pression in brackets. This result shows that f is a function of the weight-averaged axial ratio[46] only and is identical in form with the shape factor for monodisperse systems, f_i, which is given by

$$f_i = \frac{\mu_{ii}}{8V_i} = 1 + \frac{\frac{1}{4}\frac{l_i}{d}}{1 + \frac{2}{3}\left(\frac{l_i}{d}\right)^{-1}} \tag{A-5}$$

Thus, for polydisperse rodlike systems f simply corresponds to the value that one would obtain for monodisperse systems having the weight-average axial ratio and is insensitive to the precise form of the particle size distribution. This result would not be true for polydisperse spherical particles (f would be <1), but it should be approximately correct for elongated structures in general, such as the prolate ellipsoids used for calculating the theoretical curve in Figure 5.

Registry No. NaTDC, 1180-95-6.

---

[46] For prolate spherocylinders this axial ratio is given by $\bar{l}_w/d + 1$.

Mechanism of the Catalytic Reduction of Nitric Oxide by Ammonia over Cobalt–Amine Complexes in Na–Y Zeolite

Shuichi Naito* and Kenzi Tamaru

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo, 113, Japan *(Received: May 26, 1982; In Final Form: September 20, 1982)*

The mechanism of the NO–NH_3 reaction over $Co(en)_2(NO_2)_3$ complex (en = ethylenediamine), ion exchanged into Na–Y zeolite, was studied extensively and compared with that by the same complex in an aqueous solution, which has been reported previously. At room temperature, the catalytically active species are similar in both media, exhibiting similar reaction mechanisms. Ammonia treatment of the catalyst at 363 K caused the reduction of cobalt cation to Co^{II} with the removal of NO_2 groups. The catalytic behavior of this Co^{II}(en)–Y zeolite was compared to that of $Co^{II}(NH_3)$–Y zeolite, prepared by a conventional cation-exchange method. During the NO–NH_3 reaction, mononitrosyl and dinitrosyl intermediate species were much more stable in $Co(NH_3)$ zeolite than Co(en)–Y zeolite, resulting in different reaction orders and kinetic isotope effects. It is demonstrated that a zeolite cavity can be a microreactor, where residual water acts as a solvent to assist the stabilization of the catalytically active species.

I. Introduction

The catalytic reduction of nitric oxide by ammonia has been studied over transition-metal ions in zeolites, such as Cu–Y[1,2] and Co–Y zeolites.[3] In these systems, the catalysts were prepared by a cation-exchange method, and $[Cu(NH_3)_4]^{2+}$ or $[Co(NH_3)]^{2+}$ (ref 4) is postulated to be a catalytically active species in the zeolite cavity. Recently Lunsford et al.[5] compared the catalytic behavior of $[Cu^{II}(NH_3)_4]^{2+}$ in zeolite to that in an aqueous solution and concluded that cavities of the zeolite could be microreactors for the NO–NH_3 reaction, where residual water is a solvent and the zeolite framework is an anion.

We have also found a similar phenomenon in the case of the NO–NH_3 reaction catalyzed by $Co^{III}(en)_2(NO_2)_3$ complex (en = ethylenediamine), exchanged in Y-type zeolite,[6] which exhibited catalytic behavior quite similar to that in an aqueous solution.[7,8] The interesting point of this system is that the NO–NH_3 reaction proceeds only very slowly when these complexes are supported on silica, alumina, or silica–alumina, indicating that an important role of the zeolite cavity is to stabilize catalytically active species similar to that in the solution. There exists a large solvent effect in the solution reaction, and the kinetics in DMF are quite different from those in aqueous solution, which may be explained by the shift of the rate-determining step. The kinetics of the reaction over the zeolite-supported complex are similar to those in the aqueous solution, but the real structure of the complex in the cavities of zeolites and the reaction mechanism have not been clarified yet.

In this report, infrared and X-ray photoelectron spectroscopic techniques are applied to investigate the working state of the catalyst during the reaction. Detailed kinetic experiments and tracer studies using ^{15}NO and $^{15}NH_3$ are carried out to elucidate the reaction mechanism of the NO–NH_3 reaction, and the correlation between two different media, in zeolite and in solution, is discussed in depth.

II. Experimental Section

(*1*) *Catalyst Preparation.* Complexes employed in this study were prepared with a method similar to that reported by Holtzclaw, Jr., et al.[9] An aqueous solution of the complex was mixed with powdered Na–Y zeolite (Linde) and stirred at 350 K for a few hours. After filtration the catalyst was washed thoroughly with water and dried at room temperature. The amount of the complex ion exchanged was determined spectroscopically from the amount of the complex left in the solution. In the case

---

[1] W. B. Williamson and J. H. Lunsford, *J. Phys. Chem.*, **80**, 2664 (1976).

[2] T. Arakawa, M. Mizumoto, Y. Takita, N. Yamazoe, and T. Seiyama, *Bull. Chem. Soc. Jpn.*, **50**, 1431 (1977).

[3] K. A. Windhorst and J. H. Lunsford, *J. Am. Chem. Soc.*, **97**, 1407 (1975).

[4] T. Iizuka and J. H. Lunsford, *J. Am. Chem. Soc.*, **100**, 6106 (1978).

[5] M. D. Oates and J. H. Lunsford, *J. Mol. Catal.*, **9**, 91 (1980).

[6] S. Naito, *J. Chem. Soc., Chem. Commun.*, 1101 (1979).

[7] S. Naito, *J. Chem. Soc., Chem. Commun.*, 175 (1978).

[8] S. Naito and K. Tamaru, *J. Chem. Soc., Faraday Trans. 1*, **78**, 735 (1982).

[9] H. F. Holtzclaw, Jr., D. P. Sheetz, and B. D. McCarty, *Inorg. Synth.*, **4**, 176 (1953).

0022-3654/83/2087-0315$01.50/0

of silica (Aerosil), alumina (aluminium oxide C, Aerosil), and silica–alumina (Shokubai kasei) supported catalysts, the complex was impregnated on these oxides from the aqueous solution and dried at room temperature.

(2) *Reaction Procedure.* A 1–2-g sample of the catalyst was put into a U-shaped glass tube connected to a closed gas circulation system (total volume = ca. 350 cm^3) and evacuated at room temperature for a few hours (fresh catalyst) before the NO–NH_3 reaction at room temperature. For higher-temperature reactions, it was necessary to repeat several runs of the NO–NH_3 reaction to obtain reproducible activity. Before each run, the catalyst was treated by ammonia at 363 K for a few hours and then evacuated at the same temperature for 14 h. By this pretreatment, the rate of the NO–NH_3 reaction became reproducible for many runs and the amount of N_2 and N_2O formed during each run exceeded the amount of cobalt cations employed, which indicates that this reaction is catalytic. Compositional analysis of the gas phase was performed by gas chromatography (molecular sieve 13X for N_2 and NO, and Chromosorb 103 for N_2O and NH_3). For isotope-labeled experiments, ^{15}NO and $^{15}NH_3$ (nitrogen-15 purity = 96%, from Prochem. British Oxygen Company Limited) were employed without further purification. Isotope distributions of produced N_2 and N_2O were analyzed by a quadrupole mass spectrometer (UTI, Model 100C) with an ionization voltage of 70 eV.

(3) *Infrared and X-ray Photoelectron Spectroscopies.* For the experiments of infrared spectroscopy, the catalyst powder was pressed into a disk (20-mm diameter, ca. 40 mg) and placed in an infrared cell, which was treated with the same procedure mentioned above before the NO–NH_3 reaction. Infrared spectra were taken by a Jasco IRA-2 grating spectrophotometer.

Another small glass vessel with several side arms for sampling was used for the XPS experiments. At each step of the reaction procedure, a small part of the catalyst powder was shaken into one of these sampling tubes, which was removed under vacuum with a gas torch. These sample tubes were broken inside a glovebox under nitrogen atmosphere, which was connected to the XPS sample chamber, and the sample powder was mounted on the XPS sample holder. XPS measurements were carried out by a Mcpherson ESCA 36 spectrometer. For the calibration of the binding energy, Au $4f_{7/2}$ (83.7 eV) was used as a reference.

III. Results

(1) *NO–NH_3 Reaction over $Co(en)_2(NO_2)_3$ Complex Exchanged in Na–Y Zeolite.* When either NO or NH_3 is introduced separately onto a freshly prepared catalyst of $Co(en)_2(NO_2)_3$ complex exchanged in Na–Y zeolite (Co(en)–Y zeolite catalyst), no reaction occurs; this suggests that coordinated NO_2 groups or diamines do not react directly with NH_3 or NO at room temperature (Figure 1A). But when a mixture of NO and NH_3 is added, both N_2O and N_2 are formed as shown in Figure 1B. The rates of N_2O and N_2 formation decrease gradually, indicating a deactivation of the complex. These situations are quite similar to the case of the NO–NH_3 reaction catalyzed by $Co(en)_2(NO_2)_3$ complex in an aqueous solution.[8] After the reaction at room temperature, the catalyst was treated with 100 torr of ammonia at 363 K for 5 h and then evacuated at the same temperature for 14 h. When NO was introduced on this catalyst at room temperature, a large amount of N_2 was formed as shown in Figure 1C. This result is different from the experiment in Figure 1A and indicates the formation of strongly adsorbed $NH_3(s)$ by ammonia treatment at 363 K, which does not desorb by a prolonged evacuation at 363 K. From the amount of N_2 formed during this reaction, the amount of $NH_3(s)$ was estimated to be about one NH_3 molecule per one cobalt cation. When NH_3 was introduced to this system after the evacuation of gaseous NO, quick desorption of NO was observed accompanied by the formation of N_2O, as shown in Figure 1D.

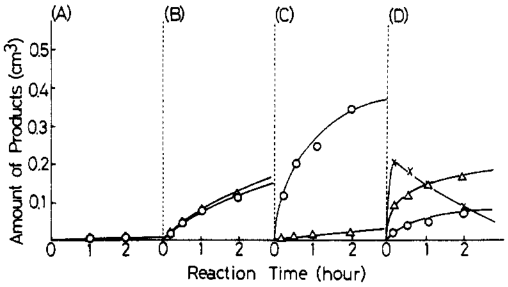


Figure 1. NO–NH_3 reaction over Co(en)–Y zeolite at room temperature; 2.5 wt % (complex) catalyst = 2 g. (O) N_2, (Δ) N_2O, (×) NO. (A) NO (230 torr) or NH_3 (33 torr) only was introduced over freshly prepared Co(en)–Y zeolite. (B) A mixture of NO and NH_3 was introduced on the catalyst after the experiment of A. (C) After B, the catalyst was treated by 100 torr of NH_3 at 363 K for 5 h and then evacuated at 363 K for 14 h. After cooling to room temperature, only NO (230 torr) was introduced. (D) After the evacuation, NH_3 (33 torr) was introduced at room temperature.

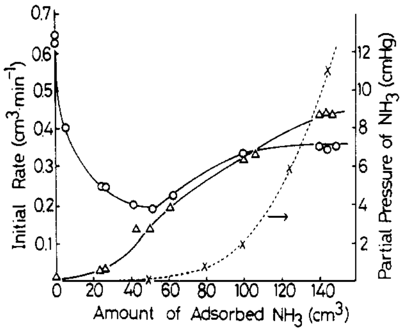


Figure 2. Dependence of the initial rates of N_2 and N_2O formation in NO–NH_3 reaction upon the amount of adsorbed NH_3 over Co(en)–Y zeolite at 353 K; 2.5 wt % (complex) catalyst = 2 g. (O) V_{N_2} (initial rate of N_2 formation), (Δ) V_{N_2O} (initial rate of N_2O formation), (×) partial pressure of NH_3. The catalyst was prepared by 100 torr of NH_3 at 363 K for 5 h, followed by the evacuation at the same temperature for 14 h before each run. Partial pressure of NH_3 was changed with the constant partial pressure of NO (230 torr).

To investigate the behavior of this strongly adsorbed $NH_3(s)$, we first prepared $NH_3(s)$ by the procedure mentioned above, and then the NO–NH_3 reaction was performed at 353 K by changing the partial pressure of NH_3 with a constant partial pressure of NO. When the amount of NH_3 was small, all the NH_3 was adsorbed on the catalyst (up to ca. 50 mL of $NH_3(a)$/2 g of catalyst) and no ammonia pressure was observed in the gas phase as indicated in Figure 2 (dotted line). In this region, the main product was N_2, whose initial rate decreased abruptly as the amount of adsorbed NH_3 increased. After going through a minimum, the rate of N_2 formation increased again and then saturated in the higher ammonia pressure region. The initial rate of N_2O formation exhibited similar behavior in this latter region. The dependence of the initial rates of N_2 and N_2O formation upon the partial pressure of NH_3 and NO in this higher-pressure region is shown in Figure 3. The initial rates are almost independent of the partial pressure of NH_3 corresponding well to the latter region of Figure 3. On the other hand, the dependence upon the partial pressure of NO was quite different, being first order for N_2 formation and second order for N_2O formation.

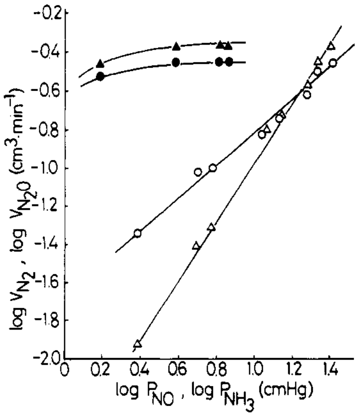


Figure 3. Dependence of the initial rates of N_2 and N_2O formation upon the partial pressure of NO and NH_3 over Co(en)–Y zeolite at 353 K; 2.5 wt % (complex) catalyst = 2 g. (○) V_{N_2}, (△) V_{N_2O} (partial pressure of NO was changed with the constant partial pressure of NH_3 = 33 torr), (●) V_{N_2}, (▲)$_{N_2O}$ (partial pressure of NH_3 was changed with the constant partial pressure of NO = 230 torr).

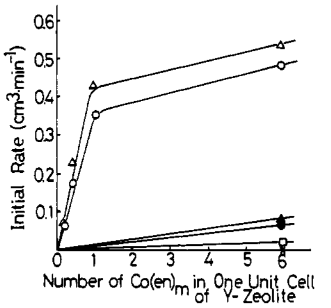


Figure 4. Dependence of the initial rates of N_2 and N_2O formation upon the amount of the complexes exchanged (impregnated) into Na–Y zeolite (silica–alumina, alumina, and silica) at 353 K. Catalyst = 2 g. (○) V_{N_2}, (△) V_{N_2O} over Co(en)–Y zeolite, (●) V_{N_2}, (▲) V_{N_2O} over Co-(en)–silica–alumina, (□) V_{N_2} (and V_{N_2O}) over Co(en)–alumina, (×) V_{N_2} (and V_{N_2O}) over Co(en)–silica.

TABLE I: ^{15}NO-$^{14}NH_3$ Reaction over Co(en)-Y Zeolite at 353 K

reaction time, h	$^{14}N^{14}N$	$^{14}N^{15}N$	$^{15}N^{15}N$	$^{14}N^{14}NO$	$^{14}N^{15}NO$	$^{15}N^{15}NO$
1	0.05	0.95	0.00	0.00	0.04	0.96
2	0.03	0.96	0.01	0.01	0.03	0.97
3	0.03	0.96	0.01	0.01	0.03	0.97
4	0.03	0.96	0.01	0.01	0.03	0.97
6.7	0.03	0.96	0.01	0.01	0.03	0.97

TABLE II: ^{14}NO-$^{15}NH_3$-$^{14}NH_3$(s) Reaction over Co(en)-Y Zeolite at 353 K

reaction time, h	$^{14}N^{14}N$	$^{14}N^{15}N$	$^{15}N^{15}N$	$^{14}N^{14}NO$	$^{14}N^{15}NO$	$^{15}N^{15}NO$
0.2	0.61	0.39	0.00	1.00	0.00	0.00
0.5	0.45	0.55	0.00	1.00	0.00	0.00
1	0.40	0.60	0.00	1.00	0.00	0.00
2	0.39	0.61	0.00	1.00	0.00	0.00
4	0.39	0.61	0.00	1.00	0.00	0.00

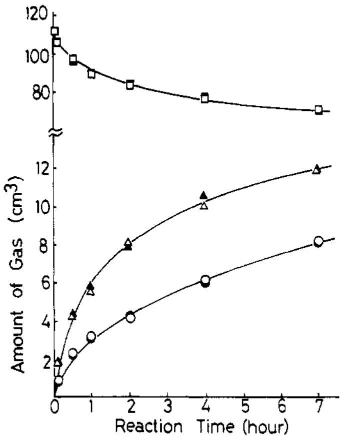


Figure 5. Kinetic isotope effects between NO–NH_3 and NO–ND_3 reactions over Co(en)–Y zeolite at 353 K; 2.5 wt % (complex) catalyst = 2 g. (○) N_2, (△) N_2O, (□) NO (NO–NH_3), (●) N_2, (▲) N_2O, (■) NO (NO–ND_3).

The dependence of the initial rates of N_2 and N_2O formation upon the amount of $Co(en)_2(NO_2)_3$ complex exchanged in Na–Y zeolite is shown in Figure 4. The abscissa of the figure represents the number of complex molecules per unit cell of Y zeolite. Up to one complex molecule per unit cell, the initial rate increased linearly with the amount of the complex, but after that the degree of dependence decreased drastically. Similar investigations were carried out in the cases of $Co(en)_2(NO_2)_3$ complexes supported on silica, alumina, and silica–alumina. The activities of these catalysts for the NO–NH_3 reaction were very low compared to that of Co(en)–Y zeolite, but the interesting point is that the slope in the case of silica–alumina-supported catalyst is quite similar to that of the latter stage of Co(en)–Y zeolite. These results suggest that only one $Co(en)_2(NO_2)_3$ molecule can enter into the supercage of a zeolite cavity by ion exchange, and this entity exhibits higher catalytic activity for the NO–NH_3 reaction.

(2) *Isotope-Labeled Experiments.* To examine the nitrogen sources of the products N_2 and N_2O, we studied the reaction between ^{15}NO and $^{14}NH_3$ over Co(en)–Y zeolite at 353 K. As is summarized in Table I, produced N_2 was mainly $^{14}N^{15}N$, indicating the reaction between ^{15}NO and $^{14}NH_3$ molecules. On the other hand, N_2O was mainly $^{15}N^{15}NO$ from two nitric oxide molecules. To investigate the role of strongly adsorbed ammonia NH_3(s) in the NO–NH_3 reaction, we carried out the following experiment. First of all, $^{14}NH_3$(s) was prepared by the procedure mentioned in section III-1, and then the ^{14}NO–$^{15}NH_3$ reaction was carried out at 353 K. At the very initial stage of the reaction, $^{14}N^{14}N$ was formed as shown in Table II, indicating the higher reactivity of $^{14}NH_3$(s) for the reduction of ^{14}NO. But at the latter stage both $^{14}N^{14}N$ and $^{14}N^{15}N$ were formed, suggesting a rapid exchange of strongly adsorbed NH_3(s) with gaseous or weakly adsorbed NH_3(w). Formed N_2O was only $^{14}N^{14}NO$ at any stage, confirming the result of Table I; in other words, N_2O is formed between two NO molecules.

The kinetic isotope effect of ammonia on the rate of N_2 and N_2O formation over Co(en)–Y zeolite was examined at 353 K, NH_3 and ND_3 being used. Before the NO–ND_3 reaction, the catalyst was treated with ND_3 at 353 K to replace all the exchangeable hydrogen with deuterium. As shown in Figure 5, there existed no isotope effect on the formation rates of N_2 and N_2O between the NO–NH_3 and NO–ND_3 reactions. The NO–NH_3–ND_3 reaction was also examined over Co(en)–Y zeolite at 353 K, which demonstrated that H–D exchange reaction of ammonia was 1 order of magnitude faster than the reduction of nitric oxide.

(3) *Infrared Spectroscopy and XPS Studies.* Infrared spectra of adsorbed species were studied during the NO–NH_3 reaction over Co(en)–Y zeolite. After an ammonia treatment at 363 K for 5 h, the catalyst disk was evacuated at the same temperature for 14 h. Spectrum A in Figure 6 was taken at room temperature after this treatment. A

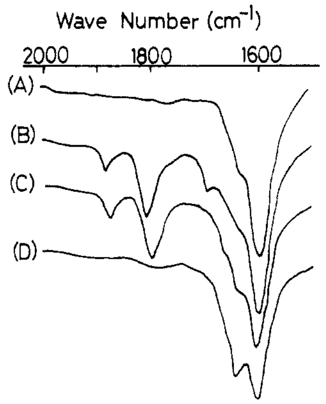


Figure 6. Infrared spectra of adsorbed NO and NH_3 over Co(en)-Y zeolite at room temperature: (A) after NH_3 treatment of the complex, (B) 50 torr of NO was introduced on A, (C) 5 torr of NH_3 was added to B, (D) the partial pressure of NH_3 was increased to 20 torr.

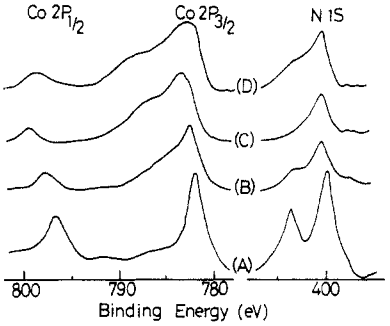


Figure 7. XPS spectra of Co(en)-Y zeolite after various treatments: (A) $Co(en)_2(NO_2)_3$ complex, (B) freshly prepared Co(en)-Y zeolite, (C) after NH_3 treatment at 363 K for 3 h, (D) after NO-NH_3 reaction at 353 K for 20 h.

large absorption band around 1600 cm^{-1} can be assigned to the bending mode of the NH_2 group of the coordinated ethylenediamine. A shoulder band around 1650 cm^{-1} can be assigned to the bending mode of strongly adsorbed NH_3(s) or residual water in the zeolite cage. When only NO was introduced to this disk at room temperature, three new bands appeared around 1880, 1800, and 1700 cm^{-1} (spectrum B). The bands at 1880 and 1800 cm^{-1} can be assigned to the symmetric and asymmetric stretching vibrational modes of adsorbed NO dimer ($Co(NO)_2$) and 1700 cm^{-1} to monomer complex (CO-NO) according to the literature.[3,4] The addition of 5 torr of NH_3 on this disk at room temperature caused the disappearance of the 1700-cm^{-1} band and the shift of the 1880- and 1800-cm^{-1} bands to 1870 and 1790 cm^{-1} (spectrum C). When more than 20 torr of NH_3 was added, these bands also disappeared, accompanied by the increase of an adsorbed NH_3 band around 1650 cm^{-1} (spectrum D). During the NO-NH_3 reaction at room temperature or at higher temperatures, no other bands except ones for adsorbed NH_3 could be observed.

An XPS study was carried out to investigate the real catalytically active species during the NO-NH_3 reaction. Figure 7A is the spectrum of the $Co(en)_2(NO_2)_3$ complex itself before ion exchange with Na-Y zeolite. Two peaks at 782.0 and 797.0 eV are due to Co $2p_{3/2}$ and Co $2p_{1/2}$ of Co^{III} ions in the complex, respectively. The separation between these two Co 2p lines is 15.0 eV, which is similar to Co^{III} ions reported in the literature.[10] Two peaks at 400.0 and 403.8 eV are due to N 1s of ethylenediamine and NO_2 ligands, respectively. After ion exchange, Co 2p and N 1s of ethylenediamine ligand peaks exhibited a shift of 0.6-0.8 eV toward higher binding energies as shown in Figure 7B, indicating some electronic interaction between the complex and the zeolite cage. But the line separation between Co $2p_{3/2}$ and Co $2p_{1/2}$ peaks was still 15.0 eV, suggesting the retention of Co^{3+} valency in the zeolite cavity. Spectrum C was taken after NH_3 treatment of fresh catalyst at 363 K. Co 2p peaks again shifted to 783.4 ($2p_{3/2}$) and 799.4 ($2p_{1/2}$) eV whose separation was now 16.0 eV. According to the literature,[10] this chemical shift and the change of the line separation seem to result from the reduction of Co^{III} ions to Co^{II} in the zeolite cavities. Moreover, the N 1s peak of the NO_2 ligand disappeared completely after ammonia treatment at higher temperatures. After a prolonged reaction between NO and NH_3, the N 1s peak of adsorbed NO_2 reappeared accompanied by the broadening of Co $2p_{1/2}$ and Co $2p_{3/2}$ peaks as shown in spectrum D. This may suggest that some part of the cobalt cation is oxidized to Co^{III} during the NO-NH_3 reaction, corresponding to the deactivation process of the catalyst.

IV. Discussion

(*1*) *Catalytically Active Species in Zeolite Cavity.* Lunsford et al. prepared cobalt(II) ions in a Y-type zeolite and examined active intermediates in the reduction of nitric oxide by ammonia with infrared spectroscopy[3-5] and XPS.[10] They observed the same infrared bands at 1880 and 1800 cm^{-1} by the introduction of NO on Co^{II}-Y zeolite as our case in Figure 6 and concluded the existence of $[Co^{II}(NH_3)(NO)_2]^{2+}$ complex in the supercage of the zeolite. They also confirmed it by their XPS study.[10] On the other hand, we started from a $Co(en)_2(NO_2)_3$ complex exchanged into Na-Y zeolite. After ion exchange, the infrared spectra of the fresh catalyst exhibited the existence of ethylenediamine and NO_2 ligands, although the intensity of the latter was considerably decreased. This means at least one NO_2^- group of counteranion is removed by ion exchange, which is supported by the XPS spectra of Figure 7B. From the results of the chemical shift of Co 2p and N 1s peaks after ion exchange and also from the catalytic behavior examined in the experiment of Figure 5, at least one complex molecule may be located inside the supercage of Y zeolite, which has a diameter of approximately 13 Å with windows of 9-Å diameter. It is not clear from these results how many ethylenediamine and NO_2 ligands stay on the coordination sphere of cobalt cation in the supercage of the zeolite, but at least we can tell that $Co^{III}(en)_m(NO_2)_n$ complex (m and n = 1 or 2) may be the catalytically active species for the NO-NH_3 reaction over fresh Co(en)-Y zeolite catalyst at room temperature.

After ammonia treatment of the fresh catalyst at 363 K, the complex was transformed considerably; that is, the valency of cobalt cation changed to Co^{II} and all the NO_2 ligands were removed from the coordination sphere. On the other hand, one strongly coordinated ammonia molecule NH_3(s) is formed by this treatment, which is very reactive with NO when weakly adsorbed ammonia is not saturated on the surface. During the steady state of the NO-NH_3 reaction at higher temperature, only adsorbed NH_3 was observed by infrared spectroscopy, indicating $Co(en)_m(NH_3)_n$ in Y zeolite as a catalytically active species.

(*2*) *Reaction Mechanism.* Freshly prepared Co(en)-Y zeolite catalyst exhibited catalytic activity and selectivity in the NO-NH_3 reaction at room temperature similar to those in the aqueous solution of $Co(en)_2(NO_2)_3$ complex.[7] As discussed in section IV-1, the catalytically active species would be the $Co^{III}(en)_m(NO_2)_n$ complex in the cavity of the zeolite, and the reaction mechanism on this catalyst may

---

(10) J. H. Lunsford, P. J. Hutta, M. J. Lin, and K. A. Windhorst, *Inorg. Chem.*, 17, 606 (1978).

be similar to that in the aqueous solution.[8]

By ammonia treatment at 363 K, all the NO_2 groups in the complex are removed as indicated by XPS, which causes reduction of Co^{III} to Co^{II} and coordination of one $NH_3(s)$. As shown in Figure 1C, when NO was added on this $Co^{II}(en)_m[NH_3(s)]$ complex at room temperature, N_2 was formed by the reaction between $NH_3(s)$ and NO, which was confirmed by tracer experiments of Table II. Infrared spectroscopic results (Figure 6B) demonstrate the formation of NO monomer and dimer adsorbed species by this procedure. As demonstrated by the experiments in Figure 1D and also in Figure 5D, these adsorbed monomer and dimer species desorb quickly by the introduction of NH_3, accompanied by the simultaneous formation of N_2O. These phenomena will be expressed as the following equations:

$$Co^{III}(en)_m(NO_2)_n \xrightarrow{NH_3} Co^{II}(en)_m[NH_3(s)] + (n/2)N_2 \quad (1)$$

$$Co^{II}(en)_m[NH_3(s)] \xrightarrow{NO} Co^{II}(en)_m(NO)[NH_3(s)] \quad (2)$$

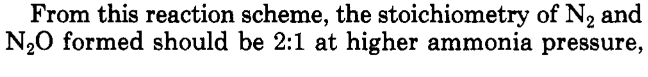
$$Co^{II}(en)_m(NO)[NH_3(s)] \xrightarrow{NO} Co^{II}(en)_m(NO)_2 + N_2 + H_2O + (H) \quad (3)$$

$$Co^{II}(en)_m(NO)_2 \xrightarrow{NH_3} Co^{II}(en)_m(NH_3)_2 + \text{NO desorption or } Co^{II}(en)_m(NH_3)_2 + N_2O + H_2O \quad (4)$$

The pressure dependence of the NO–NH_3 reaction in Figures 3 and 4 can be explained reasonably by these equations. When the partial pressure of NH_3 is very low and the surface is not saturated by weakly adsorbed $NH_3(w)$, N_2 is the main product of step 3, leaving $Co^{II}(en)_m(NO)_2$ dimer adsorbed species on the surface (from the measurements of NH_3 adsorption on zeolite only, it was recognized that 90% of $NH_3(w)$ on Co(en)–Y zeolite was adsorbed on the support, but both adsorption isotherms were similar, indicating the similarity of the NH_3 isotherm on Co(en) complex, too). The rate of N_2O formation from this NO dimer species is slow because of the small concentration of $NH_3(a)$ (step 4). As the partial pressure of NH_3 is increased, the surface is saturated by weakly adsorbed $NH_3(w)$. Because of the inhibition of NO adsorption by this $NH_3(w)$, as demonstrated in infrared experiments, coordination of NO on $Co^{II}(en)_m[NH_3(s)][NH_3(w)]$ may become a slow step in the overall NO–NH_3 reaction (step 2). Then, the pressure dependences would be zeroth order with respect to the partial pressure of NH_3 and first (for N_2) and second (for N_2O) order with respect to the partial pressure of NO. Consequently the reaction scheme of the NO–NH_3 reaction of this catalyst after NH_3 treatment at higher temperatures can be summarized as follows

$$Co^{II}(en)_m[NH_3(s)] + NO \rightarrow Co^{II}(en)_m(NO)(NH_3) \rightarrow N_2 + H_2O + (H)$$

for the lower ammonia pressure region, and



$$Co^{II}(en)_m[NH_3(s)][NH_3(w)] + NO \longrightarrow \begin{cases} Co^{II}(en)_m(NO)(NH_3) \longrightarrow N_2 + H_2O + (H) \\ Co^{II}(en)_m(NO)_2 \xrightarrow{2(H)} N_2O + H_2O \end{cases}$$

for the higher ammonia pressure region.

From this reaction scheme, the stoichiometry of N_2 and N_2O formed should be 2:1 at higher ammonia pressure, which is quite different from the experimental results in Figure 4. To elucidate this result, it is necessary to introduce another pathway for the formation of N_2O, which would be the disproportionation of NO to form N_2O and coordinated NO_2 on CO^{III}.

$$Co^{II}(en)_m(NO)_2 + NO \rightarrow N_2O + Co^{III}(en)_m(NO_2)$$

$$Co^{III}(en)_m(NO_2) + NH_3 + (H) \rightarrow N_2 + 2H_2O$$

The reduction of $Co^{III}(en)_m(NO_2)$ by NH_3 seems to be rather slow and causes the deactivation of the complex even at higher temperatures. The results of isotope-labeled experiments in Table I can be explained by this reaction scheme; N_2 is formed from $Co^{II}(en)_m(NO)(NH_3)$ mononitrosyl intermediate, and N_2O from $Co^{II}(en)_m(NO)_2$ dinitrosyl intermediate complexes. The absence of kinetic isotope effects in the NO–NH_3 and NO–ND_3 reactions and the rapid H–D exchange during the NO–NH_3–ND_3 reaction can also be explained if the rate-determining step is the coordination of NO under the reaction condition examined in Figure 5.

(3) *Comparison of the Catalytic Behavior of Co(en)–Y Zeolite with Co(NH₃)–Y Zeolite, and Also with That in Solution.* In the case of the $Co^{II}(NH_3)$ complex in Y zeolite, Lunsford et al. observed the existence of a kinetic isotope effect in NO–NH_3 and NO–ND_3 reactions ($k_{NH_3}/k_{ND_3} = 1.5$), which is quite different from this study. The reaction order of the NO–NH_3 reaction over Co(NH_3)–Y zeolite was 0.3 with respect to the partial pressure of NO, which is much smaller than in the case of the ethylenediamine complex in this study. Moreover, they could observe infrared bands of adsorbed mononitrosyl and dinitrosyl adsorbed species during the NO–NH_3 reaction, which means that NO monomer and dimer species are much more stable in the case of Co(NH_3)–Y zeolite than Co(en)–Y zeolite. Accordingly, the difference in kinetic isotope effects and reaction orders may be explained by the difference of the stabilities of the reaction intermediates and the rate-determining steps in these two complexes.

As mentioned already, the rate of the NO–NH_3 reaction over a freshly prepared Co(en)–Y zeolite catalyst is similar to that in the aqueous solution as follows: turnover frequences of N_2 and N_2O formations over Co(en)–Y zeolite are 7.2×10^{-3} and 7.5×10^{-3} s^{-1}, respectively, and those in the case of $Co(en)_2(NO_2)_3$ complex in an aqueous solution are 2.5×10^{-3} and 2.1×10^{-3} s^{-1} at room temperature. Moreover, they exhibited similar reaction orders, suggesting the operation of similar reaction mechanisms in these two different media. As has been demonstrated by the experiments in Figure 4, only one $Co^{III}(en)_2(NO_2)_3$ complex seems to be able to enter the supercage of Y zeolite, which exhibits high activities for the NO–NH_3 reaction. On the other hand, the activities of the complex supported on the outer face of Y zeolite or on silica–alumina, alumina, or silica are very low. It has been demonstrated that there exists a large solvent effect in the NO–NH_3 reaction by this complex in aqueous and DMF solutions. NMR spectroscopic studies[8] during the reaction of the solution suggest the requirement of the dissociation of the NH_2 group of the diamine ligands for the coordination of NO, which would be assisted by the solvents. Accordingly, it seems reasonable to suppose that this dissociation step is possible inside the supercage of Y zeolite.

Registry No. NO, 10102-43-9; NH_3, 7664-41-7; $Co^{III}(en)_2(NO_2)_3$, 14376-56-8; deuterium, 7782-39-0.