A NEW APPROACH OF ZEOLITE ACIDITY.
ACTIVITY COEFFICIENTS

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Examples are presented of high interactions in zeolites due to the charge density. The comparison with acidic solutions suggests then to define activity coefficients and to consider protons and cations in terms of activity rather than concentration. The consequences of such a concept in the fields of catalysis and adsorption are presented.

The study of the acidity of zeolites has been mainly devoted to the characterization of the nature, number and strength of sites. Since it now appears that zeolites behave also like ionizing solvents [1, 2] or electrolytes [2, 3] it may be interesting to look if other acidic properties of zeolites could not be deduced from the properties of acidic solutions. In this respect the paper will present some experimental facts which may be related to the well known concentration effect in solution.

Introduction

It is known for a long time that interactions between charged species occur in zeolites. For instance, recently the Si K_β X-ray emission band energies have been linearly correlated to the aluminium content of various zeolites types [4]. The results imply a regularly increasing destabilization of silicon bonding orbitals as aluminum atoms replace silicium atoms, independently of any zeolite structure effect.

Acidity studies described previously may be a second example. They showed that only a part of the acidity of faujasite-types zeolites is titrable [5]. This part is decreasing as the aluminum content increases. It was deduced that a self-inhibition effect reduced the efficiency of the aluminum atoms in generating titrable acidity. An efficiency coefficient α was defined for the various zeolites. The changes of this coefficient with the aluminum content showed that the introduction of one more aluminum atom in the faujasite structure decreases the efficiency of all the aluminum atoms by 1.45%.

Another series of results concerned with the interactions in zeolite is related to the infra-red wavenumber of acidic hydroxyl groups (high frequency band) which depends on cation and aluminum contents. With alkaline cationic forms progressively exchanged with protons, it has been observed that the hydroxyl IR wavenumber

vary almost linearly with the Si/Al ratio for series of faujasite type zeolites [6] or various zeolites [7, 8]. The Fig. 1 reports results which have been published for 9 different zeolites. Only three of them (n⁰ 2, 3, 6) belongs to the faujasite family.

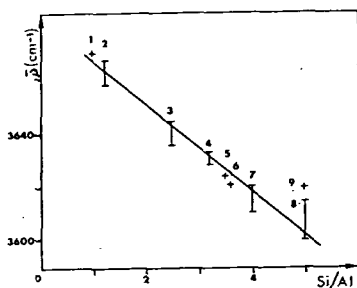*Fig. 1.* Wavenumber of the acidic hydroxyls as a function of the Si/Al ratio for the following zeolites: 1: zeolite A [9]; 2: X; 3: Y[6]; 4: L[10]; 5: Ω[11]; 6: Y Al-deficient [6]; 7: offretite [12]; 8: mordenite [13]; 9: clinoptilolite [14]

The zeolites for which a large number of results have been obtained give a range of OH wavenumbers. The low values correspond to high acid strength (low cation content) and upper value to weak acid strength (high cation content). Since for similar weak acid strengths different zeolites give various hydroxyl wavenumbers, it is inferred that the wavenumber alone is not a measure of the acid strength. The decrease in $\bar{v}_{OH}$ observed in Fig. 1 as Si/Al increases cannot then be explained only on the basis of the known increase in acid strength. Since the decrease in the aluminum content (rise in Si/Al ratio) decreases the density of charges in the zeolite, the hydroxyl groups are subjected to less intense interactions with the framework and it is suggested that the force constant k of the OH bond is then decreased which shifts the wavenumber to low values. The average IR wavenumber characterizing each zeolite would then depend mainly on the charges in the zeolite independently of the crystalline structure and of the acid strength.

Activity coefficients

The study of solutions depend whether they are dilute or not. For solutions 0.1 N to 1 N activity coefficients are used and may be calculated. The large number of interactions prevent the calculation of activity coefficients at higher concentrations. It is then interesting to look at the "concentration" of acid sites in zeolites [15]. The Table I reports the unit cell volume of a series of zeolites in Å³ and litre [16] and the corresponding proton concentration per litre of zeolites crystal. The proton concentration of the theoretically hydrogen forms lies between 4.76 and 9.5 mol

Table I

Zeolite	$\frac{Al}{Al+Si}$	V unit cell		Theoretical H+ per u. c.	Theoretical H+ per litre	Exchange % for normal solution
		Å³	litre (a) (xN)			
X	0.45	15 670	9.03	86	9.5	10.5
Y	0.29	15 350	9.03	56	6.2	16.1
L	0.24	2 794	1.68	8	4.76	21
offretite	0.20	1 160	0.70	3.6	5.16	19.4
modernite	0.17	2 207	1.33	8.4	6.32	15.8

(a): N = Avogadro Number

of H^+ litre^{-1} which corresponds to highly concentrated solutions. The last column gives the degree of exchange to have an acid concentration of one mole proton per litre. The values obtained are quite lower than those considered for commercial zeolites. Since in solution it is quite usual in all these concentration ranges to consider activity coefficients, it is suggested that activity coefficients might also be defined in zeolites. The activity of a substance is defined by HAMMETT [17] "fundamentally in terms of the statement that the quantity RT ln a represents the work that can be gained by the reversible transfer of one mole of the substance from the state in which it exists to some standard of reference state at the same temperature. Any force of interactions that tends to bind the substance to other components of the solution must therefore decrease its activity, for the work that must be done against these forces decreases the amount that becomes available when the substance is transferred to the reference state". This definition might be applied to ions and atoms of the zeolite structure.

From what was said just before, the interactions are very important in zeolites. The smaller the charge density, i. e. the smaller the Al/Al + Si ratio, the higher would be the activity coefficient. It then would depend for a large extent on the aluminum content. The Table I shows that it would increase from X to mordenite. In the case of faujasite it would be higher for Y than for X. Then it turns out that the efficiency coefficient defined just before for faujasite zeolites behaves like an activity coefficient. Such a concept of activity coefficient would need of course the definition of reference and standard state on a thermodynamical basis.

Applications to catalysis

The consequences of an activity coefficient concept in acid solids would be at first in the field of catalysis. The rate of a reaction catalyzed by a proton is given by:

$$r = k[S][H^+] \frac{f_S \cdot f_{H^+}}{f_*}$$

where [S] and [H$^+$] are the concentrations of the substrate S and of the proton; f_S, f_{H^+} and f_* are the activity coefficients of the substrate, of the proton and of the transition state.

As far as the activity coefficient of the proton depends on the catalyst, the comparison of the catalytic properties of various zeolites should involve this parameter. Up to now no general classification of zeolites with regards to catalysis has been presented since the results depend on many parameters (nature of the cations, type of reaction, pretreatment and test conditions...). However for a long time it is known that in many reactions X zeolites are less active than Y [18,19] and mordenite more active than Y [19]. In the isooctane cracking it has been observed that HKL [20] and HK-offretite [21] zeolites are more active than HKY [22] with similar cation contents. The sequence of activity is parallel to that of activity coefficients deduced from the Table I (inverse of Al/Al + Si ratio) and to that reported Fig. 1.

It has been postulated that the high acid strength generates a high catalytic activity. Nevertheless it has not been convincingly proved that the stronger acidity offsets the decrease in acid sites number as the Al/Al + Si ratio decreases [19]. Moreover the stronger acid sites are not necessary in cumene cracking on Y zeolites for example

.[23]. The *iso*octane cracking experiments also showed that even at intermediate cation content, *i. e.* similar rather weak acid strength, Y zeolites are less active then L and offretite samples [20—22]. If then the acid strength alone is not able to account for the sequence of zeolites activities, the activity coefficient might be important to consider. It may complete the series of parameters which may be involved [24].

Applications to adsorption

From the extension of the Hammett definition to the case of zeolites it is suggested that activity coefficient may exist for ions other than protons. The cations which are usually considered as the adsorption sites for various adsorbates should then be evaluated in terms of activity rather than concentration. For a given zeolite the number of charges only depends on the aluminum content since the sum (H^+ +cation) is constant. The activity of the cation, like that of the proton, would vary then mainly with the aluminum level. In the faujasite series it would be lower in X than in Y zeolites. The changes in the chemical potential of the sites $\mu = RT \ln a$ would also, in absolute, be lower in X and consequently the free enthalpy of adsorption per site.

This hypothesis could be substantiated by results of adsorption of benzene and cyclohexane on X and Y zeolites with various sodium contents. Integral enthalpies and entropies of adsorption have been calculated for a monolayer [25]. It was concluded that "in X materials each cation adsorbs a smaller amount of hydrocarbon with a smaller heat of adsorption and a smaller change in entropy than in Y zeolites". It follows that, in absolute, the free enthalpy of adsorption per cationic site, ΔG, is also lower in X than in Y zeolites [26] (about 3 times for benzene adsorption). This is in line with the predictions.

The existence of activity coefficients for adsorption sites would then modify the equilibrium of adsorption, the amounts adsorbed and the thermodynamical values of adsorption.

Conclusions

Due to the large interactions in zeolites, it is very likely that cations and protons behave like in concentrated solutions. Activity coefficients should then be defined. It is then necessary to take these activity coefficients into account when comparing the catalytic properties of various zeolites to their number of acid sites. It is also suggested that interactions in other solids may also generate activity coefficients. For instance the characterization of the acidity of amorphous silica-aluminas may very probably make necessary the use of activity coefficients.

Acknowledgments

References

[1] *Kasai, P. H., R. J. Bishop:* J. Phys. Chem. **77**, 2308 (1973).
[2] *Rabo, J. A., P. H. Kasai:* Progr. Solid State Chem. **9**, 1 (1975).
[3] *Rabo, J. A.:* Zeolite Chemistry and Catalysis, A. C. S. Washington, 1976, p. 332.
[4] *Patton, R. L., E. M. Flanigen, L. G. Dowell, D. E. Passoja:* A. C. S. Symp. Ser. **40**, 64 (1977).
[5] *Beaumont, R., D. Barthomeuf:* J. Catal. **26**, 218 (1972).
[6] *Poncelet, G., M. L. Dubru, P. A. Jacobs:* A. C. S. Symp. Ser. **40**, 606 (1977).
[7] *Jacobs P. A.:* Carboniogenic activity of zeolites, Elsevier, Amsterdam, 1977 p. 58.
[8] *Barthomeuf, D.:* J. C. S., Chem. Com. **1977**, 743.
[9] *Tempere, J. F., D. Delafosse:* J. Catal. **39**, 1 (1975).
[10] *Ballivet, D., D. Barthomeuf:* J. C. S. Faraday I. **73**, 1581 (1977).
[11] *Weeks, T. J., D. G. Kimak, R. L. Bujalski, A. P. Bolton:* J. C. S. Faraday I. **72**, 575 (1976).
[12] *Mirodatos, C., A. Abou Kaïs, J. C. Vedrine, D. Barthomeuf:* J. C. S. Faraday I. to be published.
[13] *Karge, H. G.:* A. C. S. Symp. Ser. **40**, 584 (1977).
[14] *Detrekoy, E. J., P. A. Jacobs, D. Kallo, J. B. Uytterhoeven:* J. Catal. **32**, 442 (1974).
[15] *Barthomeuf, D.:* Compt. rend. to be published.
[16] *Breck, D. W.:* Zeolite Molecular sieves, John Wiley and Sons, New York, 156—177 (1974).
[17] *Hammett, L. P.:* Physical Organic Chemistry, Mc Graw Hill, New York, 1940, p. 88.
[18] *Rabo, J. A., P. E. Pickert, D. N. Stamires, J. E. Boyle:* Actes 2° Congr. Inter. Catal. Paris, 1960, p. 2055. *Rabo, J. A., M. L. Poutsma:* Adv. Chem. Ser. **102**, 284 (1971).
[19] *Poutsma, M. L.:* Zeolite Chemistry and Catalysis (ed. Rabo J. A.), A. C. S., Washington, 1976, p. 437.
[20] *Franco Parra, C., D. Ballivet, D. Barthomeuf:* J. Catal. **40**, 52 (1975).
[21] *Mirodatos, C.:* Thesis, Lyon 1977.
[22] *Beaumont, R., D. Barthomeuf:* J. Catal. **40**, 160 (1975).
[23] *Topchieva, K. V., Huo Shi Thuang:* Dokl. Akad. Nauk SSSR **211**, 870 (1973).
[24] *Huo Shi Thuang, K. V. Topchieva, B. V. Romanovski:* Kin. i Kat. **15**, 1053 (1974).
[25] *Barthomeuf, D., B. H. Ha:* J. C. S. Faraday I. **69**, 2158 (1973).
[26] *Barthomeuf, D.:* to be published.