

Influence of Alkali and Alkaline Earth Cations on the Brønsted Acidity of Zeolites

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We report a computational study on how alkali and alkaline earth metal cations affect the Brønsted acidity of a bridging OH group in their close vicinity. The zeolite fragment is modeled as a six-ring of faujasite structure which contains two or three aluminum centers. The calculations show that charge compensation by alkali or alkaline earth metal cations decreases the deprotonation energy (DE) of the bridging OH group relative to the completely protonic forms of the clusters; i.e., mixed forms of zeolites which contain both protons and metal cations for charge compensation exhibit sites that are more acidic than the corresponding pure protonic forms. The strongest decrease in DE is found for calcium and sodium exchanged model clusters. An analysis of the properties of the bridging OH groups and the trends in calculated DE values reveals that the contribution of the metal cation to the stabilization of the deprotonated form of the cluster is important for the reduction of DE of the considered bridging OH group. We also discuss the influence of the metal cations on the core level shifts of the zeolite oxygen centers.

1. Introduction

The Brønsted acidity of bridging OH groups is among the topics that have received the most attention when zeolites and related microporous materials were studied computationally.^{1–6} The goal of the present work is to evaluate the effect of some alkali and alkaline earth metal cations on the Brønsted acidity of mixed forms of zeolites which contain both metal cations and protons as charge compensating cations. In most theoretical investigations, the deprotonation energy (DE) of hydroxyl groups was calculated as a unifying measure of the Brønsted acidity. The consequences of different computational approaches and the construction of models were recently discussed.^{6,7} Therefore, in the present context it suffices to briefly review the results of theoretical studies which simulate acidity changes that are generated by alterations of the environments of bridging OH groups.

The effect of the aluminum content of the framework on the zeolite acidity was investigated recently by a combined quantum mechanical/interatomic potential (QM–Pot.) approach.⁸ It was found that the DE increases, i.e., acidity decreases, with the number of the aluminum centers in nearest-neighbor framework positions of the silicon atom which borders the bridging OH group; however, aluminum centers distributed farther away in the framework do not affect the DE value. Using the same method, Brändle and Sauer⁵ performed extensive studies of acidity differences of several zeolite materials caused by the difference in their framework structure. They found similar DE values for the strongest acid sites in all materials; the DE values vary between 1171 and 1200 kJ/mol, corresponding to HY and HZSM-5 zeolites, respectively.

Gonzales et al.⁹ modeled various defect sites in the vicinity of bridging OH groups and found substantially reduced DE

values in the presence of Si defect sites of the form $\equiv\text{Si}^+$ (by 200 kJ/mol), while inclusion of extraframework cationic aluminum containing species, such as $\text{Al}=\text{O}^+$, in the immediate vicinity of the acid site lower the DE by about 100 kJ/mol. Similar calculations were also performed on the effect of some alkali metal and calcium cations on the Brønsted acidity of HZSM-5 zeolites.¹⁰ The model cluster used in that study comprised a branched chain with two Al centers and the cation was located next to the bridging OH group along the chain. The calculated DE values were reduced by 25 and 113 kJ/mol due to the presence of Li^+ and $\text{Ca}(\text{OH})^+$, respectively. Very recently, Barbosa and van Santen¹¹ studied the effect of zinc cations on the Brønsted acidity of protons in one or two coupled four-rings of zeolite structure. They found the acidity of a bridging OH group enhanced (by 115 kJ/mol) only when a ZnOH^+ cation is located at the same four-ring as the acidic OH group. The acidity of a proton in the neighboring four-ring remains unaffected. These authors also concluded that a Zn^{2+} cation itself has no effect on the Brønsted acidity of a OH group in the model cluster. However, this conclusion is based on calculations on a cluster containing two coupled four-rings and a Zn^{2+} cation located at one of the rings, while the OH group is in the other four-ring. Note that the Loewenstein rule¹² does not allow more than two Al atoms in one four-ring; i.e., it is not possible to have simultaneously one bi-valent cation, as Zn^{2+} and a proton for charge compensation at one four-ring. However, such a combination is allowed at six-rings containing three aluminum T-atoms.

The Brønsted acidity of zeolite materials containing both metal cations and protons as charge compensating cations is a subject of continued interest.^{13–17} In most of the experimental studies the bridging OH groups are distinguished by their vibrational frequency or its alteration after interaction with probe molecules. Hunger et al. were able to discriminate two adsorption states of ammonia on $\text{HNa}-\text{Y}$ zeolite with adsorption energies differing by about 20 kJ/mol.¹⁶ Using the IR spectra after adsorption of probe molecules, Datka et al. identified four

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different types of bridging OH groups in HNa-Y zeolite.¹⁵ The authors attributed these acidity differences to variations in the number of aluminum centers at framework positions closest to the silicon center of the bridging OH group.

We now turn to the goal of the present work, namely, a computational study of the effect of some alkali and alkaline earth metal cations on the Brønsted acidity of mixed forms of zeolites with two kinds of charge compensating cations. This type of charge compensation with a proton and a metal cation in close vicinity is restricted to zeolites with higher Al content. For this reason we will model the zeolite fragment as a six-ring of faujasite structure which contains two or three aluminum centers. This cluster model of the zeolite structure is more appropriate for the purpose of the present study than a chainlike fragment since, in addition to the stabilization of the deprotonated cluster along the chain, it also accounts for the direct interaction of the metal cation with the oxygen center of the formerly bridging OH group in the deprotonated cluster. Another advantage of six-rings as models in the present study is the possibility of having simultaneously a bi-valent metal cation and a bridging OH group at the same zeolite ring. In addition to the acidity changes, we will discuss the influence of the metal cations on the core level shifts of the zeolite oxygen centers in the model clusters as an extension of our recent investigation of sodium exchanged faujasites.¹⁸

2. Methods

2.1. Model Zeolite Clusters. We will use two types of zeolite fragment models: six-rings of faujasite structure with two (Al-2) or three (Al-3) aluminum centers (see Figures 1 and 2). For the cluster Al-2 both relative positions of the two aluminum centers in the ring allowed by the Loewenstein rule¹² were considered, para (Al-2p) and meta (Al-2m) (Figure 2b,c). Accordingly, Si and Al alternate as T-atoms of the six-ring model Al-3. A cluster with one aluminum center is considered only with H⁺ compensation because in this cluster it is impossible to simultaneously have a bridging OH group and a metal cation. Free valences of the silicon and aluminum atoms of the rings were saturated by hydrogen atoms. The initial positions of the T-atoms and the oxygen centers in the six-rings were taken from mean crystallographic values for Na-X zeolite.¹⁹ The structures of the charged clusters were optimized, keeping the positions of the T-atoms fixed at crystallographic distances. This procedure attempts to represent the actual situation in a zeolite framework where the motion of the T-atoms is restricted by two additional bonds directed outside the ring while the oxygen atoms are much more mobile.

The influence of monovalent alkali metal cations Li⁺, Na⁺, and K⁺ on the acidity of the bridging OH group was studied for the six-ring Al-2p. The effect of the cluster model on the acidity is examined by comparing the sodium containing forms of the clusters Al-2m, Al-2p, and Al-3, namely, Na-Al-2m, Na-Al-2p, and Na-Al-3, respectively. The latter cluster exhibits two bridging OH groups. Alkaline earth metal exchanged zeolites are modeled by the clusters Mg-Al-3 and Ca-Al-3. The six-ring with three aluminum centers is used because the DE calculation requires at least one bridging OH group in the initial cluster to account for the influence of these bi-valent cations. For comparison, we also modeled the completely protonic forms of the zeolite clusters, H-Al-1, H-Al-2p, H-Al-2m, and H-Al-3; in each of these cluster models, the number of protons is equal to the number of aluminum centers. The positions of the oxygen centers of the ring, the protons of the bridging OH groups, and the metal cations (when present) were optimized.

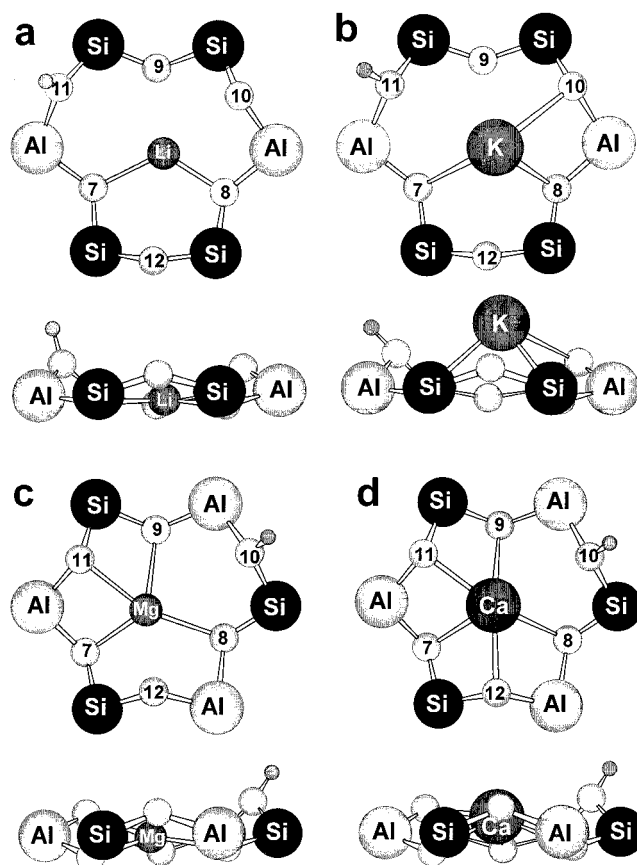


Figure 1. Calculated locations of the alkali and alkaline earth metal cations at the zeolite six-rings: (a) Li-Al-2p, (b) K-Al-2p, (c) Mg-Al-3, and (d) Ca-Al-3. For the corresponding M-O distances see Table 1. The oxygen atoms of the six-rings are numbered for easy reference in the discussion.

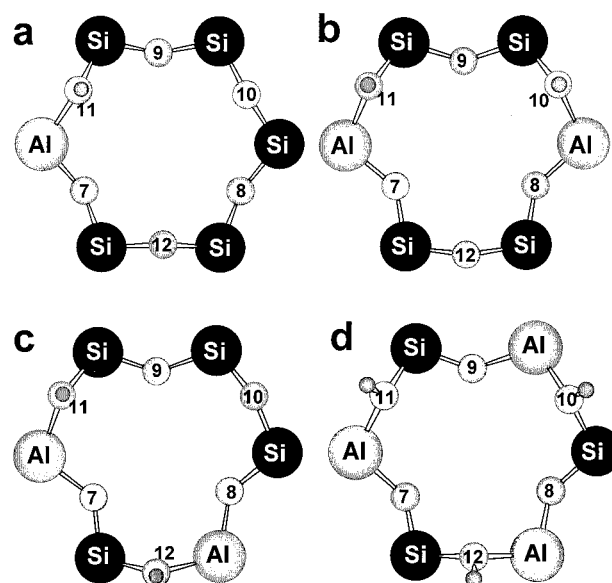


Figure 2. Structure of the model zeolite six-rings compensated by protons: (a) H-Al-1, (b) H-Al-2p, (c) H-Al-2m, and (d) H-Al-3. The oxygen atoms of the six-rings are numbered for easy reference in the discussion.

2.2. Computational Details. The calculations have been carried out with the linear combination of Gaussian-type orbitals density functional method (LCGTO-DF)²⁰ as implemented in the new program ParaGauss for parallel computers.^{21,22} The gradient corrected exchange-correlation functional suggested by

TABLE 1: Characteristics of the Metal Cations at the Six-Rings Al-2p and Al-3

	Li-Al-2p	Na-Al-2p	K-Al-2p	Na-Al-3	Mg-Al-3	Ca-Al-3
M-O7 ^a	207	237	291	225	203	229
M-O8 ^a	190	223	270	241	220	236
M-O9 ^a	226 ^b	248 ^b	312 ^b	227	223	239
M-O10 ^a	270	250	279	287 ^c	327 ^c	291 ^c
M-O11 ^a	329 ^c	307 ^c	333 ^c	234	228	236
M-O12 ^a	294 ^b	286 ^b	301 ^b	296 ^c	236	239
⟨M-O⟩ ^d	253	259	298	252	240	245
⟨M-O⟩ ^e	249	254	293	252	240	245
z(M) ^f	15	59	171	33	8	30
q(M) ^g	0.49	0.53	0.62	0.51	1.12	1.62

^a M-O distances (pm) of different oxygen centers of the six-rings. For the numbering of the centers see Figure 1. ^b Oxygen center of Si-O-Si bridge. ^c Oxygen center of bridging OH group. ^d Averaged M-O distance of all oxygen centers of the six-ring. ^e Average M-O distance of the oxygen centers of the Al-O-Si bridges. ^f Distance of the metal cations to the plane of the T-atoms (pm). ^g Mulliken charge of the cation (e).

Becke (exchange) and Perdew (correlation)²³ was used. Gaussian-type basis sets were employed to describe the Kohn-Sham orbitals: (6s1p)→[3s1p] for H, (9s5p1d)→[5s4p1d] for O and C, (12s9p1d)→[6s4p1d] for Al and Si, (9s4p)→[4s2p] for Li, (12s8p1d)→[6s5p1d] for Na, (15s10p1d)→[6s5p1d] for Mg, (15s11p1d)→[6s5p1d] for K, and (16s11p1d)→[6s5p1d] for Ca.²⁴ All contractions were of generalized form. For calculating the Hartree contribution of the electron-electron interaction an auxiliary basis set was employed to represent the electronic charge density.²⁰ The corresponding exponents were constructed by scaling the exponent of the orbital basis; a standard set of p and d polarization exponents was added on each atomic center.²⁵ The exchange-correlation energy and the matrix elements of the exchange-correlation potential have been evaluated by numerical integration.^{26,27} The structures of the clusters described in the previous section were optimized automatically using analytical energy gradients.²⁸ The charges reported in the following were obtained by a Mulliken population analysis.

After geometry optimization, a constrained frequency analysis was carried out where the vibrational modes of the bridging OH group were taken into account. Normal harmonic vibrational frequencies were calculated by diagonalizing the mass weighted force constant matrix in internal coordinates. The force constants were obtained numerically by finite differences of analytical energy gradients.

The Brønsted acidity of the different bridging OH groups was estimated by the deprotonation energy, calculated as the total energy difference between the initial (neutral) and deprotonated (anionic) forms of the zeolite clusters. This is an absolute measure for the thermodynamic acidity of the materials studied, independent of the corresponding base. For zeolites, DE values cannot be measured directly. However, at least the difference between DE values of two different OH groups can be determined as differences of the binding energies of a probe basic molecule.

Core level binding energy shifts of the oxygen centers in the zeolite six-rings were approximated as differences of ground-state (Kohn-Sham, KS) orbital energies:

$$\Delta E_b(\text{O}1s) = -[\epsilon^{\text{KS}}(\text{O}1s) - \epsilon_{\text{ref}}^{\text{KS}}(\text{O}1s)]$$

As reference in the present context we employ the orbital energy of oxygen centers of a six-ring, $\epsilon_{\text{ref}}(\text{O}1s)$, which contains only silicon T-atom (Si-6). A negative value of $\Delta E_b(\text{O}1s)$ implies that the corresponding O 1s orbital is less stable than that of the reference center. The validity of the above procedure for estimating core level binding energy shifts for the systems under study was confirmed by the so-called ASCF procedure²⁹ for several oxygen centers of different rings, compensated either by protons or metal cations. The values obtained by the two

procedures differed at most by 0.1 eV; thus the very economical estimate of $\Delta E_b(\text{O}1s)$ as the difference of ground-state KS orbital energies is fully justified in the present context.¹⁸

3. Results and Discussion

3.1. Structure of the Clusters. The position of the metal cation with respect to the zeolite ring depends strongly on the ionic radius of the cation, as is evident from X-ray diffraction (XRD) data.^{19,30} Our recent study³¹ on the location of Na⁺ at zeolite six-rings of different Al content showed that the cation interacts mainly with (i) the oxygen centers of Si-O-Al bridges and (ii) the oxygen centers directed inward in the model ring (O_{in}); also, the cation was found far from the bridging OH group. The other cations studied here show similar trends. The positions of the smaller cations, lithium at the Al-2p ring and magnesium at the Al-3 ring, are near the plane of T-atoms of the six-ring, shifted somewhat toward the plane of the oxygen centers O_{in} (Figure 1a,c and Table 1). The shortest Li-O distances are 190 pm (to the oxygen center O8 far from the bridging OH group; Figure 1a) and 207 pm (to the oxygen center O7). Similarly, a Mg²⁺ cation is closer to the oxygen center at the side opposite to the bridging OH group of the ring Al-3, at 203 pm. The Mg-O distances to the other two oxygen centers O_{in}, O8 and O9, next to the OH group, are almost the same, 220–223 pm (Table 1). The position of Mg²⁺ near the center of the six-ring agrees with the XRD data for dehydrated MgNa-X zeolite (for Mg at site SII),³⁰ while the presence of water molecules results in a shift of the cation.³⁰ Geometry optimization with different starting positions of Li⁺ or Mg²⁺ at the six-rings Al-2p and Al-3, respectively, lead to the same optimized structures, described above.

The position of Ca²⁺ at the six-ring Al-3 is very similar to that of a sodium cation at the same six-ring (Table 1); this has been expected from the similarity of the ionic radii of the two cations, 97 and 99 pm for Na⁺ and Ca²⁺, respectively.³² The calcium cation is at 30 pm above the plane of T-atoms of the ring with a shortest Ca-O distance of 229 pm.

Two local minima were found for K⁺ at the six-ring Al-2p, similar to the syn and anti positions of a sodium cation,³¹ but farther away from the plane of T-atoms. The cation is located 203 pm from the plane of the ring when K⁺ is at the side of the O_{in} oxygen atoms, i.e., in syn position, and 171 pm from the plane, when in anti position—at the opposite side of the ring (Figure 1b). At variance with Na⁺, both positions of K⁺ were also observed at the six-ring Al-1, because the cation is too big to move to the center of the ring as does the sodium cation. The shortest K-O distances of the syn position at the six-ring Al-2p are 260 and 278 pm, while for the anti position these values are slightly larger, 270 and 279 pm (Table 1). In both

TABLE 2: Characteristics of the Bridging OH Groups in Different Zeolite Clusters

cluster	$R(\text{OH})^a$	$\nu(\text{OH})^b$	DE^c	ΔDE^d
H-Al-1	98.3		1203	31
H-Al-2p ^e	98.4, 98.4	3651, 3648	1172	0
H-Al-2m ^f	98.3		1251	79
H-Al-2m ^g	98.4		1196	24
H-Al-3 ^h	98.2, 98.2, 98.3		1244	72
Li-Al-2p	98.3	3659	1133	-39
Na-Al-2p	98.5	3651	1116	-56
K-Al-2p	98.6	3635	1130	-42
Na-Al-2m	98.5	3648	1122	-50
Na-Al-3 ^e	98.5, 98.6		1173, 1177	-11, -7
Mg-Al-3	98.5	3645	1146	-26
Ca-Al-3	98.8	3600	1090	-82

^a O-H distance R (pm). ^b Vibrational frequency ν (cm^{-1}). ^c Deprotonation energy DE (kJ/mol). ^d Change of DE (kJ/mol) with respect to deprotonation energy of H-Al-2p cluster. ^e The model cluster contains two bridging OH groups in equivalent positions. ^f Values of the bridging OH group at the center O12 between the two Al centers in next-nearest T-atom position. ^g Values for the bridging OH group at the O11 center with farther Al centers. ^h The model cluster contains three bridging OH groups in equivalent positions.

structures of the cluster K-Al-2p, the cation is closer to the side of the six-ring opposite to the bridging OH group.

The Lewis acidity of the sodium cation in the two positions at the rings with two or three Al centers is different judged both by the Mulliken charge and the frequency shift of an adsorbed probe molecule carbon monoxide.³¹ The cation is more acidic in the syn position, $q(\text{Na}) = 0.61$ e, and $\Delta\nu(\text{CO}) = 38$ cm^{-1} , while for the anti position the charge is by 0.07–0.10 e smaller and so is the CO frequency shift (by 6–10 cm^{-1}). At variance with these results, the Lewis acidity of the potassium cation at both positions is essentially the same: the charge varies by 0.02 e and the CO frequency shift by 2 cm^{-1} . Since Rb^+ and Cs^+ cations are farther than K^+ from the zeolite ring due to their larger ionic radii,³² one should expect even smaller differences between the properties of these cations in the two possible positions. This comparison suggests that the existence of two cationic positions with respect to an individual six-ring with distinguishable properties is a peculiarity of Na^+ among the alkali metal cations (as mentioned above, only one position was observed for Li^+).

3.2. Influence of the Cation on the Bridging OH Group.

When one of the charge compensating protons in the cluster with two or three Al atoms is exchanged by a metal cation, the O-H bond length of the remaining bridging OH group changes only very slightly, by at most 0.4 pm for alkali metal cations and 0.6 pm for Ca^{2+} . The charge of the acidic proton, as determined by a Mulliken analysis, remains essentially the same at 0.30 ± 0.01 e. Gonzales et al.¹⁰ also found small changes of the O-H bond length and a change of 0.02 e of the Mulliken charge of the proton using a chainlike model to account for the effect of the charge compensating cation. With an embedded cluster approach,⁵ the O-H bond lengths at the four different crystallographic positions of the faujasite structure were calculated to differ by 1.5 pm, while the calculated bond lengths of the most stable OH groups of different zeolite structures were found to vary by 0.3 pm only.

The vibrational frequency of the bridging OH group was also calculated for some of the clusters (Table 2). The frequency decreases with the increase of the square of OH bond length in the model clusters (see Figure 3). In the order K-Al-2p, Na-Al-2p, Li-Al-2p, the calculated frequency slightly increases (by 24 cm^{-1}) together with the decrease of the O-H distance by 0.3 pm. Note that K^+ exerts a stronger influence on the

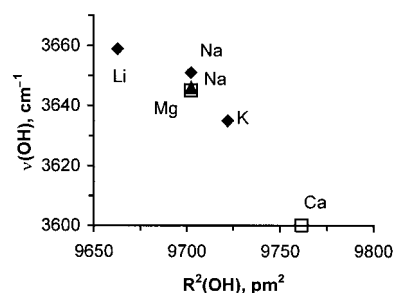


Figure 3. Correlation between the square of the bond length $R(\text{OH})$ and vibrational frequency of the bridging OH group of clusters Al-2p (rhombus), Na-Al-2m (triangle), and Al-3 (open squares).

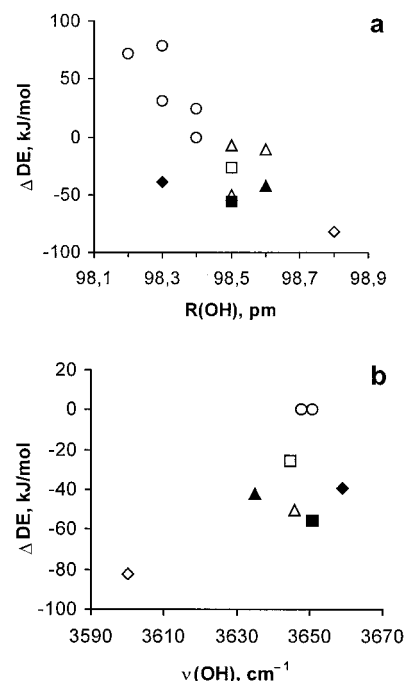


Figure 4. ΔDE values of the OH groups of various model clusters versus O-H bond length $R(\text{OH})$ (a) and vibrational OH frequency (b); clusters compensated only by protons (open circles), Li-Al-2p (solid rhombus), Na-Al-2p (solid squares), K-Al-2p (solid triangles), Na-Al-2m and Na-Al-3 (empty triangles), Mg-Al-3 (open squares), and Ca-Al-3 (open rhombus).

oxygen center of the bridging OH group [as estimated by the field of the cation $q(\text{M})/R^2(\text{M}-\text{O})$], mainly due to a higher effective charge q of potassium cation, 0.62 e, compared to 0.53 e for Na^+ and 0.49 e for Li^+ . Note that the distances K-O(H) and Li-O(H) are quite similar (see Table 1).

3.3. Deprotonation Energies. The calculated DE values of the clusters are collected in Table 2. The lower the DE value of an OH group, the higher is its Brønsted acidity. The DE value of the cluster H-Al-2p (Figure 2b) may be taken as reference, because it is the lowest among the proton compensated clusters. Not unexpectedly, the DE values of an OH group at the oxygen center between two aluminum centers in the meta position (in next-nearest-neighbor framework position), as found in the clusters H-Al-2m (deprotonated at O12 center) and H-Al-3 are about 65–80 kJ/mol higher than the DE of OH groups where the Al centers are farther from each other, as in the clusters H-Al-2p and H-Al-2m deprotonated at the O11 center (Table 2). This trend in the DE values of the clusters compensated only by protons is in agreement with the conclusions of recent calculations based on the QM-Pot. method.⁸

The DE value of the cluster H-Al-2p (Figure 2b) is lower by 31 kJ/mol than that of the cluster with one aluminum center,

TABLE 3: Location of the Metal Cations at Deprotonated Clusters Al-2p and Al-3

distances	Li-Al-2p	Na-Al-2p	K-Al-2p	Na-Al-3	Mg-Al-3	Ca-Al-3
M-O7 ^a	206	229	273	237	220	240
M-O8	206	231	278	241	221	241
M-O9	224 ^b	239 ^b	291 ^b	226	220	241
M-O10	282	259	281	249	257	246
M-O11	286	264	284	255	256	246
M-O12	310 ^b	305 ^b	311 ^b	314 ^c	261	247
⟨M-O⟩ ^d	252	255	286	254	239	244
⟨M-O⟩ ^e	245	246	279	254	239	244
z(M) ^f	13	34	140	13	6	8

^a M-O distances (pm) of different oxygen centers of the six-rings. For the numbering of the centers see Figure 1. ^b Oxygen center of the Si-O-Si bridge. ^c Oxygen center of the bridging OH group. ^d Averaged M-O distance of all oxygen centers of the six-ring. ^e Averaged M-O distance of the oxygen centers of the Al-O-Si bridges. ^f Distance of the metal cation to the plane of the T-atoms z (pm).

H-Al-1 (Figure 2a). This is due to a stabilization of the anionic form of the six-ring H-Al-2p, in which the remaining second proton (at the oxygen center O11) moves toward the center of the ring; the angle between the proton, the center O11, and the center of the six-ring decreases from 106° in the initial cluster H-Al-2p to 88° in the mono-deprotonated cluster. In this way, it partly compensates for the loss of the proton at oxygen center O10.

Exchange of one or two of the charge compensating protons at the zeolite six-rings containing two or three Al atoms by an alkali or alkaline earth metal cation leads to a decrease of the deprotonation energy of the remaining OH group (Table 2 and Figure 4). Thus, *mixed clusters containing both protons and metal cations for charge compensation are more acidic than the pure protonic forms*. The lowest DE value was calculated for the bridging OH group of the cluster Ca-Al-3. It is lower by 154 kJ/mol than the DE value of the corresponding protonic cluster H-Al-3; also, the difference ΔDE with respect to the reference cluster H-Al-2p is -82 in kJ/mol. This suggests that zeolites containing Ca²⁺ and H⁺ close to each other, e.g. HCa-X, are the most acidic among the systems studied. In order of decreasing acidity, they are followed by the zeolites HNa-Y and HNa-X, represented by the model clusters Na-Al-2p and Na-Al-2m with ΔDE from -50 to -56 kJ/mol. The calculated enhancement of the Brønsted acidity of the OH groups in the cluster Ca-Al-3, as judged by ΔDE = -154 kJ/mol with respect to the corresponding protonic form, is by 40 kJ/mol larger than the DE reduction caused by the species CaOH⁺ or ZnOH⁺, reported in previous computational studies.^{10,11}

The deprotonation energy depends both on the effect of the charge-compensating cation on the initial state of the OH group and on the stabilization of the final anionic form of the cluster. Figure 4 shows how the ΔDE values of the model clusters vary with the bond lengths *R*(OH) of the hydroxyl groups and the corresponding calculated vibrational frequencies *ν*(OH); both quantities are representative for the initial state of the OH group in the cluster. Apparently, the general trend is rather poor: longer OH bonds and lower OH frequencies correspond to lower DE values. The DE values of bridging OH groups of alkali metal compensated clusters Al-2p clearly deviate from this trend (see solid symbols in Figure 4). In this series, these values go through a minimum in the order Li, Na, K; ΔDE of Na-Al-2p is -56 kJ/mol, while for the other two alkali metal cations ΔDE is about -40 kJ/mol. Since the initial-state characteristics *R*(OH) and *ν*(OH) of the bridging OH group change synchronously with the ionic radii of the cation (Figure 3), the broken trend in ΔDE can be rationalized with the influence of the stabilization of the deprotonated form of these clusters. A weaker stabilization of potassium compared to the deprotonated sodium cluster is expected because the potassium cation is farther from the six-ring (by about 110 pm, Table 3), and, concomitantly, it interacts

TABLE 4: Effect of Different Charge-Compensating Metal Cations on the Core Level Shifts of the Oxygen Centers in the Deprotonated Clusters Al-2p and Al-3

ΔE(O1s) ^a	Li-Al-2p	Na-Al-2p	K-Al-2p	Mg-Al-3	Ca-Al-3
O7	-3.3	-3.6	-3.8	-2.8	-3.1
O8	-3.3	-3.6	-3.8	-2.8	-3.1
O9	-2.6 ^b	-2.8 ^b	-3.1 ^b	-2.8	-3.1
O10	-3.8	-3.6	-3.8	-3.3	-3.1
O11	-3.8	-3.6	-3.9	-3.3	-3.1
O12	-3.1 ^b	-3.1 ^b	-3.1 ^b	-3.3	-3.1

^a Core level binding energy shifts ΔE(O1s) with respect to the orbital energy of oxygen centers of a six-ring, which contains only silicon T-atoms. A negative value of ΔE_b(O1s) implies that the corresponding O1s orbital is less stable than that of the reference center. ^b Oxygen center of the Si-O-Si bridge. ^c Oxygen center of the bridging OH group.

weaker with the zeolite oxygen centers. On the other hand, the smaller reduction of the DE value in the cluster Li-Al-2p (compared to Na-Al-2p) can be rationalized by the smaller ionic radius of Li⁺ as follows. After deprotonation, a sodium cation moves by about 25 pm closer to the plane of the zeolite ring and also in direction to the oxygen center of the former bridging OH group (Table 3). In this way it interacts simultaneously with all oxygen centers of the six-ring, the ΔE_b(O1s) values of the oxygen centers of all four Al-O-Si bridges are the same (Table 4). This interaction stabilizes the anionic form of the cluster. On the other hand, a Li⁺ cation is too small to simultaneously interact in an effective way with all oxygen centers of the six-ring; thus, the stabilization of the deprotonated form is weaker in this case. Indeed, the O1s levels of the centers O7 and O8 closer to the cation are by 0.5 eV more stable than the levels of the other two oxygen centers of Al-O-Si bridges, O10 and O11 (Table 4).

The change in DE is maximized for the cluster Ca-Al-3 because the O-H bond of the initial cluster is significantly weakened (see Δ*R*(OH) = 0.6 pm) and the deprotonated form of the cluster is strongly stabilized. The later effect is connected with the symmetric location of the calcium cation in the anionic form: all Ca-O_{in} and Ca-O_{out} distances are very similar, 241 and 247 pm, respectively. (Note that in the Al-3 six-ring all oxygen centers are associated with Al-O-Si bridges.) This results in a simultaneous stabilization of all oxygen centers of the six-ring as judged by the same ΔE_b(O1s) values (Table 4). A magnesium cation is also located symmetrically, near the center of the six-ring; however, due to the smaller ionic radius of Mg²⁺ the difference between the distances Mg-O_{in} and Mg-O_{out} is larger: Mg-O_{in} values are about 220 pm, and Mg-O_{out} values about 260 pm (Table 3).

The lack of a high-quality correlation in Figure 4 between DE on one hand and the bond lengths *R*(OH) of the hydroxyl groups and the corresponding vibrational frequencies *ν*(OH) on

TABLE 5: Calculated Core Level Shifts and Mulliken Charges of the Oxygen Centers^a in Different Model Clusters

centers	Li-Al-2 p	Na-Al-2 p	K-Al-2 p	Na-Al-3	Mg-Al-3	Ca-Al-3	H-Al-1	H-Al-2p	H-Al-2m	H-Al-3
$\Delta E_b(\text{O}1s)^b$										
O7	0.3	0.0	0.3	0.2	0.2	-0.2	-1.1	-1.3	-0.2	-0.2
O8	-0.5	-0.9	-1.2	1.1	1.4	1.3	0.2	-1.3	-1.4	-0.2
O9	1.5	1.4	1.0	-0.5	0.8	0.7	-0.6	1.8	0.6	-0.2
O10	-0.6	-0.5	-0.8	3.3	3.3	3.9	-0.1	3.4	-0.4	2.5
O11	3.7	3.8	3.6	-1.1	0.1	-0.1	3.0	3.4	3.2	2.5
O12	-0.2	-0.2	-0.3	3.3	0.0	-0.1	1.0	-1.2	2.5	2.5
Charges										
O7	-0.77	-0.72	-0.69	-0.69	-0.75	-0.85	-0.65	-0.66	-0.65	-0.65
O8	-0.78	-0.71	-0.69	-0.71	-0.78	-0.84	-0.60	-0.66	-0.66	-0.65
O9	-0.69	-0.65	-0.61	-0.70	-0.78	-0.84	-0.61	-0.58	-0.60	-0.65
O10	-0.64	-0.67	-0.69	-0.54	-0.55	-0.59	-0.60	-0.52	-0.59	-0.52
O11	-0.54	-0.54	-0.55	-0.69	-0.72	-0.83	-0.52	-0.52	-0.53	-0.53
O12	-0.60	-0.62	-0.64	-0.55	-0.73	-0.83	-0.58	-0.61	-0.53	-0.53

^a Oxygen center of bridging OH groups are underlined. ^b Core level binding energy shifts $\Delta E(\text{O}1s)$ (eV) with respect to the orbital energy of oxygen centers of a six-ring that contains only silicon T-atoms.

the other suggests that these initial-state characteristics are not representative for the acidity of these hydroxyl groups in zeolites as evaluated by their DE. Similar indications have already been reported in other theoretical studies of zeolite acidity. Sierka et al.⁸ observed different trends of DE values on one hand and of calculated OH vibrational frequencies and ¹H NMR chemical shifts, on the other hand, when studying various bridging OH groups of protonic forms of zeolites. Moreover, Gonzales et al.¹⁰ found that also the interactions with weakly basic probe molecules cannot be used as measure of DE; both the binding energy of CO to a bridging OH group and the optimized distance between the zeolite proton and the carbon atom of CO do not correlate with the calculated DE.

3.4. Core Level Shifts of the Oxygen Centers. The optimized structures and calculated electronic characteristics of zeolite model clusters reported here present an excellent opportunity to discuss also the influence of different metal cations on the core level shifts and the charge of framework oxygen centers (Table 5). The core level binding energies are very important because they are connected with the basicity of the framework oxygen centers¹⁸ that determines various sorption and catalytic properties of zeolites.^{33,34} The O1s binding energies, calculated with respect to oxygen centers of the six-ring with six silicon T-atoms, vary strongly with the position of the oxygen centers in the ring both in the cluster compensated by protons only or by metal cations. As a rule, oxygen centers of Al-O-Si bridges have a lower $\Delta E_b(\text{O}1s)$ value; i.e., their 1s core levels are less stabilized compared to the centers of Si-O-Si bridges. Peculiar cases are provided by the oxygen centers of the bridging OH groups: their core levels are substantially stabilized, by 2.5–3.8 eV, with respect to the reference value. Their negative charges are reduced by more than 0.1 e compared to other O center of Al-O-Si bridges (Table 5). As can be seen in Table 5, the stabilization of the 1s core level is lower for oxygen centers between two Al atoms in next-nearest framework position (in H-Al-3 and O12 in H-Al-2m), about 2.5 eV, compared to 3.0–3.4 eV for oxygen centers of other OH groups (in H-Al-1, H-Al-2p, and O11 of H-Al-2m). The same trend holds also for the OH groups in the model clusters exchanged with metal cations.

In zeolite clusters with charge compensation by protons, H-Al-1, H-Al-2p, H-Al-2m, and H-Al-3, a reasonably good correlation can be observed between the Mulliken charges of oxygen centers and their $\Delta E_b(\text{O}1s)$ values (Figure 5a). However, the situation changes for clusters where charge compensation is accomplished by metal cations (Figure 5b). Apparently, protons and alkali metal cations affect core level shifts of oxygen

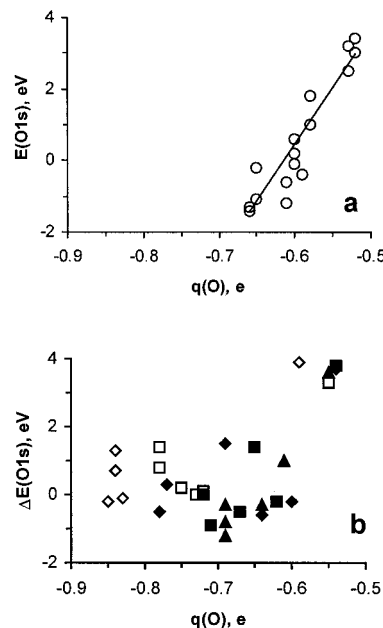


Figure 5. Core level shifts ΔE_b of oxygen centers in six-rings as function of the corresponding Mulliken charges $q(\text{O})$ for the clusters compensated by (a) H^+ and (b) metal cations: Li-Al-2p (solid rhombus), Na-Al-2p (solid squares), K-Al-2p (solid triangles), Mg-Al-3 (open squares), and Ca-Al-3 (open rhombus).

centers of zeolites in a different fashion. Protons influence the electron distribution around oxygen centers mainly via covalent bonds (and to a lesser degree via the potential effect). Metal cations, on the other hand, interact with oxygen centers mainly through the electrostatic field which implies an increase both of the negative charge on an oxygen center and a positive value of $\Delta E_b(\text{O}1s)$. The electrostatic potential of the cation affects the core level shift both directly and indirectly via inducing more electron density on the oxygen center to screen the potential due to the cation. Both effects counteract each other. The direct potential effect stabilizes the core level and thus increases the core level shift. Simultaneously, the increased negative charge is expected to decrease the core level binding energy.

Changes of both $\Delta E_b(\text{O}1s)$ and $q(\text{O})$ are stronger for those cations which generate a stronger electrostatic field (Mg^{2+} , Li^+). The negative charge of the oxygen center O8 in the cluster Al-2p, which is closer to the alkali metal cation, increases from -0.66 e in the H-Al-2p cluster to -0.78 e in Li-Al-2p (Table 5), while the corresponding O1s core level is stabilized by 0.8 eV in the lithium cluster, compared to H-Al-2p. The same trend

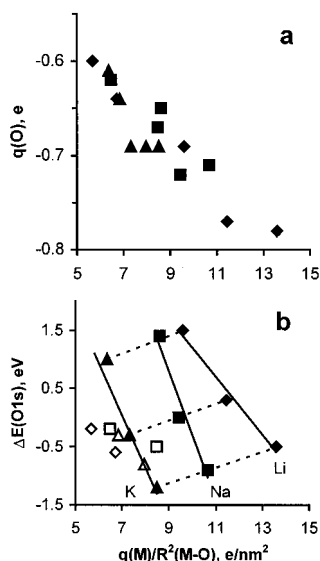


Figure 6. Oxygen charge $q(O)$ (a) and core level shift ΔE_b (b) of oxygen centers of alkali metal cation containing clusters Al-2p as function of the electrostatic field due to the cation, approximated by $q(M)/R^2(M-O)$. Li-Al-2p (rhombus), Na-Al-2p (squares), K-Al-2p (triangles). In b the O_{in} and O_{out} centers are shown as filled and open symbols, respectively. O_{in} oxygen centers for each alkali metal cation are connected with a solid line. Dashed lines connect the points corresponding to O9, O7, and O8 centers (from top to bottom) in the three model clusters.

is observed for the center O7 in the six-ring Al-2p; this center is also close to the metal cation. A similar influence of the cation on both the oxygen charge and the $\Delta E_b(O1s)$ value is found for the cluster Mg-Al-3. The core levels of the oxygen centers which do not participate in the bridging OH groups in the Mg^{2+} exchanged cluster are by 0.4–1.6 eV more stable than those of the corresponding centers in the cluster H-Al-3. At the same time, these centers of the Mg^{2+} compensated cluster carry a more negative charge, -0.75 e to -0.78 e, compared to -0.65 e in the cluster H-Al-3.

As an example for the increase of the negative charge of the oxygen centers with the increase of the electrostatic field of the cation (estimated as the field of a point charge at the corresponding M–O distance), we present the corresponding correlation for the alkali metal exchanged clusters M-Al-2p in Figure 6a. The electrostatic field of the cations influences the $\Delta E(O1s)$ values of the oxygen centers O_{in} and O_{out} differently (filled and open symbols, respectively), as shown in Figure 6b for the ring Al-2p. The two groups of oxygen centers are separated the most for Li^+ (rhombus), where the data for the centers O_{in} fall on the right-most line, while the two O_{out} centers O10 and O12, not participating in the OH group, are located on the left-hand side of the plot (open symbols). This reflects the fact that the lithium cation interacts exclusively with the centers O_{in} (O7, O8, and O9). For the cluster Na-Al-2p (squares), the data points corresponding to the two groups of oxygen centers lie closer to each other, while for K-Al-2p (triangles) the cation is far from the six-ring and the data points for the oxygen centers O_{in} and O_{out} fall essentially on one line (Figure 6b). If one compares the data points which correspond to a single type of oxygen center O_{in} (connected by broken lines; Figure 6b), one notes that the $\Delta E_b(O1s)$ values decrease with decreasing strength of the field of the cation at the location of the oxygen center, from Li^+ to Na^+ to K^+ . In the cluster Li-Al-2p, the O1s core levels of the centers O7, O8, and O9 are by 0.5–0.7 eV more stable than those of the corresponding cluster K-Al-2p, despite the fact that their charges are about

0.1 e more negative than in the cluster K-Al-2p. The changes in the core level shifts are a consequence of the stronger field of Li^+ acting on these oxygen centers.

The $\Delta E_b(O1s)$ values of the oxygen centers in the clusters M-Al-3 with charge compensation by an alkaline earth metal cation are close to zero or positive (calculated with respect to oxygen centers of Si-6 ring). The highest-lying O1s core levels in the clusters Mg-Al-3 and Ca-Al-3 exhibit shifts of 0.0 and -0.2 eV, respectively, similar to oxygen centers of the cluster H-Al-3. These levels are by about 1 eV more stable than the core levels of the cluster Na-Al-3 (Table 5). This trend agrees with the experimental finding that the experimental O1s binding energy of Ca-X zeolite, measured by XPS, is by 0.6 eV larger than the core level binding energy of Na-X zeolite.³⁵

4. Conclusions

The calculations reported here show that charge compensating cations in mixed forms of zeolites affect the Brønsted acidity of the bridging OH groups as measured by their deprotonation energy. Charge compensation by alkali or alkaline earth metal cations in the six-rings instead of protons leads to a decrease of the deprotonation energy of the bridging OH group compared to the purely protonic forms of the clusters. Thus, zeolites with mixed charge compensation by both protons and metal cations exhibit sites that are more acidic than the purely protonic forms. The most acidic sites were found for the model clusters Ca-Al-3 and Na-Al-2p with changes ΔDE of the deprotonation energies of -82 and -56 kJ/mol, respectively.

The ΔDE values of the model clusters correlate only poorly with the characteristics of the initial state of the OH group in the clusters. Thus, the DE values of the bridging OH groups considered are to a significant amount determined by final state effects, i.e., by the stabilization of the deprotonated form of the cluster due to the charge compensating cation. The present results and those of other studies^{8,10} suggest that deprotonation energies of acid sites in zeolites cannot be estimated in a reliable fashion from measured properties of the corresponding initial bridging OH groups.

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