

and Matthey Bishop Corp. for a loan of precious metal salts.

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Active Intermediates in the Reduction of Nitric Oxide by Ammonia over a CoY Zeolite

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Abstract: The reduction of nitric oxide by ammonia over a CoY zeolite has been studied using both conventional kinetic techniques and dynamic infrared spectroscopy. The $[\text{Co}^{\text{II}}(\text{NH}_3)(\text{NO})_2]^{2+}$ complex was observed under steady-state reaction conditions, and the decay of the complex in the absence of gas-phase NO yielded turnover frequencies in good agreement with those obtained from the overall kinetic data. The nitrosyl ligands react with weakly coordinated NH_3 rather than with the more strongly coordinated ammonia. In agreement with this observation the order of the reaction with respect to NH_3 varied from approximately first order at low partial pressures of NH_3 to nearly zero order at higher partial pressures. A reaction order of 0.3 was observed for NO. A kinetic isotope effect of 1.5 is consistent with the breaking of an N-H bond in the rate-limiting step of the reaction. The overall reaction rate goes through a reversible maximum at 85 °C, and the decrease in activity at higher temperatures is attributed to a decrease in the number of complexes.

Introduction

The catalytic reduction of nitric oxide by ammonia over transition metal ions in zeolites has been demonstrated, and in the case of CuY zeolites a reasonable mechanism has been proposed.¹⁻³ Cobalt(II) ions in a Y-type zeolite are likewise active as a catalyst,⁴ although the kinetics of the reaction over the two metal ions are different. With the CuY zeolite the reaction was first order with respect to nitric oxide partial pressure and the reaction was continuous at pressures approaching 500 Torr.¹ By contrast, over the CoY zeolite the reaction was <0.5 order with respect to nitric oxide, and partial pressures of nitric oxide greater than 10 Torr resulted in side reactions

which poisoned the catalyst. From a practical standpoint, this reaction has been proposed as a means of removing nitric oxide from stack gases,⁵ and in this application the lower order in NO partial pressure is an advantage since the effluent streams may contain only low levels of nitric oxide.

In the present work attention has been given to the reactive intermediates in the catalytic process. The CoY zeolite was particularly promising for this investigation since several nitrosyl complexes in the zeolite have already been characterized by infrared spectroscopy,⁶ and it was even suggested that the $[\text{Co}^{\text{II}}(\text{NH}_3)_n\text{NO}]^{2+}$ complex was an intermediate in the reaction scheme.⁴

Table I. Comparison of Turnover Frequencies Obtained from Overall Reaction Kinetics and from Infrared Data

T , °C	complexes/ Co ²⁺ total, %	half-life, min	k , min ⁻¹	infrared TOF, molec/min· Co ²⁺	kinetic TOF, molec/min· Co ²⁺
65	1.6	4.7	0.15 ± 0.03	$(2.4 \pm 0.5) \times 10^{-3}$	1.8×10^{-3}
75	1.1	2.9	0.24 ± 0.08	$(2.6 \pm 0.9) \times 10^{-3}$	2.2×10^{-3}
85	0.8	2.0	0.37 ± 0.09	$(3.0 \pm 0.8) \times 10^{-3}$	3.8×10^{-3}

The problem of establishing reactive intermediates by spectroscopic techniques is difficult since the concentration of the intermediate under reacting conditions is often below the limits of detection. Usually one obtains spectra under conditions of temperature and pressure which are far removed from those of the reaction, and the results are sometimes misleading. Ideally one would like to observe spectra under reacting conditions where variables may be introduced which would affect both the reaction rate and the concentrations of the proposed intermediates. Several intermediates in heterogeneous catalysis have now been identified by this technique.⁷ During the reduction of nitric oxide by ammonia, the formation and reactivity of a cobalt-dinitrosyl complex are such that under dynamic reaction conditions the possible role of the complex as a reaction intermediate has been determined. This information, along with other data from isotope studies, has led to a reasonably detailed understanding of the reaction mechanism.

Experimental Section

Catalyst Preparation and Pretreatment. The Co¹¹Y zeolites were prepared and analyzed for cobalt content as described in a previous paper.⁶ Three exchange levels of 11, 14, and 19.6 Co²⁺ ions/unit cell were used in this experiment, although most of the results reported here were obtained on the zeolite which contained 11 Co²⁺ ions/unit cell. The zeolite samples were activated by heating in vacuo at 350 °C for 4 h as a standard treatment. As water was removed from the zeolite by this thermal treatment, the color of the sample changed from pink to blue.

Kinetic Experiment. A flow reactor constructed from 8-mm Pyrex glass tubing was used. The catalyst bed, which varied in amount from 0.25 to 1.0 g, was placed in the reactor and heated to 350 °C under a vacuum which ultimately approached 3×10^{-5} Torr.

The NO gases diluted with He (0.1 or 0.5% NO in He) were obtained from Union Carbide Co. and NH₃ (1.0% NH₃ in He) was obtained from Matheson Corp. Anhydrous NH₃ (Matheson), ND₃ (99% D, Merck & Co.), and NO (Matheson) were used after dilution with pure He (Airco) to different partial pressures. Nitric oxide was purified by passing the gas through a trap which was maintained at -78 °C. In kinetic experiments ammonia gas was passed over the catalyst first.

During the reaction the flow rate was maintained at 40 mL/min and the reaction temperature was regulated by placing a cylindrical electric furnace around the catalyst bed. The temperature was calibrated and controlled to within ± 1 °C. The product gases were analyzed with a CEC-214 mass spectrometer. The sensitivity of the instrument was determined for each of the gases that was analyzed.

Infrared Experiments. The infrared study employed a conventional T-shaped glass cell having a diameter of 20 mm and a volume of about 70 cm³. The cell was heated by passing a current through nichrome wire which was wound on the external walls of the glass. To obtain kinetic data the cell was connected in series to the outlet of the flow reactor. In these experiments the amount of catalyst in the reactor and the flow rate were adjusted such that the conversion did not exceed 6%.

The infrared samples were in the form of self-supporting wafers which were obtained by pressing zeolite powder between stainless steel disks under a pressure of 2×10^3 kg/cm². The resulting wafers had a density of about 8 mg/cm². A thermocouple in contact with the

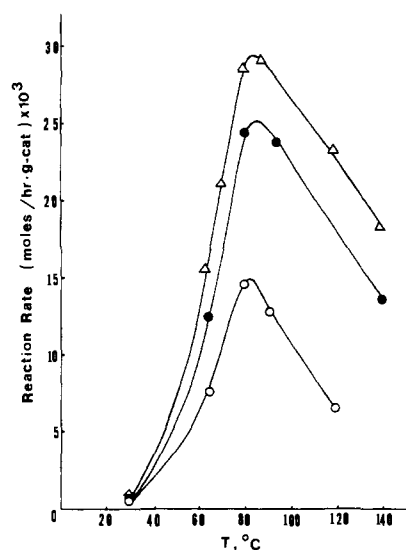


Figure 1. Catalytic activity of CoY zeolite for the NO-NH₃ reaction: (O), 0.68 Torr NO, 47.5 Torr NH₃; (●), 3.57 Torr NO, 47.5 Torr NH₃; (Δ), 7.6 Torr NO, 47.5 Torr NH₃.

wafer was used to determine the temperature. The catalyst wafer was positioned such that the inlet gases passed directly over it; thus lag times due to mixing were avoided.

The spectra were recorded using a Beckman IR-9 spectrophotometer which was usually operated in the transmittance mode. The maximum single-beam transmission for the sample was approximately 45%. The slit width was chosen such that a maximum resolution of 3 cm⁻¹ was maintained.

Results

Reaction Kinetics. The activity of CoY catalyst decreased gradually with time and reached a steady state 1-5 h after the reaction started. In the initial state of reaction, from 5 to 30% conversion to N₂O was observed, but the formation of N₂O gradually decreased along with the deactivation of the catalyst, and the products were mainly N₂ and H₂O in the steady state. The activity of CoY was essentially proportional to the exchange level of Co²⁺ in the zeolite.

The steady-state activity as a function of reaction temperature is shown in Figure 1, and in Table I the kinetic data are presented both as rate constants and as turnover frequencies (TOFs) where the latter is based on the total number of cobalt ions in the zeolite. It is evident that the activity passes through a maximum at ca. 85 °C for the three concentrations of NO in the gas stream. This was a reversible maximum in that it could be approached from temperatures either greater or less than 85 °C.

The reaction order was estimated to be 0.3 ± 0.1 order with respect to NO partial pressure in the range of 65-100 °C. As shown in Figure 2, the reaction rate varied in a nonlinear manner with respect to the partial pressure of ammonia. At higher pressures the order of the reaction with respect to ammonia partial pressure approached zero.

The reaction rate of NO with deuterated ammonia (ND₃) was compared with that of the NO-NH₃ system to determine whether a kinetic isotope effect (KIE) existed. The reaction rates and the KIE in sequential pairs of experiments are compared in Table II. The average ratio of the overall rate constants is $k_{\text{NH}_3}/k_{\text{ND}_3} = 1.5 \pm 0.1$ in the range of reaction temperatures from 65 to 120 °C.

Infrared Studies. In preparation for the infrared studies the CoY wafer was subjected to the standard treatment followed by exposure to NH₃ and evacuation of the cell at 25 °C for 8 h. Upon passing the 1% NO-He mixture over the sample at 65 °C infrared bands were observed at 1330, 1430, 1640, 1800, and 1880 cm⁻¹, as shown in Figure 3. The bands at 1430 and

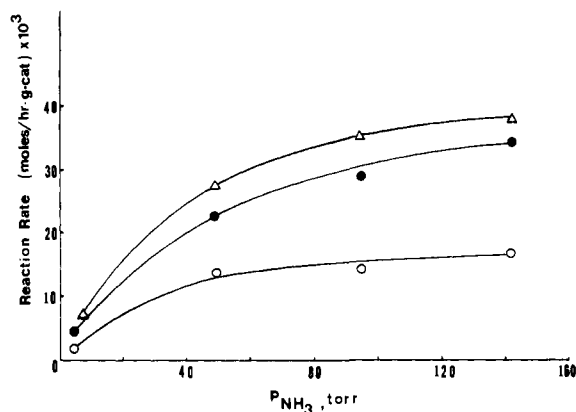


Figure 2. Rate dependence on NH_3 partial pressure at 85°C : (O), 0.68 Torr NO; (●), 3.57 Torr NO; (Δ), 7.6 Torr NO.

Table II. Summary of Reaction Rate and Isotope Effect in the Reduction of NO^a

NO, Torr	T, $^\circ\text{C}$	isotopic form	k , mol/g-cat-h $\times 10^3$	$k_{\text{NH}_3}/k_{\text{ND}_3}$
0.68	65	NH_3	7.50	1.59
0.68	65	ND_3	4.73	
0.68	81	NH_3	14.32	1.60
0.68	81	ND_3	8.93	
3.57	65	NH_3	12.26	1.40
3.57	65	ND_3	8.74	
3.57	82	NH_3	24.08	1.53
3.57	82	ND_3	15.74	

^a Ammonia partial pressure, 47.5 Torr; flow rate, 40 mL/min.

1640 cm^{-1} have been attributed to NH_4^+ and coordinated NH_3 , respectively.⁶ The band at 1330 cm^{-1} , which increased in intensity during the initial period of exposure to flowing NO, was attributed to the symmetrical deformation band of NO_2 in the $[\text{Co}^{\text{III}}(\text{NH}_3)_n\text{NO}_2]^{2+}$ complex.⁶ The antisymmetrical band of this complex occurs at 1430 cm^{-1} and was apparently superimposed on the NH_4^+ band. The bands at 1800 and 1880 cm^{-1} gradually increased in intensity when the NO gas mixture was introduced at 65°C and attained maximum intensity after 1 h. These bands have been attributed previously to the NO symmetrical and antisymmetrical stretching vibrations of $[\text{Co}^{\text{II}}(\text{NH}_3)(\text{NO})_2]^{2+}$.⁶ When the mixture of 7.6 Torr NO and 7.6 Torr NH_3 in He was passed over the zeolite containing the nitrosyl complex, the bands at 1800 and 1880 cm^{-1} shifted to 1790 and 1870 cm^{-1} , respectively, and decreased in intensity to a steady-state level (Figure 3). The steady state was also achieved by exposure of the CoY to 7.6 Torr NH_3 in He first, followed by exposure to the NO, NH_3 , and He mixture at 65 – 85°C . At these concentrations the infrared bands were not observed at temperatures of 100°C , but they reappeared upon cooling the sample back to lower temperatures.

At room temperature in a flow of 7.6 Torr NO and 7.6 Torr NH_3 in He, a strong band at 1700 cm^{-1} was observed in addition to the bands at 1790 and 1870 cm^{-1} . This band was previously ascribed to the NO stretching mode of the $[\text{Co}^{\text{III}}(\text{NH}_3)_n\text{NO}]^{2+}$ complex.⁶ Under these conditions, as shown in Figure 4, the broad bands around 1330 – 1350 cm^{-1} increased gradually and the bands at 1700 , 1790 , and 1870 cm^{-1} decreased with time. Five hours after the flow began the bands at 1700 , 1790 , and 1870 cm^{-1} disappeared, as did the catalytic activity.

Qualitatively the bands due to the dinitrosyl complex behaved in a manner which suggested that they may be an intermediate in the catalytic process. To provide quantitative

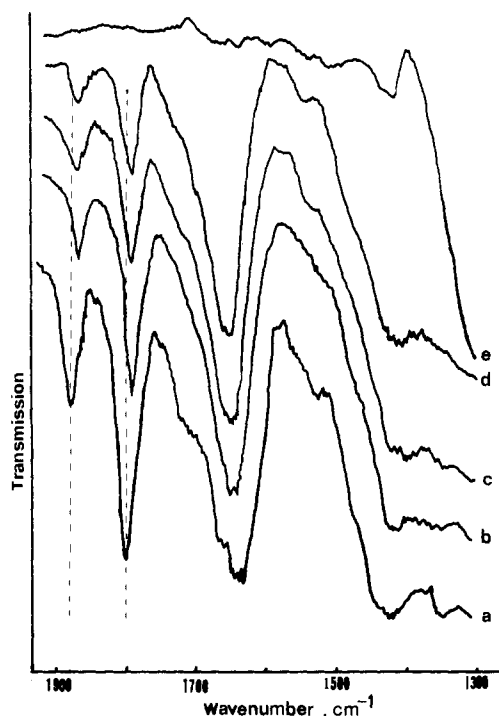


Figure 3. Infrared spectra at 65°C of CoY which had been exposed to excess NH_3 , followed by evacuation of the gas phase: (a) 1 h after the introduction of flowing NO/He mixture, 7.6 Torr NO; (b) 3 min after flowing 7.6 Torr of NO and 7.6 Torr of NH_3 in He over the sample; (c) after 1 h; (d) after 5 h; (e) background.

data in support of this hypothesis a steady state was first achieved at an elevated temperature and then the flow of NO into the cell was stopped. Subsequently the rate of decay of the dinitrosyl bands was determined, and from this value along with the absolute steady-state concentration of $[\text{Co}^{\text{II}}(\text{NH}_3)(\text{NO})_2]^{2+}$ a TOF for the complex was obtained.

In order to evaluate the absolute concentration of the dinitrosyl under reacting conditions it was necessary to determine its extinction coefficient. This was achieved by gravimetrically measuring the NO uptake in a $[\text{Co}^{\text{II}}(\text{NH}_3)]\text{Y}$ zeolite as a function of time and pressure. The gas uptake was rapid at first but became slower at longer times, particularly at the lower NO pressures. On a separate sample, which was in the form of a wafer (the same wafer that was used in the determination of TOFs), the infrared band intensity at 1880 cm^{-1} was measured over a range of time and pressure. It was necessary to consider the weaker of the two dinitrosyl bands since the one at 1800 cm^{-1} gave zero transmission. After converting to absorbance units the band intensity and the number of NO molecules/ Co^{2+} ion were compared at an adsorption time of 90 min as shown in Figure 5. By replotting these data as band intensity vs. the number of complexes per g of zeolite an extinction coefficient of $1.83 \times 10^{-18}/\text{complex}$ was determined.

It should be noted here that the infrared band intensity did not increase at pressures of NO greater than 100 Torr. Further increase was observed for the NO uptake; however, at these higher pressures the disproportionation of NO to N_2O and NO_2 becomes significant, and the NO_2 that is formed remains in the zeolite. As the reaction occurred the color of the zeolite gradually changed from blue to brown. The probable nitric oxide uptake in complex formation is indicated by the dashed line in Figure 5. The saturation value of the infrared band corresponded to 1.9 NO molecules/ Co^{2+} ion. Once formed the $[\text{Co}^{\text{II}}(\text{NH}_3)(\text{NO})_2]^{2+}$ complex was stable, as indicated by the constant intensity of the infrared bands upon evacuating the gas phase from the cell.

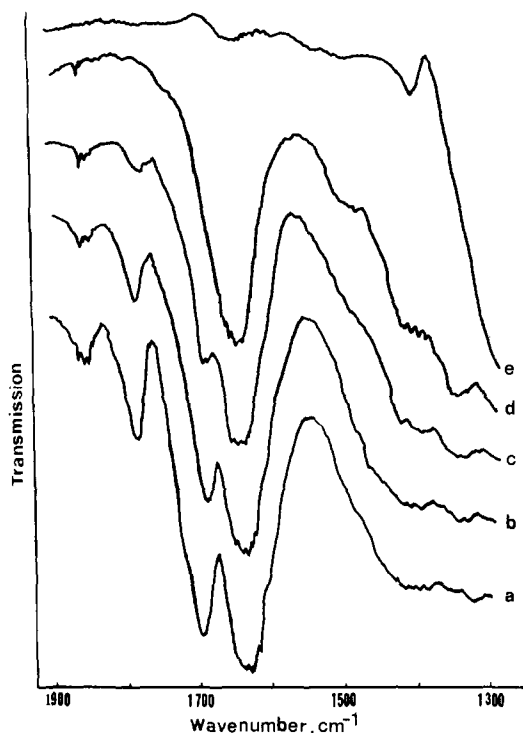


Figure 4. Infrared spectra at 25 °C of CoY in a flowing mixture of NO, NH₃, and He: (a) 10 min after the introduction of 7.6 Torr NO and 7.6 Torr NH₃ in He; (b) after 30 min; (c) after 1 h; (d) after 5 h; (e) background.

Adsorbed water had a strong influence on both the rate and the extent of complex formation. From the infrared spectra it was determined that prior exposure of the sample to 0.3 Torr of water resulted in the attainment of equilibrium during a period less than 5 min, but the amount of [Co^{II}(NH₃)(NO)₂]²⁺ formed was substantially less than when no water was present. Because of this influence of water the dynamic infrared experiments were carried out with the cell downstream from the reactor so that the zeolite would experience the same steady-state concentration of water vapor as the final section of the catalyst bed.

After steady state was obtained in a flow of 7.6 Torr NO and 7.6 Torr NH₃ in helium the percentages of Co²⁺ ions that were involved as dinitrosyl complexes were 1.6, 1.1, and 0.8% at 65, 75, and 85 °C, respectively. Upon turning off the NO flow, the infrared band at 1790 cm⁻¹ decayed with characteristic half-lives of 4.7 ± 0.7, 2.9 ± 0.7, and 2.0 ± 0.5 min at 65, 75, and 85 °C, respectively. The TOFs calculated from this data are compared with those obtained from the flow reactor in Table I, and considering the experimental error introduced by integration of the weak infrared bands, the agreement is quite good.

Determination of the Reactivity of Strongly Coordinated Ammonia. During the infrared experiments it was observed that upon removing ammonia from the gas stream which contained NO, NH₃, and He the bands at 1790 and 1870 cm⁻¹ gradually shifted to 1800 and 1880 cm⁻¹, but not further to 1830 and 1910 cm⁻¹. This suggested that even at reaction temperatures the ammonia ligand in the [Co^{II}(NH₃)(NO)₂]²⁺ was unreactive; thus [Co(NO)₂]²⁺ was not formed. This interpretation of the infrared data was tested by forming the [Co^{II}(¹⁵NH₃)(NO)₂]²⁺ complex, and then carrying out the surface reaction at 80 °C with only ¹⁴NO and He in the gas stream. Under these conditions no N₂ was observed as a product, and when ¹⁴NH₃ was added to the gas stream, only ²⁸N₂ was detected as a product. The amount of ¹⁵NH₃ con-

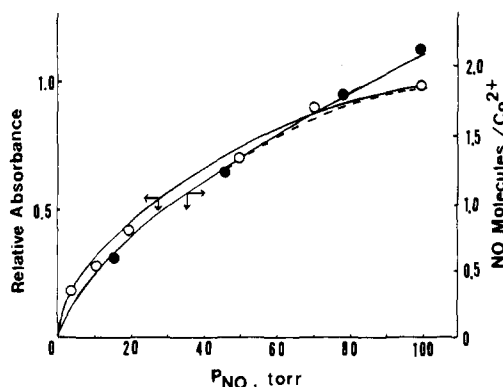


Figure 5. Adsorption isotherms of NO on CoY zeolite: (O) from infrared spectra; (●) from gravimetric data.

tained in the complex was comparable to the amount of ammonia in the gas stream.

Discussion

Zeolites having the faujasite structure, of which zeolite Y is a synthetic form, are constructed of SiO₄ and AlO₄ tetrahedra arranged such that large and small cavities exist. The large cavities or cages have a diameter of approximately 13 Å with windows of 9 Å diameter, whereas the small cavities have a free diameter of 6.6 Å with windows of 2.2 Å. As the zeolites are dehydrated the exchange cations lose their waters of hydration and take up positions relative to the zeolite structure where the ions are coordinated to the oxygen atoms of the framework. After moderate conditions of dehydration Co²⁺ ions, for example, are mainly found within the small cavities at positions which are removed by several ångstroms from the large cavities.^{8,9} One might expect that ions in such locations would not participate in catalytic reactions, even with small molecules of the type under consideration in this work; however, it is now well established that certain ligands are capable of inducing the migration of the cations to more favorable sites which are exposed to the large cavities.¹⁰⁻¹²

In the previous study it was suggested that the cobalt ion in the [Co^{II}(NH₃)(NO)₂]²⁺ complex was actually coordinated to three oxide ions of a six-membered ring with the ammonia and the nitric oxide ligands being trans to one another.⁶ Although a final decision concerning the exact site of the complex must await X-ray diffraction data, it seems reasonable on the basis of the kinetic data reported here to conclude that the NO ligands extend into the large cavities. In the following discussion we will assume this configuration as a working model.

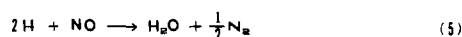
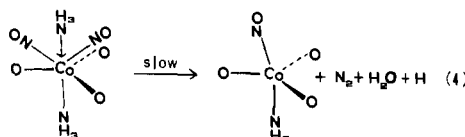
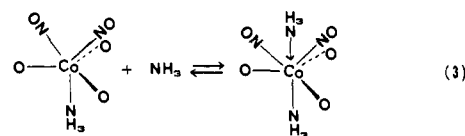
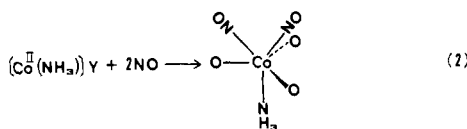
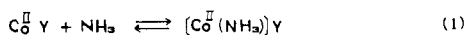
The 10-cm⁻¹ shift to lower wavenumbers upon exposure of the [Co^{II}(NH₃)(NO)₂]²⁺ complex in the zeolite to gas-phase ammonia suggests that a weak complex is formed. The shift of 10 cm⁻¹ may be compared with a shift of 30 cm⁻¹ which was observed upon the addition of the first ammonia molecule to the cobalt nitrosyl complex.⁶ The relative intensity ratio of the symmetric and antisymmetric modes of the two NO ligands indicates that the ON-Co-NO bond angle increased from 123 to 134° upon addition of the second NH₃ molecule.⁶ This ammonia ligand was relatively easy to remove either by evacuation or by reaction with nitric oxide, whereas the strongly held ammonia did not desorb or react at temperatures less than 100 °C. The kinetic effect of the weakly coordinated ammonia is apparent in Figure 2, where the zero reaction order at high partial pressures of NH₃ may be understood in terms of Langmuir-Hinshelwood kinetics. As the partial pressure increases all of the complexes become coordinated to an additional ammonia molecule and further increases in the gas-phase concentration have no effect.

The kinetic order with respect to NO is more difficult to

understand since the coordinated nitric oxide was not in equilibrium with the gas phase. In view of the ability of the nitric oxide to induce motion of transition metal ions in a Y-type zeolite, it is reasonable to expect that the steady-state concentration of $[\text{Co}^{\text{II}}(\text{NH}_3)(\text{NO})_2]^{2+}$ complexes would be related to the NO partial pressure in some nonintegral manner. At higher NO partial pressures the disproportionation reaction becomes a factor, and the catalyst is poisoned by the formation of cobalt-nitro complexes. Although this poisoning reaction was not important in the experiments described here, it probably was significant at the somewhat higher pressures used by Seiyama in a related study.³

The reversible activity-temperature profile depicted in Figure 1 is rather unusual in heterogeneous catalysis; however, it was observed previously for the same reaction over CuY zeolites.¹⁻³ In that case the decrease in activity at higher reaction temperatures was ascribed to the reduction of Cu^{II} to the inactive Cu^{I} ion. There is no indication that such a reduction takes place with the cobalt ion. At a reaction temperature of 120 °C, the color of the CoY catalyst had changed from faint pink to blue, and the infrared spectrum of the nitrosyl complex was not observed. Based upon spectroscopic data Hoser et al. showed that Co^{2+} ions in a Y zeolite changed their coordination from octahedral to tetrahedral upon heating to 120 °C in air, and they suggested that some of the Co^{2+} ions moved from the large cavities to the small cavities.¹³ Egerton et al. reached the same conclusion from magnetic susceptibility measurements.⁸ The reversible decrease in activity in the present work is likewise attributed to the decomposition of the complexes, in particular the nitrosyl complex, followed by the migration of the metal ions into the hidden tetrahedral sites. Seiyama et al. also noted a maximum catalytic activity as the temperature increased, but at the higher NO partial pressure used in their experiment the effect was not reversible.³ They observed that the color of the zeolite changed to brown which indicates that the poisoning of the catalyst at the higher temperatures may have been due to the formation of nitro complexes.

The agreement between the TOFs determined from the overall reaction and those obtained from the infrared spectra of the $[\text{Co}^{\text{II}}(\text{NH}_3)(\text{NO})_2]^{2+}$ complex (Table I) provides evidence for the role of the complex in the catalytic reaction. Moreover, the observed KIE of 1.5 indicates that the slow step in the reaction involves the breaking of N-H bonds. On the basis of this and related kinetic data, we postulate that the reaction goes by the following mechanism:



Reactions 2 and 5 are not intended to imply elementary reaction steps, but rather the origin of the dinitrosyl complex and the fate of the hydrogen from reaction 4. The role of water has not been explored in this study, except to qualitatively determine its effect on the rate of reaction 2. Nevertheless, water which is formed as a product of the reaction almost certainly competes with both nitric oxide and ammonia for the coordination sites of cobalt. Under steady-state conditions the Co^{2+} ions are distributed between several sites in the zeolite, and the possible ligands include the oxygen atoms of the lattice, water, ammonia, or nitric oxide. It is not surprising, therefore, that less than 2% of the Co^{2+} ions were present as $[\text{Co}^{\text{II}}(\text{NH}_3)(\text{NO})_2]^{2+}$ complexes.

An interesting comparison may be made between the CoY and the CuY zeolites as catalyst for the reduction of nitric oxide with ammonia. In the case of CuY no nitrosyl complexes have been observed, and the coordinated ammonia is believed to react with either gas-phase or weakly coordinated NO.¹ The reaction was first order with respect to NO and zero order with respect to NH_3 . By contrast, in CoY the cobalt was bonded more strongly to NO and the reaction was less than 0.5 order with respect to NO. A temperature maximum occurred with both metal ions, but in the case of CuY the decrease in activity at higher temperatures was attributed to the reduction of copper, whereas with CoY the decrease in activity was attributed to the loss of ligands and the motion of the cobalt into the small cavities. Thus, what may appear superficially to be a related kinetic phenomenon is in fact quite different in origin.

Conclusions

The $[\text{Co}^{\text{II}}(\text{NH}_3)(\text{NO})_2]^{2+}$ complex formed in a Y-type zeolite is an active intermediate in the reduction of NO by NH_3 . The relative rates of formation and reaction of this complex were such that dynamic infrared experiments could be carried out under reacting conditions. Spectroscopic and kinetic evidence indicate that the reaction of an NO ligand with a weakly coordinated NH_3 molecule is the slow step in the reaction mechanism. The catalyst was characterized by a reversible rate vs. temperature curve which reached a maximum at 85 °C. This phenomenon is attributed to the thermal stability of the complex and the motion of Co^{2+} ions to hidden sites within the zeolite.

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