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 (25) Co(II) has been shown to catalyze the reduction of Co(II) by hydrazine in perchloric acid medium.²⁶ Under these conditions the redox reaction is too slow to be substitution controlled and takes place by a different mechanism.
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Cobalt Nitrosyl Complexes in Zeolites A, X, and Y

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Nitrosyl complexes were formed when NO reacted with Co²⁺ ions in zeolites A, X, and Y. In the A-type zeolite the mononitrosyl complex was favored, whereas in the Y-type zeolite only the dinitrosyl complex was formed. Both complexes were formed in the X-type zeolite. The greatest thermal stability occurred in the Y-type zeolite. Infrared and XPS data suggest that there is no appreciable electron transfer between the metal ion and the ligand in either complex, although diffuse-reflectance spectra indicate that the nitrosyl group has a significant effect on the electronic structure of the cobalt ion. The propensity of the Co²⁺ to form the mono- or the dinitrosyl complex is attributed to the position of the cation with respect to the oxide ions of the lattice and the mobility of the cation under the influence of the ligand. These factors may ultimately be related to the charge density in the zeolite.

Introduction

A number of different metal ions in zeolites have been observed to coordinate with nitric oxide, forming nitrosyl complexes. These metal ions include Ag⁺, Cu⁺, Cu²⁺, Ni²⁺, Cr²⁺, Fe²⁺, and Co²⁺.¹⁻⁸ Both mono- and dinitrosyl complexes have been observed. In the case of the nickel nitrosyl complex and EPR spectrum provides convincing evidence that electron transfer occurs from the ligand to the metal ion.^{3,4} Similar interpretations have been given for the formation of nitrosyl complexes with Cu²⁺, Fe²⁺, and Cr²⁺.^{2,5,6} An unusual situation occurs in Ag-Y zeolites where nitric oxide apparently forms a bridge between Ag⁺ ions.¹

In a Y-type zeolite Co²⁺ forms a dinitrosyl complex which has been identified by infrared spectroscopy.⁷ The spectra suggest that there is no appreciable electron transfer between the metal ion and the ligand. On the basis of the electron diffraction data of Seff,⁸ one may conclude that a mononitrosyl complex is formed in an A-type zeolite. The Co²⁺ ion is coordinated to three oxide ions in the six-membered window and the bent nitrosyl ligand extends into the large cavity.⁹

It was at first believed that the M-N-O angle was approximately 180° in all complexes which had a cationic nitrosyl ligand and that the bond angle was nonlinear for complexes containing an anionic nitrosyl ligand. Additional structural data have shown that in fact there is no correlation between the effective charge on the NO group and the geometry of the molecule.¹⁰ Enemark and Feltham¹⁰ have pointed out that the ultimate geometry assumed by the NO group is dependent not only on the total number of electrons but also upon the nature of the highest occupied molecular orbital.

The present study has been an attempt to understand the role of the zeolite framework in the formation of either mono- or dinitrosyl cobalt complexes. In particular it was of interest to explain why the mononitrosyl complex was favored in the A-type zeolite and the dinitrosyl complex was favored in the Y-type zeolite. In order to evaluate the effect of charge density on this question the formations of the complexes in X- and Y-type zeolites have been compared. Both of these zeolites

are of the faujasite structure, but the X zeolite has a smaller silicon to aluminum ratio and, therefore, a greater charge density. The charge density in the A-type zeolite is even greater than in the zeolites of the faujasite structure. An additional purpose of the study was to determine whether the cobalt ion underwent any oxidation or reduction during the formation of the complexes.

Experimental Section

The experiments were performed on cobalt(II) A, X, and Y zeolite samples prepared by ion exchange as described elsewhere.⁷ The Co²⁺ exchange levels were 72, 69, and 70% for the A, X, and Y zeolites, respectively. In the preparation of a sample which contained cobalt(III) the [Co(NH₃)₆]³⁺ complex was exchanged into a Y-type zeolite from an aqueous solution. Unless otherwise indicated, all of the zeolites were degassed under vacuum (10⁻⁵ Torr) to a temperature of 300 °C.

The nitric oxide, obtained from a commercial source, was repeatedly sublimed and frozen using a pentane slush and liquid nitrogen, respectively, in order to remove nitrogen dioxide which was present as a major impurity.

A Cary 14 spectrophotometer with a type-II diffuse-reflectance attachment was used to obtain the spectra in the range from 6000 to 30000 cm⁻¹. A NaY zeolite, dehydrated under vacuum to 460 °C, was used as the reference material. Spectra were recorded with the zeolite both in the form of a loose powder and as an opaque compressed wafer. In the former case there was less of a problem with contamination of the sample, but larger amounts of material were required and it was more difficult to introduce the nitric oxide uniformly so that direct comparison could be made with the results from infrared and photoelectron spectroscopy.

The infrared spectra were recorded using a Beckman IR-9 spectrophotometer in the transmission mode. The zeolite was in the form of a self-supporting wafer which had a single-beam transmission of approximately 50%. The cell used for the infrared work was similar to that described previously.¹¹ Slit widths were set so that a minimum resolution of 1.5 cm⁻¹ was achieved. The accuracy of the band positions was estimated to be ±5 cm⁻¹.

A Hewlett-Packard 5950A ESCA spectrometer utilizing monochromatic Al Kα_{1,2} x radiation (1486.6 eV) was employed to obtain the photoelectron spectra. The cobalt-exchanged zeolite was pressed into a thin film and placed on a sample plate. The samples were

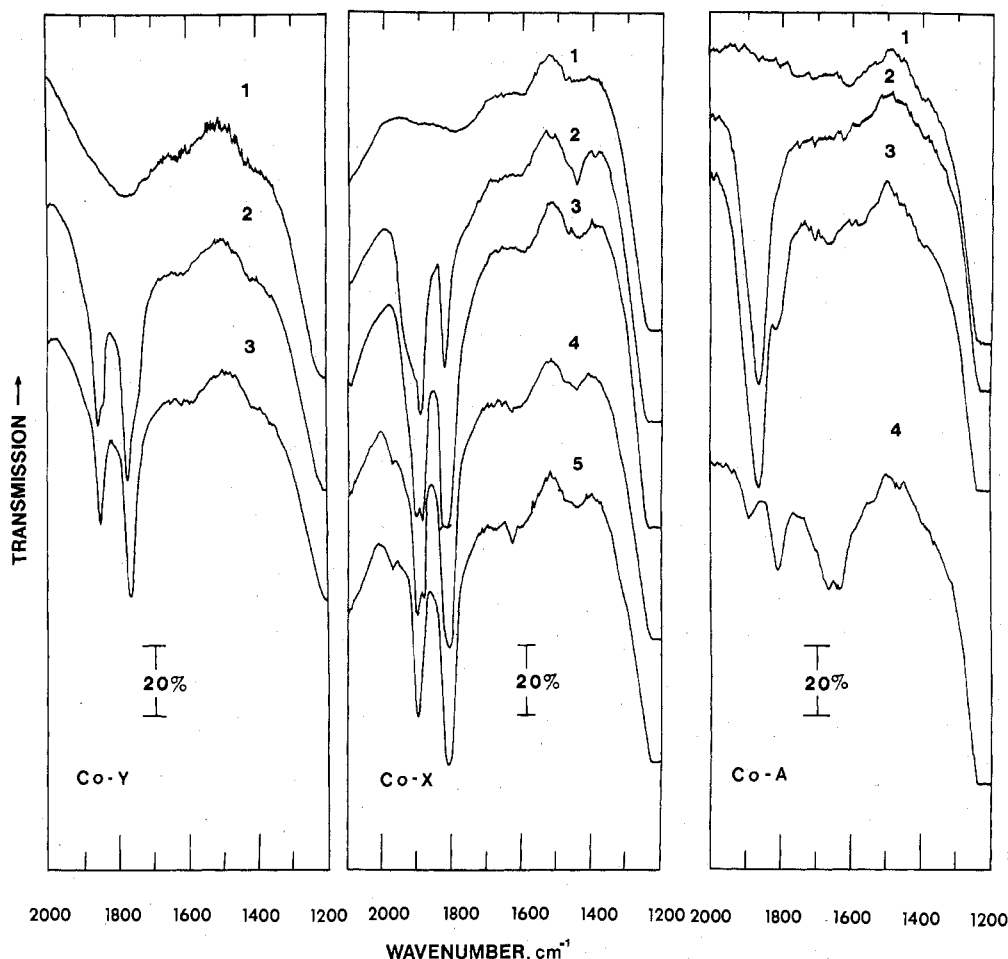


Figure 1. Infrared spectra of cobalt(II) zeolites. CoY: (1) degassed at 300 °C, (2) 10 min after addition of 40 Torr of NO, and (3) under vacuum for 1 h at 25 °C. CoX: (1) degassed at 300 °C, (2) 10 min after addition of 40 Torr of NO, (3) 16 h after addition of NO, (4) under vacuum for 3.5 h at 25 °C, and (5) under vacuum for 6 h at 25 °C. CoA: (1) degassed at 300 °C, (2) 15 min after addition of 10 Torr of NO, (3) 16 h after addition of NO, and (4) under vacuum for 6 h at 25 °C. The curves have been displaced with respect to the ordinate for clarity of presentation.

degassed at temperatures up to 300 °C in the sample preparation chamber of the spectrometer. Subsequently they were exposed to 60 Torr of NO at 25 °C for 4 h. The sample probe was cooled to -13 °C before the gas-phase nitric oxide was pumped off. Spectra of the nitrosyl complexes on Co^{II}A were recorded with the probe at -13 °C, whereas those on Co^{II}Y were recorded with the probe at both -13 and +25 °C. Typical collecting times were 3 h for the Co 2p peaks and 5 h for the nitrogen 1s peak. Binding energies were referenced to a gold spot which was deposited on the sample. The 4f_{7/2} level of Au was assigned a binding energy of 84.0 eV. A carbon 1s peak with a binding energy of 285.0 eV and a silicon 2s peak from the zeolite with a binding energy of 153.3 eV served as supplementary standards. Charge compensation was achieved by flooding the sample with nearly zero-kinetic-energy electrons. Measured binding energies were reproducible to ±0.1 eV for N 1s and ±0.2 eV for Co peaks. The data points of the XPS spectra were smoothed by a simple five-point program, and the spectra were deconvoluted using a Du Pont 310 curve resolver.

Results

Infrared Spectra. Upon admission of NO at pressures of 10–50 Torr to a Co^{II}Y zeolite at 25 °C, infrared bands at 1820 and 1905 cm⁻¹, characteristic of the dinitrosyl complex, grew in a parallel manner over a period of several hours, as previously reported (in the earlier work⁷ the positions of the bands were given as 1830 and 1910 cm⁻¹). In addition, shoulders at 1800 and 1890 cm⁻¹ were also observed, as shown in Figure 1, after short exposures of the sample to NO. Although it is not indicated in the figure, the ultimate concentration of the complex responsible for the bands at 1820 and 1905 cm⁻¹ was

more than 1 order of magnitude greater than the concentration of the complex which gave rise to the bands at 1800 and 1890 cm⁻¹. The species responsible for the shoulders was removed by evacuation for 1 h at room temperature. The bands at 1820 and 1905 cm⁻¹, however, were quite stable at 25 °C and decreased in amplitude only at temperatures in excess of 100 °C.

With the Co^{II}X zeolite similar bands were formed at 1815 and 1900 cm⁻¹, but an additional band was observed at 1880 cm⁻¹, as depicted in Figure 1. The latter band reached a maximum intensity rather quickly, whereas the pair of bands continued to grow for several hours. All three of the bands decreased in intensity upon evacuation at 25 °C, but the band at 1880 cm⁻¹ disappeared more rapidly than the other two.

Addition of NO to a Co^{II}A zeolite resulted in the rapid formation of a strong band at 1870 cm⁻¹. Over a period of several hours a weak band at 1810 cm⁻¹ also appeared, as shown in Figure 1. Upon evacuation of gas-phase NO for 3 h the band at 1870 cm⁻¹ was greatly reduced in intensity, and after evacuation for 16 h only a pair of bands at 1810 and 1890 cm⁻¹ remained. A broad band at 1650 cm⁻¹ in curve 4 of Figure 1 (Co-A) is due to a small amount of water that was readsorbed into the zeolite. An equimolar mixture of ¹⁴N¹⁵O and ¹⁵N¹⁴O resulted in a pair of bands of equal intensity at 1840 and 1870 cm⁻¹.

Previous work by other investigators⁵ had suggested that it may be possible to distinguish between nitrosyl complexes located in the small cavities and those located in the large

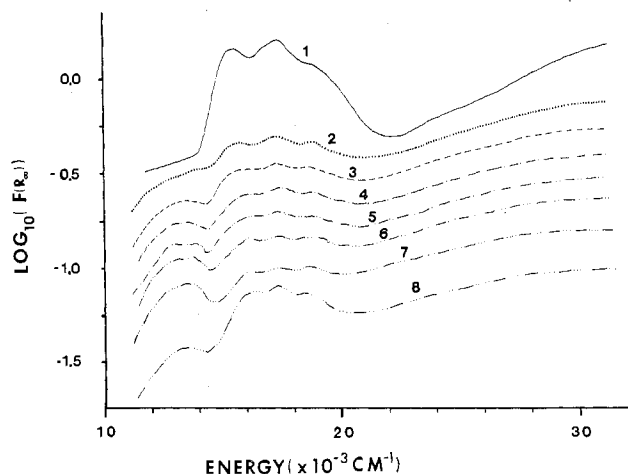


Figure 2. Diffuse-reflectance spectra of $\text{Co}^{\text{II}}\text{Y}$ zeolite: (1) degassed at 300°C ; after addition of 40 Torr of NO for (2) 10 min, (3) 1 h, (4) 2 h, (5) 3 h, (6) 9 h, (7) 19 h; and (8) under vacuum for 10 h at 25°C . The curves have been displaced with respect to the ordinate for clarity of presentation.

cavities by following the relative rates of reaction between the complexed nitric oxide and molecular oxygen. It is generally believed that NO is able to enter the sodalite cages at 25°C , but O_2 is not. In order to employ this potentially diagnostic technique the cobalt nitrosyl complexes in the A, X, and Y zeolites were exposed to molecular oxygen at 25°C , following the brief evacuation of the gas-phase nitric oxide. Surprisingly, in all three cases the half-life for the reaction was on the order of several hours. In the X zeolite the pair of bands at 1815 and 1900 cm^{-1} reacted more rapidly than the single sharp band at 1880 cm^{-1} . New bands due to N_2O_3 (1920 , 1560 , 1315 cm^{-1}) and coordinated ONO^7 (1520 cm^{-1}) appeared in the spectrum. With the A and Y zeolites the ONO band was observed, but the bands due to N_2O_3 were not. In the A zeolite a strong band at 1315 cm^{-1} was also observed which may be attributed to a chelating nitro group.¹³

Diffuse-Reflectance Spectra. Curve 1 of Figure 2 shows the spectrum of the degassed $\text{Co}^{\text{II}}\text{Y}$ zeolite. As reported previously by other investigators,¹⁴ the spectrum is characterized by three maxima in the region from 15000 to 19000 cm^{-1} . Upon admission of NO there was a distinct decrease in absorbance in this region and a shift of the band at 15260 cm^{-1} to ca. 15700 cm^{-1} . In some samples there also appeared a band at 13000 cm^{-1} ; however, its appearance was sporadic, and the band was not evident in the spectrum if the sample was exposed only briefly to the intense light source in the reflectance attachment. We believe that the band at 13000 cm^{-1} was due to a photoinduced oxidation of the cobalt since the energy is consistent with a high-spin transition of a Co^{3+} ion in a tetrahedral environment. The bands in the 15000 – 19000-cm^{-1} region of the spectrum increased only slightly in intensity upon evacuating the sample for 16 h at 25°C .

The modifications in the diffuse-reflectance spectra upon admission of NO to the $\text{Co}^{\text{II}}\text{X}$ zeolite were generally the same as those observed for the $\text{Co}^{\text{II}}\text{Y}$ zeolite. A partially reversible decrease in the spectrum was noted with a shift of the band at 15270 cm^{-1} to 15630 cm^{-1} .

Curve 1 of Figure 3 shows the typical spectrum of Co^{2+} ions in an A-type zeolite.¹⁵ Admission of NO immediately resulted in the disappearance of the 24000-cm^{-1} band and a decrease in intensity of the bands in the 14000 – 19000-cm^{-1} region. The region around 19000 cm^{-1} became relatively more pronounced. A large increase in the background was detected and the sample turned from blue to almost black. The low-energy band was shifted from 6600 cm^{-1} to 8100 cm^{-1} . Evacuation of the cell for 16 h caused most of the characteristic features of the

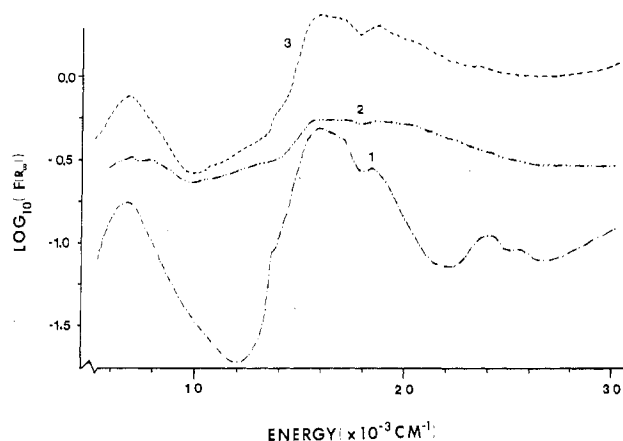


Figure 3. Diffuse-reflectance spectra of $\text{Co}^{\text{II}}\text{A}$ zeolite: (1) degassed at 300°C , (2) 10 min or 18 h after addition of 40 Torr of NO, and (3) under vacuum for 16 h at 25°C . The curves have been displaced with respect to the ordinate for clarity of presentation.

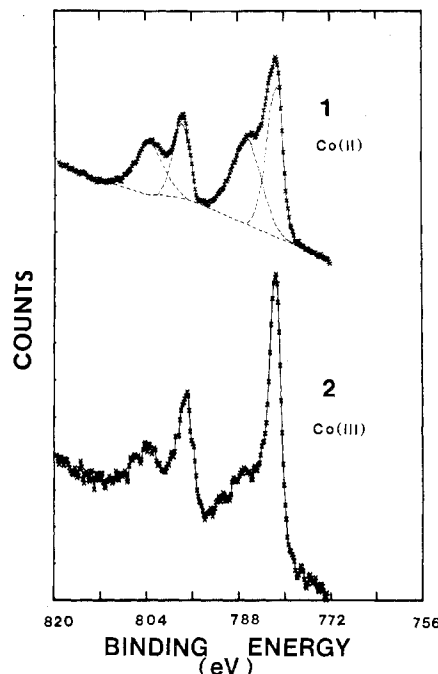


Figure 4. X-ray photoelectron spectra of cobalt-exchanged zeolites: (1) $\text{Co}^{\text{II}}\text{Y}$ degassed at 300°C and (2) $[\text{Co}^{\text{III}}(\text{NH}_3)_6]^{3+}$ -exchanged Y-type zeolite. The curves have been displaced with respect to the ordinate for clarity of presentation.

$\text{Co}^{\text{II}}\text{A}$ spectrum to reappear, although evacuation at 60°C for 1.5 h was required to fully restore the band at 24000 cm^{-1} and to return the sample to its original blue color.

X-Ray Photoelectron Spectra. There was no change in the peak positions or relative intensities of the XPS spectra of the Co 2p lines upon adsorption of NO on either the $\text{Co}^{\text{II}}\text{A}$ or $\text{Co}^{\text{II}}\text{Y}$ zeolites. The spectrum of the Co 2p lines, as shown in curve 1 of Figure 4, consisted of two primary peaks at 782.0 and 798.0 eV for the $2p_{3/2}$ and $2p_{1/2}$ levels, respectively. Satellite lines were observed at 5.0 eV greater binding energies. The separation between the Co 2p lines was 16.0 eV , and the full width at half-maximum (fwhm) of the deconvoluted $2p_{3/2}$ line was 3.5 eV . Deconvoluted curves gave a ratio of the peak heights of the satellite line to the primary Co $2p_{3/2}$ line of 0.55 . The multiplet splitting for the 3s level of the cobalt was difficult to observe due to strong interference from the Si 2p line at 102.5 eV .

Although the binding energies and the separation of the Co 2p lines were in good agreement with those reported for

high-spin cobalt(II) in salts and zeolites,¹⁶ it was of interest to establish the spectrum of cobalt(III) in a zeolite. The diamagnetic hexaamminecobalt(III) complex in a Y-type zeolite, which had been previously studied by infrared spectroscopy,¹⁷ gave a different XPS spectrum from that of the Co^{2+} ion. With the cobalt in the higher oxidation state the primary peaks were located at 781.7 and 796.7 eV for the Co $2p_{3/2}$ and $2p_{1/2}$ levels, respectively, as depicted in curve 2 of Figure 4. The satellite lines appeared at a greater binding energy of 5.5 eV and the separation between 2p lines was 15.0 eV.

For the nitrosyl ligand in the $\text{Co}^{\text{II}}\text{Y}$ zeolite the nitrogen 1s peak was observed at 400.7 eV. A value of 400.6 eV was observed for the $\text{Co}^{\text{II}}\text{A}$ zeolite although the difference is within the limits of reproducibility. The intensity of the spectrum in the A zeolite was only slightly less than in the Y, which means that the cooling of the sample effectively prevented the decomposition of the complex in the high vacuum of the spectrometer.

Discussion

The infrared results confirm the x-ray diffraction data of Seff⁸ which demonstrated that a mononitrosyl was dominantly formed upon the adsorption of NO into a $\text{Co}^{\text{II}}\text{A}$ zeolite. Furthermore, the ease with which the complex may be destroyed by evacuation of the gas-phase NO at 25 °C is consistent with the long Co-N bond length of 2.4 Å. The situation is clearly different than in the $\text{Co}^{\text{II}}\text{Y}$ zeolite where a much more stable dinitrosyl complex is formed. The $\text{Co}^{\text{II}}\text{X}$ zeolite appears to be intermediate between the A and Y zeolites in that both the mononitrosyl and the dinitrosyl complexes occur.

This difference in complex structure is at first somewhat surprising since the cobalt ions are believed to be coordinated to three oxygen ions in the six-membered rings in all three of the zeolites. On closer inspection, however, it should be noted that the cobalt ions in the zeolite A are located almost in the plane of the three oxygen ions⁸ and that coordination with two NO ligands would be unlikely because of repulsive interactions between the nitrogens and the oxygen ions of the lattice. The x-ray diffraction data show that the cobalt remains essentially in a fixed position upon complex formation in the zeolite A.

In X and Y zeolites the cobalt ions are located in distorted tetrahedral symmetry as determined from reflectance spectra.¹⁴ The x-ray diffraction data of Gallezot and Imelik¹⁸ indicated that in $\text{Co}^{\text{II}}\text{Y}$ dehydrated at 200 °C the metal ions occupy mainly sites I' and II'.¹⁹ In these sites the cobalt ion is approximately 1 Å out of the plane of the oxygens of the six-membered ring and would be available for coordination with nitric oxide. There is also evidence from the work of Gallezot et al.²⁰ that upon coordination NO may induce extensive migration of Ni^{2+} cations which are located originally in the hexagonal prisms of a Y zeolite.

This induced mobility of the cation during complex formation in zeolite Y has now been observed for several cases, and the mobility in zeolite Y is clearly greater than in zeolite X. For example, in a Y zeolite all of the Cu^{2+} ions react to form the tetraamminecopper(II) complex upon the addition of excess NH_3 at ca. 35 °C,²¹ whereas in an X zeolite only a fraction of the ions form the complex.²² This variation in the availability of the cation for multiple coordination with ligands other than the oxide ions of the lattice is presumably due to the differences in charge density among the zeolites. A high charge density such as in zeolite A would be expected to lock a cation into a hidden site. Even in the zeolite A, however, a limited number of stable dinitrosyl complexes were formed, perhaps at a few Co^{2+} ions that had migrated from the usual exchange sites or that were present in an impurity phase of the zeolite.

The relatively unstable dinitrosyl complex in the zeolite X suggests that the free-energy difference must be small between the metal ion coordinated only to the oxide ions of the lattice and the metal ion coordinated to two NO molecules. A small number of these sites of high charge density must also be available in the Y zeolite, giving rise to the fraction of dinitrosyl complexes which was relatively unstable. The mononitrosyl complex in the X zeolite is somewhat puzzling if one assumes that cobalt ions in sites I', II, and II' are at least capable of forming weak dinitrosyl complexes. In this respect it should be noted that Maxwell and de Boer²³ in the study of a faujasite crystal observed a high occupancy factor for Cu^{2+} ions in site I'A and site IIA, both of which are located essentially in the plane of three oxygens of a six-membered ring, as in the A-type zeolite. If such sites are occupied in the $\text{Co}^{\text{II}}\text{X}$ zeolite, then a mononitrosyl would be expected.

Since the reactivity of nitrosyl ligands with molecular oxygen has been suggested as a technique for distinguishing between the possible locations of complexes in a zeolite, it was important to study a case where the NO moiety was known to be in the large cavities. It is evident from the x-ray data of Seff⁸ and the infrared data reported here that even those NO ligands which are located in the large cavity react slowly with O_2 . In contrast it should be noted that the $[\text{Cr}^{\text{I}}\text{NO}]^{2+}$ complex on alumina reacted very rapidly with molecular oxygen;²⁴ thus, the slow rate of reaction reported here cannot be generalized for all mononitrosyl complexes. The cobalt dinitrosyl ligands likewise reacted slowly with O_2 ; however, it is now clear that their location cannot be distinguished on the basis of reactivity.

While the infrared data focus attention primarily on the nitrosyl ligands, the diffuse-reflectance data provide information on the metal ions. The large decreases in absorbance with only minor modifications in band positions upon NO adsorption suggest that the new spectra cannot be attributed to simple crystal-field perturbation of a trigonal environment, as described by Klier et al.,¹⁵ to interpret changes in the spectra of $\text{Co}^{\text{II}}\text{A}$ upon the adsorption of alkanes and alkenes. Rather, it seems likely that the extinction coefficients for the d-d transitions decrease as the nitrosyl complexes are formed and that ligand-to-metal charge-transfer bands occur at energies beyond the range of our instrument. The large background absorbance upon exposure of the $\text{Co}^{\text{II}}\text{A}$ to NO may well be the tail of a strong charge-transfer band at higher energies. The remaining bands in the 15 000–20 000- cm^{-1} region are attributed to uncomplexed cobalt ions. In one $\text{Co}^{\text{II}}\text{Y}$ zeolite the absorbance almost decreased to zero over a period of several days. The reversible behavior of the spectrum for $\text{Co}^{\text{II}}\text{A}$ is consistent with the infrared spectra.

The XPS data provide additional information on the state of the metal ion after complex formation. Although the binding energies alone would not allow one to distinguish between Co^{2+} and Co^{3+} , the satellite structure and the separation between the Co 2p lines provide sufficient evidence to allow the identification of the oxidation state. In agreement with the XPS spectra of Co $2p_{3/2}$ in many low-spin Co(III) compounds there exists a sharp decrease in the satellite structure and a decrease in the fwhm.²⁵ The latter effect may be due to a decrease in spin-orbit degeneracy. Furthermore, the Co(II) ion is characterized by an increased separation in the Co 2p lines which is probably the result of multiplet splitting of the 2p electrons by unpaired valence electrons. Here it is assumed that if the cobalt(III) nitrosyl complex existed, it would be in the low-spin state since NO is a strong-field ligand.

Agreement between the binding energy of nitrogen 1s electrons in $\text{Co}^{\text{II}}\text{A}$ and $\text{Co}^{\text{II}}\text{Y}$ zeolites confirms that the charge on the NO moiety is the same in both cases. The value of 400.7 eV is identical with that reported by Finn and Jolly²⁶

for a more anionic NO ligand in $[\text{Co}(\text{NO})(\text{NH}_3)_5]\text{Cl}_2$, whereas these authors reported a value of 402.3 eV for a more cationic NO in $[\text{Co}(\text{NO})(\text{diars})_2](\text{ClO}_4)_2$ (diars = $\text{C}_6\text{H}_4\text{-}[\text{As}(\text{CH}_3)_2]_2$). It is difficult, however, to make a valid comparison between these absolute binding energies, particularly since Finn and Jolly did not report the value adopted for their carbon (pump oil) standard. The infrared bands in the 1800-cm^{-1} region are consistent with a minimum electron donation into the π^* orbital of the nitrosyl ligand. Therefore, on the basis of the infrared data and the photoelectron spectra of the cobalt ions, we believe that the nitrosyl ligands are effectively neutral in the cobalt complexes of the three zeolites.

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Registry No. Co^{2+} , 22541-53-3; CoNO^{2+} , 65036-07-9; $\text{Co}(\text{NO})_2^{2+}$, 65036-08-0; $[\text{Co}^{\text{III}}(\text{NH}_3)_6]^{3+}$, 14695-95-5.

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Partial Dealumination and Healing of Faujasites by Chromium(III) Salt Solutions

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When faujasite-type zeolites such as Y and X are partially dealuminated by refluxing in aqueous chromium chloride solutions, a portion of the chromium remains in the washed zeolite. Most of this chromium cannot be removed by ion exchange. If, instead of chromium chloride, EDTA is used as the complexing agent to remove aluminum from zeolite Y, a significant amount of silicon can subsequently be digested and removed with refluxing 1.0 N sodium chloride solution. In the case of chromium, the silicon is less readily removed, particularly after calcination at 540 °C. This is evidence that the chromium is "healing" the rupture in the lattice created by hydrolysis and removal of the aluminum atoms. Others (Maher et al., Peri, Gallezot et al.) have reported that some healing can occur simply by silicon atom migration following dealumination with EDTA. We propose the empirical formula $(\text{Na} + \frac{1}{3}\text{Cr})_x(\text{Al} + \text{Cr})_y\text{Si}_z\text{O}_w$, where the ratio $y:x$ is higher than in the starting faujasite, to describe these new materials (in dehydrated form) at up to about 40% aluminum removal. Different metal ions, such as silver and lanthanum, can be added to these materials by ion exchange.

Introduction

Dealumination of dense zeolites such as erionite with hot aqueous solutions of chromium(III) salts has been reported previously by us,¹ along with evidence for a complex between chromium and the removed aluminum. The dealuminated dense zeolite residues are left with very little chromium, usually much less than 1 wt %. We now find that the larger pore faujasites respond to treatment with chromium(III) salt solutions for aluminum removal, but the dealuminated faujasite contains much more chromium, up to 7 wt %, most of which is not removed by ion exchange. Further, we have evidence that the chromium is "healing" to some extent the rupture in the lattice created by hydrolysis and removal of the aluminum atoms. Ermolenko et al. have previously reported isomorphically substituted chromium in zeolites,² where a chromium compound is used in the crystallization of the zeolite.

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Experimental Section

Procedure. As in the previous work on dense zeolites,¹ the powdered zeolites were added to chromium(III) salt solutions at either reflux or room temperature. At the end of the treatment period, the material was filtered through paper by suction and the filter cake was washed with water until the test for anion was negative. In all cases, the filtrate remained clear. The residue was dried overnight at 110 °C.

Materials. Hydrated chromium(III) chloride was obtained from Matheson Coleman and Bell. The synthetic sodium X faujasite was obtained from The Linde Co., and the sodium Y faujasite was synthesized by the procedure outlined in ref 3.

Results

Faujasite type zeolites have a large pore opening of 9 Å and a framework consisting of a tetrahedral arrangement of sodalite units linked by hexagonal faces with six bridge oxygen atoms.⁴ The apices of the sodalite cages are occupied by silicon and aluminum atoms, about five silicon to four aluminum atoms in faujasite X and five silicon to two aluminum atoms in faujasite Y. Siting of the aluminum ion in the lattice is