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Density Functional Studies of Alkali-Exchanged Zeolites: Basicity and Core-Level Shifts of Framework Oxygen Atoms

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The basicity of framework oxygen atoms in sodium-exchanged zeolites, in particular its dependence on the number and relative position of the aluminum atoms in four- and six-rings of faujasite, has been studied by a gradient-corrected density functional method using cluster models. The most basic oxygen atoms (determined by calculated proton affinities, PA) were found in a six-ring with two aluminum atoms in *meta* position (903 kJ/mol) and in a four-ring (897 kJ/mol). Exchange of Na^+ by K^+ increases the PA by about 25 kJ/mol. The PA is influenced primarily by the site potential as manifest by the orbital energies of the oxygen center probed. Similarly to the experimental relationship between the corresponding values for a series of oxygen containing molecules in the gas phase, the calculated PAs and O1*s* binding energy shifts correlate in a strictly linear fashion. For an increase of the O1*s* binding energy by 1 eV the PA increases by about 80 kJ/mol. From these findings, we suggest the O1*s* binding energy shift as a reliable measure of the basicity of oxygen centers, while we found calculated atomic charges to be of little value as basicity criterion. The oxygen position in the ring has a dominant influence on the O1*s* binding energy (resulting in shifts of up to 3 eV), while changes due to alterations of the Na^+ position or the exchange of Na^+ by K^+ causes shifts of up to 0.4 eV only. The differences in the atomic charges of the oxygen atoms between the various cation positions are rationalized by the change of the external electrostatic potential generated by the cations.

Key Words: **alkali zeolites; DF study; binding energy shift; proton affinity; basicity; atomic charge; faujasite.**

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1. INTRODUCTION

Alkali forms of zeolites are applied where basic properties are necessary or strong acidic sites would interfere (1). They are used as basic catalysts in a variety of organic reactions which are initiated by abstraction of a proton from an activated C–H bond, e.g., in side-chain alkylation of toluene (2–5), condensation reactions (6), and selective alkylation of aromatic compounds which contain oxygen or nitrogen (7, 8). It has been proposed (3–6) that the proton is abstracted by a basic framework oxygen center, while the alkali cation as a Lewis acid stabilizes the carbanion formed. Since such proton abstraction is difficult to achieve, strong basicity of the zeolite is crucial for the catalytic reaction. Over protonic zeolites these reactions either yield other products or do not occur at all. Alkali-exchanged zeolites are also used in separation processes (9, 10) where the combined effects of diffusion limitation and selective adsorption of components at suitable positions in zeolite cages are utilized (11–14). Precise knowledge of strength and relative positions of Lewis acidic centers (metal cations) and of basic framework oxygen centers is mandatory for a successful description of the catalytic and sorption capabilities of alkali-exchanged zeolites. In a parallel computational investigation (15) we focused on the location and Lewis acidity of sodium cations (as measured by the adsorption of a CO probe molecule) at six-rings of a faujasite framework. Here, we study the basicity of oxygen atoms in zeolite rings.

X-ray photoelectron spectroscopy (XPS) of O1*s* core levels (16) is employed for studying the basicity of zeolite materials due to the correlation between measured oxygen core-level binding energies (E_b) and the basicity of different molecular compounds: the lower the E_b(O1*s*), the more basic is an oxygen center. In general, the E_b(O1*s*) values of zeolite samples vary as expected according to their known basicity[3] (17, 18)—the basicity increases with the aluminum content and with the ionic radius of the charge-compensating cations from Li^+ to Cs^+. However, the factors determining the XPS binding energy shifts are still under discussion (18–21). Barr (20) rationalized the dependence of E_b on the aluminum content of the zeolite samples with the higher ionicity of the bonding in zeolite lattice when the Al/Si ratio increases. Other groups (17, 18) considered the increase of the total framework charge or the alteration of the local charge on the zeolite framework centers

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[3] In some experiments the expected dependence of E_b(O1*s*) on the type of the alkali cation was not observed. Na, K, and Cs forms had the same values, or sodium zeolite featured a slightly lower O1*s* binding energy; see Refs. (17) and (19).

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responsible for the observed trends in E_b shifts of O1*s* and Si2*p*. Grünert *et al.* (19) showed that the calculated Madelung potential (averaged over all sites, corresponding to the emitting atom) correlates with experimental shifts and concluded that it prevails over the charge effect.

Following chemical intuition, calculated atomic charges, often based on empirical or semi-empirical approaches, are also used for estimating the basicity strength of oxygen centers in zeolites (1, 18, 22, 23). Different procedures yield rather different charge values, but trends correlate with the O1*s* core level shifts and the expected basicity of the framework oxygen centers. A recent density functional (DF) study of cluster models M^+-Al$(OH)_3H^-$ (24) showed that oxygen charges obtained from either a Mulliken population analysis or a natural orbital analysis remain essentially unchanged in the series $M^+ = Li^+$ to Cs^+, while the O1*s* core levels shifts by 1.1 eV.

In the present work we employed a gradient-corrected DF method to investigate the basicity of sodium-exchanged faujasite zeolites. The zeolite fragment is presented as four- and six-rings which contain different numbers of aluminum atoms arranged according to the Loewenstein rule (25). The aim of the work is to evaluate the basicity of framework oxygen atoms and, especially, how it depends on the number and the relative position of the aluminum atoms in the ring. As an unambiguous measure of basicity, the proton affinities (PA) of individual oxygen atoms of the cluster models have been calculated. We will also provide insight into the relationship between different measures of basicity and the influence of the alkali metal cations on the local basic properties of a neighboring zeolite ring. We shall discuss the factors which influence the atomic (Mulliken) charges and the 1*s* core-level energies of oxygen centers. For comparison with experimental trends in the series of alkali cations, we shall also report results for a model cluster where the sodium ion has been exchanged by a potassium ion.

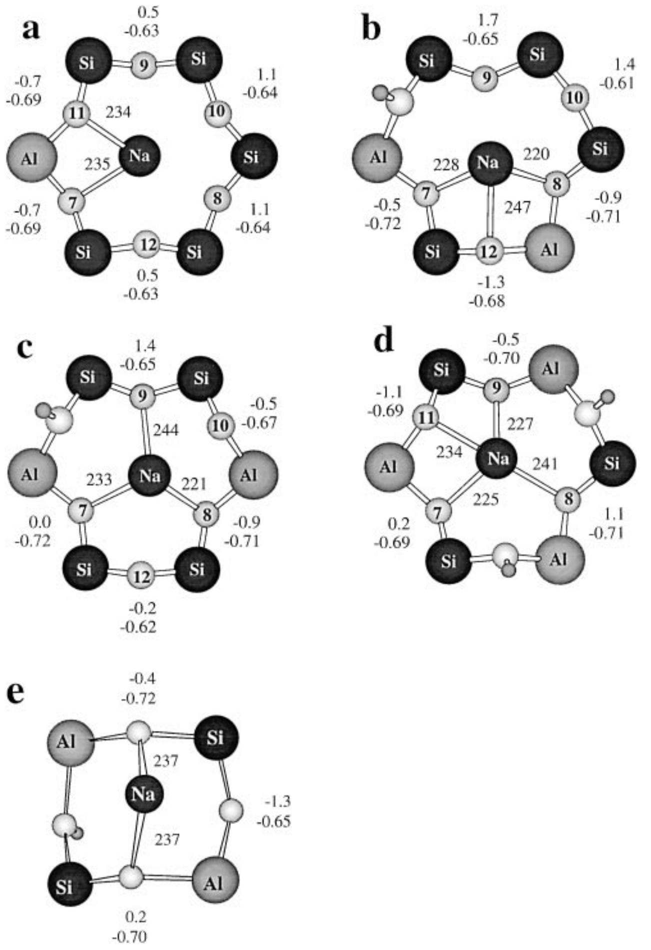

FIG. 1. Location of the sodium cation at the zeolite six-rings (in *anti* position): (a) Al-1, (b) Al-2*m*, (c) Al-2*p*, (d) Al-3, and at the four-ring with two Al atoms (e). Only Na–O distances (in pm) shorter than 250 pm are indicated. The oxygen atoms in the six-rings are numbered; for oxygen centers without a charge-compensating proton nearby the binding energy shifts ΔE_b(O1*s*) (in eV, top) and Mulliken charges are given (in *e*, bottom).

2. METHODS

2.1. Zeolite Clusters

In the present work we studied a six-ring of a faujasite structure containing one (Al-1), two (Al-2), or three (Al-3) aluminum atoms (Figs. 1a–1d). Both relative positions of the two aluminum centers in a ring Al-2 allowed by the Loewenstein rule were considered, *para* (Al-2*p*) and *meta* (Al-2*m*) configurations (Figs. 1c, 1b). In NaX and NaY zeolites this structure corresponds to sodium cations in SII crystallographic positions, where Na^+ is located inside the supercage at a six-ring window of the sodalite cage (12, 13, 26). The SIII cationic site (occupied only in X zeolites) is modeled by calculations on Na^+ at a four-ring with two aluminum centers (Fig. 1e). For comparison, a six-ring containing only silicon T-atoms (Si-6) was also considered (not shown in Fig. 1). Free valences of the silicon and aluminum atoms in the rings were saturated by hydrogen atoms. The initial positions of the T-atoms and the oxygen centers in both four- and six-rings were taken from mean crystallographic values (12, 26); 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 due to two additional bonds outside the ring while the oxygen atoms are much more mobile. The excess negative charge of clusters with two or three Al atoms was compensated by protons connected to oxygen atoms of Al–O–Si bridges which are directed outward from the ring in order to minimize the direct effect of the compensating cation on the central Na^+ ion. To estimate the effect of this additional charge-compensating proton on the oxygen basicity, the cluster Al-2*p* (Fig. 1c) was also optimized with a second Na^+ as additional charge-compensating cation.

After construction and initial geometry optimization of the rings, in all aluminum-containing rings a Na^+ ion was added near the center of the ring and the position of the oxygen centers of the ring, the sodium ion, and the charge-compensating cations (where present) were optimized. Details about the choice of the model rings and the charge compensation procedure are presented elsewhere (15).

2.2. Calculation Details

The calculations were carried out with the new density functional (DF) program ParaGauss (27) using the gradient-corrected exchange-correlation functional suggested by Becke (exchange) and Perdew (correlation) (28, 29). Gaussian-type basis sets (24), contracted in generalized form, were employed to describe the Kohn–Sham orbitals: $(6s1p) \rightarrow [3s1p]$ for H, $(9s5p1d) \rightarrow [5s4p1d]$ for O and C, $(12s9p1d) \rightarrow [6s4p1d]$ for Al and Si, $(12s8p1d) \rightarrow [6s5p1d]$ for Na, and $(15s11p1d) \rightarrow [6s5p1d]$ for K. The basis sets of all nonhydrogen atoms contain one *d*-type polarization exponent (24). The structures of the clusters described in the previous section were optimized automatically using analytical energy gradients (30). The charges reported in the following were obtained by Mulliken population analysis.

2.3. Determination of Core-Level Binding Energy Shifts

In Hartree–Fock (HF) theory, the 1*s* core-level binding energies E_b of an oxygen atom can be determined by invoking Koopmans' theorem for the O1*s* orbital (31):

$$E_b(\mathrm{O}1s) = -\varepsilon^{\mathrm{HF}}(\mathrm{O}1s).$$

On the other hand, in the Kohn–Sham (KS) approach to DF theory Koopmans' theorem is not valid. Rather, KS orbital energies of Slater's transition state may be used where the occupation of the level to be ionized is decreased by half a unit, resulting in a "relaxation" shift that is, at least in part, related to self-energy corrections (32). However, if one is interested only in core-level binding energy *shifts*, as in the present study, it is an acceptable approximation, to approximate these quantities as differences of ground state orbital energies (33):

$$\Delta E_b(\mathrm{O}1s) = -\left[\varepsilon^{\mathrm{KS}}(\mathrm{O}1s) - \varepsilon^{\mathrm{KS}}_{\mathrm{ref}}(\mathrm{O}1s)\right].$$

As reference in the present context we employ the oxygen atoms of a six-ring, $\varepsilon_{\mathrm{ref}}$ (O1*s*), which contains only silicon T-atoms.[4] A negative value of $\Delta E_b(\mathrm{O}1s)$ implies that the corresponding O1*s* orbital is less stable than that of the reference atom.

Such use of the O1*s* energy eigenvalues accounts only for the initial state effects on E_b. Since final state effects due to the relaxation of the remaining electrons after core hole creation are not evaluated (31), they are implicitly assumed to be constant if the above formula is applied. Alternatively, one may calculate ionization potentials as total energy differences of the ground and the ionized states (so-called ΔSCF procedure), just as with conventional quantum chemical methods. To check the validity of estimating core-level binding energy shifts by differences of KS orbital energies for the systems under study, we calculated $\Delta E_b(\mathrm{O}1s)$ by the ΔSCF procedure for six oxygen atoms of different rings. The values obtained by the two procedures differed at most by 0.1 eV; thus the very economical estimate of $\Delta E_b(\mathrm{O}1s)$ as the difference of ground-state KS orbital energies is fully justified in the present context.

The interpretation of binding energy shifts (in terms of initial state effects) is based on the separation of several contributions to the core-level energy (18, 19, 21, 33–35). As a first group of mechanisms we mention participation in chemical bonds, coordination number, Madelung potential due to surrounding charged atomic centers, etc. (19, 21, 34, 35). All these effects are related to changes of the surroundings of an atom which affect orbital energies of a given atom via changes of the external potential acting on the core electrons. Alterations of the external potential influence not only orbital energies but also other parameters which characterize the electronic state, such as the atomic charge, orbital occupations, and hybridization. These quantities change such in a direction to screen the external influence. This intra-atomic redistribution of electron density may be viewed as a secondary effect on the core-level shifts (18, 31, 33, 34).

For covalent molecules, the atomic charges account for the external potential generated by the neighboring atoms and correlate with ΔE_b (31, 36). In ionic substrates, the local electrostatic potential, or more generally, the Madelung potential, affects core-level shifts to a considerable extent (35). The core-level binding energy shifts ΔE_b for zeolites are often discussed in the terms of the charge-potential model (31) where ΔE_b depends linearly on the charge of the atom considered as well as on the Madelung potential (18, 19, 21). According to this model, both an increase of the negative charge on the oxygen atom and a decrease of the positive charge of surrounding atoms cause a reduction of the core-level binding energy and thus a negative value of the shift $\Delta E_b(\mathrm{O}1s)$, i.e., a destabilization of the atomic core levels.

2.4. Determination of Proton Affinies

As a measure of the basicity of a molecular system, the proton affinity is the energy gain when going from a molecule and a free proton on the one hand to the protonated molecule on the other hand. The equilibrium constant for protonation, K_p, or equivalently its pK_b value, depend

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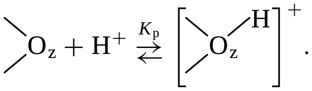
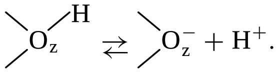
[4] The 1*s* Kohn–Sham orbital energy of oxygen centers in Si-6 is $\varepsilon_{\mathrm{ref}}$ $(\mathrm{O}1s) = -511.0$ eV.

on the PA of the base. For a basic oxygen center in the zeolite rings, the protonation equilibrium can be written as



Leaving aside temperature effects, one can estimate the PA by the total energy difference between the protonated and the initially uncharged cluster. The energy of the various protonated forms of a cluster is found by attaching a proton to the different oxygen atoms of the ring and subsequent geometry optimization under the same constraints as the corresponding initial Na^+ containing clusters. Evaluation of the basicity as total energy difference does not account for the kinetic basicity which depends on the source of the proton and is connected with the activation energy for protonation.

In the evaluation of the Brønsted acidity of protonic forms of zeolites, the deprotonation energy (37) is sometimes also referred to as proton affinity (38–40). The PA as defined there describes the energy change of the reverse reaction which deals with the proton association of negatively charged zeolite anions (right-hand side) which remain after proton abstraction from bridging OH groups:



3. RESULTS AND DISCUSSION

3.1. Optimized Structures

In Figs. 1a–1d we display the optimized locations of sodium cations at six-rings with different numbers of aluminum atoms. As can be seen, the cation preferentially interacts with oxygen atoms which are connected to aluminum centers and directed inwards the six-ring. (For Na^+ at an SII site, these oxygen atoms correspond to the crystallographic O(2) centers.) The shortest Na^+–O distances fall in the range 220–230 pm. In the ring with one aluminum atom, Al-1, the sodium cation is located almost in the plane of the T-atoms because in this ring there are only two Al–O–Si bridges and Na^+ is situated near both of those oxygen centers. For the six-rings with two and three aluminum atoms (Al-2*m*, Al-2*p*, Al-3), Na^+ positions on each side of the ring were established when H^+ as well as Na^+ were used as additional charge-compensating cations. As an example, both positions of the central Na^+ cation at the ring Al-2*m* are shown in Fig. 2. The notation *syn/anti* for these two positions refers to the oxygen atoms directed inward toward the ring which correspond to crystallographic O(2) centers. The central sodium cation is located 110–130 pm from the plane of the ring when Na^+ is in *syn* position (Fig. 2b), i.e., at the side of the crystallographic O(2) oxygen atoms, and 35–80 pm from the plane, when it is at the opposite side of the ring (*anti* position, Fig. 2a).

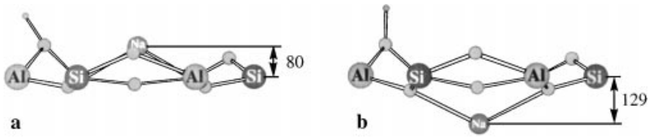


FIG. 2. Positions of the sodium cation with respect to the six-ring Al-2*m*, *anti* (a) and *syn* (b), referred to the oxygen atoms directed inward toward the ring.

After comparison of calculated distances with crystallographic data and calculated vibrational frequencies of CO probe molecules with IR spectra of CO on NaY zeolite, we recently proposed that the crystallographic SII sites of faujasites actually comprise two cation positions (15). The mean Na–O distances for the *anti* position of Na^+ are closer to the crystallographic values; this implies that most of the cations at SII sites of zeolite samples are located at the side opposite to the crystallographic O(2) centers. For this reason, we shall focus in the following on cluster models where Na^+ is in *anti* position (as shown in Figs. 1a–1d). At four-rings (Fig. 1e), the cation is about 230 pm from the plane of the ring and the shortest Na–O distances are 237 pm.

3.2. Core-Level Shift of the Oxygen Atoms

The calculated shifts ΔE_b of the O1*s* binding energy and the oxygen charges q_0 of six-rings with different numbers of aluminum centers are presented in Fig. 1. A first important observation is that the binding energy shifts vary over a range 3 eV. Both extreme shift values occur in the cluster Al-2*m* with two aluminum atoms in *meta* position (Fig. 1b).[5] For the other three six-rings, the shift values differ and span ranges of 1.8–2.3 eV. These variations are similar both to the widths of experimental O1*s* lines and to the spread expected from the Madelung effect (19). The average value of the shift ΔE_b(O1*s*) per ring decreases with the increase of the number of aluminum atoms in the ring, by about 0.5 eV from Al-1 to Al-3, in agreement with the experimental trend which shows a decrease from NaY to NaX by 0.4–0.8 eV (17, 18, 19). To distinguish the influence of the oxygen position in the ring from the contribution of the electrostatic potential of the cation to ΔE_b(O1*s*), we note the linear relationship between the calculated shifts of individual oxygen atoms in cation containing clusters (shown in Fig. 1) and shifts of oxygen centers in the initial rings (without Na^+ or K^+, see Fig. 3a). This finding shows that the cation does not substantially change the relative binding energy shifts of the oxygen atoms in the rings; rather, the cation affords a stabilization only, increasing the shifts by 3.4–4.1 eV for Na^+

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[5] The “bare” and charge compensated models of the cluster Al-2*m* are by about 22 kJ/mol less stable than the corresponding models Al-2*p*, in agreement with Dempsey’s rule; see Ref. (41).

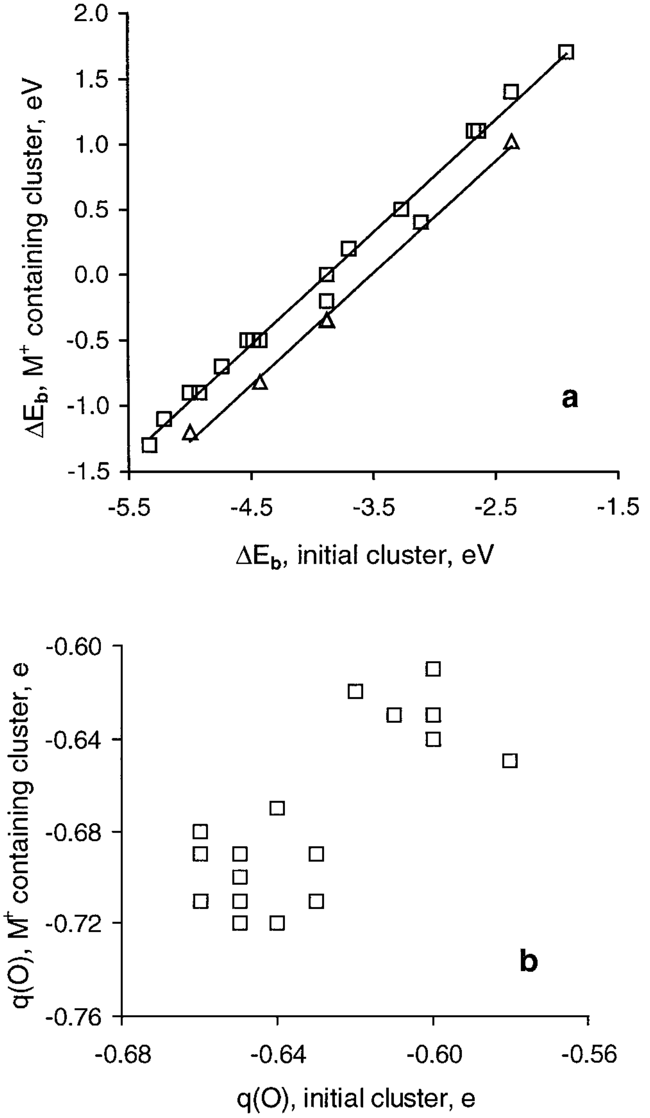

FIG. 3. Binding energy shifts ΔE_b (a) and Mulliken charges q(O) (b) of oxygen atoms of cation-containing clusters vs the corresponding values in the initial six-rings without central cation. The squares in panels (a) and (b) correspond to Na-Al-1, Na-Al-2*m*, Na-Al-2*p*, and Na-Al-3 clusters; the lower line and triangles in (a) correspond to the cluster K-Al-2*p*. The correlation coefficients of both straight lines in (a) are $r = 0.99$.

and by 3.4–3.8 eV for K^+. Thus, the variations of $\Delta E_b(O1s)$ in different clusters are mainly determined by the positions of the oxygen atoms in the ring.

In general, oxygen atoms bonded to Al exhibit a negative 1*s* binding energy shift with respect to the Si-6 ring and a higher negative charge; i.e., they are more basic. While for the initial rings (without a cation inside) a reasonable correlation between atomic charges and shifts $\Delta E_b(O1s)$ of individual oxygen centers is observed (Fig. 4a), such correlation was not found for the cation-containing clusters (Fig. 4b). As can be deduced from Fig. 3b, the irregular alteration of oxygen charges due to the presence of the cation is responsible for the loss of the correlation in the cation-containing clusters. From one point of view, such a lack of correlation is not too surprising as Mulliken charges, in particular for flexible basis sets, often exhibit artifacts. On the other hand, it will be illuminating to analyze the core-level shifts of the oxygen atoms in different clusters in some detail.

The simplest picture of the O1*s* binding energy shifts arises for the cluster Na–Al-1. The atoms O7 and O11 (Fig. 1a) are directly connected to the Al center and exhibit the largest negative shift $\Delta E_b(O1s) = -0.7$ eV; the next-nearest oxygen centers O9 and O12 feature already a positive shift of 0.5 eV, and the value for the remaining two centers O8 and O10 is 1.1 eV. The positive shift values of the latter two centers can be connected to the presence of the sodium cation in the cluster which stabilizes the 1*s* core levels of all oxygen atoms in the ring with respect to those in Si-6 ring. Note that the negative charge of the oxygen atoms in Si–O–Si bridges of the cluster Al-1 ($q = -0.63$ e) is larger than in the Si-6 ring ($q = -0.60$ e).

The binding energy shifts of the individual oxygen atoms of the other six-ring clusters are more difficult to analyze because more than one aluminum is present in the ring. Compensating cations stabilize mainly the core levels of

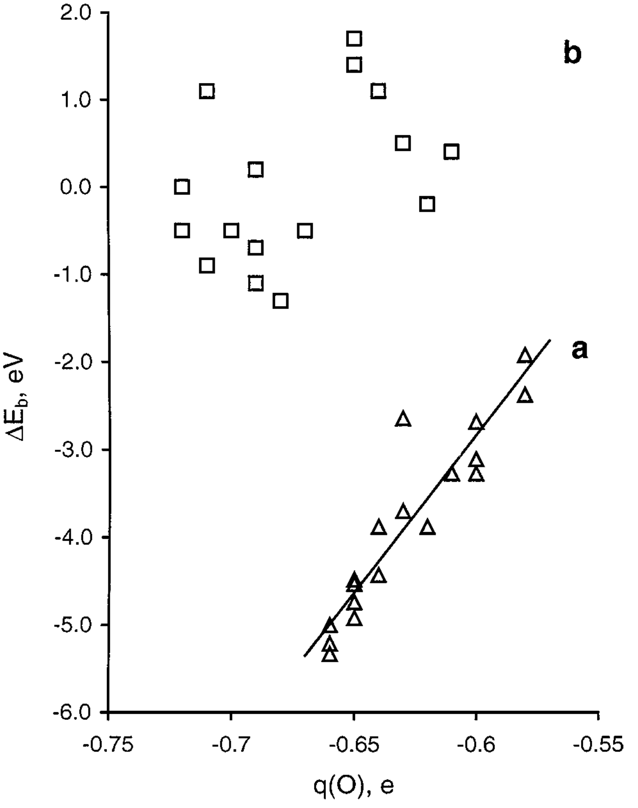

FIG. 4. Core-level shifts ΔE_b of oxygen atoms in six-rings as function of the corresponding Mulliken charges q(O) for the initial (a, triangles) and for the Na^+-containing clusters (b, squares). The correlation coefficient of the straight line (a) is $r = 0.87$.

those oxygen atoms with which they interact directly. The positive binding energy shifts $\Delta E_b(\mathrm{O}1s)$ of such oxygen centers are similar or even larger than those of Si–O–Si bridges (both when H^+ and Na^+ are used for charge compensation). In a real zeolite, such positions can be related to oxygen atoms which participate in two adjacent rings with charge-compensating cations nearby. Thus, these oxygen atoms exhibit stabilized 1*s* core levels; they are unlikely candidates for basic centers due to the correlation between the basicity and the core-level shift (see below). Compensating cations affect also the properties of other oxygen atoms in the ring, near the charge-compensating hydroxyl group; their 1*s* core levels are also stabilized, but the negative charge increases. For example, the oxygen atoms O7 in the clusters Al-2*m* and Al-2*p*, O7 and O9 in Al-3 (Figs. 1b–1d) have by 0.2–0.9 eV smaller negative ΔE_b shifts than the corresponding oxygen centers in Al-1. Center O8 of Al-3 represents a special case since it is located between the two charge-compensating bridges; it has large positive binding energy shift, +1.1 eV.

The experimentally measured increase of $\Delta E_b(\mathrm{O}1s)$ by 0.2–0.4 eV when going from pure NaY to a mixed sample HNaY (19) indicates that in our models Al-2 and Al-3 charge compensation by protons (instead of sodium cations) may overestimate the positive 1*s* core level shifts, but the qualitative effect should be correctly reproduced. Indeed, a calculation on the cluster Al-2*p*′ (see Fig. 1c), where we used a Na^+ for charge compensation instead of H^+, led to $\Delta E_b(\mathrm{O}1s)$ values by about 1 eV smaller on average than those of the cluster Al-2*p* with proton compensation. Foremost, the level shifts of the oxygen atom connected directly to the cation and of its neighbor O9 are reduced, but the increase of the negative ΔE_b shifts of the most basic oxygen atoms O8 and O10 in the ring was less than 0.4 eV.

The second factor influencing the O1*s* core level values is the relative position of the aluminum atoms in the ring. When two of the aluminum atoms are close, in *meta* position (clusters Al-2*m*, Al-3), the oxygen atoms between them exhibit the largest negative shifts ΔE_b, −1.3 eV for O12 in Al-2*m* and −1.1 eV for O11 in Al-3. For comparison, we point out that in the cluster Al-2*p* the largest negative shift is −0.9 eV (O8).

The largest negative oxygen core-level shift of the four-ring with two Al atoms is −1.3 eV, the same as the largest value of the six-rings. The shift occurs at the oxygen center which is located opposite to the compensating cation (Fig. 1e). The oxygen atoms neighboring the charge-compensating hydroxyl group are influenced in the same way as already discussed for the six-rings.

3.3. *Influence of the Sodium Cation*

As discussed above, Na^+ prefers positions near the oxygen atoms which are connected to Al centers. In that part of the ring there is an excess of electron density because the tetravalent framework position is occupied by the trivalent aluminum. Na^+ affects the properties of the oxygen atoms. However, by considering only one structure (cluster), it is difficult to discriminate the effect of the Na–O distance on the binding energy shift from that of the charge of the individual oxygen atoms in the ring. For this reason, we will compare the characteristics of some oxygen atoms of the clusters with two Al centers for both sodium locations established, *syn* and *anti*. As an example, let us discuss center O12 of the cluster Al-2*m*. In *anti* position (Figs. 1b, 2a), the cation is at 247 pm from center O12 which has a charge of −0.68 *e* and a core shift $\Delta E_b(\mathrm{O}1s)$ of −1.3 eV. For Na^+ in *syn* position (Fig. 2b), the distance Na–O12 increases to 323 pm and the negative charge is −0.63 *e*. On the other hand, the core-level shift becomes even more negative, −1.6 eV, a change in the opposite direction as expected on the basis of the change of the charge.

Opposite trends in alterations of oxygen charges and 1*s* core-level binding energy shifts with varying distance to Na^+ occur also when the motion of the cation perpendicular to the ring is modeled (Fig. 5). For the oxygen atoms O10 and O12 of Al-2*p* (Fig. 1c), the charge becomes more

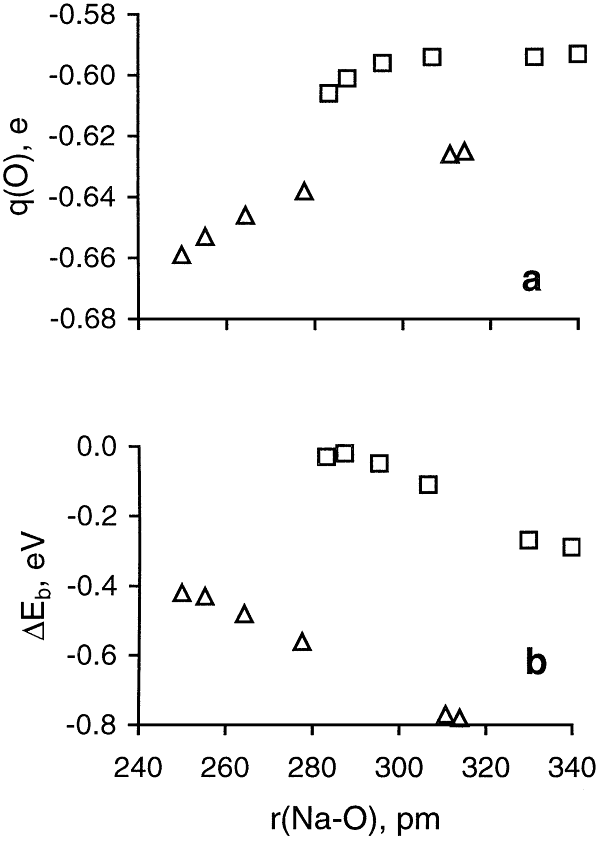

FIG. 5. Charge $q(\mathrm{O})$ (a) and core-level shift ΔE_b (b) of oxygen centers O10 (triangles) and O12 (squares) of the cluster Al-2*p* as a function of the distance $r(\mathrm{Na–O})$.

negative with decreasing Na–O distance, yet the core-level shift ΔE_b(O1*s*) becomes less negative. Despite this apparent contradiction, both observed trends can be rationalized by the response of the electronic state of the oxygen atom when the cation comes closer:

- The orbitals of the atom (including the 1*s* core level) are stabilized by the external positive electrostatic potential; thus, the core-level shift ΔE_b becomes less negative or more positive;
- The electron density around the atom increases in order to screen the external potential; i.e., the negative charge of the oxygen atom increases.

The former effect is due to the Madelung potential as accounted for in the charge-potential model for ΔE_b (19, 21, 31). Since in the cases considered here the distances between the atoms in the ring hardly change, the alteration of the Na^+ position can be used as a simplified model for the change of the Madelung potential acting on the oxygen atoms considered. If we assume for the moment that we may leave aside artifacts of a Mulliken analysis, then the observed stabilization of the O1*s* level (i.e., less negative values of ΔE_b(O1*s*)) concomitant with a higher negative charge can be interpreted as dominance of the Madelung potential effect over that of the atomic charge. This conclusion for atoms in a zeolite structure has been reached previously on the base of lattice-energy calculations (19). When applying the charge-potential model one should take into account that the atomic charge may be influenced by the strength of the Madelung potential, as seen in Fig. 6. Thus, the problem does not seem to be an incorrect description of the effect of the cation on the oxygen charges (or even Mulliken artifacts). Rather, the assumption that the different parameters of the charge-potential model are independent of each other may be an oversimplification in some cases.

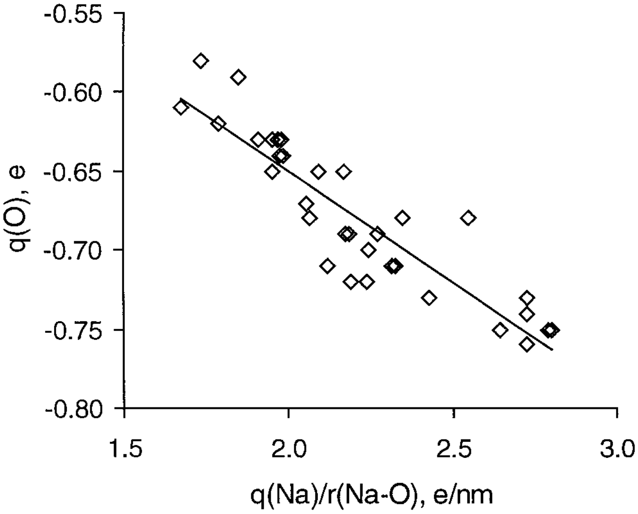

FIG. 6. Oxygen charge q(O) in the cation-containing clusters vs the field of the cation q(Na)/r(Na–O) (in e/nm). The correlation coefficient of the straight line is $r = 0.81$.

TABLE 1

Calculated Proton Affinity (PA) of Oxygen Centers[a] in Faujasite Six-Rings

Cluster	O7	O8	O9	O10	O11	O12
Al-1	849	698	751			
Al-2*m*		854				903[b]
Al-2*p*		849		832		805
Al-3	777		828		886	
Si-6	771					
K-Al-2*p*		878		855		819

[a] For the labeling of the oxygen centers, see Fig. 1.

[b] The PA for the *syn* position of Na^+ is 923 kJ/mol.

3.4. *Basicity of the Oxygen Atoms*

As seen from the previous section, core-level shifts and charges of the oxygen atoms may express contradicting trends of basicity in some cases. To obtain a reliable criterion for the oxygen basicity in the different zeolite clusters studied, the proton affinity of some of the oxygen atoms in these rings has been calculated as defined in Section 2.4. This requires additional computational effort, but it is a convincing and unambiguous procedure for evaluating the oxygen basicity. The calculated proton affinities of different oxygen positions are presented in Table 1.

For the *anti* position of Na^+, the most basic oxygen atoms are O12 in Al-2*m* (PA = 903 kJ/mol) and O11 in Al-3 (PA = 886 kJ/mol), which are located between the two aluminum atoms in *meta* position and far from the charge-compensating cations. The same atoms are even more basic for Na^+ in *syn* position (by about 20 kJ/mol) because the distance to the cation is longer (cf. Fig. 2b). When Na^+ is at the SII crystallographic position, both centers correspond to O(4) crystallographic oxygen atoms. On the other hand, the less basic oxygen centers correspond to the O(2) crystallographic position (oxygen atoms directed inward toward the ring) and to Si–O–Si bridges, O8 and O9 in Al-1 with PA = 698 and 751 kJ/mol, respectively. Center O7 of Al-3, which is connected to an Al center, also has low PA value of 777 kJ/mol because it is close to one of the charge-compensating OH groups. The PA of the oxygen atoms of the six-ring Si-6, which contains only silicon T-atoms, is 771 kJ/mol. The oxygen atoms of the four-ring with two aluminum centers have similar basicity as those of the six-ring models; the most basic oxygen has PA = 897 kJ/mol.

To compare the strength of basic centers in zeolites, we mention the PA of ammonia which, calculated in the same way, is 885 kJ/mol. This value is somewhat smaller than the strongest basic sites in the zeolite rings. The PA of water

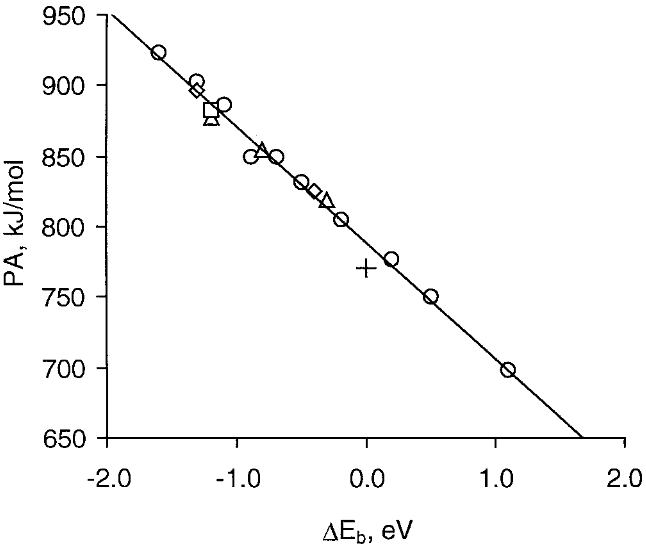

FIG. 7. Linear correlation of calculated proton affinities (PA) of zeolite oxygen centers and their core-level binding energy shifts ΔE_b. The various symbols represent oxygen atoms of different clusters: circles, Na-Al-1, Na-Al-2*m*, Na-Al-2*p*, and Na-Al-3; triangles, K-Al-2*p*; diamonds, Na-Al-2p^1 with a second Na^+ instead of H^+ for charge compensation; squares, four-ring with two Al atoms; cross, Si-6. The correlation coefficient of the straight line is $r = 0.986$.

is 724 kJ/mol, close to that of the less basic zeolite oxygen atoms.

The PA values of oxygen atoms exhibit a clear linear correlation with the corresponding core-level shifts $\Delta E_b(O1s)$ (Fig. 7). In this evaluation oxygen atoms from Al–O–Si and Si–O–Si bridges of all clusters studied are included. On the other hand, no meaningful quantitative correlation between the PA values and the Mulliken charges of the oxygen centers was found (cf. Fig. 4b). The excellent linear correlation suggests that the above discussion of factors influencing the O1*s* core-level shifts can be directly transferred to their PA as well as to their basicity. The slope of the straight line in Fig. 7 is $\gamma = -0.84$ when both PA and ΔE_b are measured in eV. Since the PA value is usually measured in kJ/mol, it is more practical to state that a negative shift of the O1*s* binding energy by 1 eV implies an increase of the proton affinity by 82 kJ/mol.

Experimentally such a linear correlation has been observed for PA and $E_b(1s)$ values of a series of oxygen- and nitrogen-containing molecules in the gas phase (42). Surprisingly, for oxygen atoms of alcohols or ethers the slope of the straight line is $\gamma = -0.95$, close to the value derived from Fig. 7 for oxygen atoms of zeolite rings. This correspondence with the experimental findings shows that the linear dependence found here is not a computational artifact but a real phenomenon that deserves special attention. The linear correlation of PA and ΔE_b values underline the close connection between the proton affinity and the electronic potential at the individual oxygen sites. Therefore, from a chemical point of view, one can expect that also the energy of other orbitals located on the oxygen center under investigation will correlate with the PA, in particular the highest occupied molecular orbital (lone pair) at that center. The higher the lone pair orbital energy, the larger the PA of that center should be. According to the experimentally observed correlation between $E_b(O1s)$ and the first ionization potential of small molecules (42, 43), the 1*s* core-level shift is representative for the relative shifts of the electronic levels of the oxygen atom considered.

Unfortunately, experimental confirmation of the relationship presented in Fig. 7 can not be expected for zeolite materials because the differences between the 1*s* core levels for individual oxygen atoms in zeolite rings are small. Also, in a sample it is not trivial to assign PA and XPS peaks to the specific framework oxygen centers. Actually, experimental estimates of the basicity (PA), by IR spectra of adsorbed acidic molecules or by the catalytic activity of the samples, evaluate the PA of the most basic oxygen centers, while the XPS peak is averaged over all oxygen atoms of a zeolite. Nevertheless, the correlation of the computational results demonstrates that oxygen 1*s* core-level shifts (measured or calculated) provide a reliable criterion for the basicity of zeolite oxygen atoms, certainly much preferable to calculated charges.

3.5. *Comparison with Potassium Zeolite*

We also performed calculations for the cluster K^+-Al-2*p* in the same fashion as for the sodium analogue in order to check whether the model developed so far is able to represent trends that are experimentally established among alkali-exchanged zeolites. The geometry optimization yielded similar results. A potassium cation may be located on either side of the ring, at longer distances from the plane of the ring compared to Na^+, 203 pm for the *syn* and 171 pm for the *anti* configuration. The charges of the individual oxygen atoms of the ring change differently from the cluster Na^+-Al-2*p*, due to the influence of the larger K^+ charge of 0.67 *e* in both positions (compared to 0.51/0.61 *e* for the two corresponding positions of Na^+) and the longer distance to the oxygen atoms. However, the E_b value is systematically lower by 0.1–0.4 eV compared to the cluster with sodium; this difference is close to that measured for the decrease of the O1*s* binding energy, 0.0–0.4 eV, when going from the sodium to the potassium forms of Y and X zeolites (17, 18). The small alteration of the core-level energies induced by the change of the cation as compared to the differences calculated for the various positions of the oxygen atoms in the ring suggests that bonding in the ring affects the potential and thus the 1*s* core-level energies most prominently. The calculated proton affinities of oxygen atoms of the K^+ cluster model are by 23–29 kJ/mol higher than those of the corresponding Na^+ model. This agrees with the experimentally observed higher basicity of potassium-exchanged zeolites compared to their sodium forms. However, note that the values corresponding to the oxygen atoms of the cluster K-Al-2*p* cluster (triangles) fall on the same line as the oxygen atoms of sodium-containing clusters (Fig. 7).

4. CONCLUSIONS

The highest negative shifts ΔE_b and the highest negative charge values are calculated for oxygen atoms of Al–O–Si bridges, followed by those oxygen centers which connect two silicon atoms, while the highest positive ΔE_b are calculated for those oxygen atoms which directly interact with the charge-compensating cation (both for H^+ and Na^+). However, the charge on an oxygen atom and the shift of the core-level binding energy do not correlate with each other for the cation-containing clusters. Moreover, we found these two parameters to often change in opposite directions, depending on the position of the central sodium cation. This suggests that the factors affecting these characteristics of zeolite oxygen atoms exhibit a more complex interplay. In summary, the main findings of our computational model cluster study concerning the calculated 1*s* binding energy shifts of oxygen atoms are as follows:

(a) The shifts $\Delta E_b(O1s)$ differ mainly with the position of the oxygen centers in the ring, relative to the Al centers and the charge-compensating cation. $\Delta E_b(O1s)$ differences range up to 3 eV.

(b) The second factor affecting the O1*s* core-level shifts is the electrostatic potential of the cation which reflects the changes of the Madelung potential. Variation of the Na^+ position or exchange with K^+ induces alterations of the shift ΔE_b by up to 0.4 eV.

(c) The effect of the variations of the oxygen charge can not be separated from that of the Madelung potential. However, the charge of the oxygen center under study has only minor influence, judged by the fact that the core-level binding energies shift in the direction opposite to that expected from the charge alterations.

Proton affinities were calculated for several oxygen atoms in rings of different Al content (for the *anti* position of Na^+). Most basic, i.e., exhibiting the highest PA values, are oxygen atoms in the six-rings where the aluminum atoms are in *meta* position, modeled by the clusters Al-2*m* and Al-3 with PA = 903 and 886 kJ/mol, respectively. Oxygen atoms in a four-ring with two aluminum centers feature a similar basicity, with a PA of 897 kJ/mol. The exchange of Na^+ by K^+ leads to an increase of the oxygen basicity, both measured by the binding energy shifts and the calculated proton affinities; PA values are 23–29 kJ/mol higher.

An excellent linear correlation is established between the calculated PA values and 1*s* binding energy shifts $\Delta E_b(O1s)$ of individual oxygen atoms, similarly to the experimental relationship between the PA and $E_b(O1s)$ values for series of oxygen and nitrogen molecules in the gas phase. Since this linear correlation holds for such different systems as organic molecules and zeolites, we can speculate that it is of general validity, applying to organic and inorganic oxygen-containing systems alike.

The observed correlation shows that O1*s* binding energies may profitably be used as convenient measure for the basicity of zeolite oxygen centers. Core-level shifts provide a more reliable basicity criterion than atomic charges. Since the O1*s* core-level shift is (in general) representative for the relative shifts of the electronic levels of the oxygen atom under study, one can conclude that the proton affinity is primarily influenced by the orbital energies, likely by the highest occupied level of oxygen center. It is difficult to separate contributions of different atomic orbitals in the HOMO range for such a complicated system as the zeolite rings studied, but one expects the lone pair levels to be immediately relevant for determining the proton affinity of an oxygen center.

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