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Zeolite Electronegativity Related to Physicochemical Properties

W. J. MORTIER

Centrum voor Oppervlaktescheikunde en Colloïdale Scheikunde, Katholieke Universiteit Leuven, De Croylaan 42, B-3030 Heverlee, Belgium

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The influence of the Al content and cation type on the physicochemical properties of aluminosilicates is explained using Sanderson's electronegativity scale. Atomic charges can easily be derived from the compound formula and correlate with acidity, T–O vibrations and interactions of sorbed molecules with the cations. Complicated chemical systems can be compared on the basis of their composition and predictions of their overall properties can be made.

INTRODUCTION

An infinite number of zeolites with the general formula $M_{x/n}{}^{n+}Al_xSi_{1-x}O_2$ can be obtained by ion exchange, dealumination treatments, etc. All of them will show varying catalytic properties related to the Al content, the nature of the cation loading and the presence of adsorbed molecules. An overwhelming amount of data is available in this field using test reactions or ir studies on framework properties, Brønsted acidity, and interactions between the gas and solid phase. Disregarding structural variations in the zeolite group, some general properties are common for all zeolites or amorphous silica–alumina. The Brønsted acidity (derived from test reactions or variation of the OH stretching frequency) increases with increasing Si content and with decreasing cation content or increasing electrostatic potential of the cations (*1*). Framework vibrations are subject to variations with the Al content (*2*). The interaction with sorbed molecules such as CO, CO_2, and water depends on the cation type and the framework composition (*3*). All these factors have an effect on the catalytic properties. Excellent reviews by Jacobs (*1*), Ward (*2*), and Flanigen (*3*) cover these topics.

A comparison between the properties of different samples is not always straightforward. Differences in zeolite type, Al content and cation loading are sometimes sufficient to prevent an adequate discussion based on only one criterion. A single quantitative model, related to the physicochemical properties, is therefore required. It will follow that Sanderson's electronegativity model (*4*) provides us with an excellent tool for a classification of aluminosilicates which is based simply on the chemical composition. The average electronegativity of the compound is easily related to its various physical and chemical properties, and includes, simultaneously, the effects of Si/Al ratio, cations, and sorbed molecules.

SANDERSON'S ELECTRONEGATIVITY MODEL (*4*)

The electronegativity (*S*) is defined as the power of an atom in a molecule to attract electrons to itself. Pauling's electro-

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negativity scale (*5*) allows us to distinguish only between two atoms indifferently of the chemical composition of the compound. In an extreme example, H_3O^+, H_2O, and OH^- would show the same ionicity for all OH bonds. In a molecule consisting of atoms with differing electronegativity the electrons will be redistributed such that they are equally attracted to the nuclei in the bond. Sanderson therefore introduces the principle of electronegativity equalization which is stated as: "When two or more atoms initially different in electronegativity combine chemically, they become adjusted to the same electronegativity within the compound." This intermediate electronegativity (S_{int}) is very satisfactorily postulated to be the geometric mean of the component atoms that make the compound formula. For a compound $P_pQ_qR_r$, the intermediate electronegativity is given as

$$S_{\text{int}} = [S_P{}^p \cdot S_Q{}^q \cdot S_R{}^r]^{1/(p+q+r)}.$$

This allows us to determine the electronegativity depending on the composition of a compound. The partial charge can be derived as the ratio of the change in electronegativity undergone by an atom in joining the compound to the change $\Delta S\,[=2.08(S)^{\frac{1}{2}}]$ it would have undergone in acquiring or losing one electron. For the atom Q, the partial charge is then given by $(S_{\text{int}} - S_Q)/\Delta S_Q$. The electronegativity scale Sanderson developed could be used very successfully in evaluating binding energies. Bond energy will not be considered here since accurate bond distances are very difficult to obtain for zeolites and certainly also for amorphous aluminosilicates. However, it will be possible to correlate electronegativity or partial charges (which are linearly related to each other) with various physicochemical properties. The electronegativity data used here are given in Table 1. An example of the calculation of the average electronegativity of SiO_2 is:

$$S_{SiO_2} = (2.84 \times 5.21^2)^{\frac{1}{3}} = 4.26,$$

and the charge on Si:

$$(4.26 - 2.84)/[2.08(2.84)^{\frac{1}{2}}] = +0.40.$$

TABLE 1

Data for Calculating Partial Charges on Combined Atoms (*4*)

Element	S	Element	S
H	3.55	K	0.42
C	3.79	Ca	1.22
N	4.49	Zn	2.98
O	5.21	Rb	0.36
F	5.75	Sr	1.06
Na	0.70	Cd	2.59
Mg	1.56	Cs	0.28
Al	2.22	Ba	0.78
Si	2.84	Ag	2.57
Ge	3.59		

SOLID ACIDS AND BASES

The acidity of a zeolite is one of the most thoroughly investigated properties. Several reactions are catalyzed by proton transfer between surface and adsorbed molecules. Protons in the zeolite appear after thermal decomposition of NH_4^+-exchanged forms or after hydrolysis during the dehydration step (especially for multivalent cation-exchanged zeolites). Both are important, the total number of protons and the acid strength of the individual Brønsted acid sites. The acid strength will directly correlate with the electronegativity. The electronegativity of several fully cation-exchanged forms of zeolite X and Y and of several other molecules as calculated following Sanderson's method is given in Fig. 1. HX and HY zeolites have different electronegativities and therefore a different acid strength (related to the hydrogen charge, see also Fig. 1) of the protons is predicted. If protons are present in the structure of fully cation-exchanged samples after dehydration (through water hydrolysis), their acid strength can also be estimated. The presence of a few water molecules per unit cell will have only a minor influence on the total electronegativity of the zeolite. It is

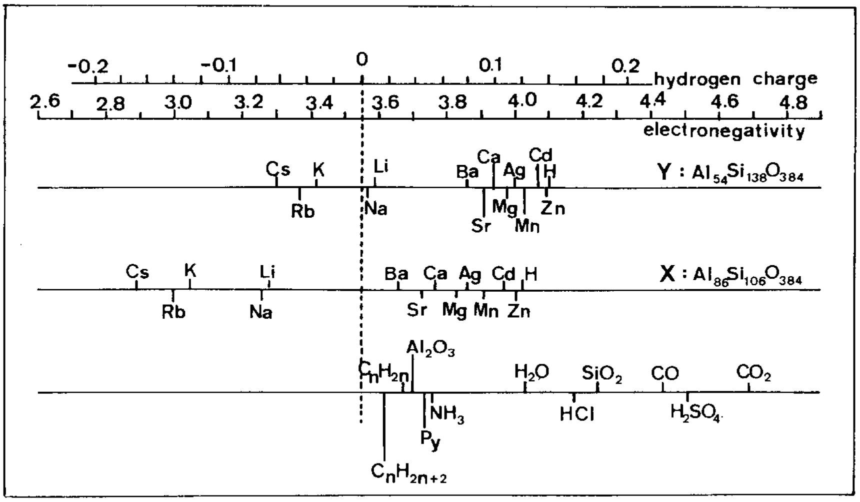

FIG. 1. Electronegativity scale of several fully exchanged X and Y zeolites and other compounds together with the scale indicating the hydrogen charge at the corresponding electronegativity.

important to emphasize here that for partially decationated samples the number of cations and their nature will be of extreme importance.

During the formation of an adsorption complex, the equalization principle predicts an intermediate electronegativity for the entire compound. If the zeolite has a higher electronegativity, an equalization can be promoted by a proton transfer from the zeolite to the molecule. This is analogous with the generation of H_3O^+ upon interaction of HCl with water molecules. If, however, the adsorbed molecule has a higher electronegativity, proton transfer will be very difficult. The proton transfer rate will therefore decrease with decreasing charge on the proton.

Since only overall properties of the zeolite can be considered, application to catalysis will only be straightforward in those cases where the majority of the protons are known to be involved in the reaction. Alcohol dehydration and olefin isomerization are typical examples [see Ref. (*1*), p. 169], while for cracking reactions only trace amounts of the protons are active. The influence of the change in acidity on *n*-butene isomerization was recently investigated for protonated germanic X-type sieves, X and Y zeolites by Poncelet *et al.* (*6*). Calculating the proton charge on the basis of the given composition, a linear variation of the turnover number with the acid strength could be observed. This explains again the change in activity by a change in acid strength, as was stated by the authors.

INFLUENCE OF THE Al CONTENT

The calculated variation of the proton charge vs the Al fraction for fully decationated zeolites ($H_xAl_xSi_{1-x}O_2$) is given in Fig. 2 and illustrates the decreasing acidity with increasing Al content. This variation being linear in the mole fraction is certainly not linear with the molar ratio. X and Y zeolites are only representatives of a very limited composition range. A variation of properties such as OH stretching frequency would show only an apparent linearity with the Si/Al ratio for experiments limited to this range. Indeed, a comparison of the OH stretching frequency with other zeolites [see Ref. (*1*), p. 58] no longer obeys

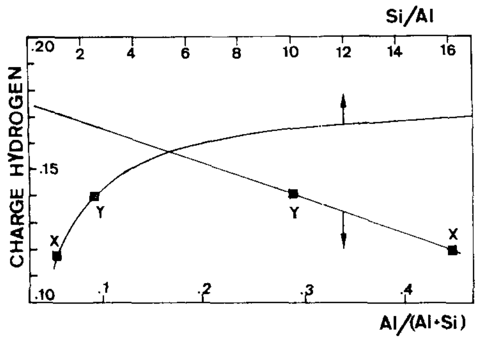

FIG. 2. Variation of the hydrogen charge with the Al fraction for fully decationated zeolites ($H_xAl_xSi_{1-x}O_2$).

the linearity with the molar ratio. Jacobs and Uytterhoeven (*7*) have shown that the frequencies of the components I and III of the OH stretching band (see also below) varied linearly with the Al content (and therefore also with the mole fraction). This was only true after conversion to the same exchange level, indicating again the importance of the cation content.

Structure sensitivity resulting in a multiplicity of stretching frequencies, is not surprising regarding for example the influence of T–O–T and O–T–O bond angles (T stands for Al or Si) on the bond length and consequently also on the atom charges as extensively discussed by Tossel and Gibbs (*8*). A comparison of the OH stretching frequencies is therefore not straightforward when comparing different structure types or when a comparison with amorphous samples is made. A narrowing of the T–O–T angle results in an increased T–O bond length, a decreased overlap population and an increased negative charge on the oxygen. This explains the sequence of OH stretching frequencies of decationated faujasite-type zeolites (*7*). If a proton is attached to the bridging oxygens, the frequency will vary with the OH bond strength, which will be larger for more negatively charged oxygens, i.e., a lower T–O–T angle. A classification on the basis of the T–O–T bond angle in hydrogen faujasite (*9*) (O_1: 138.6°; O_2: 147.4°; O_3: 139.7°; and O_4: 145.3°) predicts the $O_1 > O_3 > O_4 > O_2$ sequence. Jacobs and Uytterhoeven (*7*) decomposed the OH bands and assigned their I, III, IV, and V components to oxygens in the same sequence, with the exception of the IV and V bands which were explained by coupling effects of protons attached to the O_2 and O_4

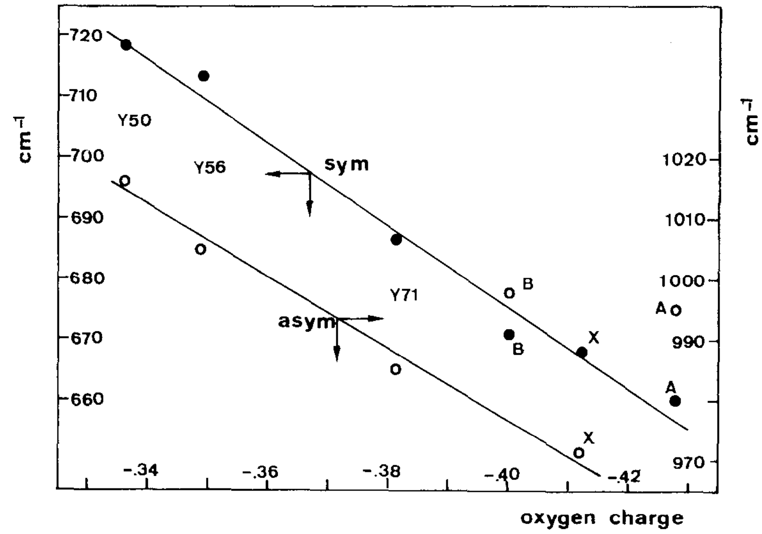

FIG. 3. Variation of the symmetric (●) and asymmetric (○) T–O stretching frequency with the oxygen charge for fully exchanged NaX, NaY, NaA, and NaB zeolites.

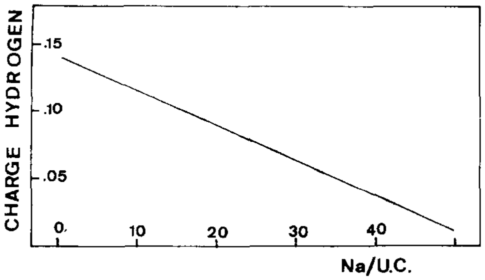

FIG. 4. Calculated influence of the variation of the number of Na ions per unit cell on the hydrogen charge for NaHY zeolites.

oxygens. This sequence can therefore be explained on the only basis of framework properties and illustrates the influence of the structure on the ir frequencies. It is therefore clear that only OH stretching frequencies for OH groups in comparable configurations can be compared successfully. However, within the same homologous series, the electronegativity will be quantitatively related to the physicochemical properties. A further discussion, assigning amounts of protons attached to the different oxygens on the basis of the T–O distances corrected for bond angles, was given earlier (*10*).

Flanigen *et al.* (*11*) studied the influence of the mole fraction of Al in the T atoms on the T–O stretching frequency. The symmetric stretching was found to vary linearly with the Al content and was structure insensitive. The asymmetric stretching frequency also varied linearly with the Al fraction but only within the faujasite-type structure. Figure 3 shows that the T–O stretching frequency shift is consistent with the oxygen charge variation for the zeolites X, Y (three compositions), A, and B. All these samples are supposed to be fully exchanged with Na and to show only the influence of the varying Al content.

INFLUENCE OF THE CATIONS AND HALOGENATION

A variation of the hydrogen charge in gradually decationated NaY zeolites is shown in Fig. 4. A linear relation with the exchange level is predicted. The same type of relation will also be found for a mixed occupancy of cations with different electronegativities. However, not only the acid strength of the protons will be influenced by the nature of the exchangeable cations, but also other properties. A number of studies have been made on the influence of different cations on the Brønsted acidity and on the interactions with adsorbed molecules such as CO, CO_2, and water. The frequency of ir absorption bands could be related to the many properties which influence the electrostatic field strength such as cation radius, electronegativity, and

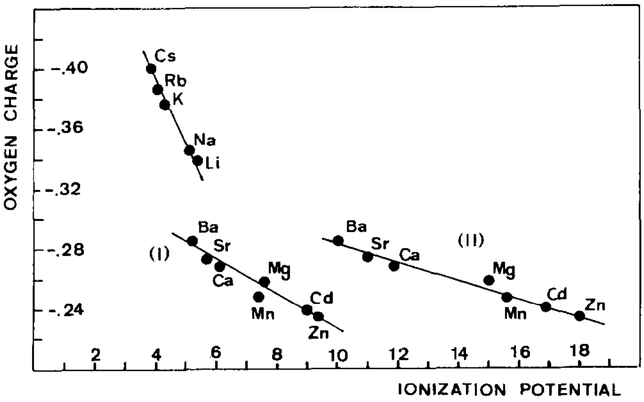

FIG. 5. Influence of the various cations (presented by the ionization potential; I and II: first and second ionization potential) on the framework oxygen charge for fully exchanged Y zeolites.

ionization potential (*2*). The Brønsted acidity was shown to vary linearly with the ionic radius and electrostatic field for Mg, Ca, Sr, and Ba-exchanged zeolites (*12*). The CO_2 2349–2374 cm^{-1} absorption band (asymmetric stretching vibration) varied in a regular manner with the electrostatic field (*13*). The shift of the hydroxyl stretching frequency on water adsorption for alkali-exchanged Y zeolites is linear with the ionization potential (*14*). The water bending frequency band was furthermore also influenced by the cation type (*15, 16*). All these interactions can be related to the charge on the oxygens, the protons or the cations of the zeolites or adsorbed molecules. Following the electronegativity equalization principle, framework and adsorbed molecules will acquire the same mean electronegativity. Oxygen charges of the framework or adsorbed molecules (CO, CO_2) will show an equal variation with the total electronegativity of the compound. The linear variation of the oxygen charge with the ionization potential is shown in Fig. 5 for fully exchanged Y zeolites. The hydrogen charge is subject to a similar variation. Linear variations are also calculated between the oxygen charge and the ionic radii for the series Na, K, Rb, and Cs and also for Mg, Ca, Sr, and Ba-exchanged zeolites. There is no need to redraw the above relations given in the literature (*11–15*), since both the abovementioned properties and the electronegativity as well as the oxygen and proton charges vary linearly with the ionization potential or the ionic radii. Moreover, in most cases the chemical composition of the samples was not given.

The more complicated systems (X and Y zeolites with mixed cation loadings) studied by Angell and Schaffer (*15, 16*) will further illustrate the validity of the method. Since not all compositions of the samples were given, some assumptions have to be made (see caption of Fig. 7). The 2200 cm^{-1} stretching frequency varies linearly with the oxygen charge as plotted in Fig. 6 explaining the shift by the change in charges on the CO molecule. If plotted against the cation charge (Fig. 7), two distinct groups emerge. Indeed the *d* orbitals of the transition metal ions allow back donation of electrons in the π^* orbitals of the CO molecule. This explains the different sensitivity of the CO molecule to the charge of the cations which indeed shows a weakening of the bond unlike extrapolation of the relation for the alkaline earth cations would predict. By plotting against the different charges of the atoms involved in the formation of the CO adsorption complex information can thus be obtained on the nature of the complex itself. The water bending frequency (Fig. 7) also varies linearly with the cation charge.

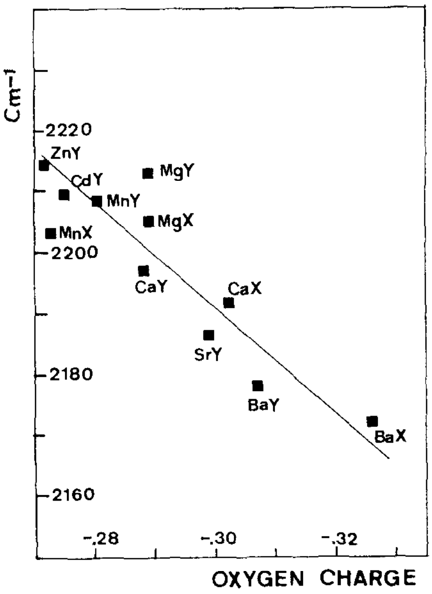

FIG. 6. Variation of the 2200 cm^{-1} CO stretching frequency with the charge on the oxygens for the same samples as described in the caption of Fig. 7.

The replacement of OH groups by halogenes in the framework is known to enhance the acidity of the residual protons [see, e.g., Ref. (*17*)]. A linear increase of the proton charges with the fluorine content is predicted.

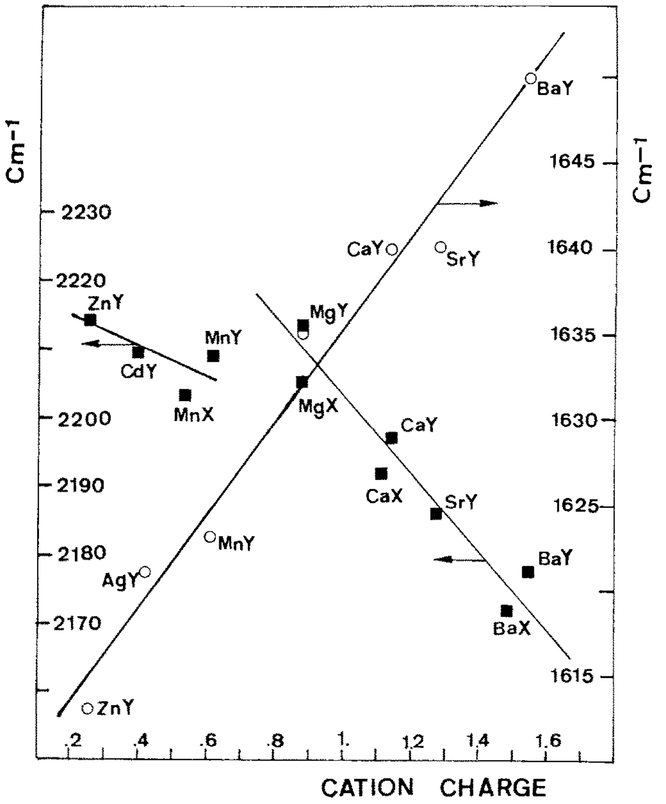

FIG. 7. Variation of the 2200 cm^{-1} CO stretching frequency (■) and the 1615 to 1650 cm^{-1} water bending frequency (○) with the cation charge. Composition of the samples: $Na_{16}Mg_{20}Y$; $Na_{10}Ca_{23}Y$; $Na_{16}Zn_{20}Y$; $Na_{16}Cd_{20}Y$; $Na_{16}Mn_{20}Y$; $Na_{1}Ca_{40}X$; $Na_{1}Ag_{55}Y$. The composition of the following samples was supposed to be: $Na_{16}Sr_{20}Y$; $Na_{16}Ba_{20}Y$; $Mg_{43}X$; $Ca_{43}X$; $Ba_{43}X$; $Mn_{43}X$.

CONCLUSION

Sanderson's electronegativity scale allows a prediction of several physicochemical properties of aluminosilicates with the use of only the chemical compound formula. Complicated systems (e.g., mixed cation loadings and Si, Al content) can now be compared. The already known influences of the Si/Al ratio and cations can be rationalized on a single basis. However, structural differences cannot be explained but trends within a homologous series are certainly valid. Another drawback is the limited number of cations that can be studied in this way. Indeed, electronegativity values for most transition metal ions are not available. It might be possible, however, in the future to derive them indirectly from experiments on clearly defined systems.

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Note added in proof. The applicability of the present method was proved experimentally in a recent paper (Jacobs, P. A., Mortier, W. J., and Uytterhoeven, J. B., *J. Inorg. Nucl. Chem.* (1978), in press) relating the acidity, carboniogenic activity and strength of interaction in transition metal complexes to the electronegativity.

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