J. Am. Chem. Soc. 1986, 108, 3178–3186

ESCA Studies of the Surface Chemistry of Zeolites

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Abstract: It has been demonstrated that the constituents on the surfaces of various pure zeolites, clays, silicas, and aluminas yield reproducible ESCA peaks with unique binding energies. The collective patterns realized by these different binding energies strongly suggest the registration of selective "group" rather than "elemental" chemical shifts. The two primary chemical groups identified in many of the zeolites seem to be a unit that resembles SiO_2 and another that mimics $N^{+(+)}–Al_2O_4^{2-}$ (where N symbolizes the cations, usually alkali or alkaline earth species that balance the aluminate charge), a feature supported by quantum calculations, relatively narrow line widths, and reproducible valence band and loss data. These results have been employed to determine the relative purity of the surface region of different conventionally prepared zeolite systems. High-resolution ESCA studies of mordenite, ZSM-5, and silicalite surfaces always seem to exhibit Al(2p) spectra that are significantly broadened into patterns that suggest several Al-containing species. The nonzeolites present at the surface of these systems generally constitute more than 50% of the total aluminum. The primary "impurity" species have been identified as metal aluminates and aluminas in differing ratios apparently depending upon the cation (e.g., sodium) concentrations. The possible presence of silica on the surface of some freshly prepared zeolite systems is suggested, but unconfirmed. Binding energy differences have been found between the ZSM-5 and silicalite systems that are consistent with the aforementioned group substitution pattern. It is uncertain, as of yet, whether the latter differences result simply from the change in the Si/Al ratio or are indicative of some unique structural dissimilarity between the two systems.

Despite their importance, surprisingly few studies of zeolite surfaces exist in the literature.[1,2] Several recent publications[3-5] reported from this laboratory described results which suggest the ability to utilize ESCA binding energy shifts to identify the surface (chemical) characteristics of different alumino-silicate systems, particularly of different zeolites. In establishing these results, care was employed to try to ensure that the materials were, in fact, of sufficient purity to justify the proported identifications. It is well-known, however, that many zeolites, particularly those of commercial origin, often may be compromised by variously dispersed "impurities". If these impurities exist, they should be primarily "clusters" of aluminas, silicas, metal aluminates or silicates, or perhaps complicated aluminosilicate byproducts. These species may result from the preparation process or perhaps may be generated during some subsequent degradation. For some systems, the presence of these impurities has been suggested to be particularly prevalent at sites at or near the surface.[6,7] In view of the present results, one should consider with care the extremely relevant studies of Dwyer et al.,[6] who utilizing fast atom bombardment mass spectrometry (FABMS) detected (for systems similar to those in the present study) surface Si/Al ratios that differed dramatically from the bulk, and also evidence for bulk dealumination that seemed to indicate deposition of the aluminum at the surface. [The term *surface* employed herein will be restricted to the outer ~50 Å of material, the *bulk* technically refers to the balance; however, one should note that there is, in reality, a largely undetected area (X) (where $50\ \text{Å} < X < \sim 1000\ \text{Å}$) that lies between the regions detected by surface techniques and that *primarily* detected by bulk methods (e.g. NMR, X-ray fluorescence, EDX, etc.). This may not be a problem for zeolites since the restrictions of their structure provide little space for novel features in these "intermediate" regions. In fact, many researchers seem to question the conventional use of "surface" and "bulk" terminology for these extremely porous systems. Results from many laboratories, including this one, however, strongly dispute the oft repeated claim that zeolites are "all surface". However, a companion assertion that surface spectroscopies examine only the compromised outer (physical) layer of material is more difficult to challenge. Our results (and those of others) seem to negate this assertion, but proof awaits further study.] One may question the absolute accuracy of the quantitation obtained by surface mass spectrometry, but the reproducible variations reported in the results of Dwyer et al.[6] can only be adequately explained in terms of significant differences between the bulk and surface composition. It is important, therefore, to "challenge" the utility of the aforementioned ESCA identifications by examining a variety of zeolite systems to see if the surface impurities and variations suggested by FABMS are also detected by ESCA and if so if there are any chemical patterns, both qualitative and quantitative, detectable in these features.

In the following, therefore, the ability to detect ESCA variances between different aluminosilicate species is extended to the aforementioned zeolite impurity problems. It is important to realize that (1) all of the materials described are fresh preparations made by conventional techniques outside our organization and obtainable in the same or similar lot by other researchers and (2) all materials exhibited bulk composition and structural characteristics within the specificiations stated by their producers.

Experimental Section

(A) Materials Examined. The materials featured in this study were obtained from common outside suppliers. All were purported to have excellent composition and structural integrity. These materials were obtained as fine mesh powders and were all (lightly) pressed into thin (relatively) smooth cylindrical wafers in the specially designed HP ESCA platens. The question of the "state of presentation" of this type of sample has been previously examined and described.[3] Suffice it to say, at present, that, although small ESCA variations have been found that may (in some way) relate to sample preparation (e.g., the pressure employed in preparing the cylindrical disks may perhaps affect such properties as surface hydration, etc.), these differences have been found to be inside of the error bars of the present study and, as of yet, are of unknown origin. Therefore, at present, any effects related to sample presentation will be assumed to be negligible and ignored. This feature is a point for subsequent studies.

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(1) Auger examples include the following: Suib, S. L.; Stucky, G. D.; Blattner, R. J. *J. Catal.* **1980**, *65*, 174, 179. Suib, S. L. Coughlin, D. F.; Otter, F. A.; Conopask, L. F. *J. Catal.* **1983**, *84*, 410.

(2) ESCA examples include the following: Dejaifve, P.; Vedrine, J. C.; Bolis, V.; E. G. Derouane, E. G. *J. Catal.* **1979**, *59*, 248.

(3) Barr, T. L. *ACS Div. Petrol. Chem.* **1978**, *23*, 82.

(4) Barr, T. L. *Appl. Surf. Sci.* **1983**, *15*, 1.

(5) Barr, T. L. In *Practical Surface Analysis by Auger and Photoelectron Spectroscopy*, Briggs, D.; Seah, M. P., Eds.; John Wiley & Sons, Ltd.: New York, 1983; Chapter 8.

(6) Dwyer, J.; Fitch, F. R.; Machado, F.; Quin, G.; Smyth, S. M.; Vickerman, J. C. *J. Chem. Soc., Chem. Commun.* **1981**, 422. Dwyer, J.; Fitch, F. R.; Qin, G.; Vickerman, J. C. *J. Phys. Chem.* **1982**, *86*, 4574.

(7) (a) Tempere, J. F.; Delafosse, D.; Contour, J. P. *Chem. Phys. Lett.* **1975**, *33*, 95. (b) Kneckt, J.; Stork, G. *Z. Anal. Chem.* **1977**, *283*, 105. (c) Tempere, J. F.; Delafosse, D.; Contour, J. P. *Molecular Sieves-II*; Katzer, J. R., Ed. ACS Symposium Series 40; American Chemical Society: Washington, DC, 1977.

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(B) Analysis Equipment. All surface studies were conducted with a Hewlett-Packard (HP) 5950A ESCA spectrometer. Most of the attachments of this system that are key ingredients in these analyses have been described elsewhere in some detail,[8] therefore, these descriptions will not be repeated herein. It should be noted that both the resolution and stability of the HP system, and the conventional (HP 18623A) electron flood gun, played integral roles in the present analyses. In particular, all readers interested in the "mechanics" of these examinations should study in detail the methodology employed to remove the charging shift inherent to all these systems and also the resulting lack of a fixed Fermi edge.[4,5,8,9] In the present case, similar procedures were employed, and the authors acknowledge that these controversial areas may present problems, particularly in view of the possibilities of differential charging. However, despite these potential pitfalls, it is our contention that the results and conclusions to be described herein were successfully achieved and not compromised. These aspects will be described in some detail in a subsequent section of this paper. In general it should be noted that *the excellent reproducibility of results is one of the strongest features supporting the suppositions to follow.* In this regard, in all of these measurements, the HP system was operated such that it generated the following (optimal) binding energy scale:

$$\mathrm{Au}(4f_{7/2}) = 83.95 \pm 0.05\ \mathrm{eV}$$

$$\Delta(\mathrm{Au}(4f_{5/2}) - \mathrm{Au}(4f_{7/2})) = 3.70 \pm 0.05\ \mathrm{eV}$$

$$\mathrm{Cu}^{\circ}(2p_{3/2}) = 932.55 \pm 0.05\ \mathrm{eV}$$

Also, unless stated otherwise, the reported binding energies for the silica-aluminate systems exhibited a precision of

$$\Delta\mathrm{BE} = \pm 0.15\ \mathrm{eV}$$

Most of the semiquantitative information generated in this study was achieved while utilizing an HP-2100A 32K minicomputer and the HP System Three software for data generating, storage, and treatment. Unfortunately, only a few of the reported examinations were conducted while utilizing a more versatile, new data system capable of detailed peak deconvolution and more exact relative quantitation. Because of this, the error bars attached to the composite of the numbers realized on System Three are much broader than are presently being realized. A reexamination of all of these materials will be completed in the near future and more precise values reported for the relative quantitation.[10] The most important features of these total results, however, are the type of species detected and their *approximate* surface distribution. This information may be obtained from the present analysis. Preliminary evaluation of the more accurate quantitative results now being generated (see below) indicates that *the general conclusions will not change.* (It should be noted that a more precise evaluation of the relative quantitation is probably an interesting demonstration but is almost certainly not a very meaningful one, because it is doubtful that the batch preparative and handling procedures that are employed in manufacturing and transporting these materials can physically reproduce surfaces within these finer limits.)

The H.P. ESCA system was employed at an analyzer pressure of $\sim 1 \times 10^{-9}$ torr. The temperature in the analyzer chamber was maintained at ~ 25 °C. The "soft" nature of the monochromatized Al Kα X-rays produced no materials damage that could be *detected by the ESCA.* Leaving these zeolites in the X-ray beam for several days did, however, result in a slight brown "stain" in the exposed area. The exact source of this problem is unknown; however, comparisons with other related effects suggest it may be due to either surface dehydration or the trapping of a free electron in a hydrated cation unit. ESCA analysis of these species after the appearance of the brown stain produced essentially the same result as before the stain.

In addition to the analysis of the outer surface of these "fresh" zeolites, referenc has been made to results achieved by argon ion sputter etching.[4] This process was conducted in a 99.99% argon gas that was further purified over a titanium ion sublimation pump. Sputtering was accomplished with a PHI sputtering system, with a gas pressure of $\sim 5 \times 10^{-5}$ torr, at beam currents of $\sim$10–15 μamps and energies of 500–900 eV. The results will only be referred to in the present study. The details of their generation, meaning, and limitations are described elsewhere.[4]

Results

(A) Pure Species. (1) Establishment of the Binding Energy Scale. As stated above, methods were developed employing the electron flood gun to remove the charging shift inherent to all of these systems. Similar, but significantly different, current settings were found to be necessary for aluminas (0.4 mA), silica (0.5 mA), and zeolites (0.3 mA). No additional kinetic energy seems to be needed.[3] Slight current variations may be appropriate between different zeolites, but the uncertainties of the methodology place these variations inside of our error brackets. The shift removal was "optimized" against the production of the narrowest possible ESCA lines with standard Lorentzian features. Some systems (generally of heterogeneous composition) have been examined that defy this approach, but this is not the case for any of the present materials. Several specific examples of the use of this procedure were displayed in ref 4.

After removal of the charging shift it is still necessary to "locate" the Fermi edge.[5,9] This process is even more uncertain and, therefore, potentially more inaccurate than the removal of the charging shift.[9] There are several (possible) procedures for establishing, in the ESCA, an energy level that loosely resembles a Fermi edge for nonconductive materials (such as those being described in the present study). Several useful approaches for singular, alumino-silicate systems were described in some detail in previous publications.[4,5] These deal primarily with trying to fix the binding energy of one of the elemental constituents on the surface of the materials system. In some cases this constituent may be a persistent surface impurity such as adventitious carbon.[11] One must be very wary in the use of this approach, however, as the classification of an uncontrolled contaminate as a singular, scale-establishing species does not assure one of its origin or final form. For example, ESCA examination of more than one thousand nonconductive species in our HP ESCA laboratory has revealed *several chemically different types of adventitions carbon* (even when the surfaces are carefully exposed only to clean air). In general, however, it has been found that most zeolites and aluminas, with similar (*nonuse*) histories, exhibit nearly identical adventitious carbon components. From these it is generally possible to separate out the polymeric hydrocarbon part that is commonly sought as the key to the binding energy scale. The relative quantitation of C–C, C–H, C–O, and other carbonaceous species may still vary in ways that presently defy exact description.[12] All of these problems generally make it inappropriate to use the C(1s) peak as the *sole* means for establishing the binding energy scale. Therefore, the use of additional checking procedures is strongly recommended. In the present studies these have included the following:

(a) The Auger parameter has been measured.[13] (Note that Wagner et al. have also detected similar zeolite shifts with this procedure, see below.)[14]

(b) The XPS-induced loss shift has been measured. Characteristic values have been detected for some zeolites. These will be described elsewhere.[5,15]

(c) The ESCA-induced valence band spectra were measured. It has been determined that the valence band spectra for different zeolites differ from one another in several key (reproducible) ways, e.g., their shape, the binding energy of the (half-height) leading edge, and their band width.[4,5,16] Representative examples of these results are displayed in Figure 1.

(d) A set of fixed binding energies for a common *silica-alumina* impurity were used; for example, the Si(2p) and O(1s) values for α-quartz have been fixed (based upon our best judgement) and all other binding energies for the elemental constituents of many

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Table I. Bulk and Surface Si/Al Ratios for Selected Zeolites

	R_b bulk Si/Al[a]	R_s surface Si/Al[b]
NaA	1.0	1.0
NaX	1.2	1.3
NaY	2.4	2.7
mordenite (Na form)	5.0	6.7
ZSM-5 (Na form)	23.3	25.2

[a] Determined primarily by X-ray diffraction $\Delta \cong \pm 0.20$. [b] Determined primarily through ESCA peak areas of Si(2p) and Al(2p), employing for the cross-section ratio $K_{Si/Al} \cong 1.5$ and a depth of analysis of $\lambda Si/\lambda Al \approx 1.0, \Delta \cong \pm 0.2$ except for ZSM-5 where $\Delta \cong \pm 0.4$.

systems have been simultaneously referenced to these values, as well as the aforementioned C(1s).

(e) There was also an understanding that the chemical binding energy shifts ($\Delta E_B{}^{1\alpha}$) for any element (1) and photoelectron (α), e.g., $E_B{}^{Si(2p)}$(CaX) - $E_B{}^{Si(2p)}$ (NaX) for these physically similar materials, are essentially independent of the establishment of a fixed Fermi edge, after the charging shift (which depends dramatically upon the *physical* conditions of a system) has been removed.[3]

In the case of the binding energies reported hereafter in this paper, all were verified by independent agreement from at least two of the above methods. In all cases reproducibility was achieved to within the range of precision stated in the Experimental Section, even when examining the "same" material from different manufacturers.

Note that the technique of doping the surface of the system in question with a pure elemental (conductive) species of known binding energy, e.g., Au, has been purposefully ignored. This procedure has been called to question by one of the present authors[9] because a conductive material that is "imbedded" into a surface insulator often does not have its Fermi edge coupled to that of the spectrometer. Therefore, the conductive material may be either part of the phase that supports a charge (if reasonably dispersed in the insulating phase) or may, at least, have a Fermi edge that is "floating" off of that for both the spectrometer and the wide band gapped (insulating) material. These facts make this procedure (often called dotting) suspect, although, if adroitly employed, this method sometimes may make a useful addendum to the above list.

(2) **Purity of the Materials Examined.** As mentioned above, all of the zeolite systems described in these studies have significant amounts of adsorbed adventitious carbon on their surfaces due primarily to atmospheric exposure. [This fact is, of course, also true for *all* solid surfaces not cleaned and retained in ultra-high ($<10^{-10}$ torr) vacuum.] In addition, all materials examined in these studies are known to have varying amounts of surface hydration (or hydroxides). The relative amount of the latter is hard to determine, because H cannot be detected in the ESCA and the O(1s) peak for OH^- is hard to separate from many of the other "oxide" peaks detected for these glass-forming oxide systems.[16] Since surface hydration may differ substantially from bulk hydration this is an important unknown feature. Attempts are presently under study to describe the effects that variable hydration has on the ESCA results. Although anticipated to create small variations, these effects are not expected to modify the present "general" conclusions.

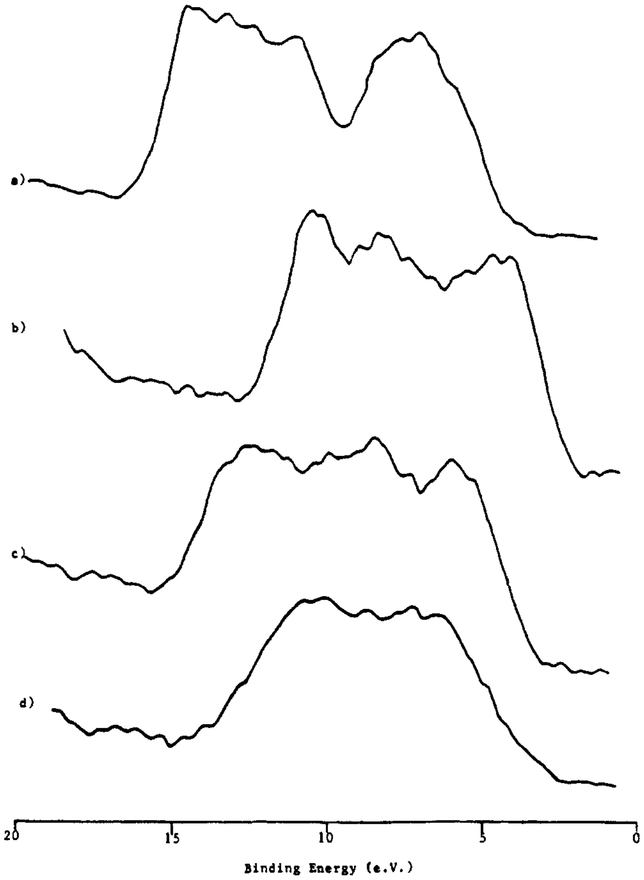

Figure 1. Representative valence band spectra of (a) (clean) ZSM-5, (b) NaA, (c) NaY, and (d) α-Al_2O_3.

Except for the above impurities, the sodium forms of most of the "pure" zeolite species obtained from commercial suppliers or produced by conventional recipes appear to have sufficiently *clean* surfaces to validate all results, see, for example, Table I. In the case of the systems whose specified cation is not sodium, substantial impurities of at least a second cation (usually sodium) were sometimes detected, e.g., in CaA. Although somewhat confusing, these facts do not appear to affect the present conclusions. For example, when incomplete exchange occurs, the binding energy shifts attributed to the newly introduced cations seem only partially realized. These effects were taken into consideration in constructing the subsequent tables for "pure" species.

(3) **Binding Energies, Line Widths, Valence Bands, and Sputter Etching.** Tables II and III list the key elemental (ESCA) peak binding energies and line widths identified as those for the "pure" silica-aluminates in question. [In addition to the problems described above, the reason for the point of emphasis on the word "pure" will become more apparent in succeeding sections of this paper.] On the basis of the procedures described above, it has been established that given a reference scale, which has been fixed *primarily* to the C(1s) of the *appropriate part of the adventitious carbon* at 284.4 eV (see above), the binding energies listed in Table II are reasonably precise and, therefore, the shifts detected between the various reported elemental binding energy peaks are purported

Table II. Representative Binding Energies in eV (±0.1 eV); Charge Shifts Removed C(1s) = 284.4 eV

	SiO_2	ZSM-5	NaY	bentonite	CaX	NaX	kaolinite	γ-Al_2O_3	NaA	$NaAlO_2$[b]
Si(2p)	103.35	102.90	102.35	102.50	102.25	101.75	102.25		100.90	
Al(2p)		74.50	74.00	74.60	74.35	73.70	74.10	73.60	73.20	73.20
O(1s)	532.65	532.25	531.55	531.80	531.40	530.85	531.30	530.35	530.20	530
Na(1s)				1073.15[a]		1072.05	1071.75[a]		1071.45	
Na(2s)			63.80	64.05[a]		63.55			63.00	
$Ca(2p_{3/2})$					347.90					

[a] Impurity—Note that there may be small to moderate quantities of other cations in the zeolites due to incomplete exchange. [b] The surface of air-exposed sodium aluminate suffers extensively from carbonation[8] (Na_2CO_3 formation). Cleaning can be difficult producing enhanced uncertainties in the stated results, particularly in sodium values.

Table III. Selected Line Widths for Zeolite Peaks Listed in Table II (eV ± 0.15 eV)

	NaY	CaX	NaX	NaA
Si(2p)	1.68	1.82	1.77	1.72
Al(2p)	1.55	1.86	1.60	1.56
O(1s)	2.05	2.08	1.65	1.75
Na(2s)	1.65		1.67	1.65
Na(1s)	1.95		1.95	1.92
C(1s)	1.50		1.52	1.44
Ca($2p_{3/2}$)		1.94		

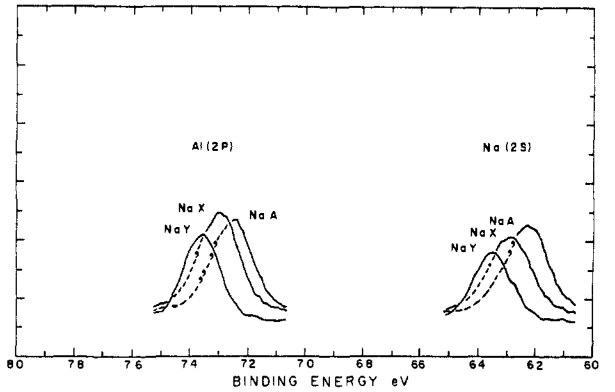

Figure 2. Al(2p) and Na(2s) spectra for NaA, NaX, and NaY. Note the obvious "structural" shift.

to be real. As described in our previous publications,[3-5] the most disturbing feature of these binding energy shifts is not their presence but rather the direction that these shifts seem to follow, e.g., during an examination of first NaA and then NaX the Na, Si, Al, and O peaks *all increase* in binding energy, see, for example, Figure 2. This seems to be contrary to the common trend, where positive binding energy shifts in some elemental (cation-like) constituents are usually countered by negative shifts in other elemental (anion-like) species. These cases are, of course, complicated by the fact that for zeolites it is the elemental distribution that varies rather that the kind of element. A possible explanation for these confusing features may be realized by noting that the basic cation–anion units in these silica-aluminate species (e.g., NaA, NaX, etc.) *are not elemental* but rather *group "clusters"*, represented by the replacement of, for example, $Na^+AlO_2^-$ with SiO_2 units.[4] Noting the respective binding energies of the elements in SiO_2, $Na_2Al_2O_4$, and Al_2O_3, it is apparent that the substitution of silica for aluminate "promotes" a positive binding energy shift in the aluminate unit and a corresponding negative shift in the silica unit. Additional justification for these conclusions, based upon analogies with changes in charge densities, have been found in the results of simple quantum calculations made by others[17] and confirmed in this laboratory.[4,10]

Other researchers have pointed out examples of apparent unidirectional "group" binding energy shifts for some "complex" molecular units,[18] but the present case is perhaps the most detailed example yet reported. *In summary, for zeolites and silica-aluminate type clays, the silica seems to function as the cation-like unit, whereas the aluminate exhibits anion-like characteristics,* (see Table IV).

Several features in Tables II and III support the contention that the formation of the zeolitic (crystalline) unit from alumino-silicate components exerts an influence on the resulting binding energies and line widths. For example, there is evidence that some of the line widths may narrow as a result of zeolite formation (e.g., Bentonite compared to NaY). In addition, zeolite formation may in some cases actually change the binding energies of the elemental constituents. For example, this feature may be the cause of the significant lowering of the binding energies of the common constituents of NaA compared to kaolinite. (Note that both systems have $[\mathrm{Si/Al}]_b \cong 1$). However, it should be noted that kaolinite is not an aluminate, but rather an alumina-containing system, and the higher binding energies of the latter compared to sodium aluminate may actually dictate the aforementioned differences. The higher binding energies of bentonite ($[\mathrm{Si/Al}]_b \approx 2.0$) compared to NaY ($[\mathrm{Si/Al}]_b \cong 2.5$) are perhaps further proof of a *zeolite formation effect* on the binding energy shifts. These results seem to suggest that aluminates are more negative than aluminas and thus the former "induces" larger negative shifts in the relatively positive SiO_2 unit. Several other effects seem to "mimic" these shifting patterns, including the resulting changes in the aforementioned valence band and ion sputter etching studies.[4] For example, the valence band width (at half-maximum) grows progressively with Si/Al ratio in the sequence $Al_2O_3 \rightarrow$ through various zeolites $\rightarrow SiO_2$, see Table 6 in ref 4. Thus, the shifts documented in Table II may result from changes in structural as well as compositional features.[3,4]

Table IV. Groupings of Selected Binding Energy Shifts (in eV ± 0.1 eV)[a]

	NaY–NaA	NaY–NaX	CaY–CaA
Si(2p)	1.45	0.70	0.80
O(1s)	1.25	0.75	0.80
Al(2p)	0.90	0.35	0.45
Na(2s)	0.95	0.40	0.35[b]
Ca($2p_{3/2}$)			0.35

ΔSi(2p) for SiO_2–NaA ≅ 2.5 eV
ΔAl(2p) for bentonite–NaA ≅ 1.5 eV

[a] Note that in general Si and O shift as a group, whereas Al and the cation do also!
[b] Extensive impurity.

Table V. Comparisons of Common Binding Energies Achieved by Wagner et al. (W)[14] and Barr (B)[2] Adjusted to C(1s) = 284.6 eV[a]

		Al(2p)	Si(2p)	Na(1s)
NaA	W	73.46	101.23	1071.5
	B	73.40	101.10	1071.65
NaX	W	73.93	101.96	
	B	73.90	101.95	
NaY	W	74.25	102.64	
	B	74.20	102.55	
α-Al_2O_3	W	73.52		
	B	73.80		
α-SiO_2	W		103.45	
	B		103.55	

[a] Picked as an intermediate point between the range of values presently suggested, i.e., 284.8 ↔ 284.4 eV.

As will become more apparent below, the progressions exhibited in the line widths (Table III) are also very important parts of this analysis. For example, there seems to be a tendency for zeolite formation to cause a narrowing of all peaks, particularly for the sodium zeolites. Thus, the average value for the Si(2p) and Al(2p) line widths for NaA, X, and Y is ~1.6 eV, whereas these same lines are significantly broader for SiO_2, the aluminas, and even some clays. In view of the aforementioned differences in the binding energies of the elemental constituents it is anticipated that mixtures of pure systems will also create line broadening and possibly even shoulder effects (see below). (Note that "absolute" line widths are only meaningful when compared to each other, since line widths reflect the resolution of the particular detection system and therefore should not be compared to those obtained with other spectrometers.)

Many of the aforementioned arguments are supported by the existence of independent corroboration. Wagner et al.[14,19] have recently published detailed XPS results of silica–aluminate sys-

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(17) Clarke, T. A.; Rizballa, E. N. *Chem. Phys. Lett.* **1976**, *37*, 523.

(18) See for example: Evans, S.; Thomas, J. M. *J. Chem. Soc., Faraday Trans. 2* **1975**, *2*, 313. Thomas, J. M.; Tricker, M. J. *J. Chem. Soc., Faraday Trans. 2* **1975**, *2*, 329.

(19) Wagner, C. D.; Passoja, D. E.; Hillery, H. F.; Kinisky, T. G.; Six, H. A.; Jansen, W. T.; Taylor, J. A. *J. Vac. Sci. Technol.* **1982**, *21*, 933.

tems, primarily designed to demonstrate the attributes of the Auger parameter (which they seem to confirm). During the generation of these Auger parameters, core binding energies were also obtained for many of the systems investigated in the present study. The binding energies from both studies are in excellent agreement, see Table V. Note also that Wagner et al.[14] also report a progressive development in the Auger parameter for the "family" NaA, NaX, and NaY that seems to "map" the trend detected in our binding energies.

Corroboration from one laboratory, such as Wagner's, is supportive, but confirmation by several laboratories is ideal. Because of the general lack of binding energy studies of zeolites this type of detailed corroboration would appear to be out of the question, except that one study does exist that resulted in the collective examination of the key binding energies for NaA, SiO_2, and an alumina by more than one dozen independent laboratories. This study, commissioned and reported by ASTM,[20] would seem to be a poor choice for the confirmation of anything because of the disturbing, broad spread in the resulting binding energies. However, close examination of the average or "centroid" of the ASTM results (see Figure 8.1 in ref 5) reveals several features that strongly support the progression and relative sizes of the shifts described in the present study. Thus, in the ASTM study[20] the key average shifts ($\langle\Delta\rangle$) are: Si(2p) for SiO_2–NaA $\sim +2.3$ eV and Al(2p) for Al_2O_3–NaA ~ -0.5 eV. These values compare quite well with those realized in the present study, see Table II.

(B) Freshly Prepared Standard Zeolites—Characteristics and Impurities. (1) General Considerations—Surface and Bulk Si/Al Ratios, R_s and R_b. Previous XPS studies of zeolites have often been concerned with the surface Si/Al ratio, R_s, and its relationship to the corresponding bulk value, R_b. This attention has produced a minor controversy because some researchers[7a] have detected substantial variation in the R_s/R_b ratio claiming a value of ~ 1 near $R_b = 1$ and values greater than 2 for $R_b = 5$. (These results have led to the prediction of a (selective) surface dealumination that seems to grow with increasing R_b.) Other researchers examining supposedly the same materials have found distinctly different results.[7b] Results have been reported from this laboratory[5] that suggest a growth in R_s/R_b with increasing R_b (for some zeolites, see Table I), but, if real, we find the growth to occur at a much more gradual rate than suggested by Tempere et al.[7a] (Note that Tempere has since communicated to one of us (T.L.B.) the observation of a more gradual rise in R_s/R_b.[7c] The FABMS results of Dwyer et al.[6] also seem to suggest that there is dealumination in the surface region of some zeolites but that in some cases it occurs in the "subsurface" area and that the migrating aluminum may subsequently deposit on the surface (probably as an alumina).

All of this seems to suggest that freshly prepared zeolites of supposedly the same composition may vary substantially in their surface composition with a resulting uncertainty as to the purity and, if present, the position of any impurities. The results seem to suggest, for example, a possible tendency for some impurities to concentrate at or near the surface.

With these "prospects" in mind, it is of interest to carefully examine the surface properties detected by ESCA for fresh and commercially prepared reagent grade zeolites, with the intent of (a) detecting the extent (if any) of the deviations from bulk composition and (b) attempting to use the "chemical shift" capability described above to actually detect the types of nonzeolite surface components and their relative concentrations.

All of these arguments are, of course, predicated upon the assumption that the bulk of the zeolite system under study may be assumed to contain the zeolite in question, with excellent (uniform) chemical and structural integrity. For some of the "fresh" zeolites to be described this last feature may, in fact, be untrue. For example, studies have recently indicated that ZSM-5 systems may often grow in very selective layer zones (SiO_2 rich, etc.).[21] Similar selective layers may indeed form during the growth of many zeolitic systems, and because they may be so superficial (by bulk standards), they may not have been "detected" by conventional bulk (X-ray spectroscopic and NMR) techniques.[22] There is some evidence from a combination of our surface and subsurface (sputter etching) results that the ESCA may actually have detected some of these zonal layers.[4,10] However, without further supportive studies these possibilities remain unconfirmed. Therefore, the analyses to be described in the balance of this paper must, at present, be restricted to the description of the surface anomalies (if any) detected during ESCA studies of (in most cases) freshly prepared zeolite systems, whose properties seem to exhibit sufficient bulk integrity to be classified as of acceptable chemical and structural purity.[6]

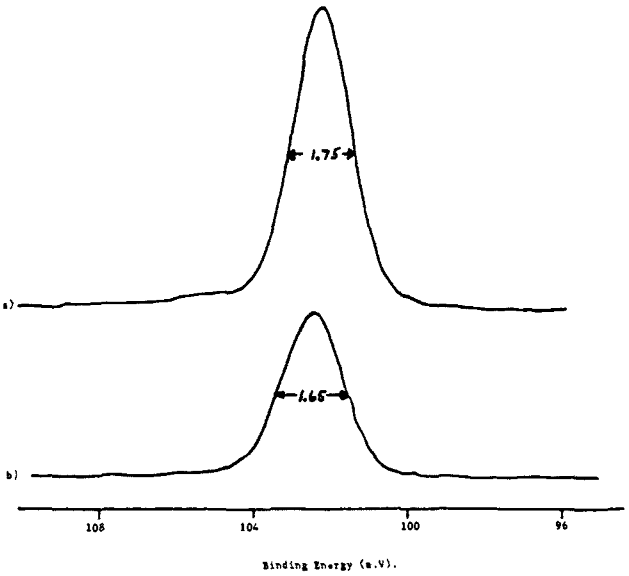

Figure 3. Si(2p) spectra of (A) mordenite and (B) representative ZSM-5. Note relatively narrow lines and shift.

(2) Examination of the Components Detected at the Surface of Zeolites. (a) Initial Description of the High-Resolution Results for NaA, NaX, and NaY. The sodium version of the common zeolites formed around the basic sodalite cage structure,[5,6] e.g., A type and faujasites, generally produces ESCA results that strongly suggest the presence at the surface of relatively pure zeolite species. This purity is reflected in part by the repetition achieved in the binding energy measurements and also by the narrow line widths realized in the high-resolution scans of all of the components in NaA, NaX, and NaY, Table III. However, only the Al(2p) is consistently narrow, the Si(2p) generally seems to be somewhat broader, whereas the O(1s) spectrum also may be broadened by a factor of ~20%. The broadening of the Si(2p) line may be indicative of a slight increase in surface dealumination as previously suggested to occur when R_b increases,[6,7] thus perhaps leaving behind a slight SiO_2 residue(?). The rather broad O(1s) line width has also been obtained in the ESCA results of numerous other zeolite systems. This broadening of the O(1s) line may also be attributed to dealumination or perhaps other anomalies, such as different states of surface hydration. (It should be noted that tests designed to detect small quantities of silica purposefully mixed with NaA zeolite have as yet proven inconclusive.)

Therefore, despite the possibility of some dealumination, particularly for the Y system, the uniform, narrow line widths and lack of evidence for distinct nonzeolitic Al(2p) or Si(2p) shoulders suggest the surface presence of *essentially* pure zeolites for these zeolites constructed around the sodalite cage.

(b) High-Resolution Results for Mordenite, ZSM-5, and Silicalite. Several zeolite systems with $R_b > 4$ have been found to

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(20) Madey, T. E.; Wagner, C. D.; Joshi, A. *J. Electron Spectrosc. Rel. Phenomena* **1977**, *10*, 359.

(21) Derouane, E. G.; Detremmerie, S.; Gabelica, Z.; Blom, N. *Appl. Catal.* **1981**, *1*, 201.

(22) Klinowski, J.; Thomas, J. M.; Fyfe, C. A.; Gobbi, G. C.; Hartman, J. S. *Inorg. Chem.* **1983**, *22*, 63. Fyfe, C. A.; Gobbi, G. C.; Klinowski, J.; Thomas, J. M.; Ramdas, S. *Nature (London)* **1982**, *296*, 530.

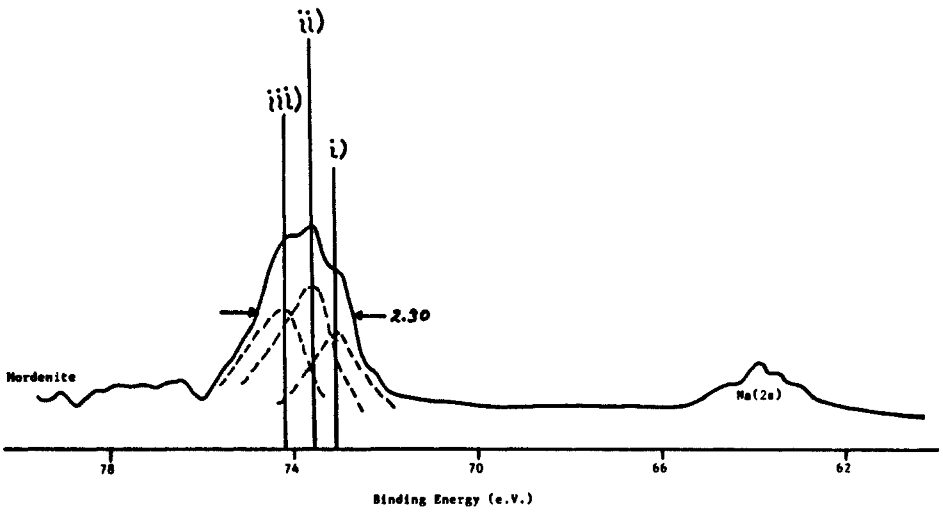

Figure 4. Al(2p) spectrum of representative mordenite. Note line width and multiplicity of proposed peaks. Binding energy scale not Fermi edge referenced.

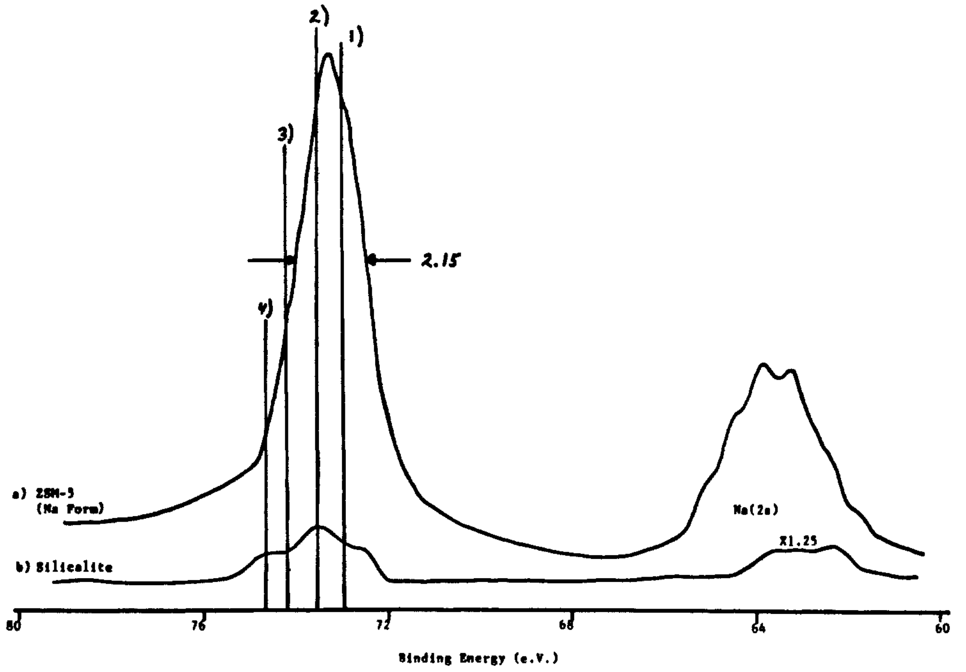

Figure 5. Al(2p) spectra of representative (a) ZSM-5 (Na form) and (b) silicalite.

exhibit significant, selective deviations from the patterns described previously for zeolites formed from the sodalite unit. In addition, many of the patterns displayed by those systems with large Si/Al ratios bear striking similarities. For example, the sodium-hydrogen forms of mordenite,[6] ZSM-5,[23] and silicalite[24] all exhibit narrow Si(2p) and O(1s) lines, whose characteristics are similar in structural "appearance" to those previously described for the sodalite-containing systems. ("Similar", of course, except for the expected "group" shifts, see Table II.[3,4]) Examples of these features are displayed in parts a and b of Figures 3, where the Si(2p) binding energies suggest zeolites of large Si/Al ratio and the line widths (~1.7 eV) exemplify relatively pure materials. These results are, however, in sharp contrast to those obtained for the Al(2p) peaks of these same ($R_b > 4$) systems.

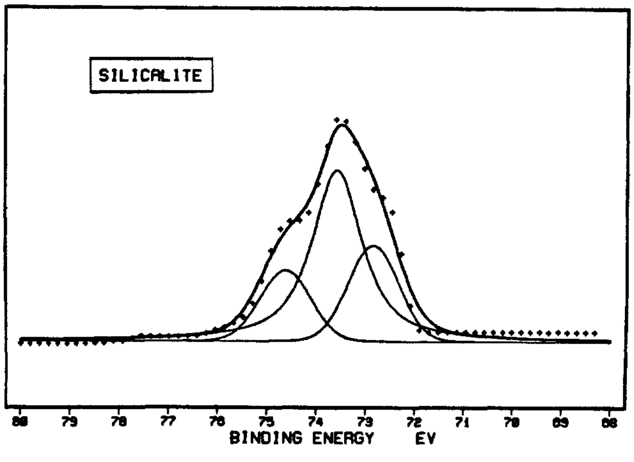

Figure 6. Computer deconvolution of the point rendition of the Al(2p) line of the Silicalite spectrum in Figure 5. None of these results are Fermi edge referenced.

All of the Al(2p) peaks for the systems in question are substantially (and rather uniformly) broader than their corresponding Si(2p) and O(1s) lines; to confirm this statement compare the linewidths reported in Table III with those shown in Figures 3, 4, and 5. The extent of this broadening is ~35–60%, and this plus the appearance of several reproducible humps under the general Al(2p) manifold (see Figure 4) strongly suggest the presence on the surface of a variety of different aluminum-con-

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(23) Argauer, R. J.; Landolt, G. R. U.S. Patent 3 702 886, assigned to Mobil Oil Corp., 1972.

(24) Flanigen, E. M.; Pattan, R. L. U.S. Patent 4 073 685, assigned to Union Carbide Corp., 1978.

taining species. In view of the aforementioned uncertainties with the O(1s) spectra of Y systems, additional evidence is needed to support this multiple species concept. This evidence may be provided through binding energy alignment and deconvolution of the high-resolution versions of Al(2p) peaks for the mordenite, ZSM-5, and silicalite systems, Figures 4, 5, and 6. In addition, as described below, attempts to "clean" these systems strongly support these contentions.

(i) Curve Fitting of the ESCA Results. Mordenite. Figure 4 reveals three primary Al(2p) peaks (for a Mordenite sample) whose binding energies have been reproduced in several independent measurements of various fresh mordenite systems. The only significant differences detected between these independent results are the relative quantitative distributions of these three peaks, labeled (i), (ii) and (iii). In Figure 4 they are roughly distributed as 3.5 (i):4.0 (ii):2.5 (iii) (on a scale of 10), but other cases with distributions such as 5 (i):3 (ii):2 (iii) and 3.5 (i):2.5 (ii):4 (iii) have been found. Thus, although these three principal peaks vary substantially in relative size, each is always a significant contributor to the total spectrum. In addition, other lesser species may be indicated in some of these spectra, but these have not yet been verified. In any case, it is contended that freshly prepared Mordenite surfaces always exhibit several species, each of which contains enough unique aluminum to produce the three aforementioned Al(2p) peak ratios. Crude curve fitting produces the binding energies for the three peaks (reproducible to within ±0.2 eV) as exhibited in Figure 4. Note also that based upon the shift results described above only one of these three peaks produces a binding energy in the range suggested for a zeolite system with [Si/Al] $>$ 4. In addition the approximate line widths for the individual (deconvoluted) peaks are within the range suggested above for "pure" species, whereas the total manifold is much too broad for a "pure" zeolite. *On the basis of these results these peaks are assumed to result from the appearance of three unique (surface) components.*

ZSM-5 and Silicalite. The Al(2p) spectra for selected ZSM-5[23] and Silicalite[24] systems are presented in Figures 5a,b and 6. These spectra again suggest mixed systems which, although somewhat more complex than the previously described mordenite, appear to yield very similar results. In the present case, four major components (1, 2, 3, and 4) are detected, Figure 5. The ZSM-5 example (one of several independent ZSM-5 systems that produced similar results) produced a somewhat narrower Al(2p) line than the aforementioned mordenite sample, suggesting that the former has fewer aluminum-containing components. At the same time, the binding energy of the principal part of the ZSM-5 Al(2p) appears to be even more shifted to a low binding energy than the mordenite case (based upon anticipated results for zeolites with Si/Al $>$ 4). The silicalite example, on the other hand, is very broad and noticably triple humped, features that we have *generally* reproduced by using computerized curve fitting, see, for example, Figure 6. Note that some distortion of features and unrealistic line widths were created by the computer in realizing this simulation.

Before trying to adjudge the identity of the components producing peaks 3 and 4, it is instructive to note that the species i and ii from the mordenite analysis appear to duplicate 1 and 2, respectively, from the analysis of the pentasil-type systems. In fact, peaks or shoulders with these binding energy values have been found in numerous zeolitic samples. In addition, the species at 73.20 eV seems to be most prevalent *when* there is substantial sodium ion present in the system, e.g., Figure 5, see below. This sodium in turn produces a broad Na(2s) line, peaked at values of ~63.20 ± 0.2 eV. The ESCA results for this sodium-containing impurity are quite similar to those for $NaAlO_2$.

In all of the cases under consideration, the relative concentrations of the species identified are difficult to determine; however, it seems plausible to suggest the following hypotheses:

(a) The species producing i and 1 are assumed to be the same. The same is true for ii and 2.

(b) The species identified as i (or 1) is directly associated with Na^+. Removal of Na^+ destroys peaks i and 1.

(c) The two Al-containing species with the lower Al(2p) binding energies, i.e., i and ii (or 1 and 2), are always major constituents of these freshly prepared zeolite systems of large [Si/Al], constituting from ~60 to 90% of the *total aluminum part of the species* found on the outer surface of these systems.

(d) *The Al(2p) peaks at 74.05 eV (iii), 74.20 eV (3), and 74.70 eV (4) are all also produced by distinct species.* The resolution achieved in these studies would probably be insufficient to differentiate between species iii and 3 if they were mixed together, but that was never the case. For the systems presently under study, iii and 3 are assumed to be different, with the peak produced at 74.05 (iii) apparently occurring just above 74.0 eV, whereas 3 always occurs at a slightly larger binding energy.

(e) Analyses of freshly prepared ZSM-5 systems with significantly larger R_b than the species producing Figure 5a exhibited a three-peak structure with peaks 1 and 2 and the third peak 3′ of higher binding energy than 3.

(f) In addition, reexamination of all of these materials and also examinations of other supposedly similar systems with the same R_b produced essentially the same general results, except for the relative amounts of i (1) and ii (2). *However, it should be noted that the relative "presence" of i + ii (or 1 + 2) was always large.*

(ii) "Cleaning" of the Zeolites with $R_b > 4$. It is apparent that the above results support the contention that a substantial fraction of the Al on the surfaces of these freshly prepared zeolites with $R_b > 4$ may be nonzeolitic. To further confirm this assertion, attempts have been made to "clean" these zeolites based around procedures (acid wash, calcinations, etc.) developed for performing similar tasks when the zeolite bulk is "dirty". In view of the inherent uncertainties surrounding these surfaces it is not surprising that these cleaning studies have not been entirely successful, but they have proven sufficiently so to support the aforementioned assumption. In these cases cleaning removed substantial part of the species creating peaks i and ii (or 1 and 2 depending upon the system), *narrowing the resulting Al(2p) lines* and shifting the peak maximum toward the deconvoluted values iii, 3, or 4.

Discussion and Conclusions

(A) Charge Shift Removal and Binding Energy Scale (Fermi Edge) for Silica–Aluminate Materials. Procedures were described earlier in this paper and in other publications[3-5] that claim the successful removal of the charging shifts inherent to the silica–aluminate systems in this study. These techniques involve the utilization of the HP Electron Flood Gun. The method requires slightly different, controlled-current settings for selected types of these materials. These differences seem to be primarily dictated by the principal constituent in the materials system (e.g. SiO_2, NaA, etc.); however, for the procedures to be successful it is necessary that any significant subsidiary components have similar charging characteristics and/or be contiguously dispersed in the primary species (i.e., charge removal from clusters of Au lodged in SiO_2 would be difficult by this procedure).[5,9] It seems that all of the zeolite systems in the present study are sufficiently contiguous to be successfully "treated" for charging by the aforementioned procedure. [Note, for example, that the detected line broadening and multiplicity of the Al(2p) in some of the previously described systems only occurs for the Al lines and thus the splitting is *not* explicable as a residual differential charging effect.[9]]

Procedures were also presented for establishing a quasi-Fermi edge for these insulating materials system, and thus fixing the binding energy scale.[4,5,9] These techniques are based upon the criteria that the binding energy of one or more of the constituents that are detected in all of the systems should occur at previously specified values. Note that this step is *not* taken until after the charging shift has been successfully (?) removed.[5] For a variety of reasons, the procedure for fixing the Fermi edge is often less reliable than that for removing the charging shift.[9] However, in the present case, repetition of results, obtained on hundreds of different samples, and the excellent general agreement with independent data obtained by others[14,20] (see Table V) suggests that the values reported in Table II are reasonably accurate. In that regard, it should be noted that the chief points of interest and utility

Table VI. Identification of Species on Surfaces of Fresh Zeolites with $R_b > 4$

		BE in eV	(±0.2 eV)
designation	suspected species	Al(2p)	Si(2p)
(i) = 1	$NaAlO_2$[a]	73.20	
(ii) = 2	Al_2O_3[b]	73.60	
(iii)	mordenite (mixed Na^+ and H^+ form)	74.05	102.45
3	NaZSM-5 and TPA–ZSM-5 ($R_s \cong 40/1$)	74.20	102.65
5	NaZSM-5 and TPA–ZSM-5 ($R_s \cong 90/1$)	74.50	102.95
4	silicalite ($R_s > 120/1$)	74.75	103.10

[a] Identification drawn primarily from inference. [b] ESCA differentiation may be possible for γ-Al_2O_3, α-Al_2O_3, and the hydrated forms of alumina (see Wagner et al.[14] and Barr[5]). However, the present study does not have sufficient precision for further, unequivocal identification.

of the results in that table are the binding energy "*shifts*", and the accuracy of determination of the latter has been shown to be independent of many of the errors that may plague the absolute values.[3,4]

(B) The ESCA Description of *Pure* Silica–Aluminate Systems. Having established a binding energy scale, it is possible to catalogue the ESCA results for different zeolites, clays, silicas, and aluminas. In addition to binding energies (Table II), line width data (Table III), valence band results (Figure 1), sputter etching studies,[4] and loss spectra (not shown) have all been employed to identify and characterize a particular pure silica–aluminate species. The use of the word *pure* points out one of the major difficulties in this type of analysis. As will be summarized in the next section, many of the freshly prepared versions of these systems display sufficient selective surface impurities to affect significantly the ESCA results. *This fact may occur even when the system exhibits exceptional bulk purity.* As a result, certain adjustments in binding energies (particularly of Al(2p)) may be necessary to establish the *true* values for the *pure* systems. These adjustments were made in Table II. These binding energies were estimated on the basis of the previously described deconvolutions and partial cleaning of the aforementioned mixed surfaces. The presence of these residual impurities also seems to significantly broaden the Al(2p) line widths by 30 to 60%.

The presence of small residual surface impurities is probably not realizable in the rather broad featureless valence band spectra.[4] The situation may be different, however, for the sputter etching[4,6,10] and loss spectra results,[5,15] and studies are presently underway to try to determine if these techniques can detect these effects.

(C) Identification of the Residual "Impurities" Detected on the Surface of Select Zeolites. In the previously described results, several zeolite systems with $R_b > 4$ were found to have substantial parts of the aluminum on their surfaces compromised, such that at most 40% of the total aluminum seemed to be truely zeolitic. It is our contention that in addition to adjudging the relative quantitation, the general chemical nature of the species present on all of these surfaces may be predicted as a result of peak alignments, spectral deconvolution, and comparisons with the results obtained during examinations of pure (and partially cleaned) zeolites, aluminas, and clays.[4] All of the results necessary for these inferences are presented in section B and Tables II and III. Table VI summarizes our suppositions by demonstrating that when these zeolites are produced in the sodium form a significant $NaAlO_2$ impurity always seems to arise. In addition, variable amounts of some form of alumina are generally present. Results with nonsodium zeolites of $R_b > 4$ (e.g., TPA–ZSM-5, not shown) indicate that nearly the same total percentage of nonzeolitic species are found (at the surface) but the vast majority of the "residue", in these cases, is some type of alumina. *Note that although these alumina- and aluminate-type impurities always constitute more than 50% of the total aluminum present on these $R_b > 4$ systems (because of the lack of total aluminum), these nonzeolitic residues are still less than 10% of the total system and in the case of the Silicalite system may actually be less than 1%!*[24]

Approximate deconvolutions of the Al(2p) peaks for the aforementioned systems indicate that when both $NaAlO_2$ and Al_2O_3 are present, each contributes substantially to the total residue, see, for example, Figure 5.

Attempts to identify other residues in the zeolite systems by this approach have, so far, not been very successful. On the basis of studies with numerous related materials, it is assumed that zeolites examined in our HP ESCA will produce an optimal line width of ~1.6 eV for both the Si(2p) and Al(2p) peaks. If this is true, then the slightly broader Si(2p) line produced by those zeolites with $R_b < 2.5$ may indicate a selective silica residue for these systems, but this can only be inferred from the inconclusive results, particularly because selective surface hydration and other effects may also explain these effects.

(D) Final Conclusions. Results have been provided that demonstrate that high-resolution ESCA studies permit accurate identification of a variety of pure zeolites, aluminas, silicas, and clays. These procedures have also been shown to be sensitive enough to permit the detection and identification of the "residues" found on the surfaces of certain commercial and other freshly prepared zeolites. Zeolite systems with $R_b > 4$ were shown to exhibit an extensive surface presence of both alumina and sodium aluminate impurities (always >50% of the total aluminum). When sodium is removed from these zeolite systems, the "residue" present is still often substantial and is primarily some form of Al_2O_3.

Some evidence is presented that may also suggest the (selective) surface presence of a silica-like species, but these results are inconclusive.

The binding energy differences suggested above for ZSM-5 and silicalite may provide a way to differentiate between the surface of these zeolites. One should note, however, that these inequalities refer to ZSM-5 systems with Si/Al ratios <90/1 and may only reflect, therefore, the differences in Si/Al ratio. Thus, a unique structural shift, such as that between NaX and NaY, cannot be inferred or denied.[23-25]

Perhaps the most important question to ask about these results concerns the source of the detected alumina and aluminate residue and what that residue signifies about the integrity of the material system in the area "vacated" by the alumina. In this regard, nothing definite may be said, but it is possible to speculate about several possible sources. For example, the residue may originate in the bulk, perhaps resulting from incomplete zeolitic formation or internal dealumination that is subsequently washed out to the surface or perhaps reprecipitate onto the surface during the final stages of zeolite preparation.[21] Alternatively, these (Al) residues may represent a persistent (and perhaps growing) lack of "integrity" that may always exist on the outer surface of any crystallite material that has not been annealed (or otherwise treated) to ensure *surface crystallinity*. Or perhaps the species detected may be the residue of a true surface dealumination,[6,7] i.e., a selective (surface) destructive process that preferentially removes aluminum from the outer surface of some zeolites, thus increasing R_s relative to R_b, but for some reason leaving behind a residue largely of alumina and/or aluminate.

All of these suggestions are complicated by the question "why alumina?" or perhaps more appropriately "where is the silica?". Most of these hypothetical processes suggest either the incomplete formation or the destruction of some of the "true" zeolite. Since the latter also contains a silica component, many of the aforementioned processes should also produce some sort of silica residue. The uncertain detection of any silica may suggest that either it produces a Si(2p) spectrum too similar to that of the pure zeolite to differentiate or it does not lodge on the surface, perhaps being washed away. Thus, perhaps, the systems examined are inappropriate for this type of (ESCA) surface analysis of silicon. It should also be noted that the role played in these processes by (selective?) surface hydration is, as of yet, not understood.

An additional comment seems in order on the interesting R_s (surface) vs. R_b (bulk) results of Dwyer et al.[6] The reduction in

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(25) Whyte, T. E., Jr.; Dalla Betta, R. A. *Catal. Rev.-Sci. Eng.* **1982**, *24* (4), 567.

J. Am. Chem. Soc. 1986, 108, 3186-3197

R_s with sputter etching detected in that study was also observed in the present study.[4] However, this was suggested to arise from preferential sputtering of Si[4] (compared to Al), rather than the exposure of selective layer structures.[6] The former conclusion was reached because the R_s following sputtering eventually dropped substantially below R_b. The counter arguments of Dwyer et al., however, cannot be ruled out.[6] In addition, one should not preclude differences resulting from the choice of distinctly different sputter etching energies and other conditions. The excellent reproducibility achieved by Dwyer et al.[6] employing bombardment techniques is a persuasive feature in their arguments and may counter any criticism of the quantitation of these techniques. The present results agree with a number of Dwyer's hypotheses. The present study also provides possible chemical identifications of the mixtures formed at zeolite surfaces. Additional, better-coordinated studies are needed, however, in order to establish the interconnections between these two approaches.

In general, it may be concluded that the *surfaces of certain zeolites are compromised such that substantial proportions of their total surface (Al) are actually present in alumina or sodium aluminate residues.* Note that since the Si/Al ratio (R_s) reported in most previous ESCA studies does not reflect the substantial presence of these nonzeolitic residues, the (R_s) of *true* zeolites may actually be much larger than these reported values.

UV Resonance Raman Excitation Profiles of the Aromatic Amino Acids

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Abstract: The first total differential resonance Raman cross-section excitation profiles have been measured throughout an electronic transition of a simple aromatic molecule. The excitation profiles of the aromatic amino acids phenylalanine, tyrosinate, and tryptophan were measured between 217 and 600 nm. The mechanism for resonance enhancement for each of these benzene derivatives is discussed. The ν_1 symmetric ring stretch at 750 cm^{-1} in phenylalanine derives its preresonance enhancement from the $B_{a,b}$ transitions, while the other vibrations are enhanced by the L_a transition at ca. 210 nm. The excitation profiles for tyrosinate indicate that the L_a state has little charge-transfer character, while the L_b and states further in the UV have significant charge-transfer character. The excitation profile data are used to assign the resonance enhanced vibrations. The relationship between resonance enhancement of a vibrational mode, the atomic displacements in the vibration, and the molecular electronic transition is examined. The cross sections are used to determine the optimal excitation wavelength required to selectively enhance particular aromatic amino acids in proteins. The resonance Raman spectra of lysozyme are discussed. Photochemical and optical saturation processes which commonly occur with pulsed laser excitation can change the apparent contributions of aromatic amino acid intensities in the Raman spectra. Transient species can also form and alter the measured Raman spectra. These processes can cause artifactual Raman spectral changes.

Recently, a number of reports have appeared on the use of UV resonance Raman (UVRR) spectroscopy as a new probe for studying both the excited states[1-14] and the ground states of molecular species.[15-22] A major inducement for some of these UV spectral measurements is the potential utility of UVRR spectroscopy as a new technique for the study of biomolecular structure and function.[15,19-22] Indeed, recent UVRR investigations of aromatic amino acids, proteins, and model peptide compounds have clearly illustrated the potential of UVRR spectroscopy. These studies indicate that selective enhancement of protein aromatic amino acids is possible.[19,22] Other studies suggest that peptide backbone vibrations can be selectively enhanced with ca. 190-nm excitation.[4,11,22] A major revolution in insight accompanied visible wavelength RR studies of the mechanism of energy transduction in the visual pigments[23,24] and the mechanism of ligand binding and the structure and function in heme proteins.[23-26] Similar important strides are expected with the application of UV Raman spectroscopy to the structure, bonding, and intermolecular interactions of aromatic amino acids in proteins.

In this report we carefully characterize the UV resonance Raman excitation profiles of aqueous solutions of phenylalanine, tyrosinate, and tryptophan from 217 to 600 nm. We also discuss and review some of the photophysics which accompany UV pulsed laser excitation in these molecules.[6,27] The excitation profiles indicate the selectivity available for resonance Raman excitation of a particular type of aromatic amino acid. The detailed excitation profile patterns can be used to obtain information about the excited state. The degree of enhancement of a vibration is intimately related to the molecular electron density differences

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