

ARTICLES

The Effect of Chemical Composition and Structure on XPS Binding Energies in Zeolites

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The effect of zeolite composition and structure on XPS core level binding energies has been studied for a large class of zeolites (FAU, MFI, MOR, LTA) differing in their counterions (Na, K, Rb, Ca, Mg, Ba) and Si:Al ratio (1 to 160). Whereas absolute binding energies cannot be determined to any reasonable degree of accuracy, relative peak positions can be found with high precision. In this paper, we show that the main effect on binding energy differences between silicon, aluminum, and oxygen is caused by the aluminum content of the zeolite. The effect of the zeolite structure and the co-cation is only minor. It was found that the Si(2p) to Al(2p) XPS peak separation decreases with increasing aluminum content. Quantum chemical calculations have been performed that rationalize these findings in terms of a nonhomogeneous charge distribution in the zeolite framework.

Introduction

The interpretation of shifts in binding energy for a given element in (chemically) different environments has a long standing history. Especially for organic compounds it has a well-established basis,¹ the spectrum of ethyl tri-fluoroacetate being still a textbook example.^{2,3} Whereas organic substances can often be measured in the gas phase where no charge reference problems occur, inorganic compounds are commonly insulators and surface charge is almost always present. Thus “observed” binding energies must be corrected for this effect.⁴ Commonly employed methods are the use of flood guns, internal standards (such as peaks from the support material of a supported catalyst) or the use of external standards, such as adventitious carbon.⁵ The use of added gold particles as a standard for the absolute value of observed binding energies has also been reported,⁶ but a consistent and correct charge compensation is still a matter of debate.⁷

If we want to study the binding energies of silicon, oxygen, and aluminum in different types of zeolites there is no a priori reason to assume that a given XPS peak can be used as an internal standard. Data acquisition at high temperatures has been advocated as a means to reduce charge in zeolites,^{8,9} where the materials become ionic conductors. However, migration of ions must necessarily mean migration of charge and this might influence the observed results. Thus, correlations of absolute binding energies with other properties must be done with care

as the reported changes in absolute binding energies are invariably small.^{10–13} In this case, the use of the Auger parameter is of little use, as the Si Auger peaks are not amenable to experimental observation in present day equipment with Mg and/or Al X-ray sources. It has been used rather cleverly in the study of chemical state plots of many silicon–aluminum compounds by employing the brehmsstrahlung from a beryllium window,^{14,15} which is absent in most systems now.

Many studies of XPS binding energies in zeolites have been reported in a recent review.¹² They mostly focus on an accurate determination of the O(1s) binding energy and possible correlations with other (catalytically) relevant parameters. The influence of the amount of aluminum in the zeolite on binding energies has been noted¹⁰ and attributed to differences in the Si–O and Al–O bond ionicity. The influence of the Si:Al ratio on Auger line intensities and oxygen binding energies has been reported as well¹⁶ and ascribed to rehybridization of valence orbitals of the zeolite. Absolute values of changes in binding energies have also been reported and correlated with the electropositivity of the cation.¹⁷ The present study complements earlier work in the sense that we study a wide range of composition, a wide range of zeolites, and different counterions. As we will show, the only important parameter for binding energy differences is just the Si:Al ratio of the zeolites. We will rationalize our findings using a simple representation of a zeolite, which is amenable to ab initio quantum chemical calculations, so as to gain insight into the physical processes occurring when aluminum is substituted for silicon in a zeolite.

Experimental Section

The XPS data were obtained with a Vacuum Generators XPS system, using a CLAM-2 hemispherical analyzer for electron

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TABLE 1: Survey of the Different Types of Zeolites Studied with Their Silicon-to-Aluminum Ratio, Mole Fraction of Aluminum (f_{Al}) in the Framework, Topology, and Origin

zeolite material	Si/Al ratio	f_{Al}	zeolite topology	origin
A	1.0	0.50	LTA	Ventron
X	1.27	0.44	FAU	Ventron
ZK4	2.08	0.32	LTA	ExxonMobil Chemical Europe
Y	2.49	0.29	FAU	Ventron
Y	2.71	0.27	FAU	Zeocat
Y	3.5	0.22	FAU	ExxonMobil Chemical Europe
mordenite	5.74	0.15	MOR	Norton
ZSM-5	160.0	0.0062	MFI	ExxonMobil Chemical Europe

detection. Nonmonochromatic Al $K\alpha$ X-ray radiation was used for exciting the photo electron spectra using an anode current of 20 mA at 10 keV. The pass energy of the analyzer was set at 20 eV in order to obtain a better peak resolution. The results were essentially unchanged when using a 50 eV pass energy. Specimens were mounted in the analysis chamber attached to double-sided tape. No sputter cleaning or further treatment was applied to the samples.

Data for SiO_2 were taken on well-defined powders (Degussa) with surface areas of 50, 90, 200, and 380 m^2/g . Also, two samples of pure quartz were investigated, one consisting of finely ground powder and the other a larger crystal, crushed into millimeter-sized fragments. For comparison, two commercial samples were measured. They were kindly provided by Sibelco (Antwerp, Belgium). The first consisted of pure silica (Sand of Mol) and the second was in the form of cristobalite, a structurally different form of silica.

The zeolite materials were put in their Na^+ , K^+ , Rb^+ , Cs^+ , Mg^{2+} , Ca^{2+} , and Ba^{2+} form by four successive exchanges with a 1 M solution of NaCl (Aldrich, p.a.), KCl (Aldrich, p.a.), RbCl (Merck, p.a.), CsCl (Merck, p.a.), $MgCl_2$ (UCB, p.a.), $CaCl_2$ (UCB, p.a.), $BaCl_2$ (Aldrich, p.a.), respectively. The samples were washed Cl^- -free and dried in air at room-temperature overnight. The crystallinity of the zeolite samples before and after ion exchange was confirmed with XRD and SEM techniques. In all cases, exchange was virtually complete as evidenced by XPS. Chemical analysis of the zeolite materials after ion exchange indicated that after four successive ion-exchange steps the degree of exchange was above 98% for all materials under study. Their properties are given in Table 1.

Quantum chemical calculations were done with the GAMESS-UK program.¹⁸ The program uses ab initio methods to solve the nonrelativistic Schrödinger equation in the restricted Hartree–Fock case and is able to converge on excited core hole states. Binding energies can be computed in two different ways. The first approximation is to use Koopmans theorem, where orbital energies are equated to the adiabatic ionization potentials. In this approach all changes in ionization potential due to external perturbations (e.g., charges) are accounted for by their influence on the initial energies only. Binding energies can also be calculated as the difference in total energy between, say the $Si(1s^2 2s^1 2p^6 3s^2 3p^2)$ core hole state and the $Si(1s^2 2s^2 2p^6 3s^2 3p^2)$ ground state for the $Si(2s)$ transition with an analogous procedure for the other states considered. In this method the difference in self-consistent field total energies (ΔSCF) is taken as the ionization potential. Now, external perturbations influence both the initial and final states. All calculations were performed with a double- ζ basis set.¹⁹ Atomic charges were computed with the aid of the distributed multipole analysis module,²⁰ as implemented in GAMESS-UK. Our procedure is different from that employed recently by Vayssilov and Röscher,²¹ who used density functional theory to describe the core ionization process

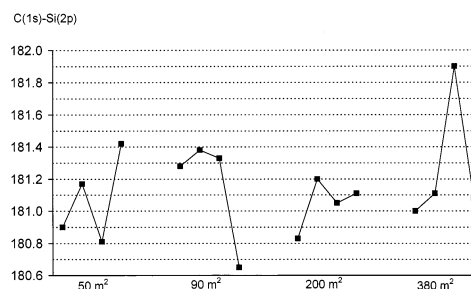


Figure 1. The observed distance (eV) between the carbon 1s and the silicon 2p peak for four different silica samples with surface areas of 50, 90, 200, and 380 m^2/g . The data for each type of silica were collected four times. For ease of comparison, related data have been connected by lines. Gridlines are given in intervals of 0.1 eV.

and Mulliken populations to estimate the charges on atoms in zeolites. Their primary interest, however, was to study the relation between basicity and O(1s) binding energy in zeolites, whereas our work focuses on the (relative) shifts of the silicon, aluminum, and oxygen XPS peaks.

Results and Discussion

As a first test we must investigate the ability of XPS to obtain reasonably accurate values of the relevant binding energies in nonconducting solids. The effect of sample charge invalidates the absolute value of any energy as measured directly. The use of a fixed binding energy of ubiquitous (adventitious) carbon must be advised against. Figure 1 shows the results obtained for the binding energy difference between the carbon 1s and the silicon 2p peaks in four samples of pure SiO_2 with different surface areas. Each measurement was repeated four times with a newly prepared sample. As can be seen, the change in the peak position difference is very large and may amount to almost 1 eV. Thus, assigning a universal value to (adventitious) carbon would imply a large shift of up to 1 eV for the absolute $Si(2p)$ peak position and is inadmissible for data on the same samples. Similar results were found with the zeolite samples. Also adding additional elements, such as gold dust, to the samples proved to be inadequate, as the observed Au–Si peak differences fluctuated widely between identical samples. Thus, we must conclude that absolute binding energies cannot be obtained with any degree of accuracy in a simple fashion. Only if the exact chemical nature of the carbon contamination overlayer were known in advance could this procedure be used. It has been applied, however, by several authors.^{9,22}

Differences in binding energy between the constituting elements of a nonconducting sample can, however, be measured with a high degree of accuracy. The differences between the $Si(2p)$ and $Si(2s)$ peaks and the difference between the O(1s) and $Si(2p)$ peaks for the samples described above as well as those for quartz and cristobalite are remarkably constant, despite a change in overall charging of the samples. The $Si(2s)$ to $Si(2p)$ distances are all accurate within ± 0.1 eV. The O(1s) to $Si(2p)$ peak separations are reproducible to ± 0.2 eV. The data also indicate that overall structure is not an overriding factor in the relevant peak positions. This is to be expected as core ionization is a very localized process. Only local effects, such as a nontetrahedral arrangement of oxygen, may lead to substantial changes.

Bearing in mind the restrictions outlined above we have investigated a large number of zeolites, with varying Si/Al content and different counterions in order to find a possible correlation between binding energies and zeolite composition. An often-used correlation is that between binding energy and

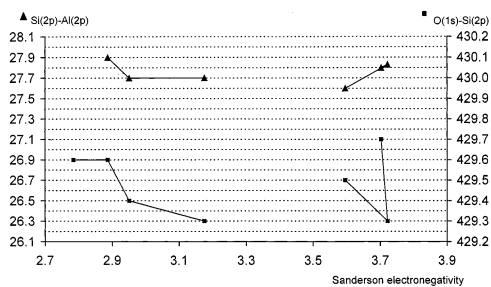


Figure 2. The observed distance (eV) between the Si(2p) and the Al(2p) XPS peak energies (left-hand axis) and the O(1s) and Si(2p) peak energy (right-hand axis) for zeolite A (Si/Al = 1) as a function of the Sanderson electronegativity of the zeolite.

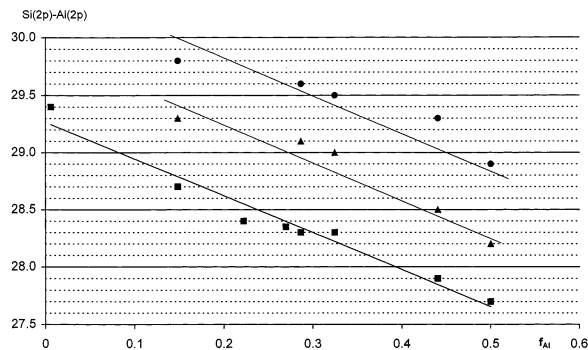


Figure 3. The observed distance (eV) between the Si(2p) and the Al(2p) XPS peak energies for a number of zeolites as a function of the aluminum mole fraction for different mono-valent counterions: ■ Na, ▲ K, ● Rb. The data for K and Rb have been shifted upward by 0.5 and 1.0 eV, respectively. The (least-squares) line through the points for sodium has also been shifted upward for potassium and rubidium so as to show the similarity in the trend in the data.

electronegativity. Figure 2 shows our data, when plotted as a function of the average Sanderson electronegativity (S.E.) of the zeolite.^{23,24} No obvious trend can be found if the total collection of data is considered, although a limited selection may indeed show a relation. It must be admitted that in Figure 2 we plot binding energy differences, not absolute values. However, if one of the absolute binding energies, e.g., the O(1s) level should show a good correlation with any conceivable property, our results indicate that the location of the Si(2p) level is completely uncorrelated. Similar results were found when plotting the data for different zeolites, all with different Si:Al ratios, in this fashion.

The results can be better correlated when we plot the binding energy differences considered as a function of the aluminum content, or rather the mole fraction of aluminum, for different zeolites with a given counterion. Figure 3 shows the data for sodium as a counterion, which was investigated extensively, as well as data for the other alkali metals. The results indicate a clear trend, the Si(2p) to Al(2p) separation decreases with increasing amounts of aluminum in the zeolite. The straight line for sodium is a least-squares fit to all datapoints. This line has just been shifted upward for the other alkali metals. Thus it appears that charge within the zeolite framework, rather than the kind of compensating ions, is the important parameter. The distance between the oxygen 1s and silicon 2p peaks is rather insensitive to the mole fraction of aluminum as shown in Figure 4. A slight increase in the absolute differences may be seen in going from sodium to the other alkali metals, but no clear-cut trend is evident.

The same plots can be made for di-valent cations and is shown in Figures 5 and 6. Though the O(1s) to Si(2p) remains

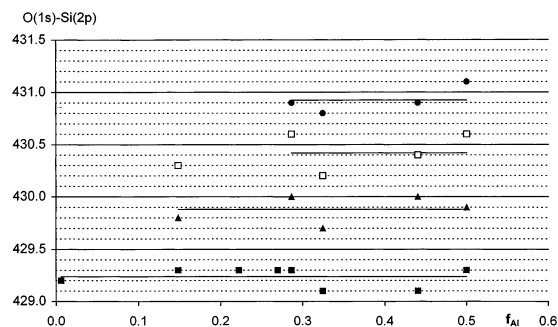


Figure 4. The observed distance (eV) between the O(1s) and the Si(2p) XPS peak energies for a number of zeolites as a function of the aluminum mole fraction for different mono-valent counterions. ■ Na, ▲ K, □ Rb, ● Cs. The data for K, Rb, and Cs have been shifted upward by 0.5, 1.0, and 1.5 eV, respectively. The average value of each data set is indicated by a horizontal line.

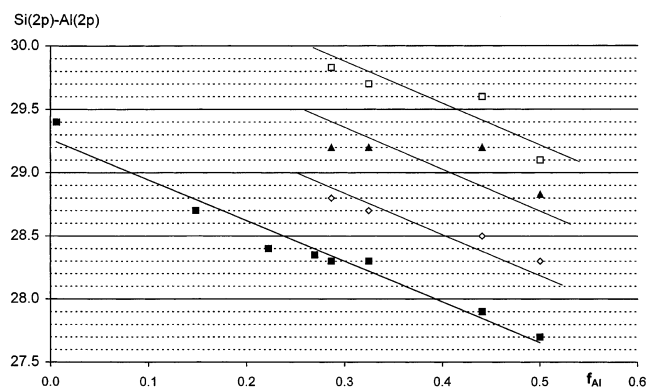


Figure 5. The observed distance (eV) between the Si(2p) and the Al(2p) XPS peak energies for a number of zeolites as a function of the aluminum mole fraction for different di-valent counterions, as compared to those for sodium: ■ Na, ◇ Mg, ▲ Ca, □ Ba. The data for Mg, Ca, and Ba have been shifted upward by 0.5, 1.0, and 1.5 eV, respectively. The (least-squares) line through the points for sodium has also been shifted upward so as to show the similarity in the trend in the data.

essentially constant, the effect on the Si(2p) to Al(2p) separation is hardly different from that of the mono-valent cations and still shows the same trend. Taking into account the experimental accuracy of our methodology we must conclude that for a given zeolite there exists no simple correlation between observed binding energy differences and the nature of the cation. Rather, there is a correlation for a given cation and the aluminum content of the zeolite, irrespective of the framework topology of the zeolite.

Changes in core binding energy levels are usually interpreted with the aid of the following equation:²⁵

$$E = E_0 + kq + \sum_i \frac{q_i}{r_i} \quad (1)$$

where E is the observed binding energy for a particular transition, E_0 a reference value, and q the charge on the atom involved with k an (unknown) constant. The last term represents the electrostatic (Coulomb) energy, caused by the presence of charges q_i at positions r_i and is often called the Madelung potential. Note that the equation as written presupposes the use of either esu units or atomic units. We will use it with atomic units as the unit of energy. This equation appears to be quite reasonable, it just states that in order to remove an electron from an atom it has to overcome the binding energy E_0 for an isolated, unperturbed atom. This energy is augmented by the second term

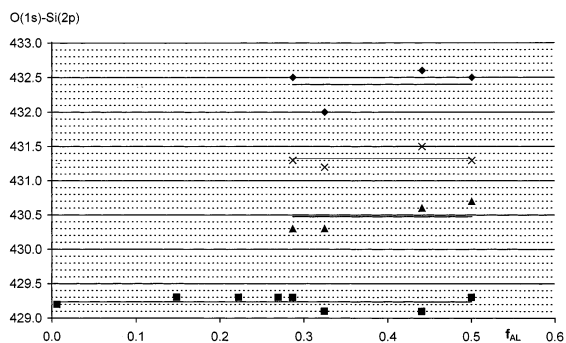


Figure 6. The observed distance (eV) between the O(1s) and the Si(2p) XPS peak energies for a number of zeolites as a function of the aluminum mole fraction for different di-valent counterions as compared to those for sodium. ■ Na, ▲ Mg, x Ca, ◆ Ba The data for Mg, Ca, and Ba have been shifted upward by 1.0, 2.0, and 3.0 eV, respectively. The average value of each data set is indicated by a horizontal line.

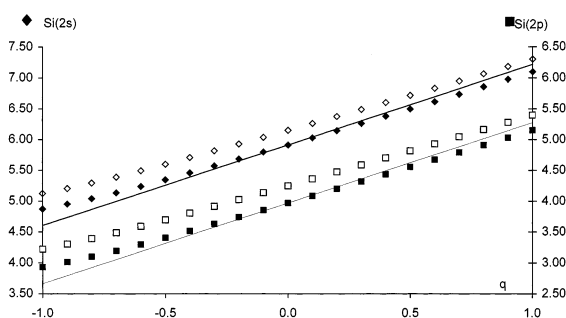


Figure 7. The theoretical transition energies for a Si(2s) and Si(2p) core hole ionization (in atomic units) in an isolated silicon atom tetrahedrally surrounded by four point charges with varying strength q at a distance of 1.62 Å. Open symbols refer to orbital energies derived from Koopmans theorem. The expected dependence (eq 1) is given by the solid lines.

if the atom involved is charged. The last term is just Coulomb's law, the potential energy of an electron in the charged region of space. The experimental validation of the equation is rather difficult, if not impossible, due to the fact that no (model) system can be made that obeys exactly the conditions imposed, i.e., a fixed (possibly nonintegral) charge on the atom and a fixed configuration of charges around it. It is, however, possible to investigate the validity of the equation by quantum-chemical means and consider the effect of the last two terms separately.

To do this we have performed ab initio quantum chemistry calculations on an isolated silicon (or aluminum) atom, tetrahedrally surrounded by four point charges with varying strength. This configuration resembles at least the actual primary building block in a zeolite. In this case, the net charge on the central atom is zero and any effects that may occur are due to the four point charges (the last term in eq 1) only. Figure 7 shows the results for the Si(2s) and Si(2p) binding energies as a function of the strength of the (four) point charges q_i , located at a distance of 1.62 Å. The charge on the silicon atom is zero in this case, so only the last term in eq 1 contributes to any effects found. The calculations were done assuming the binding energies to be given by Koopmans theorem (open symbols) and by assigning them to the difference in total energies of the excited ion and ground-state atom. The latter values are of course somewhat lower, since the final state is allowed to relax to a new equilibrium configuration. As can be seen, the influence of external charges on the ionization energies are mostly confined to the initial state. The theoretical slope of the line is given by four times the inverse distance to the charges in both

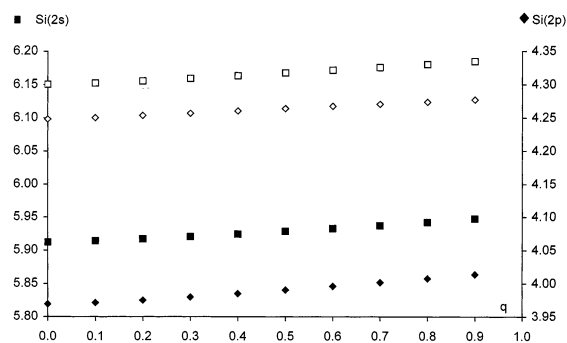


Figure 8. The theoretical transition energies for a Si(2s) and Si(2p) core hole ionization (in atomic units) in an isolated silicon atom tetrahedrally surrounded by four point charges with alternating opposite charge at a distance of 1.62 Å as a function of the magnitude of this charge. Open symbols refer to orbital energies derived from Koopmans theorem. The expected dependence (eq 1) is a constant value for the two energies.

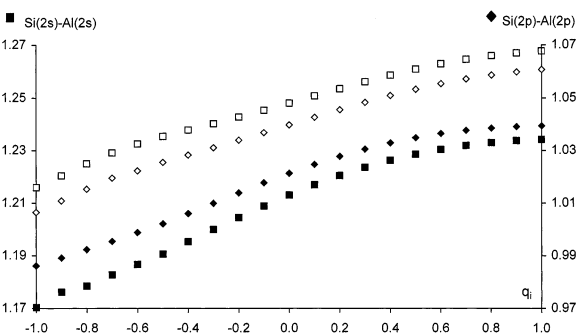


Figure 9. The difference in the theoretical transition energies for the Si(2s)–Al(2s) and the Si(2p)–Al(2p) core hole ionization (in atomic units) in an isolated atom tetrahedrally surrounded by four point charges with equal charge at a distance of 1.62 Å as a function of the magnitude of this charge. Open symbols refer to orbital energies derived from Koopmans theorem. The expected dependence (eq 1) is a constant value for the difference between the two energies.

cases and its expected dependence, as given by eq 1, is also included. The agreement is rather good, the calculated points fall along a straight line with almost the correct slope. The slope is equal for the Si(2p) and Si(2s) levels. It must be remembered, however, that shifts in binding energies are rather small and that, on the scale used in Figure 7, a difference of 0.5 au represents 13.6 eV.

The situation becomes worse when we consider a silicon atom, surrounded by four charges with alternating opposite signs, imposing a quadrupole field. This configuration is rather difficult to realize in practice, but can be used to test the validity of eq 1 in a rather stringent way. It predicts that in this case no change in binding energy must occur as the four terms in the sum add up to zero. This is evidently incorrect as shown in Figure 8 for both Koopmans theorem and the Δ SCF method. In this figure a distance of 0.01 au corresponds to an energy difference of 0.27 eV.

Another prediction of eq 1 that can be verified is to consider the difference in binding energies between a silicon and an aluminum atom in otherwise identical surroundings of point charges. The binding energy difference should remain constant as a function of charge as now only the difference between the two values of E_0 plays a role in the equation. The results are shown in Figure 9, which defies this prediction, even in the region near $q = 0$.

The effect of charge on the atom that emits the photoelectron, the second term in eq 1, can be studied with a slightly more

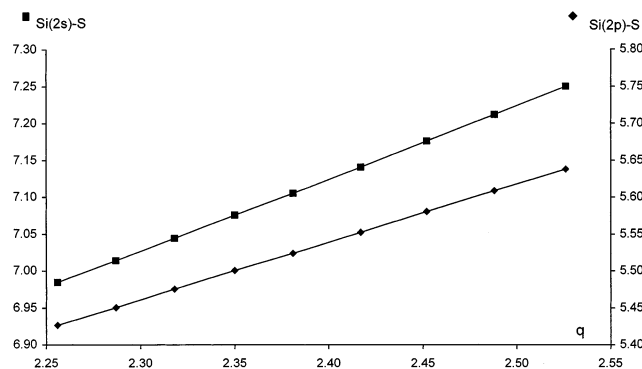


Figure 10. The transition energy for a Si(2p) and Si(2s) core hole ionization process corrected for the presence of external charges (eq 2) as a function of charge q on the silicon atom for SiO_4^{4-} using the ΔSCF method to calculate the ionization potentials. The results should fall on a straight line.

complicated model. If we perform a calculation for the molecule SiX_4 , with X for instance Cl, we can find the equilibrium Si–X distance by a geometry optimization. In this configuration there will be a nonintegral (positive) charge on the central silicon atom and an identical (negative) charge on the four X atoms together. This charge is known after performing the quantum chemical calculation from the results of a distributed multipole analysis. If we rearrange eq 1 to

$$E - \sum_i \frac{q_i}{r_i} \equiv E - S = E_0 + kq \quad (2)$$

we may evaluate the left-hand side of this equation from the computed value of E , the computed charges q_i , and the known distance r_i . As the charge q equals four times q_i , but with opposite sign, the right-hand side contains only E_0 and k as unknowns. If we now perturb the equilibrium geometry slightly, by moving the surrounding X atoms to a different position, the calculation will result in different charges q_i on X and a different charge q on the central silicon atom. Thus we can plot the left-hand side as a function of q , where q changes due to the imposed change in the interatomic distances Si–X and obtain a straight line with slope k . Figure 10 shows the result for the case of SiO_4^{4-} using the ΔSCF method to find the ionization potentials. The points fall indeed on a more or less, but not quite, straight line. The slope of the line is different for the Si(2p) and Si(2s) transition, as it does not represent the actual change in binding energy as in Figure 9. However, if we include other data with X = H, F, (OH), or Cl, the picture changes substantially. Figure 11 shows the data for the Si(2p) and Si(2s) core level peaks. If eq 1 were entirely correct, all points for a given transition should fall on one single straight line, when plotted as a function of q , the charge on the silicon atom. This is obviously not the case.

The failure of eq 1 to predict numerically correct binding energies or shifts in binding energy is of course not due to a failure of Coulomb's law or the failure of classical electrostatics. Rather it is caused by the fact that electrons cannot be considered as fixed and unpolarizable point charges. This point has also been discussed recently by Bagus et al.²⁶ and Mårtensson and Nilsson.²⁷ The calculations presented here take into account explicitly the rearrangement of the electrons in the presence of an external field, which leads to a change in orbital energies in the neutral atom. This change is large and correcting ionization potentials for final state effects, the rearrangement of electrons in the (positively) charged atom after ejection of the photo electron has only a relatively minor effect. Both effects are not

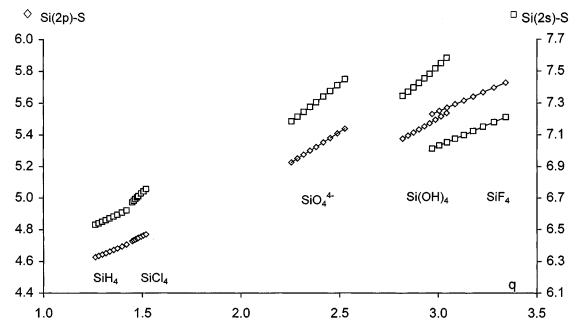


Figure 11. The transition energy for a Si(2p) and Si(2s) core hole ionization process corrected for the presence of external charges (eq 2) as a function of charge q on the silicon atom for several compounds SiX_4 , using the ΔSCF method to calculate the ionization potentials. All results should fall on a straight line if eq 2 were entirely correct.

fully included in the simple eq 1, and although the sign of the shifts is of course predicted correctly, its magnitude is easily off by about 0.1 of an atomic unit, or 2.7 eV. Thus, the equation cannot be used to predict absolute values for shifts in binding energy, except in a very qualitative way, and certainly not when comparing data on systems with different ions, which cause charges to be present with different magnitudes and at different distances.

To rationalize our experimental results, which indicate a large effect of the Si/Al ratio on the binding energy differences between the Si(2p) and the Al(2p) core levels, we must resort to a more elaborate computational scheme. To this end we consider a zeolite to be composed of SiO_4 and AlO_4 tetrahedra and include all five atoms in these units in the quantum chemical calculation. This unit, or cell, is uncharged in a zeolite consisting of only silicon and oxygen as each oxygen is bridged to two silicon atoms. Chemically, however, a formal charge of -4 is assigned to the SiO_4 unit. We compensate for this negative charge by placing four point charges with strength q in the system along every Si–O bond at a distance of two times 1.62 Å, which was taken as the interatomic spacing between silicon and oxygen. These four charges are supposed to represent the rest of the zeolite, not explicitly included in the quantum chemical calculation. For a system with only SiO_4 units or cells the charge q of each point charge must be $+1$, but this value must change if aluminum is substituted for silicon in the molecular framework. The model neglects the effect of the relative spatial arrangement of tetrahedra completely, the interconnection of the various tetrahedra is not considered. However, this neglect can be justified by the fact that our experimental data indicate that the primary effect on the Si(2p) and Al(2p) binding energy difference is caused by the Si-to-Al atomic ratio, and not related to the detailed structure of the zeolite.

Next we consider the total charge in the system. If the Si-to-Al ratio is denoted as x , the mole fractions of Si and Al will be

$$f_{\text{Si}} = \frac{x}{1+x}$$

$$f_{\text{Al}} = \frac{1}{1+x} \quad (3)$$

The net excess negative charge per cell is equal to the mole fraction of aluminum, as each Al atom, substituted for a Si atom, contributes an amount of -1 . The presence of the positive charges outside the framework is neglected in the calculation as experimentally their influence seems to be of less importance.

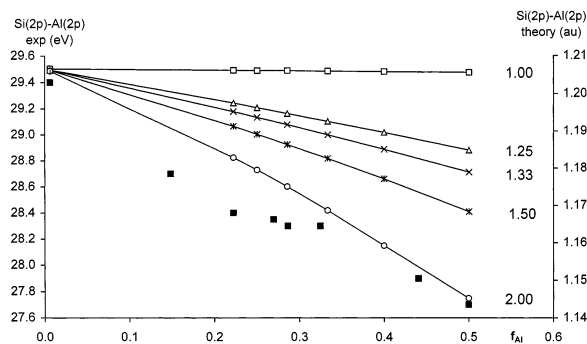


Figure 12. The experimental results for the difference in binding energy in eV of the Si(2p) and Al(2p) peaks as a function of the mole fraction of aluminum in the zeolite framework (left-hand axis) for sodium counterions. The right-hand axis shows the calculated results (in atomic units) with the model outlined in the text for different values of the charge ratio r on the silicon and aluminum entities, using the Δ SCF method to calculate the ionization potentials.

This net excess charge must be distributed over SiO_4 and AlO_4 units. If we denote their charge by Q_{Si} and Q_{Al} , respectively, and their ratio by r , we have the following equations for the charge in the system:

$$\frac{x}{1+x}Q_{\text{Si}} + \frac{1}{1+x}Q_{\text{Al}} = -\frac{1}{1+x}$$

$$\frac{Q_{\text{Si}}}{Q_{\text{Al}}} = r \quad (4)$$

These equations can be solved for the charges Q_{Si} and Q_{Al} to yield

$$Q_{\text{Si}} = -\frac{r}{1+rx}$$

$$Q_{\text{Al}} = -\frac{r}{1+rx} \quad (5)$$

This equation implies that if $x = 1$ (or a zeolite with as much silicon as aluminum) and $r = 1$ (or an equal distribution of charge between silicon and aluminum cells) the net charge on each of them is equal to $-1/2$ as it should. The values for the point charges q used to describe the rest of the zeolite are calculated by a charge balance for each unit or cell:

$$Q_{\text{Si}} = -\frac{r}{1+rx} = 4 - 4 \times 2 + 4 \times q_{\text{Si}}$$

$$Q_{\text{Al}} = -\frac{r}{1+rx} = 3 - 4 \times 2 + 4 \times q_{\text{Al}} \quad (6)$$

where the numbers refer to the formal charges of silicon (+4), four oxygen atoms (-2), and aluminum (+3).

The calculations are now done for a $\text{SiO}_4/4q_{\text{Si}}$ unit and a $\text{AlO}_4/4q_{\text{Al}}$ unit using the appropriate values of the mole fraction and using the charge ratio $r = Q_{\text{Si}}/Q_{\text{Al}}$ as a parameter. Again, the energies were calculated with the GAMESS-UK program as outlined above, but now including all electrons on the silicon (or aluminum) and those on the four oxygen atoms using the Δ SCF method. The results for the difference in energy between the Si(2p) and Al(2p) levels are shown in Figure 12 as a function of the mole fraction of aluminum for various values of the charge ratio r on the right-hand axis. As we would expect silicon to be more amenable to the accommodation of excess charge,

only values of $r > 1$ were considered. The general shape of the curves for $r > 1$ is in good agreement with the observed data. These have also been included for the case of sodium as counterion and all zeolites studied. The maximum change in the binding energy difference (about 0.06 au or 1.6 eV) is in good agreement with the experiments, which give 1.7 eV for this number. The agreement could be improved by shifting the calculated curves along the y-axis, as the absolute values of these numbers may not be as reliable as their difference.

Calculations were also performed for the oxygen O(1s) level. The results indicate that the difference in binding energies Si(2p)–O(1s) remains extremely constant, with changes of only 0.01 eV between calculated points. This is also in agreement with experiment. It must be remarked though, that in the calculations the oxygen atom is not treated in a “symmetrical” way. The oxygen atom is bound directly to only one silicon atom and the extra point charge, whereas the silicon atom has a symmetrical environment of four oxygen atoms and four point charges. So this agreement, albeit satisfactory, might be fortuitous.

The physical reasoning behind our approach, which seems to give sensible results, is in fact quite simple. If we imagine a zeolite to be composed completely of tetrahedral SiO_4 units, the influence of the electrons on the core ionization of a silicon atom will be caused predominantly by the electrons on the neighboring oxygen atoms, so structure (in the sense of the detailed spatial arrangement of the SiO_4 units) will be less important. If we now remove a proton from a silicon atom, changing it into an aluminum atom, the effect will be 2-fold. An extra “free” electron will be found in the system, but still within the framework of the zeolite. The compensating positive charge must be located rather far away from most silicon (and aluminum) atoms if it is caused by a positive ion. The extra electron released by the change of a silicon atom into an aluminum atom will not remain localized near the aluminum atom, but its charge will be redistributed over the whole zeolite framework through the various bonds. This redistribution will not take place in a symmetrical manner, more charge will be accumulated near a silicon atom than close to an aluminum atom. So their binding energies will be influenced in a different way. Both will decrease with increasing electron density, but the decrease for aluminum is less than that for silicon, leading to a smaller separation between the Si(2p) and Al(2p) peaks with increasing aluminum content.

The influence of a change in cation may be rationalized in a similar way using the arguments given above. Taking sodium as the reference ion in the plot for the Si(2p) to Al(2p) binding energy difference, we would first order expect that changing it to potassium or rubidium would not lead to a large effect, as indeed it does. Of course sodium does affect the charge on the oxygen atoms, and in this way the charge seen by the silicon and aluminum atoms, but the effect of a different mono-valent ion will be small, as evidenced by the data in Figure 3. The shift in the energy differences might be at most 0.1 to 0.2 eV.

Replacing sodium ions by di-valent ions must have a larger influence on the charge in the zeolite framework than the replacement by a mono-valent ion. First of all there is the effect of a higher valency but, probably more importantly, also the number of counterions must go down. This will lead to a less well-defined charge distribution within the framework, which makes a prediction of their effect on the observed binding energy differences at best speculative. However, we note again from Figure 5 that the trend remains unaffected and that the change in energy differences for the di-valent cations is small.

Conclusions

The results obtained in the present paper can be summarized as follows:

(1) Absolute binding energies of the nonconducting samples studied in this paper cannot be obtained by simply referencing them to the value of adventitious carbon. This procedure should not be used, unless the nature of the carbon species is known in advance.

(2) The differences in the binding energies of Si(2p) and O(1s) are negligible for all zeolites studied here with different framework topology (FAU, MFI, MOR, LTA) and different mono- and divalent counterions.

(3) A significant trend in the difference in binding energy is found for the Si(2p) and Al(2p) peaks as a function of the aluminum content of the zeolite, irrespective of its framework topology or counterion. The energy difference decreases almost linearly with increasing aluminum mole fraction.

(4) The effect on the difference in binding energies of Si(2p) and Al(2p) can be rationalized by an increased charge in the zeolite framework upon substituting Al for Si. This charge is redistributed over the various Si–O and Al–O bonds, but leads to an unequal charge distribution in and around SiO₄ and AlO₄ units.

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