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X-Ray Photoelectron and Electron Spin Resonance Spectroscopic Studies of Cu-NaY Zeolites

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X-Ray photoelectron spectroscopic (XPS) studies of hydrated, dehydrated, and reduced Cu-NaY zeolites were carried out. With sufficient analyzer resolution, both the Cu $2p_{1/2}$ and $2p_{3/2}$ transitions were resolved into two components in hydrated Cu-NaY. The higher-binding-energy component and the shake-up satellites decreased in intensity with dehydration. By correlation with electron spin resonance (ESR) and X-ray diffraction results the higher-binding-energy component is assigned to octahedrally coordinated Cu^{2+} in the large α-cages of the zeolite and the lower-binding-energy component to tetrahedrally coordinated Cu^{2+} in the small β-cages of the zeolite. On hydrogen reduction of dehydrated Cu-NaY the XPS transitions shift by ~1 eV to lower binding energies which correlated with an order of magnitude decrease in the Cu^{2+} ESR intensity. These shifted transitions are assigned to Cu^+ or possibly to Cu^0. © 1985 Academic Press, Inc.

INTRODUCTION

Copper-exchanged X and Y zeolites have been shown to be highly active and selective catalysts (*1–3*) and consequently have been the subject of numerous studies involving various physical techniques (*4–9*). The effects on the catalytic properties of various preparation procedures of Cu-Y zeolites have been discussed (*3, 8*) in terms of different oxidation states of Cu. The photoelectron and Auger chemical shifts observed in the X-ray photoelectron spectra (XPS) on changing the oxidation state from Cu^{2+} to Cu^+ to Cu^0 are significant (*10, 11*). However, little use has been made of these significant shifts for characterization of copper-exchanged zeolites (*12, 13, 15*). The change in oxidation state from Cu^{2+} to Cu^+ can also be followed by loss of electron spin resonance (ESR) since only Cu^{2+} is paramagnetic. Thus a combination of XPS and ESR may provide firm assignment of the oxidation state of Cu in zeolites under various treatment conditions.

Recently Chon *et al.* (*15*) studied the vapor-phase hydrogenation of furfural on Cu-Y zeolite by ESR and XPS. They used ESR to study the organic radicals formed and to detect Cu^{2+} although they did not assign the Cu^{2+} to any specific copper species in the zeolite. They assigned the XPS data by comparison with $CuCl_2$ and CuCl. The assignment of the XPS data to specific copper species is important because some reduction might occur during various sample treatments such as dehydration (*12*). In this paper we have used ESR and X-ray diffraction information to assign the observed Cu 2*p* XPS binding energies to specific zeolitic copper species obtained by various treatments of Cu-NaY zeolites. We also find that the associated shake-up satellite intensities depend on the coordination geometry of the metal ion as well as on the oxidation state, thus the satellite intensities alone do not uniquely correlate with the oxidation state.

EXPERIMENTAL

Linde NaY zeolite (LZY52) was used after washing with 0.1 *M* NaCl and $NaCH_3COO$ solutions. The exchange of copper was done with 0.01 *M* cupric nitrate solutions at pH values of 5.5 to 5.9. Zeolites with 18 to 46% of the Na^+ exchanged with

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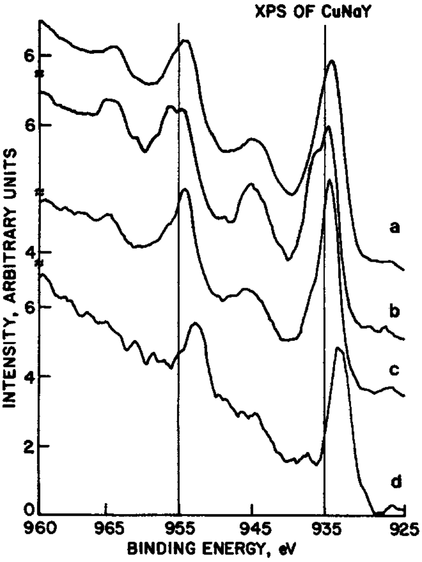

FIG. 1. X-Ray photoelectron spectra of Cu-NaY zeolite in the Cu 2*p* region. (a) Freshly prepared sample, evacuated for 2 h in the ESCA spectrometer before recording the spectrum at 100-eV analyzer pass energy; only one type of copper species is indicated. (b) Freshly prepared sample treated similar to (a) but recorded at 25-eV analyzer pass energy; note that now two types of Cu^{2+} are resolved. The higher-binding-energy components at 936.2 and 956.2 eV are attributed to $Cu(H_2O)_6^{2+}$ and the two lower-binding-energy components are assigned to $Cu(O_z)_3X^{2+}$ where X could be O, OH, or H_2O. (c) Sample dehydrated in the ESCA spectrometer for 6 h at 523 K and recorded at 25-eV analyzer pass energy; note the decrease in the $Cu(H_2O)_6^{2+}$ component intensities. (d) Sample dehydrated at 573 K for 12 h and reduced with 100 Torr of H_2 at the same temperature for 3 h. The sample was evacuated at 573 K for 3 h before transferring to the ESCA spectrometer under a nitrogen atmosphere. The features of $Cu(H_2O)_6^{2+}$ have disappeared and the components at 932.8 and 952.8 eV are assigned to Cu^+ or Cu^0. Acquisition time was 8 min for (a), 5 min for (b) and (c), and 20 min for (d).

Cu^{2+} were prepared but most of the XPS experiments were made with the Cu-NaY zeolite containing 10 cupric ions per unit cell corresponding to 36% of the Na^+ exchanged. The zeolite after ion exchange was dried in air at room temperature (60% relative humidity) and pressed in a hydraulic die at about 200 kg to form a thin, smooth ½-in. round pellet which was then positioned on a sample holder by means of a silver clamp. The photoelectron spectra were measured in a Perkin–Elmer PHI Model 550 ESCA/SAM spectrometer using Mg*K*α X-rays at 1253.6 eV as the excitation source. All binding energies were referenced to the adventitious carbon 1*s* line presumably due to hydrocarbon contamination, at 285.0 eV. The reproducibility of the binding energies for samples treated in an identical manner was less than ±0.2 eV. Data smoothing, subtraction of inelastic scattering, and deconvolution of the spectra were performed using the PHI software available in the spectrometer. ESR measurements were made with a Varian E-line spectrometer at 9 GHz.

RESULTS AND DISCUSSION

Figure 1a shows the photoelectron spectrum of Cu-NaY zeolite in the Cu 2*p* region after evacuation at room temperature for 2 h to 10^{-8} Torr in the main vacuum chamber of the ESCA spectrometer. The resolution was low and the spectrum is similar to that of 60% exchanged Cu-NaY reported by Chon *et al.* (*14*, *15*). Two main lines corresponding to the $2p_{3/2}$ and $2p_{1/2}$ Cu transitions are observed at 933.8 and 954.0 eV, respectively, along with their associated shake-up satellites (*10*, *11*). However, on increasing the resolution of the analyzer, from 100-eV pass energy to 25-eV pass energy, the $2p_{3/2}$ and $2p_{1/2}$ peaks clearly show a resolved shoulder indicating the presence of a higher-binding-energy component as shown in Fig. 1b. The intensity and resolution of these two components did not alter on keeping the sample in the main chamber of the spectrometer for 48 h at 10^{-9} Torr before recording the spectra. The resolution into two components is supported by a deconvolution of the $2p_{3/2}$ peak and its satellite as shown in Fig. 2. Such deconvolution, with the assumption of a Gaussian lineshape, yields binding energies of 936.2 and 933.9 eV for the shoulder and main peak, respectively. Such resolved structure was not reported by either Bravo *et al.* (*13*) or Chon *et al.* (*15*) in previous Cu-NaY zeo-

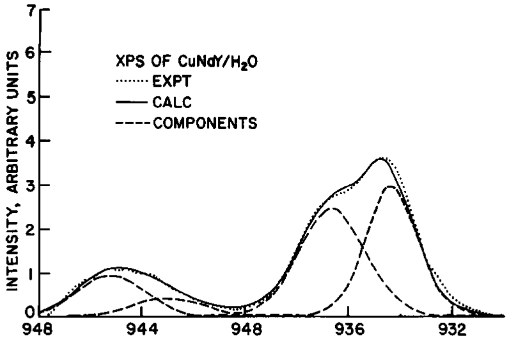

FIG. 2. Deconvoluted spectra, based on a Gaussian lineshape of the Cu $2p_{3/2}$ line and its main satellite, compared with the experimental spectrum (in Fig. 1b) after subtraction of inelastic scattering.

lite studies. Minachev *et al.* (*12*) show some structure in their photoelectron spectra of Cu-NaY zeolite but did not comment on it. Careful examination of the XPS data for several copper-exchanged X and Y zeolites in our laboratory has shown similarly resolved higher-binding-energy components which are sensitive to the concentration of copper in the zeolite (*16*).

After dehydrating the sample by raising the temperature to 523 K and evacuating it for 2 h the sample became dull gray and the photoelectron spectrum showed much decreased intensities of the higher-binding-energy component and of the satellite lines while the main component showed a slight increase in intensity (see Fig. 1c). There were no measurable differences between the ESR spectra or spectral intensities of hydrated and such dehydrated samples. ESR spectra of both samples at room temperature exhibit a somewhat broad isotropic line at $g = 2.17$ similar to reports in the literature (*7, 17, 18*). Thus the significant decrease in the satellite and higher-binding-energy component intensities are not due to changes from Cu^{2+} to Cu^{+} via an autoreduction process. To further study the changes in the XPS data a Cu-NaY sample was dehydrated at 10^{-6} Torr with a gradual increase of temperature from 300 to 523 K over 12 h followed by reduction at 523 K with 100 Torr of H_2 for 3 h. This sample had a grayish brown color compared to the light blue color of fresh and room-temperature evacuated samples. The ESR spectrum of this reduced sample still showed a broad line at $g = 2.17$ but it was an order of magnitude weaker than the ESR spectrum of fresh or room-temperature evacuated Cu-NaY zeolite. The photoelectron spectrum of such a reduced sample is shown in Fig. 1d; it indicates the complete disappearance of the higher-binding-energy component and the satellite lines. The main peaks show a shift of ~1 eV to lower binding energies. The binding energies and widths of the observed XPS lines in hydrated, dehydrated, and reduced samples of Cu-NaY are summarized in Table 1.

Chon *et al.* (*15*) also observed a decrease in the satellite intensities and shifting of main peaks to lower binding energies when furfural was adsorbed on Cu-NaY. They attributed this to a change of oxidation state from Cu^{2+} to Cu^{+} on adsorption. However, it is not clear to us whether they compared the photoelectron spectra of a fresh hydrated sample or a dehydrated sample to that of Cu-NaY with adsorbed furfural. From the intensity of the satellites in their

TABLE 1

Linewidths and Binding Energies of the Cu $2p_{3/2}$ XPS Transition in Cu-NaY Zeolites

Zeolite	Hydration status	Binding energy[a] (eV)	Full width at half maximum (eV)	Ref.
Cu-NaY	Hydrated	933.8[b]	4.6[b]	This work
Cu-NaY	Hydrated	933.9[c]	2.8	This work
		936.2[c]	2.8	This work
Cu-NaY	Dehydrated	934.2	3.3	This work
Cu-NaY	Dehydrated, reduced	932.8	3.2	This work
Cu metal	—	933.0	1.9	(*32, 33*)
Cu_2O	—	932.9	1.9	(*32, 33*)
$CuSO_4 \cdot 5H_2O$[d]	—	935.9	—	(*33*)
CuO–ZnO[e]	Dehydrated	933.9	3.5	(*24*)
$Cu(OH)_2$	—	934.4	2.6	(*34, 35*)

[a] Referenced to carbon 1*s* at 285.0 ± 0.2 eV.

[b] Low resolution (100-eV analyzer pass energy).

[c] High resolution (25-eV analyzer pass energy) with spectral deconvolution as shown in Fig. 2.

[d] Cu^{2+} is in octahedral coordination.

[e] Cu^{2+} is in tetrahedral coordination.

data it appears that they compared a hydrated sample to the sample with adsorbed furfural.

As shown in Figs. 1b and c there is a significant decrease in the intensity of the satellite lines on dehydration alone. While the origin of these satellite lines in the XPS data of transition metal ions is still not clearly understood (*10, 11, 19–23*) it has been observed that they are sensitive to factors such as the ligand electronegativity, the delocalization of the unpaired electron, the coordination number, and the extent of distortion in the coordination geometry of the transition metal ion. By examining the XPS data of a series of CuO–ZnO catalysts Okamoto *et al.* (*24*) have shown that the intensity of the shake-up satellites of Cu^{2+} decreases significantly as Cu^{2+} changes coordination from distorted octahedral to symmetric tetrahedral geometry. Escard *et al.* (*23*) also observed a low satellite intensity for tetrahedral alkyl ammonium copper(II) complexes.

A similar argument can be used to explain our XPS data of Cu-NaY zeolites. The higher-binding-energy component observed in fresh samples is most likely due to Cu^{2+} in distorted octahedral coordination. From ESR studies it is known that a significant amount of Cu^{2+} exists as the $Cu(H_2O)_6^{2+}$ complex in the large cages of the zeolite in highly exchanged samples of Cu-NaY (*17, 18, 25–27*). X-Ray diffraction results also support this. Maxwell and DeBoer (*28*) were able to locate only 6 out of 26 Cu in a fully exchanged hydrated Cu faujasite which has the same structure as Y zeolite but a lower Si/Al ratio by X-ray diffraction and they concluded that the majority of the Cu^{2+} are mobile and in the hexaaquo form. Even in very low exchanged copper Y zeolites, Ichikawa and Kevan (*29*) have shown by electron spin echo modulation studies that Cu^{2+} is in a distorted octahedral arrangement with three zeolite oxygens and three water molecules in the large cage. Thus the high-binding-energy component can be assigned to Cu^{2+} in octahedral coordination in the large cages of the zeolite. It should be noted that its binding energy is quite close to that of Cu^{2+} in $CuSO_4 \cdot 5H_2O$ (*20*) where Cu^{2+} is in octahedral coordination (see Table 1).

On evacuation at higher temperatures some of the water ligands are lost and Cu^{2+} moves to specific sites in the zeolite lattice. Gallezot *et al.* (*30*) as well as Maxwell and DeBoer used X-ray diffraction to suggest that more than 75% of the Cu^{2+} occupies the small cage sites SI′ and SII′ in dehydrated faujasite. In such sites Cu^{2+} is in trigonal coordination with three oxygens of a six-ring or in distorted tetrahedral coordination with a fourth ligand from a nonframework oxygen. Chao and Lunsford (*7*) suggested that two such Cu^{2+} are weakly coupled to produce the observed isotropic ESR spectra. Conesa and Soria (*9*) postulated pairing of Cu^{2+} at SI′ and SII′ positions in the zeolite lattice to explain their ESR spectra of Cu-NaY zeolites dehydrated at 873 K. Iwamoto *et al.* (*31*) concluded from their temperature-programmed desorption studies of Cu-NaY zeolites that Cu^{2+} are located at SI′ and SII′ sites in the sodalite cage and are coupled through a nonframework oxygen. They also observed that the ESR intensities of Cu-NaY zeolites remain constant over a dehydration temperature range of 273–673 K which agrees very well with our observations. Thus there is reasonable evidence to indicate that the lower-binding-energy component in XPS spectra of hydrated or dehydrated Cu-NaY zeolites is due to Cu^{2+} in tetrahedral coordination at SI′ or SII′ positions. It should be noted here that the six Cu^{2+} that Maxwell and DeBoer (*28*) were able to locate in hydrated Cu-NaX were at SI′. This is a reason why in all the hydrated samples the Cu 2*p* lines were split into two components which we assign as octahedrally and tetrahedrally coordinated Cu^{2+}. As dehydration proceeds the Cu^{2+} in octahedral coordination in the α-cage loses some or all of the water ligands and migrates to SI′ or SII′ sites which fits very well with the observed decrease of the

936.2-eV shoulder and the increase of the 933.9-eV peak in the XPS data of Cu-NaY zeolite dehydrated at 523 K as shown in Fig. 1c. The observed decrease in the intensities of the satellite lines also correlates with the change in the coordination number and geometry of Cu^{2+} associated with such migration.

It is interesting to note that bulk $Cu(OH)_2$ has a higher binding energy than bulk CuO as shown in Table 1 (*34, 35*). These two bulk copper species have the same valence state and formally differ in their degree of hydration with the "hydrated" species having the higher binding energy. This is qualitatively similar to what we observe in the zeolites. However, we can be reasonably sure that we are not observing bulk CuO or $Cu(OH)_2$ species in the zeolites since ESR is not observable for these copper compounds due to extremely short relaxation times, while in zeolites we do observe Cu^{2+} ESR with an intensity that accounts for all of the Cu^{2+} in both hydrated and dehydrated cases. From extensive ESR and electron spin echo studies in zeolites discussed above it is clear that Cu^{2+} undergoes a change in coordination on dehydration. This correlates with the change in the XPS spectral energies. However, we cannot differentiate effects of dehydration from the change in coordination if such do exist.

Reduction of Cu^{2+} to Cu^+ does appear to be associated with a 1.0-eV shift toward lower binding energy. This shift seems best assigned to a change in the Cu oxidation state. It is difficult to decide whether the reduction leads to Cu^+ or Cu^0 because their binding energies are quite similar (*10, 11, 20*). Although Cu^0 is paramagnetic it readily forms clusters which have very broad ESR lines which are often not observable. Sufficiently large Cu^0 clusters show a pink color which can be generated with more than 15 Cu^{2+} per unit cell and dehydration above 973 K according to our observations. Under our more moderate conditions we do not believe the absence of a pink color distinguishes between Cu^0 and Cu^+. Larson (*10*) has shown that the Auger chemical shifts can be used to distinguish between Cu^0 and Cu^+ but in our case the X-ray-induced Auger lines were too weak to be quantitatively measured. Without causing X-ray-induced reduction and decomposition it was not possible to enhance their intensities.

We conclude that a decrease in intensities of satellite lines in Cu photoelectron spectra does not necessarily mean a change in the oxidation state but can also be caused by changes in the coordination number and geometry. To determine changes in the oxidation state more precisely by XPS, it might be necessary to study the Auger and valence band transitions along with the core electron spectra of the metal ion in question. Bravo *et al.* (*13*) observed a decrease, on progressive dehydration of Cu-NaX zeolites at higher temperatures, in the binding energies of Cu and they attributed such a decrease to the migration of loosely bound Cu^{2+} species. We also suggest that such migration, resulting in different coordination geometry, is correlated with the decrease of satellite intensities in the photoelectron spectra of partially dehydrated Cu-Y zeolites.

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