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Electronegativity and Brønsted Acidity of Mordenites

If the chemical composition of a zeolite is known, its physicochemical properties can be quantitatively explained with the help of Sanderson's model of electronegativity (*1*). Mortier (*2*), Jacobs *et al.* (*3*), and Hočevar and Držaj (*4*) recently reported the influence of the aluminum content and of cation exchange on the physicochemical properties of faujasite-type zeolites on the basis of their chemical composition. In this note an attempt has been made to calculate the acidity of mordenites from their chemical composition. The calculations involved were carried out following the procedure of Hočevar and Držaj (*4*). The structural formula of mordenite is

$$\mathrm{Na}_x\mathrm{Al}_x\mathrm{Si}_{(48-x)}\mathrm{O}_{96}$$

According to Loewenstein's rule (*5*) the isomorphous exchange of Si for Al can be carried out only up to the ratio Si : Al = 1 : 1. Therefore the values of x have been considered between 0 and 24. The intermediate electronegativity (S_{int}) of mordenite as a function of Al was calculated using the atomic electronegativities (1) and the equation,

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

where S_i is the atomic electronegativity of the element E_i and p_i is its stoichiometric coefficient in the chemical formula. The S_{int} values for mordenite at different number of Al atoms (N_{Al}) in elementary cell are shown in Table 1. The function of $S_{\mathrm{int}}(N_{\mathrm{Al}})$ shows the following linear equation,

$$S_{\mathrm{int}}(N_{\mathrm{Al}}) = -0.0450 \times N_{\mathrm{Al}} + 4.21 \qquad (2)$$

The partial charge (σ_i) of an element is the ratio of the change in electronegativity undergone by an atom in joining the compound to the change ΔS [where $\Delta S = 2.08(S_i)^{1/2}$] it would have undergone in acquiring or losing one electron. σ_i can be derived from the equation,

$$\sigma_i = \frac{S_{\mathrm{int}} - S_i}{2.08(S_i)^{1/2}} \qquad (3)$$

The regressions for average partial charges are obtained by inserting the above regression into Eq. (3):

$$\begin{aligned}
\sigma_{\mathrm{Al}}(N_{\mathrm{Al}}) &= -0.0145 \times N_{\mathrm{Al}} + 0.642\\
\sigma_{\mathrm{Si}}(N_{\mathrm{Al}}) &= -0.0124 \times N_{\mathrm{Al}} + 0.384\\
\sigma_{\mathrm{O}}(N_{\mathrm{Al}}) &= -0.0094 \times N_{\mathrm{Al}} - 0.211\\
\sigma_{\mathrm{Na}}(N_{\mathrm{Al}}) &= -0.0259 \times N_{\mathrm{Al}} + 2.02 \qquad (4)
\end{aligned}$$

If we sum the regressions for the average partial charges of the elements that constitute the zeolite as a function of N_{Al} this would illustrate the best tendency of changes occurring in the interaction of the atoms of zeolite forming elements:

$$\sum_i \sigma_i(N_{\mathrm{Al}}) = -0.0622 \times N_{\mathrm{Al}} + 2.835$$

where i = Al, Si, O, Na. (5)

The maximum number of Al atoms in the elementary cell of a homologous series of mordenites is according to Loewenstein's rule, 24. If this number is considered as a reference state, the tendency of the sum of the regressions of the average partial charges of mordenite-forming elements as a function of N_{Al} is

$$\sum_i \sigma_i(N_{\mathrm{Al}}) - \left(\sum_i \sigma_i(N_{\mathrm{Al}})\right)_{N_{\mathrm{Al}}=24} = -0.0622 \times N_{\mathrm{Al}} + 1.500$$

or

$$\alpha_0 = -0.0622 \times N_{\mathrm{Al}} + 1.500 \qquad (6)$$

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TABLE 1

Intermediate Electronegativity and "Structural Acidity Parameter" (α_0) of Mordenite as a Function of Number of Al Atoms (N_{Al}) in the Elementary Cell

N_{Al}	24	20	16	12	8	6	4	2	0
S_{int}	3.175	3.314	3.467	3.635	3.820	3.921	4.026	4.138	4.256
α_0 (model caln)	0.007	0.256	0.505	0.754	1.002	1.127	1.251	1.376	1.500
α_0 (normalized)	0.005	0.171	0.337	0.503	0.668	0.751	0.834	0.917	1.000

Hočevar and Držaj (*4*) determined the values of α_0 [the "structural acidity parameter" (*6*)] as a function of N_{Al} and they considered the activity coefficient f_{H^+} to be equal to α_0. The activity of the protons may be calculated from the equation,

$$a_{H^+} = [H^+] \cdot f_{H^+} \quad (7)$$

They found the relation,

$$\alpha_0 = -1.45 \times 10^{-2} \times N_{Al} + 1.4 \quad (8)$$

for faujasite-type zeolites which was in agreement with the experimental values reported by Beaumont and Barthomeuf (*6*). Barthomeuf (*7*) postulated that the increase in the acidity which is directly related to the aluminum content in a zeolite cell may be explained on the basis of an analogy with inorganic acids in solution. The "structural acidity parameter," α_0 ($= f_{H^+}$), increases with decrease of the aluminum atoms in a zeolite cell (Eqs. (6) or (8)).

Using Eq. (7) it is possible to calculate the activity of the protons of a zeolite of known composition. Hočevar and Držaj (*4*) considered the activity of the protons as the effective number of acidic sites in faujasite-type zeolites. The authors discussed the physicochemical properties of the zeolites considering the values of N_{Al} between 27 ($\alpha_0 = 1.009$) and 96 ($\alpha_0 = 0$).

The existence of Al atoms in the mordenite cell is very similar to that of protons in solution. The acidity parameter α_0 increases with decrease of the aluminum content (Al + Si) being considered as diluent. Table 1 shows that α_0 has the highest value of ~1.5 when N_{Al} tends to zero. When the ratio Al/(Al + Si) tends to zero, that is aluminum in the system is highly diluted, the system approaches ideal behavior and the values of α_0 may be normalized considering $\alpha_0 = 1$ when N_{Al} tends to zero. The normalized values of α_0 are shown in Table 1 and the function of $\alpha_0(N_{Al})$ [normalized] is

$$\alpha_0(\text{norm}) = -4.14 \times 10^{-2} N_{Al} + 1.0$$

The actual concentration of protonic sites is directly proportional to the number of aluminum atoms in the zeolite cell, but the effective number of protons is related to the actual concentration of protons and the value of α_0,

$$a_{H^+} = [H^+] \cdot \alpha_0$$

The effective number of protons of hydrogen mordenites are shown in Table 2. It can be seen that at about $N_{Al} = 12$ the proton activity is a maximum at 2.30 mmol/g. Mordenites are usually available with $N_{Al} = 8$

TABLE 2

Acidity of Hydrogen Mordenites as a Function of N_{Al}

N_{Al}	24	20	16	12	8	6	4	2	0.5
$[H^+]$/(mmol/g)	12.500	6.928	5.527	4.549	2.778	2.063	1.388	0.687	0.174
a_{H^+}/(mmol/g)	0.063	1.185	1.863	2.288	1.856	1.549	1.158	0.630	0.170
σ_{H^+}	−0.107	−0.061	−0.015	0.031	0.077	0.100	0.122	0.145	0.163

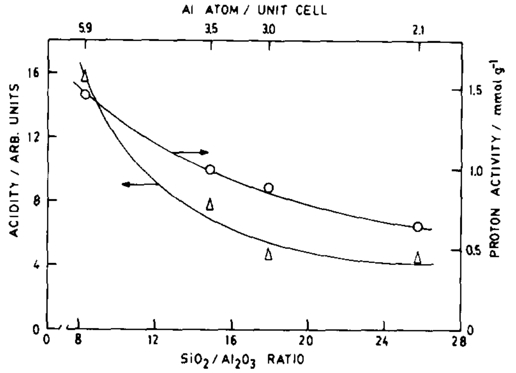

FIG. 1. Acidity determined by i.r. ammonia adsorption and proton activity as a function of aluminum content in hydrogen mordenite cell.

and on dealumination the effective number of acid sites decreases.

A series of hydrogen mordenites with different Si/Al ratios were studied by infrared spectroscopy. The details of the infrared study have been reported in an earlier paper (*8*). The calculated proton activity and the protonic acidity (in arbitrary units) using ammonia adsorption are shown in Fig. 1 and the acidity found in both the cases is the same, which is an indication that the calculation of proton acidity from the chemical composition is satisfactory.

The average partial protonic charge in the mordenite elementary cell was calculated from the equation,

$$\sigma_{H^+} = \frac{S_{int} - S_H}{2.08(S_H)^{1/2}}$$

where σ_{H^+} is the average partial protonic charge, S_{int} the intermediate electronegativity of the zeolite, and S_H the electronegativity of hydrogen. The average protonic charge at different values of x (i.e., number of Al atoms) was calculated and is shown in Table 2. It shows that the protonic charge, i.e., the strength of the sites, increases with decrease of Al atoms in the mordenite cell. This is in agreement with previous findings (*8*, *9*).

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