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THE EFFECT OF CHEMICAL COMPOSITION AND STRUCTURE ON XPS BINDING ENERGIES IN ZEOLITES

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ABSTRACT

The effect of the composition and structure of zeolites on the XPS core level binding energies has been studied for a large class of zeolites, viz. FAU, MFI, MOR and LTA with Si:Al ratio chabging from 1 to 160. Also the effect of the difference in the counter ions (Na, K, Rb, Ca, Mg, Ba, La) was investigated. As absolute binding energies cannot be determined to any reasonable degree of accuracy we focuss in this work on relative peak positions, which can be found with high precision. The main effect on binding energy differences between silicon, aluminium and oxygen in the zeolites is caused by their aluminium content. Effects of the zeolite structure and the co-cation are far less important. The Si(2p) to Al(2p) XPS peak separation decreases regularly with increasing aluminium content. We performed quantum chemical calculations that enable us to rationalise these findings in terms of a non-homogeneous charge distribution in the zeolite framework.

Keywords: Zeolites, XPS, binding energies, quantum chemistry

INTRODUCTION

Shifts in binding energy for a given element in (chemically) different environments have been noted for a long time. Especially for organic compounds it has a well established basis [1]. Organic substances can often be measured in the gas phase where no charge reference problems occur. Inorganic compounds on the other hand, are commonly insulators and surface charge is almost always present. Thus "observed" binding energies must be corrected for this effect [2], using flood guns, internal standards (such as peaks from the support material of a supported catalyst) or using external standards, such as adventitious carbon [3]. A consistent and correct way of charge compensation is still a matter of debate [4].

In studying the binding energies of silicon, oxygen and aluminium 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. Although data acquisition at high temperatures has been advocated as a means to reduce charge in zeolites [5,6], where the materials become ionic conductors, 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 [7-10].

In a recent review [9] many studies of XPS binding energies in zeolites have been reported. They mostly focus on an accurate determination of the O(ls) binding energy and possible correlations with other (catalytically) relevant parameters. The influence of the amount of aluminium in the zeolite on binding energies has been noted [9] and attributed to differences in the Si-O and AI-O bond ionicity. The influence of the Si:Al ratio on Auger line intensities and oxygen binding energies has been reported as well [11] and ascribed to rehybridisation 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 [12]. The present study complements earlier work in the sense that we study a wide range of composition, a wide range of zeolites and different counter-ions. We will show that the use of adventitious carbon as an internal standard may lead to meaningless results for the absolute value of observed binding energies. Only binding enrgy differences can be obtained with high precision. We will show the only important parameter for binding energy

differences is just the Si:Al ratio in the zeolites. Our findings can be rationalised using a simple representation of a zeolite, which is amenable to ab-initio quantum chemical calculations. In this way we can gain insight in the physical processes occurring when aluminium is substituted for silicon in a zeolite. A full discussion of the material presented here has been given previously [13].

EXPERIMENTAL

The XPS data were obtained with a Vacuum Generators XPS system, using a CLAM-2 hemispherical analyser for electron detection. Non-monochromatic Al(K_α) 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 analyser 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 SiO2 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 millimetre 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 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. Their properties are given in table 1.

Table 1. Survey of the different types of zeolites studied with their silicon to aluminium ratio, mole fraction of aluminium (fAl) in the framework, topology and origin.

Zeolite material	Si/Al ratio	fAl	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

Quantum chemical calculations were done with the GAMESS-UK program [14]. The program uses abinitio methods to solve the non-relativistic 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 ionisation potentials. In this approach all changes in ionisation 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($1s\ 2s^1\ 2p\ 3s^2\ 3p^2$) 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 ionisation potential. Now external perturbations influence both the initial and final state. All calculations were performed with a double zeta basis set [15].

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 non-conducting 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 one eV. Thus, assigning a universal value to (adventitious) carbon would imply a large shift of up to one electron volt for the absolute Si(2p) peak position and is inadmissible for data on the same samples.

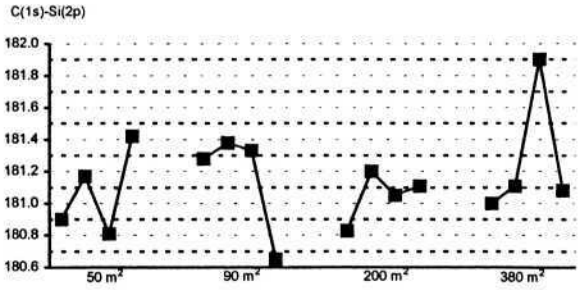

Figure 1. The observed distance (eV) between the carbon 1s and the silicon 2p peak for four different silica samples with surface areas of 50, 90, 200 and 380 m^2/g. The data for each type of silica were collected four times. For ease of comparison related data have been connected by lines. Gridlines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

Differences in binding energy between the constituting elements of a non-conducting sample can, however, be measured with a high degree of accuracy. Figure 2 shows the results obtained for the four SiO_2 samples described previously when plotting the differences between the Si(2p) and Si(2s) peaks and the difference between the O(1s) and Si(2p) peak. The results are remarkably constant and very reproducible. Data for other types of SiO_2 materials (quartz, Sand of Mol) and a different crystal modification of SiO_2 (cristobalite) are also included. Thus we observe that binding energy differences between elements present in the bulk of the sample can be measured with high precision. 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 ionisation is a very localised process. Only local effects, such as a non-tetrahedral arrangement of oxygen, may lead to substantial changes.

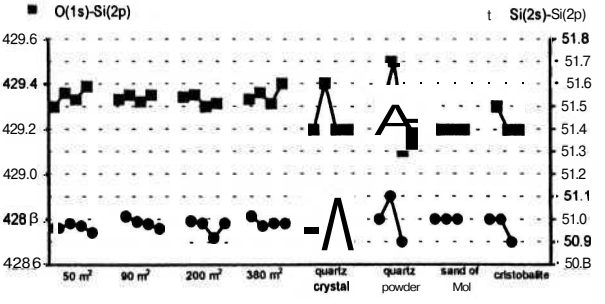

Figure 2. The observed distance (eV) between the oxygen 1s and the silicon 2p peak (left hand axis) and the distance between the silicon 2s and silicon 2p peak (right hand axis) for four different silica samples with surface areas of 50, 90, 200 and 380 m^2/g. Data for a coarse ground quartz crystal, a finely ground quartz powder, Sand of Mol (silica) and cristobalite are also included. Related measurements are connected by lines.

Bearing in mind the restrictions outlined above we have investigated a large number of zeolites, with varying Si/Ai content and different counter ions in order to find a possible correlation between binding energies and zeolite composition. As an example we show in figure 3 the data for zeolite A (with Si/Al=1) and varying counter ions. The results are simply plotted as a "function of ion", so as to show the unbiased data. No obvious correlation can be found, the Si(2p) to Al(2p) distances appear uncorrelated and may even be constant. Points for cesium cannot be obtained, due the overlap of the Cs(4d) and Al(2p) peaks. The O(1s) to Si(2p) binding energy differences are rather constant as well. As, especially for the alkali metals, any physical property varies in a regular fashion when going down a column in the periodic table, there is no simple relation with for instance (ionic) radius or ionisation potential.

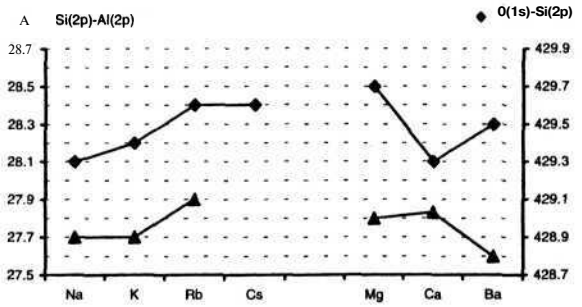

Figure 3. The observed distance (eV) between the Si(2p) and the Al(2p) XPS peak energies (left hand axis) and the O(ls) and Si(2p) peak energy (right hand axis) for zeolite A (Si/Al=1) as a function of the counter-ion.

The data can be replotted in many ways. An often-used correlation is that between binding energy and electronegativity. Figure 4 shows our data, when plotted as a function of the average Sanderson electronegativity (χ) of the zeolite [16,17]. Again 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 4 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.

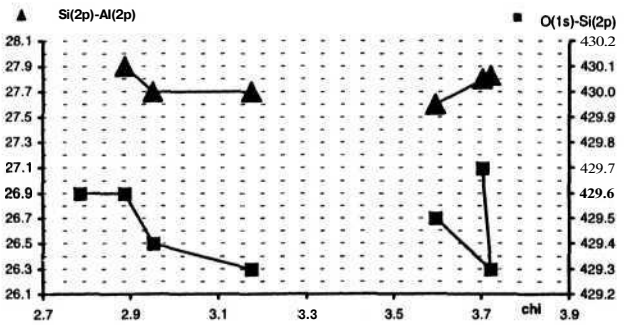

Figure 4. The observed distance (eV) between the Si(2p) and the Al(2p) XPS peak energies (left hand axis) and the O(1s) and Si(2p) peak energy (right hand axis) for zeolite A (Si/Al=1) as a function of the Sanderson electronegativity of the zeolite.

The results can be better correlated when we plot the binding energy differences considered as a function of the aluminium content, or rather the mole fraction of aluminium, for different zeolites with a given counter ion. Figure 5 shows the data for sodium as a counter ion, 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 aluminium in the zeolite. The straight line for sodium is a least square fit to all datapoints. This line has just been shifted upwards 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 aluminium as shown in figure 6. 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.

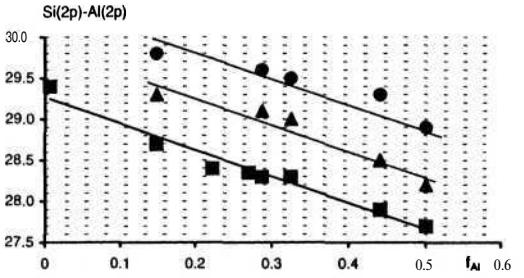

Figure 5. The observed distance (eV) between the O(ls) and the Si(2p) XPS peak energies for a number of zeolites as a function of the aluminium mole fraction for different mono-valent counter-ions. · Na, A K · Rb. The data for K and Rb have been shifted upward by 0.5 and 1.0 and eV, respectively.

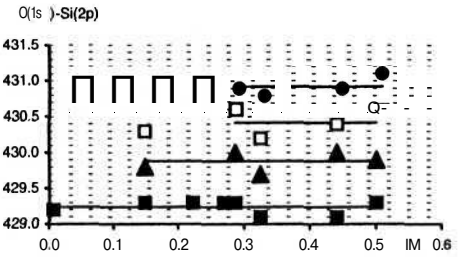

Figure *6.* The observed distance (eV) between the O(1s) and the Si(2p) XPS peak energies for a number of zeolites as a function of the aluminium mole fraction for different mono-valent counter-ions. · Na, A K, D Rb, · Cs. The data for K, Rb and Cs have been shifted upward by 0.5, 1.0 and 1.5 eV, respectively. The average value of each dataset is indicated by a horizontal line.

In order to rationalise our experimental results, which indicate a large effect of the Si/Ai ratio on the binding energy differences between the Si(2p) and the Al(2p) core levels we consider a zeolite to be composed of SiO4 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 A, 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 aluminium 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:

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

The net excess negative charge per cell is equal to the mole fraction of aluminium, 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. This net excess charge must be distributed over SiO_4 and A1O4 units. If we denote their charge by Qsi and Q_{Al} respectively and their ratio by r we have the following equations for the charge in the system:

$$\frac{x}{1+x} Q_{Si} + \frac{1}{1+x} Q_{Al} = -\frac{1}{1+x}$$
$$\frac{Qsi}{Q_{Al}} = r \quad (2)$$

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

$$Q_{Si} = -\frac{r}{1+r\,x}$$
$$Q_{Al} = -\frac{1}{1+r\,x} \quad (3)$$

This equation implies that if x=l (or a zeolite with as much silicon as aluminium) and r=l (or an equal distribution of charge between silicon and aluminium 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:

$$Q_{Si} = -\frac{r}{1+r\,x} = +4 - 4*2 + 4*q_{Si}$$
$$Q_{Al} = -\frac{1}{1+r\,x} = +3 - 4*2 + 4*q_{Al} \quad (4)$$

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

The calculations are now done for a $SiO_4/4q_{Si}$ unit and a $AlO_4/4q_{Al}$ unit using the appropriate values of the mole fraction and using the charge ratio $r=Q_{Si}/Q_{Al}$ 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 aluminium) and those on the four oxygen atoms using the ΔSCF method. The results for the difference in energy between the Si(2p) and Al(2p) levels are shown in figure 7 as a function of the mole fraction of aluminium 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>l 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 counter-ion 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.

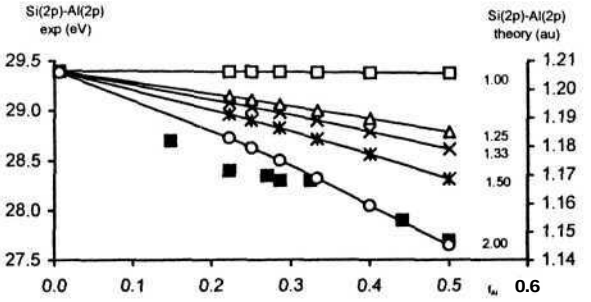

Figure 7. The experimental results for the difference in binding energy in eV of the Si(2p) and Al(2p) peaks as a function of the mole fraction of aluminium in the zeolite framework (left hand axis) for sodium counter-ions. The right hand axis shows the calculated results (in atomic units) with the model outlined in the text for different values of the charge ratio r on the silicon and **aluminium** entities, using the ΔSCF method to calculate the ionisation potentials.

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 ionisation of a silicon atom will be caused predominantly by the electrons on the neighbouring 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 aluminium atom, the effect will be twofold. 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 aluminium) atoms if it is caused by a positive ion. The extra electron released by the change of a silicon atom into an aluminium atom will not remain localised near the aluminium atom, but its charge will be redistributed over the whole zeolite framework. This redistribution will not take place in a symmetrical manner, more charge will be accumulated near a silicon atom than close to an aluminium atom. So their binding energies will be influenced in a different way. Both will decrease with increasing electron density, but the decrease for aluminium is less than that for silicon, leading to a smaller separation between the Si(2p) and Al(2p) peaks with increasing aluminium content.

The influence of a change in cation may be rationalised 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 to first order expect that changing it to potassium or rubidium would not lead to a large effect, as indeed is does. Of course sodium does affect the charge on the oxygen atoms, and in this way the charge seen by the silicon and aluminium atoms, but the effect of a different **mono-valent** ion will be small, as evidenced by the data in figure 5. 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 counter-ions 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 7 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 summarised as follows:

1. Absolute binding energies of the non-conducting samples studied in this paper cannot be obtained by simply referencing them to the value of adventitious carbon.
2. Differences in binding energies can be measured with high precision.
3. The differences in the binding energies of Si(2p) and O(ls) are negligible for all zeolites studied here with different framework topology **(FAU, MFI,** MOR, LTA) and different mono- and di-valent counter-ions.
4. A significant trend in the difference in binding energy is found for the Si(2p) and Al(2p) peaks as a function of the aluminium content of the **zeolite,** irrespective of its framework topology or counter-ion.

The energy difference decreases almost linearly with increasing aluminium mole fraction.

5. The effect on the difference in binding energies of Si(2p) and Al(2p) can be rationalised by an increased charge in the zeolite framework upon substituting A! for Si. This leads to an unequal charge distribution in SiO_4 and AlO_4 units.

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