JOURNAL OF CATALYSIS 65, 179–184 (1980)

# Auger Studies of Zeolites

## II. Ion Migration in Rare Earth and Transition Metal Exchanged Zeolites

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Received October 24, 1979; revised February 19, 1980

X-Ray photoelectron spectroscopy (XPS) has been used in the past to study various metal substituted zeolites (*1*). In these studies Minachev proposed an ordering of the degree of reduction of certain metals and subsequent migration to the external surface of the zeolites. We report here Auger spectroscopy results for the dehydration and migration of the cations in each of the zeolites in Minachev's sequence. Our findings are in essential agreement with those of Minachev, confirming that silver is most easily reduced and migrates more rapidly than the other cations examined. In mixed metal zeolites our results compare remarkably well with those of Minachev. Some doubt has arisen concerning the XPS data concerning migration of cations to the external surface of the zeolite material, rather than the external surface of the large supercage of the zeolites (*2*). Our results with CsY zeolite indicate that the Auger depth resolution is limited to the external surface of the zeolite material.

### INTRODUCTION

The presence of metal ions influences the Bronsted acid sites in zeolites (*3*). Another consequence of metal cation ion exchange in zeolites is that the metal cation itself may modify catalytic activity (*4*). The selectivity and reactivity of the zeolite can therefore be modified by appropriate metal cation incorporation.

The selectivity of a particular zeolite is in itself a problem of great interest. In general, selectivity is determined by geometry and composition, including cage and channel size, metal cation substitution, and the (Si/Al) ratio. We previously reported that the surface composition of zeolites is about the same as that of the bulk material as determined by Auger electron spectroscopy (*5*). The results of Auger surface composition studies on a variety of zeolites, including a depth profile of a zeolite single crystal, were reported.

Recently it has been shown that the properties of zeolites have a solution-analogy in terms of chemical potential and acid base properties (*5, 6*). Solution properties such as cation mobility, proton mobility, ionizing ability of the zeolite, and the ability of the zeolite to function as a ligand in transition metal migration are discussed. Both structural (*7*) (EXAFS) and dynamic (*8*) (pulsed NMR) probes reveal solution characteristics of certain cations in hydrated zeolites. Uytterhoeven (*9*) has reported

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0021-9517/80/090179-06$02.00/0

that the reducibility of a cation varies with redox potential and that zeolite cations have similar properties to the analogous cations in solution. The results of X-ray photoelectron spectroscopy (XPS) studies have shown similar cation reducibilities although the order of metal reduction is not quite the same (*1*). The XPS study also showed that in the presence of mixed metals, the more easily reduced metal does reduce on dehydration (either in vacuum or under $H_2$) and that it migrates to the external surface of the zeolite. Other XPS studies (*10*) have shown that cerium Y zeolites are different when dehydrated in air and in vacuum in terms of color and the amount of cerium on the surface after dehydration.

In this study we have prepared rare earth and transition metal ion exchanged zeolites and monitored their surface composition using Auger electron spectroscopy (AES). The metal exchanged zeolites were dehydrated in vacuum and their AES spectra were compared with that of hydrated zeolites. Mixed transition metal zeolites were also studied. The specific purpose of these studies was to demonstrate the feasibility of using Auger electron spectroscopy as a probe for observing metal migration in zeolites.

## EXPERIMENTAL METHODS

### *A. Procedure*

The Auger electron spectrometric analyses were performed with a Physical Electronics Model 545 scanning Auger microprobe. Procedures similar to those previously reported (*5*) were used for these analyses. Beam damage tests were undertaken as was previously indicated. Hydrated and dehydrated powdered zeolite samples were pressed into indium foil with a Teflon spatula and placed on the standard PHI carrousel for measurement. The dehydrated samples were immediately loaded from sealed vials onto the foil and placed in the Auger chamber under flowing nitrogen and then pumped overnight in vacuum to a pressure of $<1 \times 10^{-9}$ Torr. The samples were individually checked by visual examination for electron beam damage after the analysis. Slight discolorations could be detected after beam damage had occurred.

### *B. Materials*

Zeolites A and Y were obtained from Alfa–Ventron Corporation. Metal-exchanged zeolites were prepared in the following manner: Approximately 2.0 g of zeolite NaY or NaA was added to 200 ml of a 0.1 *N* metal chloride aqueous solution and exchanged while stirring for 24 hours in a round bottom flask at room temperature. The resulting metal-exchanged zeolites were filtered through a medium frit and stored in capped vials. In the case of silver, copper, and zinc, the nitrate salt solutions were used. All silver ion exchange procedures were done in the dark. All water used was distilled, deionized, and degassed.

The dehydrated samples were prepared in a vacuum line by heating to 550°C at a pressure of $\sim 5 \times 10^{-6}$ Torr. After dehydration the samples were closed off from the line with a greaseless stopcock and brought into a Vacuum Atmospheres Company drybox equipped with a HE–493–Train. The He atmosphere in the box was monitored by a Panametrics Model 1030 hydrometer with the water content of the atmosphere kept below 0.5 parts per million. The oxygen content of the box was periodically tested with a Ti–Zn compound as previously described and was maintained at a level below 1 part per million (*11*). After placing the dehydrated samples into the drybox they were immediately stored in capped vials.

Neutron activation analyses for various transition metal, rare earth and main group elements in the zeolites were obtained through the Environmental Sciences Department of the University of Illinois.

## RESULTS

Table 1 shows the quantitative Auger

TABLE 1

AES (Si/Al) and (RE/O) ratios and colors

| Zeolite | Si/Al | RE/O | Color |
|---|---|---|---|
| CeY Hydrated | 1.7(2) | 0.31(2) | White |
| CeY Dehydrated, air | 2.0(2) | 0.18(2) | Yellow |
| CeY Dehydrated, vacuo | 1.9(2) | 0.11(2) | Grey |
| EuA Hydrated | | Fluoresces | |
| EuA Dehydrated | 1.1(1) | 0.18(1) | White |
| EuA Rehydrated | 1.1(1) | 0.20(1) | White |

spectroscopy results for the cerium and europium exchanged zeolites. The three cerium Y zeolite samples have different colors and different Auger peak height ratios as seen in the table. These results are based on at least three repetitive measurements. The hydrated EuA zeolite system fluoresced strongly in the Auger chamber on electron beam bombardment. No Auger spectrum could be obtained for this sample due to severe surface charging. The EuA rehydrated sample was prepared by dehydration of the hydrated starting material and subsequent addition of water on removal from the drybox.

A series of transition metals (Ag, Ni, Co, Cu, and Zn) were exchanged for Na in NaY. Some of the subsequent hydrated materials were dehydrated. The data in Table 2 show the quantitative Auger results for each of these hydrated and dehydrated samples. The normalized metal concentration represents the intensity of metal signal divided by the sum of the intensity of metal signal, silicon signal, and the aluminum signal on the surface. The labelled surface metal depletion is the amount of change from the hydrated metal concentration. Thus, the 1.8 value for Ag means that there is 1.8 times more Ag on the zeolite surface after dehydration compared to the hydrated sample. Negative numbers like −3.0 for CoY show that the Co concentration has decreased by a factor of 3 on dehydration. The numbers reported are again an average of at least 3 analyses. All numbers have been averaged and standardized using pure element spectra (*12*). The data for cesium-exchanged Y zeolite show that on dehydration the amount of Cs detected on the surface is very small and the Cs transition is very broad and not resolved into its usual doublet.

The mixed metal zeolites listed in Table 3 have been analyzed in a similar fashion. The normalized metal concentrations reported under each column correspond to the ordering of the metals noted under the sample column. The column marked "surface metal depletion" refers to the increase or decrease in the metal to metals plus silicon plus aluminum ratio of the first metal listed under the sample column, for example Ag, for Ag and Cu, respectively.

TABLE 2

Auger Results for Transition Metal Y Zeolites

| Sample | Normalized metal concentration | | Surface metal depletion[a] | Si/Al | |
|---|---|---|---|---|---|
| | Hydrated | Dehydrated | | Hydrated | Dehydrated |
| AgY | 0.24(2) | 0.44(1) | 1.8 | 1.8(2) | 1.9(1) |
| NiY | 0.33(3) | 0.20(1) | −1.65 | 1.7(2) | 1.7(1) |
| CoY | 0.28(1) | 0.09(1) | −3.0 | 1.5(2) | 1.9(1) |
| CuY | 0.11(2) | 0.10(1) | −1.1 | 1.5(1) | 1.8(1) |
| ZnY | 0.27(2) | 0.16(1) | −1.68 | 1.5(1) | 1.5(1) |
| CsY | 0.09(2) | 0.09(2) | 1.00 | 1.8(1) | 1.8(1) |

[a] The surface metal depletion column is determined by the $M/(M + Si + Al)$ ratio of the dehydrated sample to the hydrated sample.

TABLE 3

AES Results for Mixed Metal Y Zeolites

| Sample | Normalized metal concentration | | | | Surface metal depletion[a] | Si/Al | |
|---|---|---|---|---|---|---|---|
| | Hydrated | | Dehydrated | | | Hydrated | Dehydrated |
| | $M_1$ | $M_2$ | $M_1$ | $M_2$ | | | |
| AgNiY | .29(1) | .03(2) | .38(1) | 0 | 1.3 | 1.5(2) | 1.7(1) |
| AgCoY | .49(1) | .08(2) | .64(2) | 0 | 1.3 | 1.6(1) | 1.9(2) |
| CuNiY | .14(1) | .08(2) | .10(1) | 0 | −1.4 | 1.6(1) | 1.8(1) |

[a] The surface metal depletion column is determined by the $M_1/(M_1 + M_2 + Si + Al)$ ratio of the dehydrated sample to the hydrated sample.

Neutron activation analyses of the single substituted metal zeolites of Table 2 indicate that the metals have substituted for at least 50% of the bulk sodium cation present in the starting material. Microanalyses of the mixed metal systems yielded the following approximate compositions:

AgNiY—$Ag_{25}\ Ni_2\ Na_{27}\ Al_{56}\ Si_{136}\ O_{384}\ 250\ H_2O$
AgCoY—$Ag_{37}\ Co_3\ Na_{10}\ Al_{56}\ Si_{136}\ O_{384}\ 250\ H_2O$
CuNiY—$Cu_{12}\ Ni_3\ Na_{26}\ Al_{56}\ Si_{136}\ O_{384}\ 250\ H_2O$.

Finally it is noted that impurity peaks for carbon were observed at times when the samples were dehydrated in vacuum. These peaks diminished if the samples were dehydrated in air.

## DISCUSSION

Tempere (*10*) and coworkers have reported XPS results for the three CeY zeolites in Table 1. We have observed the same colors as did Tempere et al (*10*) on dehydration of the zeolites in air and vacuum. They conclude that the yellow species is a cerium (IV) oxide species on the surface of the zeolite.

Our results show that the Si/Al ratio is fairly constant on dehydration and that on dehydration of the CeY hydrated sample the amount of Ce detected decreases. It is known from a number of X-ray diffraction results that dehydration of the zeolites causes the rare earth ions to migrate to the smaller (sodalite) cages (*13, 14*). This would account for the decrease in the (Auger visible) rare-earth ion concentrations for the cerium system. Further evidence that rare-earth ion migration is irreversible is shown for the EuA rehydrated sample where there is no significant change in rare-earth concentration following rehydration of the dehydrated sample. This conclusion of irreversible ion migration of rare earth ions is consistent with published ion exchange (*15*), X-ray (*13*), and Mössbauer (*16*) results.

Since the rare-earth ion concentration is higher for the CeY sample dehydrated in air, the proposed $CeO_2$ species is likely. Further supporting evidence from the Auger spectra is that the CeY sample dehydrated in air shows a distinct doublet for Ce. Standards of sintered ceria, ($CeO_2$), also show this doublet. Neither the hydrated CeY Zeolite nor the CeY dehydrated in vacuum gave Ce Auger peaks that were doublets. It is noted, however, that cerium metal also shows a Ce doublet. Nevertheless, the proposed $CeO_2$ species accounts for the color and the Auger observations. A carbon impurity for the dehydrated systems is larger when dehydrated in vacuum than in air since in the latter case the carbon can be burned away. The observed carbon impurity may arise either from the oil diffusion pumped vacuum system or from the starting carbonaceous material.

Based on XPS measurements, Minachev (*1*) has proposed a decreasing order for the reduction of certain metals and their subsequent migration to the external surface of metal-exchanged zeolite Y. He also argued that in mixed metal zeolites, migration is hindered by interaction of the metals and that only the most easily reduced metal migrates. His order of decreasing ease of metal reduction and migration in zeolite Y is as follows:

$$\mathrm{Ag} > \mathrm{Zn} > \mathrm{Cu} > \mathrm{Ni} > \mathrm{Co}.$$

In Table 2, we have reported the Auger peak height ratios after dehydration and migration for each of the zeolites in Minachev's sequence. The decreasing order for external versus internal site preferences during dehydration in vacuum is the following:

$$\mathrm{Ag} > \mathrm{Cu} > \mathrm{Ni} > \mathrm{Zn} > \mathrm{Co}.$$

Our findings for silver are in partial agreement with Minachev, confirming that Ag is most easily reduced and migrates more rapidly than the other cations. It is significant that we observe that zinc does not readily reduce or migrate since volumetric techniques (*7*) indicate that zinc does not reduce. Perhaps the differences between our work and that of Minachev result from differences in sample treatment. Yates (*17*) reported that zinc in zeolites reduces in vacuum only during $H_2$ treatment. The reducibility of all the metals besides zinc can be explained systematically in terms of electro-chemical potentials as has been suggested by Barthomeuf's zeolite solution analogy (*6*). Zinc should be the least easily reduced ion in the present series. Clearly in light of the behavior of the zinc ion, other factors are also important. No beam damage was directly observed during the analyses when analysis time and beam current density were kept to a minimum. Visual inspection, however, did reveal beam "burning" after extended exposure on some of the samples—most notably those containing silver (25 min analysis). Evidence for reduction of ions (Ag) from the Auger experiment comes from Auger line shape analysis, subsequent local charging on reduction, and Auger imaging techniques.

The Auger experiment with cesium is extremely important in that cesium cannot be reduced and subsequently migrates to the external surface. In addition cesium does not penetrate the sodalite cages since the ions are too large and can reside in the supercage only (*18*). Cesium can therefore be used as a structural standard. Our Auger results for the dehydrated CsY zeolite show, therefore, that the Auger depth resolution is limited basically to the external surface of the zeolite because small amounts of cesium and broad Cs peaks are observed in the Auger spectrum. This may involve the escape depth of the Auger electrons since areas of high electron density decrease the Auger intensities due to electron–electron interaction.

In the case of the mixed-metal zeolites our Auger results in Table 3 compare remarkably well with those of Minachev. In all cases of mixed-metal silver systems, silver is always enhanced at the surface whereas the other element (Co, or Ni) is depleted. In the case of CuNiY, more Cu is present on the surface than nickel, although the amount is minimal. Alloying effects have previously been observed in this system by EPR and magnetic methods when the zeolite is subjected to hydrogen at 550°C (*19*). Finally, the (Si/Al) ratios from Tables 2 and 3 do not markedly change on dehydration.

## CONCLUSION

In our previous work (*5*) we have shown that Auger electron spectroscopy can be used to study zeolites to obtain information concerning handling techniques, mineral identification, semiquantitative (Si/Al) ratios, and surface composition. In the present work we have extended the use of Auger electron spectroscopy in studying zeolites in order to learn about specific rare-earth and transition-metal reduction and migration. Considerable care must be taken to minimize or eliminate sample charging which can be circumvented by using a flat, smooth pressed powder sample at glancing incidence to the electron beam. Beam damage effects can be minimized by operating with low beam currents (0.1 aup) spread over relatively large areas (~500 $\mu$m × 500 $\mu$m). When these techniques are employed, useful information about the surface composition of these complex materials may be obtained in a reasonably routine fashion.

## ACKNOWLEDGMENTS

We would like to thank L. E. Iton for numerous discussions and advice throughout this work. We also would like to thank P. K. Hopke of the Environmental Sciences Department of the University of Illinois for the neutron activation analyses. Financial support for this research was provided by the National Science Foundation under grants NSF CHE 77-24964 and NSF DMR 77-23999. This material is taken in part from the Ph.D. thesis of S. L. Suib of the University of Illinois, 1979.

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