

The Influence of Framework-Gallium in Zeolites: Electronegativity and Infrared Spectroscopic Study

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Based on the influence of the composition (Si/Al and Si/Ga ratio) on the framework vibrations of zeolites with different structure types (FAU, LTL, BETA, MOR, MEL, MFI, TON, and MTW), an electronegativity value for gallium substituted into zeolite frameworks is proposed (Sanderson electronegativity scale). The present electronegativity value agrees with the known physicochemical properties of gallium substituted zeolites. © 1991 Academic Press, Inc.

INTRODUCTION

Electronegativity equalization as a (predictive) tool for characterizing the physicochemical properties of zeolites was first introduced by Mortier (1). Sanderson's formalism, i.e., the evaluation of the average electronegativity by a geometric average of the compound composition (2), allowed the rationalization of several physicochemical properties as a function of the zeolite composition, irrespective of the framework type. This concept was applied for explaining the following effects: (i) the variation of the hydroxyl stretching frequency as a function of the [Al]-content and cation loading (1, 3–5); (ii) the frequency shift of the high-frequency band of [H]-zeolites upon interaction with benzene (5), (iii) the rate of dehydration of isopropanol for zeolites with high [Al]-content and the turnover frequency of *n*-decane hydroconversion of [Pt]-loaded [H]-zeolites with high [Al]-content (5) and (iv) the variation of

the framework vibration frequencies (1, 6). It has been recognized as a powerful tool in the design of catalysts (7).

Elements such as Ga, Ce, Be, B, Fe, Cr, P, and Mg can also be substituted for Si and Al in the zeolite framework (8). This substitution influences the physicochemical properties of these materials which must correlate with Sanderson's average compound electronegativity. There is however an exception for Ga, as follows for instance from a study on the acidity of the surface hydroxyls for [Ga]- and [Al]-substituted MFI-type zeolites by Chu and Chang (9). The Brønsted acidity is found to be greater for Al(OH)Si than for Ga(OH)Si. This is contrary to what we would expect from Sanderson's principle (1, 3–5), since the electronegativity (10) of Ga (2.419) is suggested to be greater than that of Al (1.714).

The spectroscopic study of Chu and Chang (9) is consistent with the work by Simmons *et al.* (11) revealing that the catalytic activity for *n*-butane cracking is considerably lower for [Ga]-MFI compared to [Al]-MFI for a given SiO₂/M₂O₃ molar ratio. The dealkylation of cumene follows the same trend: the vacuum-pre-

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TABLE 1
 Framework Type, Chemical Composition, Si/Al Ratio, and Average Electronegativity (S) of the [Al]-Zeolites used in the Study

Sample No.	Framework type ^a	Anhydrous unit cell composition	Si/Al	S
1	FAU	$\text{Na}_{86}\text{Al}_{86}\text{Si}_{106}\text{O}_{384}$	1.24	2.9571
2	FAU	$\text{Na}_{69}\text{Al}_{69}\text{Si}_{123}\text{O}_{384}$	1.80	2.9768
3	FAU	$\text{Na}_{60}\text{Al}_{60}\text{Si}_{132}\text{O}_{384}$	2.25	2.9877
4	FAU	$\text{Na}_{48}\text{Al}_{48}\text{Si}_{144}\text{O}_{384}$	3.00	3.0004
5	LTL	$\text{K}_{13}\text{Al}_{13}\text{Si}_{23}\text{O}_{72}$	1.75	2.9754
6	LTL	$\text{K}_{9,0}\text{Al}_{9,0}\text{Si}_{27,0}\text{O}_{72}$	3.00	3.0004
7	LTL	$\text{K}_{8,5}\text{Al}_{8,5}\text{Si}_{27,5}\text{O}_{72}$	3.25	3.0037
8	BETA	$\text{Na}_{0,074}\text{Al}_{0,074}\text{Si}_{0,926}\text{O}_2$	12.5	3.0396
9	BETA	$\text{Na}_{0,025}\text{Al}_{0,025}\text{Si}_{0,975}\text{O}_2$	39	3.0506
10	MOR	$\text{H}_7\text{Al}_7\text{Si}_{41}\text{O}_{96}$	6.05	3.0244
11	MOR	$\text{H}_{5,5}\text{Al}_{5,5}\text{Si}_{42,5}\text{O}_{96}$	7.50	3.0298
12	MOR	$\text{H}_{2,4}\text{Al}_{2,4}\text{Si}_{45,6}\text{O}_{96}$	9.50	3.0348
13	MOR	$\text{H}_{0,95}\text{Al}_{0,95}\text{Si}_{47,05}\text{O}_{96}$	23.9	3.0472
14	MOR	$\text{H}_{0,60}\text{Al}_{0,60}\text{Si}_{47,40}\text{O}_{96}$	38.1	3.0504
15	MFI	$\text{H}_{2,3}\text{Al}_{2,3}\text{Si}_{93,7}\text{O}_{192}$	40	3.0507
16	MFI	$\text{Si}_{96}\text{O}_{192}$	∞	3.0562
17	TON	$(\text{H}, \text{Na})_{0,52}\text{Al}_{0,52}\text{Si}_{23,48}\text{O}_{48}$	45.7	3.0513
18	MTW	$\text{H}_{0,42}\text{Al}_{0,42}\text{Si}_{27,58}\text{O}_{56}$	65	3.0528
19	MEL	$\text{Si}_{96}\text{O}_{192}$	∞	3.0562

^a The mnemotechnical code is taken from W. M. Meier, D. H. Olson, "Atlas of Zeolite Structure Types," Butterworths, London, 1987.

treated catalyst containing [Ga]-MFI as active component is less active than the vacuum-pretreated [Al]-MFI (12). Furthermore, the desorption of ammonia from the ammonium-exchanged materials (11, 12) requires a temperature of up to 500°C

for zeolite [Al]-MFI, whereas for [Ga]-MFI, 400°C is sufficient.

There is thus certainly sufficient evidence that the electronegativity value of Ga should be reconsidered. A new value is proposed based on an extensive study of the frame-

TABLE 2
 Framework Type, Chemical Composition, Si/Ga Ratio, and Frequency (f) of the Asymmetric Stretching Vibration of the Internal Tetrahedra of the [Ga]-Zeolites used in this Study

Sample No.	Framework type	Anhydrous unit cell composition	Si/Ga	f (cm^{-1})
20	FAU	$\text{Na}_{59}\text{Ga}_{59}\text{Si}_{133}\text{O}_{384}$	2.25	987
21	LTL	$\text{K}_{10,4}\text{Ga}_{10,4}\text{Si}_{25,6}\text{O}_{72}$	2.45	1009
22	LTL	$\text{K}_{9,0}\text{Ga}_{9,0}\text{Si}_{27,0}\text{O}_{72}$	3.00	1007
23	BETA	$\text{Na}_{0,074}\text{Ga}_{0,074}\text{Si}_{0,926}\text{O}_2$	12.5	1057
24	MFI	$\text{H}_{2,0}\text{Al}_{2,0}\text{Si}_{94,0}\text{O}_{192}$	47.5	1103
25	LTL	$\text{K}_{9,7}\text{Ga}_{1,0}\text{Al}_{8,7}\text{Si}_{26,3}\text{O}_{72}$	$\frac{\text{Si}}{\text{Al} + \text{Ga}}$ 2.70	1018

work vibrational characteristics of Ga-substituted zeolites.

EXPERIMENTAL

A. Materials

The materials considered in this study are given in Tables 1 and 2, together with their structure type and chemical composition.

B. Infrared Studies

The infrared spectra of the (hydrated) zeolites were recorded by using the KBr pellet technique: a mixture of zeolite/KBr in a ratio 1/100 was pressed during 10 min at a pressure of about 10^8 Pa at room temperature. The spectra were recorded with a Fourier Transform infrared Spectrometer (FTS-40, Digilab) in a nitrogen atmosphere in the wavenumber range 400–4000 cm^{-1} .

C. Average Electronegativity Calculations

The average compound electronegativity (S) given in Table 1 was calculated as the geometric mean (2) of the free atom electronegativities of those atoms present in the molecule under consideration.

For a compound $P_p Q_q R_r$, the intermediate electronegativity is given as

$$S = (S_p^p S_q^q S_r^r)^{1/(p+q+r)}, \quad (1)$$

where S_p , S_q , and S_r denote the free atom electronegativities of atoms P , Q , and R , respectively. Except in the case of gallium, their values are taken from Ref. (10) and are retabulated in Table 3. The (extra-framework) cations and water molecules were not considered for calculating S (see Discussion).

RESULTS AND DISCUSSION

The T–O asymmetric stretching frequency and other framework vibrations for 19 different [Al]-zeolites are plotted in Figs. 1 and 2 against the calculated average electronegativity. The band assignment is hereby based on Flanigen's classification (13, 14): the region 1250–950 cm^{-1} is as-

TABLE 3

The Atom Electronegativity Values of Oxygen, Aluminium, Silicon, and Gallium According to Sanderson (Ref. (10)), as Well as the Electronegativity Values, Applicable to Zeolite Frameworks

Atom	Electronegativity value according to Sanderson	Electronegativity value applicable to zeolites
O	3.654	3.654
Al	1.714	1.714
Si	2.138	2.138
Ga	2.419	<i>1.59</i>

Note. The value in italics is the electronegativity value of gallium proposed in this article.

signed to the TO asymmetric stretching vibration of internal tetrahedra, the regions 820–750 cm^{-1} and 720–650 cm^{-1} are assigned to the TO symmetric stretching vibration of external linkages and of internal tetrahedra, respectively, and the region 650–500 cm^{-1} is assigned to the double six-ring vibration, which occurs for instance in FAU-type zeolites.

The data reported in this work agree very well with earlier observations (13–15), but the frequencies are obviously shifted to somewhat lower values (13) with respect to dehydrated zeolites (6). Water molecules adsorbed into zeolites form hydrogen bonds with lattice oxygens, which will weaken the T–O (Si–O and/or Al–O) bonds adjacent to the site of interaction. These water molecules also strongly interact with the extra-framework cations, considerably weakening their interaction with the framework oxygens. Therefore, in the calculations of the average compound electronegativity, the charge-compensating cations were excluded. The correlations between the average electronegativity and all IR bands investigated (Figs. 1 and 2) indicate that this is a correct way of proceeding for these hydrated zeolites, which encompass a diverse selection of structure types, composition, and cation loading.

The sample composition and the fre-

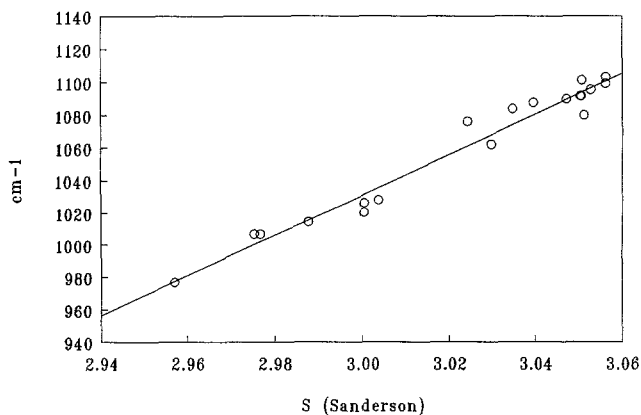


FIG. 1. Frequency of the TO asymmetric stretching vibration of internal tetrahedra for [Al]-zeolites as a function of the average electronegativity (S).

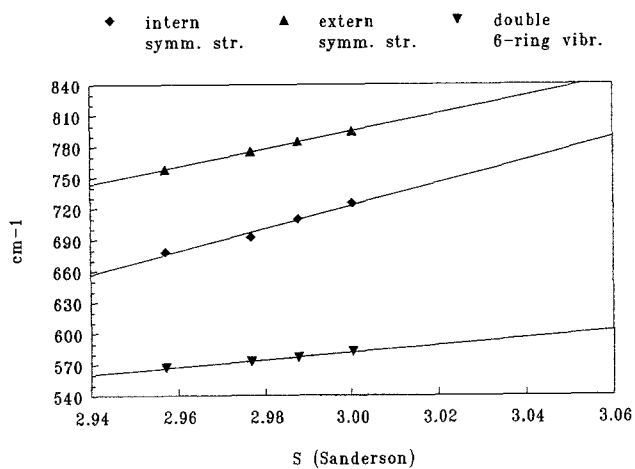


FIG. 2. Frequencies of the TO symmetric stretching internal vibration (\blacklozenge), of the TO symmetric stretching vibration of external linkages (\blacktriangle) and of the double six-ring vibration (\blacktriangledown) for [Al]-FAU-type zeolites as a function of the average electronegativity (S).

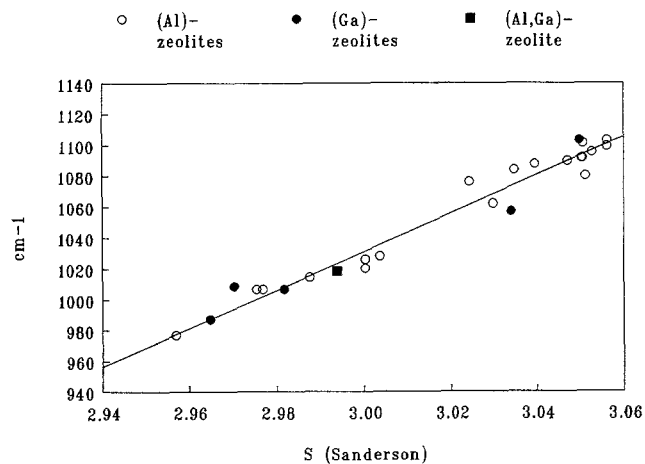


FIG. 3. Frequency of the TO asymmetric stretching vibration of internal tetrahedra for [Al] (\circ), [Ga] (\bullet), and [Al,Ga] (\blacksquare) zeolites as a function of the average electronegativity (S).

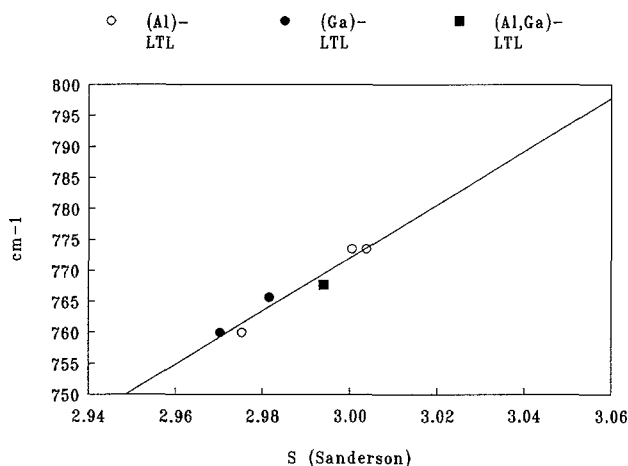


FIG. 4. Frequency of the TO symmetric stretching vibration of external linkages for [Al] (○), [Ga] (●), and [Al,Ga] (■) zeolites of the LTL type as a function of the average electronegativity (S).

quency of the TO asymmetric stretching internal vibration of the [Ga]-containing zeolites are summarized in Table 2. The frequencies are much lower for the [Ga]-zeolites than for the [Al]-zeolites for a given Si/M^{3+} ratio, indicating a lower electronegativity value for Ga compared to Al.

Accepting the correlations for the [Al]-zeolites, and knowing the chemical composition and IR frequencies for the [Ga]-containing zeolites, the electronegativity value of Ga which fits the general relation for T-O framework vibrations can be calculated numerically.

In this way, and using a weighted average contribution for the different samples (the error on the calculated value will be larger when the [Ga]-fraction in the zeolite is lower), leads to a mean electronegativity value for Ga of 1.59. Using this value, the data points for [Ga]-zeolites are highlighted in Fig. 3. The proposed value for Ga (1.59) was then tested for other IR bands. This is illustrated in Fig. 4 for the frequency of the symmetric stretching external vibration of the LTL-type zeolites. These data again suggest that the proposed electronegativity value for Ga incorporated in zeolite frameworks of 1.59 is very satisfactory. Mulliken is the only one so far who indeed gives an

electronegativity value of Ga lower than of Al (16).

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