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Auger Spectroscopy Studies of Natural and Synthetic Zeolites

I. Surface and Bulk Compositions[1]

S. L. SUIB[2] AND G. D. STUCKY[3]

School of Chemical Sciences and the Materials Research Laboratory, University of Illinois at Urbana–Champaign, Urbana, Illinois 61801

AND

R. J. BLATTNER[4]

Materials Research Laboratory, University of Illinois at Urbana–Champaign, Urbana, Illinois 61801

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It has previously been reported that the surface composition of various zeolites is quite different from that of the bulk (*1*, *2*) as determined by X-ray photoelectron spectroscopy (XPS). The selectivity of a zeolite for a particular catalytic reaction may be strongly influenced by the surface chemical composition. Consequently, we have studied the elemental surface composition of various single crystalline and powdered natural and synthetic zeolites using Auger electron spectroscopy (AES). Quantitative analyses were performed using peak-to-peak heights from conventional derivative spectra of zeolites A, X, Y, and ZSM-5. Auger depth profiles of single-crystal natural zeolites were obtained using 1 keV Ar^+ ion sputtering to compare surface and bulk compositions. Electron dose effects were studied to assess the extent of beam damage during analysis. Our results indicate that the surface silicon–aluminum ratio (Si/Al) for the zeolites invesitgated is very similar to that of the bulk in contrast to the XPS studies.

INTRODUCTION

Since the discovery of the catalytic properties of zeolites, the nature of active surface sites and the mechanisms of zeolite catalysis have been extensively studied. Basic molecules have typically been empoyed as surface probes because many of these reactions are of the carbonium ion type. Adsorbed surface species can sometimes be identified spectroscopically by means of characteristic frequencies, or they may be distinguished thermodynamically by measuring characteristic enthalpies in a desorption mode of analysis. Of these various approaches infrared spectroscopy has been most commonly used.

During the past several years, surface analysis techniques, most notably Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS), have been employed to solve a variety of surface-related materials problems. Both techniques utilize energy analysis of electron emissions from a sample under either electron (AES) or X-ray (XPS) irradiation. These emissions emanate from the outer few atomic layers of the solid and thereby provide the surface sensitivity.

Except for some well-calibrated materials systems surface analyses tend to be

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[2] Author to whom all correspondence should be sent.

[3] Present address: Division 5152, Sandia Laboratories, Albuquerque, N. Mex. 87115.

[4] Present address: Charles Evans & Associates, 1670 South Amphlett Blvd., Suite 120, San Mateo, Calif. 94402.

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qualitative or semiquantitative at the present time. There has recently been considerable interest in obtaining accurate quantitative data from these techniques. Tempere *et al.* (*1*) have studied zeolites by XPS. In this report they conclude that the silicon–aluminum ratio (Si/Al) of the outer zeolite surface is about twice that of the bulk for a variety of synthetic compounds. Subsequent work by the same authors (*2*) led to the conclusion that partial dealumination of the surface occurs for the zeolites investigated.

In this paper we discuss the use of scanning Auger microprobe (SAM) techniques to investigate various surface properties of both natural and synthetic zeolites. These materials are subject to two basic problems in an Auger analysis, viz., electron beam damage and sample charging. We have been able to circumvent these problems through the use of low electron doses during the analysis and thus have been able to obtain Auger spectra representative of the surface. These results combined with single crystal Auger depth profile data indicate no major Si/Al deviations at the surface from that of the bulk. In addition, we have found that AES of zeolites using a SAM is useful for zeolite mineral identification, for the detection of impurities introduced by sample handling and for quantitative microanalysis.

EXPERIMENTAL METHODS

A. Materials

Zeolites A, X, and Y were obtained from ALFA-Ventron Corporation. Zeolite ZSM-5 was prepared according to example 27 of Patent 3,702,886 (*4*). Single crystals of chabazite and faujasite were obtained from the U.S. National Museum, Division of Mineralogy.

B. Procedure

Auger electron spectrometric analyses were performed using a Physical Electronics Model 545 scanning Auger microprobe. Powdered zeolite samples for Auger analysis were pressed into indium foil with a Teflon spatula. Single crystal zeolites were mounted directly. These samples were positioned on the standard carousel at 30° grazing incidence to the primary electron beam. The sample chamber residual vacuum was less than 1×10^{-9} Torr prior to all analyses. Primary electron energies of up to 5 keV were employed in the spectroscopy, depth profiling, and imaging modes. Depth profiles were obtained by repetitively monitoring the appropriate Auger transitions with simultaneous 2 keV Ar^+ ion sputtering at an Ar partial pressure of about 5×10^{-5} Torr. A specimen bias which varied from sample to sample was used for calibration of the oxygen Auger transition at 510 eV. The required target bias generally ranged from +2 to +10 V. All zeolite samples were run at low electron beam current densities in order to minimize charging and damage. Damage tests with the beam current three times the normal value used for the analyses yielded no significant indications of beam burning or beam damage after up to 25 min of exposure. The total analysis time was kept to a minimum and was always less than 10 min. Samples were also visually examined for electron damage after removal from the AES vacuum system.

The (Si/Al) ratios for the various zeolites reported in this paper are based on local standards as well as elemental sensitivity factors. The procedure for using these elemental sensitivity factors has been reported previously (*3*).

Europium-exchanged ZSM-5 was obtained by stirring 100 ml of a 1.0 *M* $EuCl_3 \cdot 6H_2O$ solution with 1 g of ZSM-5 zeolite for about 1 day at room temperature. Dehydration of this material was carried out at 600°C at a pressure of $\sim 5 \times 10^{-6}$ Torr.

RESULTS

Figure 1 shows a plot of the bulk silicon/aluminum concentration (Si/Al)

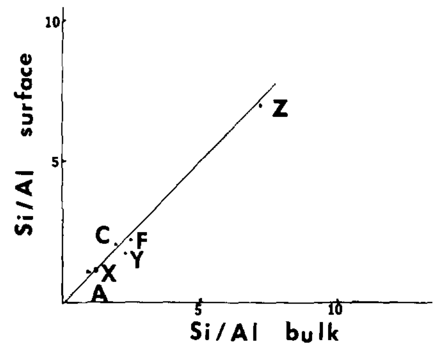

FIG. 1. Zeolites A, X, Y, chabazite, faujasite, and ZSM-5.

versus the surface Si/Al ratio as determined by Auger electron spectroscopy. The ratios reported are an average of at least three reproducible analyses. Deviations from the line indicate the relative difference between the surface and the bulk. Bulk (Si/Al) ratios were determined by conventional wet chemical techniques and from known stoichiometries. Severe charging was observed in both the sodium and acid forms of mordenite and therefore is not included in these data. A typical depth profile from a single crystal of chabazite is shown in Fig. 2. The (Si/Al) ratio of the chabazite in depth has been plotted versus depth with the sputtering rate calibrated using standard thickness of SiO_2 sputtered under the same conditions. Auger electron spectra taken before and after depth profiling yielded a (Si/Al) ratio of ~2.1 before and ~1.96 after sputtering. Faujasite single crystals also showed a slight decrease in (Si/Al) ratio on sputtering.

The Auger spectrum of a dehydrated europium ion-exchanged ZSM-5 zeolite is shown in Fig. 3. The peaks for Si, Al, O, C, and Eu are attributable to the sample. Fluorine is probably due to contamination from the Teflon spatula during sample mounting. The In peak arises from incomplete coverage of the indium foil used to hold the powder.

An analysis of single crystalline faujasite from Sasbach, Germany, revealed the usual Si, Al, and O AES transitions as well as peaks for Ca, Na, and Mg, typical of this naturally occurring mineralogical material.

DISCUSSION

The data in Fig. 1 show that the surface Si/Al ratio is very similar to that of the bulk for all the zeolites investigated. This observation is in opposition to the XPS results of Tempere *et al.* (*1*, *2*). Although these two electron spectroscopies (AES and XPS) are quite similar, they have inherent distinctions which may give rise to such discrepancies for insulating materials with AES being somewhat more reliable.

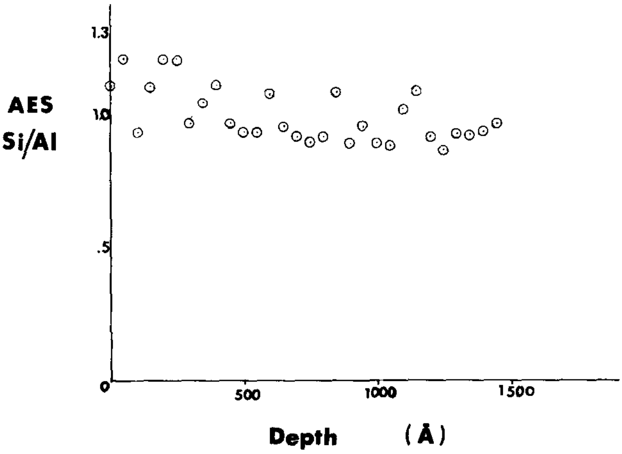

FIG. 2. Depth profile of chabazite.

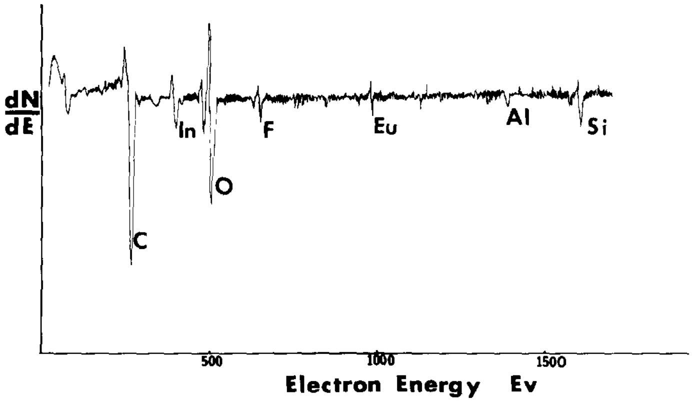

FIG. 3. Eu ZSM-5 (600°C).

In the case of XPS, X-ray bombardment is used to generate the electron emission which provides the analytical information from the sample. As these electrons leave the sample the surface becomes positively charged. In the absence of leakage currents or a charge neutralization source, this surface potential will shift the electron energy spectrum toward lower energies. Furthermore, this surface potential will steadily increase with time until it is sufficiently great to induce leakage currents to flow and thus create a dynamic equilibrium. Due to the relatively small electron fluxes involved this can take appreciable amounts of time so that conditions may change during the normal course of the analysis. Alternatively, AES utilizes a relatively large electron beam current to produce the analytical signal, and at the same time generates a large secondary electron emission current. It is often possible to balance exactly the current in with the current out and thus minimize or eliminate sample charging. Equilibrium charge transport occurs almost instantaneously with the equilibrium surface potential measurable by observing the oxygen Auger transition energy which is usually insensitive to the chemical environment. Once an equilibrium surface potential is achieved, the true energy scale can be established using a target bias supply built into the system to produce an oxygen peak at 510 eV. Once this is accomplished the energy scale is quite stable and quantitative measurements can be made in routine fashion. It is still important that the analysis be performed quickly because although the sample charging problem is circumvented, beam damage due to electron irradiation can still occur which might distort the measured Si/Al ratios. X-Ray irradiation damage is a much less serious problem and can be ignored in zeolites for all practical purposes. Another possible explanation for the discrepancy stems from the fact that adsorbed species and cations could cause a "screening effect" on the element analyzed using the XPS technique as has been previously suggested (*1*). There is also some variation in the intensity coefficients used in calculating the surface Si/Al ratio by XPS. The single crystal depth profile should reveal any compositional gradients normal to the surface. No major in-depth compositional variations could be detected in terms of the Si/Al ratio within approximately the outer 1500 Å as noted in Fig. 2. The gradual decrease from 2.1 at the surface to 1.96 in the interior may be real or could be the result of a preferential sputtering artifact. A slight decrease in depth is in general agreement with the conclusions of Tempere *et al.* (*1*, *2*) in that the surface may be partially dealuminated. Our data do not show, however, the factor of 2 decrease in the surface aluminum concentration they report.

The spectrum in Fig. 3 shows most interestingly that the largest intensity peak for dehydrated europium-exchanged zeolite ZSM-5 is for carbon. This is very likely due to the decomposition of the tetrapropylammonium (TPA) cations which are used as a template for the zeolite crystallization. The starting hydrated ZSM-5 does not show a peak for carbon since the tetrapropylammonium cations are in the inner cavities of the zeolite. Thermogravimetric analysis experiments carried out in our laboratory (*5*) show that the TPA cations begin to decompose at 350°C yielding ethylene, propylene, and carbon monoxide. The carbon data may be reflecting extracrystalline C in the dehydrated zeolite. The spectrum clearly shows a peak for F which was probably introduced as an impurity by handling the zeolite with a Teflon spatula. The F peak disappears when a stainless-steel spatula is used. The indium peak is due to the indium support.

Our results with faujasite could be very important to a mineralogist. It has been observed (*6*) at Sasbach, Kaiserstahl, German that faujasite crystals lined cavities before the growth of phillipsite tuffs. The phillipsite (a common natural zeolite) and faujasite vary in chemical composition from grain to grain. Auger electron spectroscopy could be used to study these zeolites to observe differences between them and possibly to track geologically the movement of ion-exchange pore waters.

There are obvious applications of this technique to catalytic reations and ion migration in zeolites on dehydration. We are presently studying the ion migration of various transition metal and rare earth ions in zeolites by Auger electron spectroscopy. This work is described in a following companion article.

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