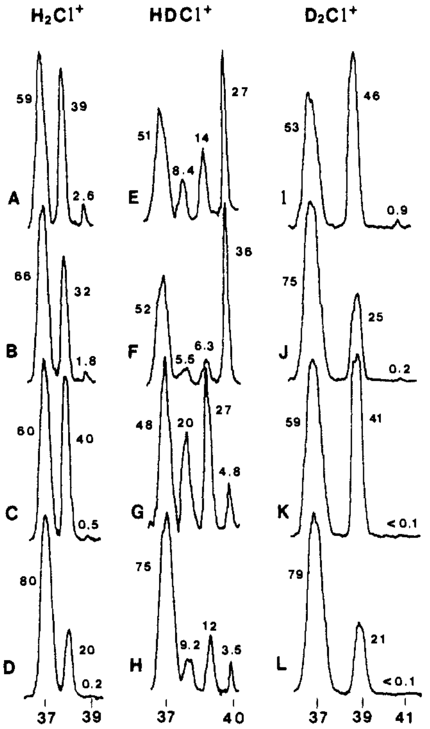

Figure 1. Hg/He neutralization–reionization (NR) mass spectra of H_2Cl^+ (A–D), DHCl$^+$ (E–H), and D_2Cl^+ ions (I–L) at lower ion source pressures ($[H_2Cl^+]/[HCl^{\cdot +}] = 0.04$; A, E, I, B, F, J) or higher source pressures ($[H_2Cl^+]/[HCl^{\cdot +}] = 3.1$; C, G, K, D, H, L). He reionization was achieved at transmittances of the neutral beams of 90% (A, E, I, C, G, K) and 30% (B, F, J, D, H, L). The figures adjacent to the peaks give peak areas in percent of the spectrum total. The absolute abundances of the reionized precursors (percent of the precursor ions collected without ion deflection): spectra B and D, *m/z* 39, 0.00032 and 0.00004; spectra F and H, *m/z* 40, 0.017 and 0.0015; spectra J and L, *m/z* 41, 0.000 04 and <0.000 02.

radical, it seems surprising that these effects combined would give the observed difference of ~400 × (Figure 1, part F vs. part J).[2,3d]

A possible alternative explanation is that the H–Cl$^+$–H structure initially formed[9] rearranges in the absence of thermalizing collisions to a more stable isomer; for this the structure Cl–H$^+$–H would be consistent with production on neutralization of the more stable[1b] Cl–H–H structure, for which various geometries are conceivable. The 12 kcal mol^{-1} exothermicity of H_2Cl^+ formation[7,8] would approximate the maximum activation energy for H–Cl$^+$–H → Cl–H$^+$–H. If this involves migration of one hydrogen, the isomerization would be slowed substantially be perdeuteration but little by monodeuteration. On the other hand, for the Cl–H–H product the isotope effect should reduce the dissociation of either Cl–D–H or Cl–D–D. Thus the HDCl observable would be favored over either H_2Cl or D_2Cl.

Consistent with these structural postulates, neutralization of the supposed Cl–D$^+$–H (Figure 1E, low source pressure) gives $[Cl^+] > [(H,D)Cl^{\cdot +}]$,[10] while that of D–Cl$^+$–H (Figure 1G, higher source pressure) gives equivalent abundances, with Cl$^+$ formed in substantial part from HCl$^{\cdot +}$ dissociation (vide infra). Rearrangement is required for formation of $Cl^{\cdot} + H_2$ from H–Cl–H[10] but not from Cl–H–H. A surprisingly high stability of $H_2Cl^{\cdot}$ for collisional dissociation[10] is also indicated. Increasing the He pressure from 90% to 30% transmission increases the average number of collisions for affected precursors from 1.06 to 2.12.[11] The NR spectrum of D_2Cl^+ under high ion source pressures shows only DCl$^+$ and Cl$^+$ (Figure 1K); increasing the helium pressure causes substantial collisional dissociation of DCl and DCl$^{\cdot +}$ (Figure 1L). However, increasing the helium collision pressure under conditions giving high formation of HDCl (Figure 1E) shows (Figure 1F) a much greater reduction in $[HCl^{\cdot +}]$ and $[DCl^{\cdot +}]$ than in $[HDCl^+]$. Sophisticated ab initio studies of the potential energy surfaces of both H_2Cl^+ and $H_2Cl^{\cdot}$ should be helpful in the further understanding of these systems.

Acknowledgment. We are indebted to R. Hoffmann, R. F. Porter, J. A. Pople, L. Radom, and H. Schwarz for helpful discussions and to the National Science Foundation (Grant CHE-8406387) for generous financial support. The National Institutes of Health and The Army Research Office funded instrument construction.

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(10) $\Delta H_f°$ (products) = 30 kcal mol^{-1} for $H^{\cdot} + HCl$, and 29 kcal mol^{-1} for $H_2 + {}^{\cdot}Cl$.[8]

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Surface Metal Ion Enhancement of Thermally Treated Zeolites[†]

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During the past several years the area of zeolite science has received increasingly intense attention owing to the preparation of new molecular sieves[1] and the availability of modern spectroscopic methods for the study of these materials.[2] The majority of spectroscopic studies of zeolites have focused on measurements of bulk magnetic, electronic, and structural properties, but few surface studies have been reported.[3,5,6] Surface-inhomogeneous aluminum and silicon species have recently been reported by Barr and co-workers.[3] In this study we have heated metal ion containing zeolites under controlled conditions in order to probe interactions between the zeolite and the metal ion. Here we present preliminary results for Ag$^+$/NaY and Cs$^+$/NaY zeolites studied by X-ray photoelectron spectroscopy (XPS), static secondary ion mass spectrometry (SSIMS), and ion scattering spectroscopy (ISS).

Zeolites Ag$^+$/NaY and Cs$^+$/NaY were prepared by ion-exchange procedures. After exchange both samples were filtered, washed with distilled deionized water, and dried at room temperature in a vacuum line at a pressure of 1×10^{-4} kPa. The silver sample was prepared in the absence of light. Samples were pressed into pellets and then mounted in a Leybold-Heraeus spectrometer for surface studies. The bulk concentrations of these materials were obtained by a combination of atomic absorption and thermogravimetric analysis. The resulting approximate emperical formulas are $Na_{3.1}Ag_{52.9}Al_{56}Si_{136}O_{384}\cdot 213H_2O$ and $Na_{18.9}Cs_{37.1}$-

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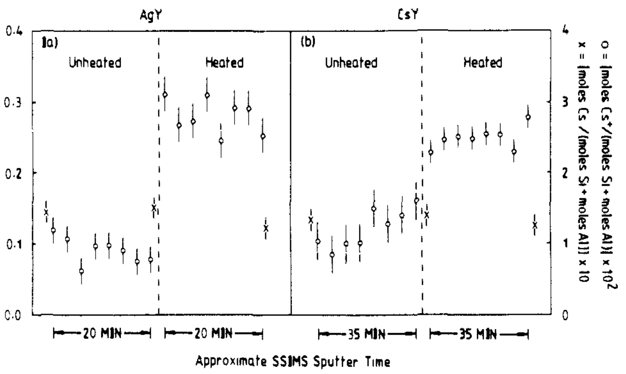

Figure 1. (a) (O) $Ag^+/Si + Al$ concentration from SSIMS. (×) $Ag^+/Si + Al$ concentration by XPS.[13] Successive SSIMS and XPS experiments on horizontal axis from left to right. (b) (O) $Cs^+/Si + Al$ concentration from SSIMS. (×) $Cs^+/Si + Al$ concentration from XPS. Successive SSIMS and XPS experiments on horizontal axis from left to right.

$Al_{56}Si_{136}O_{384}\cdot 187H_2O$. The data for Ag^+NaY are consistent with X-ray diffraction results,[7a] and those for Cs^+NaY are consistent with absorption isotherm data.[7b] Samples were first introduced into a preparatory chamber, evacuated to a pressure of 1×10^{-9} kPa, and then introduced to an analysis chamber, which was at a pressure of 1×10^{-10} to 1×10^{-11} kPa. The samples were then analyzed successively by XPS, SSIMS, and ISS. The reason for this order of analysis is that XPS is the least destructive of these methods. There may be uncertainties regarding such data due to preferential sputtering in the ISS and SIMS experiments and ion beam damage.

After this succession of surface experiments of the untreated metal-containing zeolites, the samples were moved to an attached catalysis chamber and were heated to 823 K under ultrapure N_2. Samples were moved to the preparatory chamber and then similar procedures as described above were used to determine surface properties of these thermally treated metal-containing zeolites. For the Ag^+/NaY sample all of the windows of the spectrometer were covered and the emission filaments were turned off during these experiments. No evidence of photochemical degradation of the sample was obtained from XPS studies.

Figure 1 summarizes the results of the SSIMS experiments. In the case of unheated Cs^+/NaY, a slight increase in surface Cs^+ ion concentration due to preferential sputtering is suggested by these data; however, no systematic changes were observed after heating, or in the analysis of Ag^+/NaY. The SSIMS data clearly show an increase in the concentration of surface heavy metal atoms (Ag^+ or Cs^+) upon heating. Ion scattering spectra using ^3He were collected on the samples to confirm the SSIMS results. Since SSIMS intensities depend on the yield of sputtered cations, it is conceivable that matrix effects could change as a result of heat treatment to give an appearance of an increase in surface metal ion concentrations after heating. Since ISS depends on the intensities of scattered primary ions, such matrix effects are absent.

The height of the ^3He ion scattering peak due to heavy metal atoms (Ag^+ or Cs^+) increases relative to silicon and aluminum ions of the zeolite (Figure 2). For Cs^+/NaY, this was confirmed by using a sample for which no spectroscopies other than ISS were done.

Analysis of the peak areas of the ISS data for the Cs^+NaY zeolite before heating yields a $Cs/Si + Al$ ratio of 1.8 compared to a $Cs/Si + Al$ ratio of 3.0 after heating. This corresponds to a relative increase of 1.7. These results are in good agreement with the SSIMS data of Figure 1 which show a change from 1.2 to 2.5 or a relative increase of 2.1.

Similar analyses of the ISS data for Ag^+NaY before heating yield a $Ag/Si + Al$ ratio of 1.4 compared to a $Ag/Si + Al$ ratio of 3.9 after heating. This relative increase is 2.7. Note that the $Si + Al$ ISS signal is not clearly resolved from the O and Na signal of the dehydrated Ag^+NaY. The $Ag/Si + Al$ ratio for the dehydrated Ag^+NaY was determined by using the latter part (1573–1715 eV) of the O, Na, Si, Al region (1342–1715 eV). The SSIMS data of Figure 1 show a change in $Ag/Si + Al$ from 0.1 to 0.28 or a relative increase of 2.8. There is excellent agreement between the ISS and SSIMS data here.

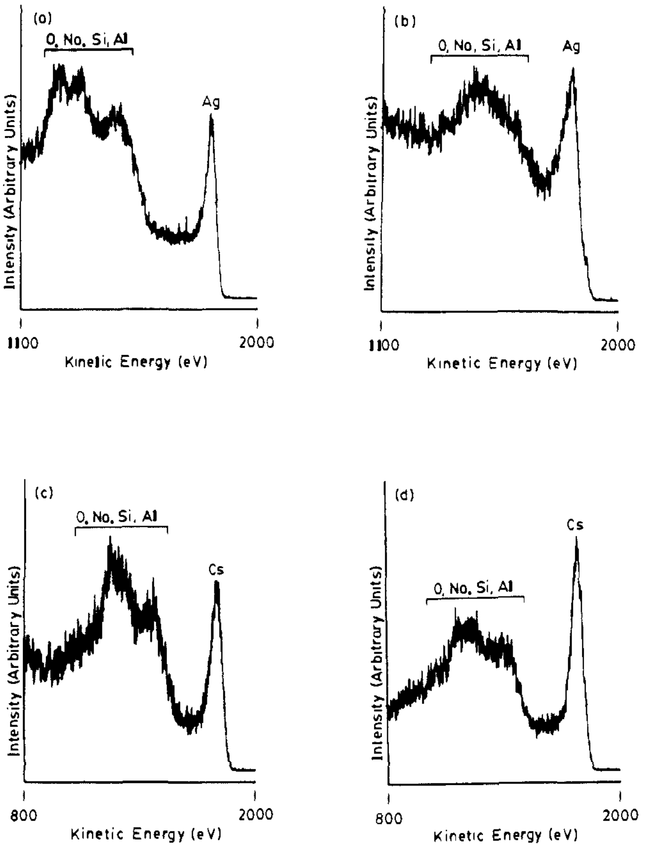

Figure 2. Ion scattering spectra using ^3He ion having a kinetic energy of 2000 eV. (a) Ag^+/NaY before heating. (b) Ag^+/NaY after heating. (c) Cs^+/NaY before heating. (d) Cs^+/NaY after heating.

The XPS results are also shown in Figure 1. When Ag^+/NaY is exposed to either visible light or to X-rays, no surface Ag^+ enhancement is observable with SSIMS after heating. When Ag^+/NaY is protected from X-rays and visible light, an increase in surface Ag^+ concentration after heating is detected by SSIMS and ISS, but not by XPS. Similarly, and in contrast to SSIMS and ISS, XPS data for Cs^+/NaY also show no significant change in concentration of surface Cs^+ ions after heating.

To explain these results, we propose the following model. When the sample is heated, the surface of the zeolite becomes richer in metal ion content in a thin layer (0–10 Å) which is only detectable with methods like SSIMS that have excellent surface sensitivity.[4]

Previously we have observed similar surface metal ion enhancements by scanning Auger microscopy[5a] and SSIMS/ISS methods[5b] for various (Cu^{2+}, Ni^{2+}, Co^{2+}) metal-containing zeolites but thermal treatments were done outside the vacuum system. The present method of studying the same sample with several surface methods allowed testing of samples for beam damage or other experimental artifacts without exposure of the samples. There is one other report[6] of a surface enhancement of Cu^{2+} in NaX zeolite as a result of thermal treatment by SSIMS, but no explanation of this phenomenon has been given.

The driving force for this surface enhancement is likely due to the release of water molecules from the metal ion during dehydration and subsequent attraction of the ion to surface oxide ions and defect sites. While several of the ions can be retained in inner sites of the zeolite, a significant number of ions migrate to external sites. Reasons for such surface ion migration could be that discontinuities and defect sites are present on external surfaces that need to be charge-compensated. These external

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surface sites are coordinatively unsaturated. The chemical potentials[8] of these surface sites may also be different than bulk sites.

To summarize, the present work demonstrates that during heating to 823 K, Ag$^+$ and Cs$^+$ ions migrate to the external surface of the zeolite. Under exposure to light, Ag$^+$ ions in these zeolites are reduced to elemental Ag(0) as determined by XPS.[15] Such species have been proposed to be active in water splitting reactions[10] and have also been characterized by electron spin echo and electron spin resonance experiments.[11] Taken together these results illustrate that surface metal ion enhancements occur during thermal treatment of zeolites. Normal XPS measurements[12] do not allow the observation of such surface enhancements because the sampling depth of the XPS experiment is too large to distinguish this thin surface layer of metal ion enhancement. Our results suggest that an integrated surface analysis of these types of materials is superior to the use of any one single method. Surface metal ion enhancements should be considered when these materials are used for adsorptive and catalytic purposes.

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(12) Angular resolved XPS experiments[14] may allow the observation of such surface metal ion enhancements for these samples. Such studies are under way in our lab.

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*Book Reviews**

Metalloproteins. Part I: Metal Proteins with Redox Roles. Part 2: Metal Proteins with Non-redox Roles. Edited by Pauline M. Harrison (University of Sheffield, England). Verlag Chemie: Deerfield Beach, FL 33442-1705. 1985. Part 1: xi + 256 pp. $55.00. ISBN 0-89573-120-6. Part 2: xii + 339 pp. $66.00. ISBN 089573-211-4.

These two volumes represent numbers six and seven in a series on "Topics in Molecular and Structural Biology". Taken together, they offer a major slice of what we know about metalloproteins. The first volume presents six articles which deal with metal proteins with redox roles, as follows: Structure and Function of Small Blue Copper Proteins; Cytochromes *c* and Cytochromes *c* Containing Enzymes; Iron-sulfur Proteins; Superoxide Dismutases; Structure and Chemistry of Cytochrome P-450; and Nitrogenase. In Part 2, devoted to metal proteins with non-redox roles, there are six more articles, as follows: Metalloproteinases; a Comparative Study of the Occurrence, Structure and Function of Troponin C and Calmodulin; Structure and Mechanism of the (Na$^+$, K$^+$) and (Ca^{2+})-ATPases; Metallothionein; Transferrins; and Oxygen Carrier Proteins.

As carefully explained by Pauline M. Harrison in two informative prefaces, her objective was to provide *fresh* and *stimulating* reviews of metalloproteins. Most of the twelve articles are timely and well written with appropriate depth, attesting to the success of her mission. However, several important topics were neglected as a result of the selection and organizational process. The reference to cytochrome *c* oxidase does not match up to its role as the most important oxidative enzyme in aerobes. Ceruloplasmin (ferroxidase), the blue copper protein of vertebrate plasma, is mentioned only once, despite the fact that this essential metalloprotein combines both redox and non-redox roles. Also lost was an opportunity to recognize the monumental achievement of Frank W. Putnam and co-workers, who in 1983 announced the complete amino acid sequence of ceruloplasmin, a single-chain metalloprotein of 1064 amino acids and six copper atoms. None of these suggestions should detract from the value and the usefulness of these two volumes to the growing literature on metalloproteins and inorganic biochemistry.

Earl Frieden, *Florida State University*

Catalysis, Science and Technology. Volume 7. Edited by J. R. Anderson (CSIRO Division of Materials Science) and M. Boudart (Stanford University). Springer-Verlag: New York. 1985. v + 222 pp. $49.50.

This book is Volume 7 of a series on heterogeneous catalysis which, as the editors correctly point out, is neither an "advances" nor a review series, but rather a collection of special topics. The topics in this issue include a chapter on the history of the catalytic synthesis of ammonia by S. A. Topham, a chapter on electron microscopy by J. V. Sanders, and a chapter on surface structures by B. E. Koel and G. A. Somorjai.

The chapter on ammonia synthesis is a fascinating presentation which places this technologically important process in a proper perspective with respect to the impact of science and engineering on human affairs. The discovery of catalysts by Fritz Haber and later by Alwin Mittasch, the process development of Carl Bosch, and the financial support by BASF established a pattern which subsequently has been repeated, to varying degrees, throughout the chemical industry.

The second chapter, which covers scanning electron microscopy (SEM), transmission electron microscopy (TEM), and scanning transmission electron microscopy (STEM), is an adequate introduction to these important techniques, although it suffers somewhat from organizational problems. Throughout the chapter, Sanders is very careful to point out limitations in the techniques and to direct the reader to the original literature for more comprehensive discussion.

In the final chapter, two surface-analysis techniques, low-energy electron diffraction (LEED) and high-resolution electron-energy loss spectroscopy (HREELS), are shown to be of major importance in structural determinations of the solid phase and the adsorbed phase. This structural information, which is largely restricted to metal single crystals, is essential for understanding catalysis on these materials at the most fundamental level.

This volume will be useful as a reference to those who are working in the field and for those who are interested in the history of science and technology (Chapter 1).

Jack H. Lunsford, *Texas A&M University*

Houben-Weyl Methoden der Organischen Chemie. 4th Edition. Supplement Volume E11: Organische Schwefelverbindungen, Parts 1 and 2. Edited by D. Klamann. Georg Thieme Verlag: Stuttgart. 1985. lxxiv + 1821 pp. DM 1950.00 (ca. $875.00). ISBN 3-13-218104-8.

This remarkably thorough work brings the subject of organic sulfur chemistry up to date from the original work (Volume 9) published in 1955 to 1984. All types of sulfuriferous functional groups except the sulfur derivatives of the carboxyl group are included, from mercaptans to esters of sulfuric acid. The 1955 volume required only about half so many pages to cover the same subject, a fact that brings to the fore the dramatic increase in publication on the subject in the last 30 years.

The exposition of the material in this work has evidently been given much more than the usual care and thought. It is hard to find a page without equations and structures. The latter are of outstanding clarity, and in addition, quick recognition of the part that is undergoing change is aided by setting that part in heavy type. The defective state of the nomenclature of organic sulfur compounds and the consequent uncertainity among many chemists about the names by which sulfur functional groups are known have been recognized; the very extensive table of contents contains prominently displayed part-structures as well as words. Even so, the nomenclature used has been carefully considered, and one sees "sulfane", a systematic name for the parent compound H$_2$S, used in combination form when it improves comprehension (e.g., "diorganooxysulfane", R^1-O-S-O-R^2, and "dialkoxydisulfane", R^1-O-S-S-O-R^2).

The coverage is not restricted to open-chain structures, although the focus of the work is on functional groups. A substantial amount of material on sulfur heterocycles is given in those areas in which other review sources are not available. Thus, thietes, thiirenes, thiazetidines, and thiapyrans are discussed, but not thiophenes or thiazoles.

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*Unsigned book reviews are by the Book Review Editor.