonic charge, frequency of stretching vibrations of this bond, etc.

We will exemplify the evaluation of the relative acid strength in the homologous series of faujasite by making use of the protonic charge, because it can be calculated from the chemical composition of a zeolite according to Sanderson (*16, 17*). What we obtain here is only the average protonic charge of the elementary cell of the zeolite, which has a larger number of acidic functions:

$$\sigma_H = \frac{S_{int} - S_H}{2.08 \cdot (S_H)^{1/2}}, \qquad (13)$$

where σ_H is the average partial hydrogen charge, S_{int} intermediate electronegativity of the zeolite, and S_H electronegativity of hydrogen.

Table 6 presents the calculated values of

TABLE 7

Dependence of Acidity on the Number of Al Atoms (N_{Al}) in the Elementary Cell of the Homologous Series of Faujasites

Sample no.	Experimental[a]			Theoretical			
	N_{Al}	Degree of ion exchange α	Quantity of adsorbed NH_3 (mmol/g)	Activity coefficient (α_0)	Proton activity (mol/el.c.) A	Molar mass (g/el.c.) M	Proton activity a_{H^+} (mmol/g)
5	66.2	0.65	0.98	0.440	18.9	12,044	1.57
4	60.3	0.65	1.18	0.526	20.6	11,187	1.84
7	56.0	0.62	1.10	0.588	20.4	12,001	1.70
6	52.6	0.49	1.41	0.637	16.4	11,299	1.45
11	46.4	0.82	1.62	0.727	27.7	11,260	2.46
8	42.8	0.74	2.21	0.779	24.7	10,978	2.25
10	40.7	0.76	1.90	0.810	25.0	9757	2.57
9	34.9	0.95	2.53	0.894	29.6	10,307	2.88
13	30.6	0.62	1.83	0.956	18.1	10,384	1.75
12	27.0	0.64	2.02	1.009	17.4	8932	1.95

[a] Refs. (*29, 30*).

the intermediate electronegativity and of the average partial hydrogen charge as a function of the degree of ion exchange for the same systems as those treated in Section III. 1.

Figure 2 shows the interdependence of the calculated values of the hydrogen charge (and indirectly, of the acid strength) and of the activity of protons for various ion-exchanged forms of the Y-type faujasite with $N_{Al} = 56$. We observe that it is the H form that has the strongest activity of protons and the largest average hydrogen charge. The activity of protons in di-, tri-, and tetravalent elements is in inverse proportion to their valence. Forms exchanged with alkaline-earth ions have the same activity of protons, but they differ markedly as to their acid strength (hydrogen charge) which decreases in the sequence MgY > CaY > SrY.

Experimental data obtained quite some time ago point to the fact that the catalytic activity of the Y-type zeolite with alkaline-earth ions at the same degree of ion exchange and under the same activation conditions decreases in the sequence MgY > CaY > BaY. This activity scale is valid, e.g., for isomerization and transalkylation of 1-methyl-2-ethyl benzene (473–723 K), for isomerization of *ortho*-xylene (523–753 K), and for the cracking of isopropylbenzene (533 and 723 K) (*28*). However, the interdependence between the number of acid centers and their strength has not yet been (adequately) defined in terms of whether such a sequence of the catalytic activity is determined by the acidity

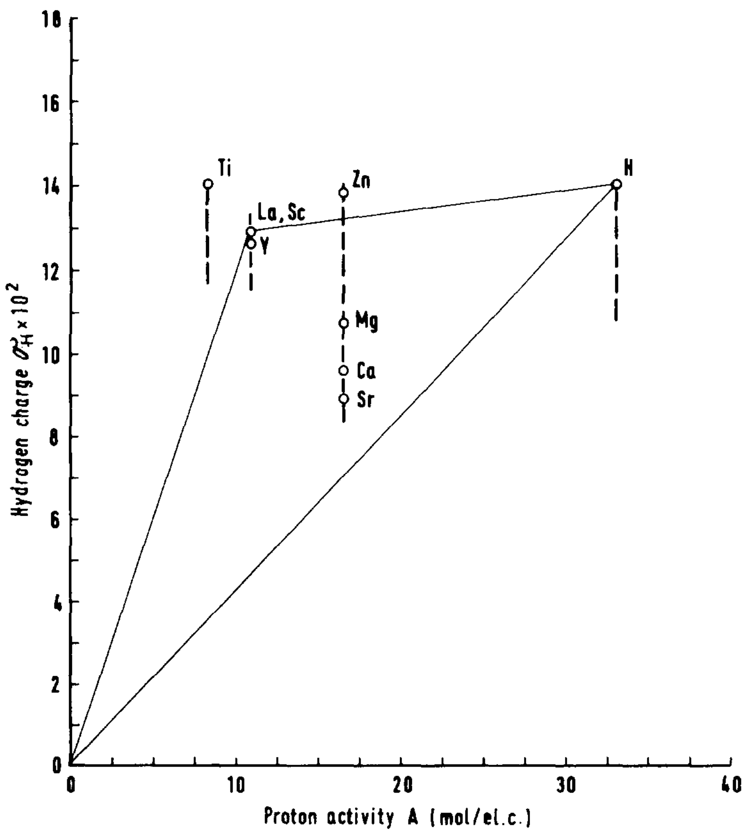


FIG. 2. Interdependence of the calculated values of hydrogen charge and of the activity of protons for various ion-exchanged forms of Y-type faujasite with $N_{Al} = 56$.

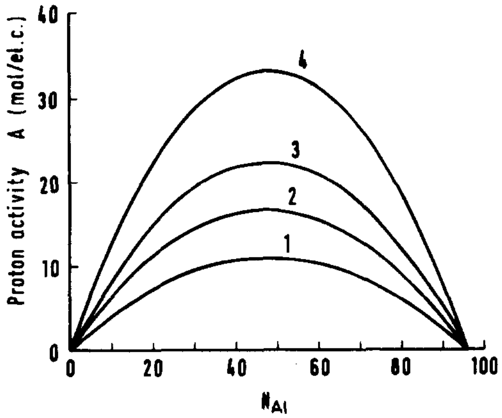


FIG. 3. Activity of protons as a function of the number of Al atoms in the elementary cell of faujasites. 1—LaY(T_2); 2—CaY(T_2); 3—LaY(T_1); 4—HY(T_2).

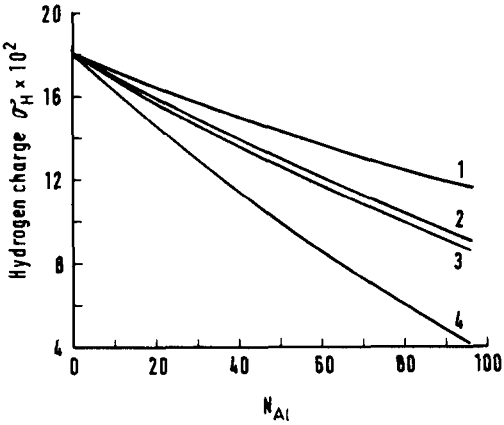


FIG. 4. Hydrogen charge as a function of the number of Al atoms in the elementary cell of faujasites. 1—HY(T_2); 2—LaY(T_2); 3—LaY(T_1); 4—CaY(T_2).

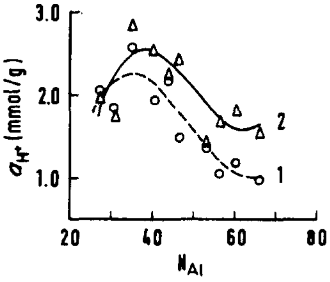


FIG. 5. Activity of protons as a function of the number of Al atoms in the elementary cell of faujasites. 1—Experimental values; 2—calculated values.

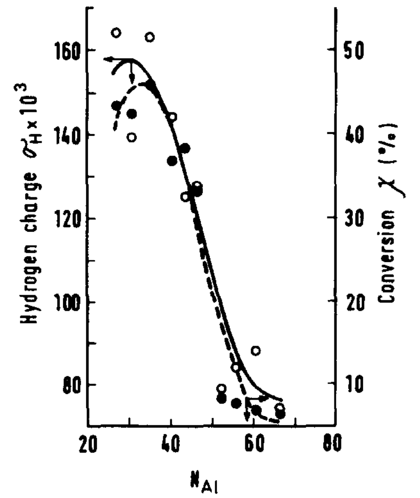


FIG. 6. Hydrogen charge and conversion in the reaction of disproportionation of toluene as a function of the number of Al atoms in the elementary cell of faujasites. ●---●, conversion; ○——○, hydrogen charge.

strength or by the number of acidic centers. In such cases we deal, in conformity with Axiom 3, with the reactions of general acidic catalysis, which depend upon the acidic strength of individual ion-exchanged forms of the Y zeolite.

3. The Dependence of Proton Activity and of Hydrogen Charge (Acidity Strength) upon the Number of Al Atoms (N_{Al}) in the Elementary Cell of the Homologous Series of Faujasites, and Their Correlation with Acidity and Catalytic Activity

Acidity and catalytic activity of zeolites are most strongly affected by the SiO_2/Al_2O_3 ratio, that is, by the number of Al atoms in the elementary cell of the zeolite of a certain structural type (*6–8, 10, 16, 17, 19, 28*). It follows from Axioms 1 and 2 that the dependence of proton activity upon N_{Al} is a function that has an extremum, while it follows from the calculation of intermediate electronegativity and of hydrogen charge that the acid strength (hydrogen charge) increases as a function of the decrease in the number of Al atoms

TABLE 8

Dependence of Catalytic Activity in the Reaction of Isopropyl Alcohol Dehydration and of Proton Activity upon the Number of Al Atoms in the Elementary Cell of Faujasites

Experimental[a]			Theoretical			
Ratio SiO_2/Al_2O_3 in the samples (La^{ex}, H^{ex}, Na)-Y	Degree of ion-exchange α La^{3+}	Catalytic activity ($kK \times 10^5$) (mol/g s atm)	N_{Al}	α_0	A (mol/el.c.)	Hydrogen charge σ_H
3.7	0.83	295	65.6	0.449	13.2	0.090
4.5	0.85	340	57.4	0.568	14.1	0.102
5.6	0.80	460	49.0	0.690	15.8	0.107
7.7	0.83	350	38.3	0.845	14.5	0.125
9.2	0.95	242	33.1	0.920	11.2	0.141

[a] Ref. (*8*).

in the zeolitic framework. Figure 3 indicates the dependence of the activity of protons (A) (mol/el.c.), while Fig. 4 shows the dependence of hydrogen charge on the number of Al atoms (N_{Al}) in the elementary cell of the homologous series of faujasites.

Table 7 presents the experimentally determined composition of partially decationized faujasites and the acidity of these samples, which was established by high-temperature adsorption of ammonia (*29, 30*), in comparison with the theoretical values of the activity of protons (expressed in mmol/g). Figure 5 indicates both experimental and calculated values graphically. The agreement between the measured and the calculated values is satisfactory.

In conformity with Axiom 3 we may expect in the matter of whether we deal with specific or general acid catalysis that the catalytic activity will correlate either with the proton activity or with the hydrogen charge (i.e., acid strength). In the case of the reaction of isopropyl alcohol dehydration (*8*), the catalytic activity correlates with the proton activity rather than with the acid strength, which is seen in Table 8. It is likely that this reaction is an example of specific hydrogen ion catalysis (*31*). In the reaction of disproportionation of toluene (*29, 30*), however, the catalytic activity correlates with the hydrogen charge, and this is shown in Figs. 6 and 7.

IV. CONCLUSIONS

The entire theorem of the acidity and catalytic activity is based on a highly limited input, namely, on the chemical formula of the compound. It is nevertheless by way of such a limited input that we are able to elucidate quantitatively the dependence of the acidity and of the catalytic activity of

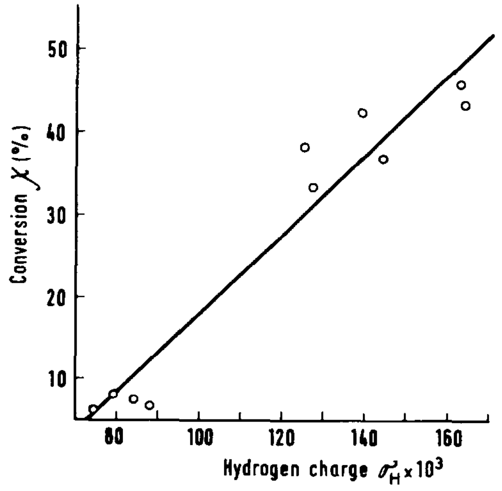


FIG. 7. Conversion in the reaction of disproportionation of toluene as a function of hydrogen charge. (Coefficient of determination $r^2 = 0.93$).

zeolites in a given series of homologues upon the Al content, and upon the content and type of exchange cations in the elementary cell.

Intermediate electronegativity and atomic charges represent the average properties of a compound and can therefore be applied only in the interpretation of the overall properties of the compound.

Within the framework of heterogeneous acid–base catalysis with zeolites, the theorem presented above is of fundamental significance for the prediction of catalytic activity and for other overall physicochemical properties of zeolites within each homologue series.

ACKNOWLEDGMENTS

We are indebted to Drs. V. Penchev and V. Mavrodinova for providing the results of high-temperature adsorption of ammonia measurements cited in Table 7 of this article. We also appreciate helpful discussions with Drs. W. J. Mortier, D. Barthomeuf, K. G. Ione, and G. V. Echevskii. This work was funded by the Research Community of Slovenia.

REFERENCES

1. Loewenstein, W., *Amer. Mineral.* **39,** 92 (1954).
2. Kühl, G. M., and Sherry, H. S., *in* "Proceedings, Vth Int. Conf. on Zeolites Naples, 1980" (L. V. C. Rees, Ed.), p. 813. Hayden, London, 1980.
3. Lohse, H., Alsdorf, E., and Stach, H., *Z. Anorg. Allg. Chem.* **447,** 64 (1978).
4. Klinowski, J., Thomas, J. M., Audier, M., and Vasuderan, S., *J. Chem. Soc. Chem. Commun.*, 570 (1981).
5. Barrer, R. M., *in* "Proceedings, Vth Int. Conf. on Zeolites, Naples, 1980" (L. V. C. Rees, Ed.), p. 273. Hayden, London, 1980.
6. Jacobs, P. A., "Carboniogenic Activity of Zeolites." Elsevier, Amsterdam, 1977.
7. Ward, J. W., *in* "Zeolite Chemistry and Catalysis" (J. A. Rabo, Ed.), ACS Monograph 171. Amer. Chem. Soc., Washington, D.C., 1976.
8. Topchieva, K. V., and Ho Si Thoang, "Aktivnost i fizikokhimicheskie svojstva vysokokremnistykh ceolitov i ceolitsoderzhashchikh katalizatorov." Izd. Moskovskogo Universiteta, Moscow, 1976.
9. Barthomeuf, D., *J. Phys. Chem.* **83,** 249 (1979).
10. Beaumont, R., and Barthomeuf, D., *J. Catal.* **26,** 218 (1972).
11. Sanderson, R. T., *J. Chem. Educ.* **29,** 539 (1952).
12. Sanderson, R. T., *J. Chem. Educ.* **31,** 2 (1954).
13. Sanderson, R. T., *J. Chem. Educ.* **31,** 238 (1954).
14. Sanderson, R. T., "Chemical Periodicity." Van Nostrand–Reinhold, Princeton, N.J., 1960.
15. Sanderson, R. T., "Chemical Bonds and Bond Energy," 2nd ed. Academic Press, New York, 1976.
16. Jacobs, P. A., Mortier, W. J., and Uytterhoeven, J. B., *J. Inorg. Nucl. Chem.* **40,** 1919 (1978).
17. Mortier, W. J., *J. Catal.* **55,** 138 (1978).
18. Mortier, W. J., Geerlings, P., Van Alsenoy, C., and Figeys, H. P., *J. Phys. Chem.* **83,** 855 (1979).
19. Beran, S., and Dubsky, J., *J. Phys. Chem.* **83,** 2538 (1979).
20. Dubsky, J., Beran, S., and Bosaček, V., *J. Mol. Catal.* **6,** 321 (1979).
21. Dubsky, J., Beran, S., Bosaček, V., and Jiru, P., *in* "Proceedings, IVth Int. Symp., Heterog. Catal., Varna 1979," p. 421. Bulgarian Acad. Sci., Sofia, 1979.
22. Plank, C. J., *in* "Proceedings, 3rd International Congress on Catalysis," Amsterdam, 1964," p. 727. North-Holland, Amsterdam, 1965.
23. Barthomeuf, D., *Acta Univ. Szeged. Acta Phys. Chem.* **24,** 71 (1978).
24. Karapet'yants, M. H., "Khimicheskaya termodinamika." Khimiya, Moscow, 1975.
25. Morita, Y., Kimura, T., Kato, F., and Tamagawa, M., *Bull. Japan Pet. Inst.* **14,** 192 (1972).
26. Yoneda, Y., *in* "Proceedings, 4th International Congress on Catalysis, Moscow, 1968," Vol. II, p. 449. Akademiai Kiado, Budapest, 1971.
27. Boreskov, G. K., "Kataliz," Parts I and II. Nauka, Sibirskoe Otdelenie, Novosibirsk, 1971.
28. Poutsma, M. L., *in* "Zeolite Chemistry and Catalysis" (J. A. Rabo, Ed.), ACS Monograph 171. Amer. Chem. Soc., Washington, D.C., 1976.
29. Penchev, V., and Mavrodinova, V., *Acta Univ. Szeged. Acta Phys. Chem.* **24,** 263 (1978).
30. Penchev, V., and Mavrodinova, V., private communication.
31. Wiberg, K. B., "Physical Organic Chemistry." Wiley, New York, 1964.