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Ammonia Oxidation over Cu(II)NaY Zeolites

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Ammonia oxidation to nitrogen and water over CuY zeolites has been studied in the temperature range from 160 to 185°C. The reaction rate was first order in NH_3 and zero order in O_2. The rate was proportional to the degree of Cu^{2+} ion exchange up to a level of about one ion per large cavity. An activation energy of 36.7 ± 2.6 kcal/mol was observed for the three exchange levels which were studied (3, 14, 44%). For the 14%-exchanged sample a turnover number of 0.169 NH_3 molecules per minute per Cu^{2+} ion was observed at 175°C and an ammonia pressure of 300 Torr. Infrared and electron paramagnetic resonance studies indicate that a $[Cu(II)\,(NH_3)_4]^{2+}$ complex was formed in the large cavities of the zeolite. The slow step in the reaction mechanism was the reduction of Cu(II) to Cu(I) by the NH_3. The reoxidation of the Cu(I) complex to a Cu(II) complex was very rapid under the reacting conditions. A detailed mechanism is proposed which is consistent with the experimental data. These results show that Cu^{2+} ions can be extracted from hidden positions within the zeolite framework to form complexes within the large cavities of the zeolite where catalytic reactions can freely occur.

INTRODUCTION

The oxidation of ammonia at elevated temperatures is of commercial importance in the manufacture of nitric acid; whereas, at lower temperatures the products nitrogen or nitrous oxide prevail and the oxidation has significance in air pollution control. At temperatures greater than 750°C ammonia oxidation over platinum and its alloys results in the formation of nitric oxide in the first steps of the production of nitric acid (*1*). At temperatures less than 350°C nitrogen and nitrous oxide become the principle products as the nitric oxide is reduced by ammonia in the presence of oxygen. Although platinum catalysts remain the most effective for ammoxidation, various mixed catalysts, metals, and transition metal oxide catalysts have also been utilized. The ammoxidation studies are reviewed in reference (*2*).

Y-type zeolites ion-exchanged with cupric ions have been shown to be catalysts for propylene and ethylene oxidation (*3*). Water vapor had a very positive effect on the catalytic activity. The Cu(II)Y catalyst was reported to have an activity tenfold higher than a cupric oxide catalyst for propylene oxidation (*3*c). Naccache and Ben Taarit (*4*) have attributed the oxidizing properties and activities of the cupric Y zeolite to the presence of cupric ions. In an electron paramagnetic resonance (EPR) study Vansant and Lunsford (*5*) found that ammonia adsorption in Cu(II)Y zeolites resulted in a square planar $[Cu(NH_3)_4]^{2+}$ complex. Sorption studies by Huang and Vansant (*6*) further indicated that a considerable amount of ammonia was coordinated to the copper(II) ions, mainly in the form of a $[Cu(NH_3)_4]^{2+}$ complex in the zeolite. Both EPR and reactivity data suggest that this complex requires a migration of Cu^{2+} ions from the sodalite cages into the supercages upon adsorption of excess ammonia.

In Y-type zeolites X-ray diffraction studies by Gallezot *et al.* (7) indicated that Cu^{2+} ions occupy mainly S_I and $S_{I'}$ sites. This means that at moderate exchange levels, the Cu^{2+} ions are unavailable for catalysis, unless they can be induced to take up positions in the large cavities. Although ammonia may readily enter the sodalite cage, molecules such as molecular oxygen are apparently too large to enter the 2.2 Å aperture at moderate temperatures.

The purpose of this research was to investigate the catalytic activity of Cu(II)Y zeolites in the oxidation of ammonia using EPR spectroscopy, infrared spectroscopy, and kinetic data. It was of particular interest to determine the role of the copper–ammonia complex in this oxidation reaction and to compare this solvated transition metal complex with the more conventional metal or metal oxide catalysts.

EXPERIMENTAL METHODS

Catalyst preparation and pretreatment. The copper(II) zeolites were prepared by treating a NaY zeolite (Linde Lot No. 13544-76) with aqueous $Cu(NO_3)_2$. Three Cu^{2+} exchange levels were prepared by digesting NaY with 0.01, 0.02, and 0.045 *N* $Cu(NO_3)_2$ at 80°C for 24 hr. After the single exchange the samples were washed with deionized water and dried at 120°C. The zeolite samples were activated by degassing at room temperature for 1 hr, and then in increments of 100°C/hr to 500°C. The catalysts were treated with 360 Torr of oxygen and heated at 500°C for 2 hr to complete the oxidation of all copper and to remove any organic contaminants. After briefly heating the zeolites *in vacuo* at 500°C, the dehydrated samples were cooled to room temperature. The zeolites had a light green color.

The exchange levels of copper were determined by exchanging the Cu(II)NaY zeolites with $AgNO_3$ and analyzing the resulting solutions for copper by atomic absorption. The analyses indicated exchange levels of 0.8, 4.0, and 12.8 Cu^{2+} ions/unit cell (3, 14, and 44% CuY, respectively).

The reactant gases, anhydrous ammonia and oxygen, were obtained from Matheson Gas Products and were used without further purification.

Kinetic experiments. A closed circulating system was employed in this study. The gases were usually circulated over the catalyst at a rate of about 0.4 liters/min. By varying the pumping speed it was demonstrated that diffusion within the reactor did not limit the reaction rate. The volume of the reactor was 0.50 liter.

For the kinetic experiments a weighed sample of catalyst (0.25–0.6 g) was placed on a porous Vycor plate in the reactor and given the standard pretreatment. Following the catalyst pretreatment the reactor was filled with ammonia and oxygen. A 10–15% decrease in activity of the catalyst was noted between the first and second runs, but thereafter the activity remained essentially constant. Therefore, after the initial pretreatment of each catalyst the oxidation reaction was carried out overnight to stabilize the catalyst.

In preliminary studies the order of the reaction was determined by varying the pressures of ammonia and oxygen for reaction. The initial ammonia pressures ranged from 105 to 500 Torr, while oxygen pressures varied from 130 to 350 Torr. Following the initial studies the catalyst was always treated with stoichiometric amounts of ammonia and oxygen, i.e., the ammonia:oxygen partial pressure was 4:3. Ammonia was absorbed in the catalyst at room temperature to an equilibrium pressure of 285 Torr. Oxygen (215 Torr) was subsequently introduced to the reactor for a total pressure of 500 Torr at 26°C.

The reactor was then attached to a CEC

21-614 residual gas analyzer whereby small amounts of gas could be removed during the reaction to monitor the concentrations of oxygen and nitrogen in addition to other possible products such as NO and N_2O. The reaction temperature was regulated by placing the reactor in a silicone oil bath which was maintained within ±1°C of a given temperature by a temperature controller. The kinetic studies included temperatures from 158 to 184°C. The reaction time ranged from 5 to 50 hr, depending upon the reaction temperature and upon the particular catalyst used for the oxidation. An attempt was made to maintain a uniform pumping speed to insure a constant temperature of gases circulating through the catalyst bed. Catalyst temperatures at the bed were calibrated relative to the bath temperature.

Infrared experiments. The infrared cell described by Uytterhoeven *et al.* (*8*) consisted of a Pyrex cell fitted with calcium fluoride windows. The cell allowed spectra to be recorded at elevated temperatures which were measured by means of a thermocouple attached to a stainless steel sample holder. The spectra were recorded on a Beckman IR-12 spectrophotometer. The resolution in the bending region was better than 3 cm^{-1}. To correct for sample emission at temperatures greater than 70°C the second chopper of the instrument was stopped. This avoided the detection and modulation of thermally emitted radiation.

The binderless zeolite powder was pressed into wafers between stainless steel plates using a pressure of 3.3 $tons/cm^2$. These self-supporting wafers had a dry thickness of 3–6 mg/cm^2 and were supported on a stainless steel sample holder within the cell. All infrared spectra were recorded with the sample at 170°C.

Electron paramagnetic resonance studies. The EPR studies were conducted in a separate reactor having a volume of 60 ml. Weighed amounts of catalysts (0.06–0.07 g) were pretreated in the same manner as described previously. The EPR spectra were recorded with the sample at −196°C, using a Varian E6S spectrometer which was operated in the X-band region.

RESULTS

Reaction kinetics. The order of the reaction was established by determining the rate dependence on the partial pressures of ammonia and oxygen. At ammonia pressures of 105, 300, and 500 Torr at 175°C with a constant oxygen pressure of 225 Torr, the rate of oxidation indicated a first-order dependence upon ammonia. Changes in oxygen pressures within a range from 130 to 350 Torr with a constant ammonia pressure of 300 Torr had no effect upon the rate of reaction, i.e., the reaction was zero order in oxygen. Nitrous oxide was not observed as a reaction product and the ratio of N_2 produced to oxygen consumed was 2:3. Thus, for the oxidation reaction,

$$4\ NH_3 + 3\ O_2 \rightarrow 2\ N_2 + 6\ H_2O, \quad (1)$$

the rate law can be expressed as

$$\frac{d[NH_3]}{dt} = -k\ [NH_3]^1\ [O_2]^0. \quad (2)$$

Here $d[NH_3]/dt$ is the rate of change in ammonia concentration; k is the first-order rate constant which contains the amount of catalyst or copper in the system; and $[NH_3]$ and $[O_2]$ are the concentrations of ammonia and oxygen at time t.

Upon integration, the rate Eq. (2) for the first-order heterogeneous reaction takes the form

$$-kt = \ln \frac{[NH_3]}{[NH_3]_0}, \quad (3)$$

where $[NH_3]_0$ is the initial concentration of ammonia. Since water is a reaction product, water droplets condensed in the cooler portions of the reactor after several hours of reaction. Considering the solubility of ammonia in the water formed and expressing the amount of ammonia reacted in terms of oxygen reacted, the overall first-order rate equation takes the form

$$-kt = \ln\left[1 - \frac{4}{3}\frac{[O_2]_0 - [O_2]}{[NH_3]_0} - \frac{[NH_3]_d}{[NH_3]_0}\right], \quad (4)$$

where $[NH_3]_d$ is the amount of ammonia dissolved in the condensed water at time t; $[O_2]_0$ and $[NH_3]_0$ are the initial concentrations of oxygen and ammonia, respectively.

The overall first order rate constants for the reaction were determined by plotting the right hand side of Eq. (4) as a function of time. The least squares analyses of the results are given in Table 1 for the three Cu(II)Y samples studied. The activation energies were determined by conducting the reaction at four or five reaction temperatures on the same catalyst. Between each run the reactor was evacuated for 12 hr at 26°C. The Arrhenius plots are depicted in Fig. 1 for the reaction rate as a function of $1/T$. A least squares treatment of the data yields activation energies of 35.4, 36.9, and 37.7 kcal/mol for the 3, 14, and 44% Cu(II)Y, respectively. The reaction rates in Table 1 have an average standard deviation of 2.4% of the rate constant while the activation energies have a standard deviation of 7.2% or ±2.6 kcal/mol. There is no significant difference between the three activation energies; therefore, an average value of 36.7 ± 2.6 kcal/mol may be deduced.

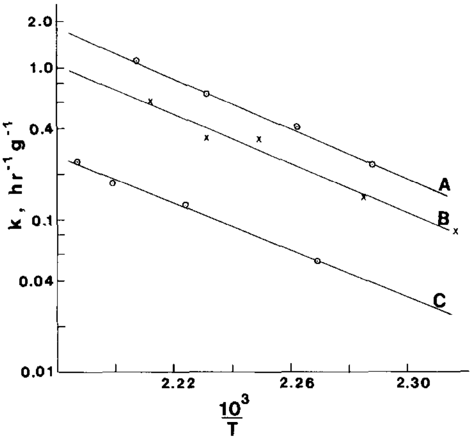

FIG. 1. Rate constants for the oxidation of ammonia over Cu(II)Y as a function of $1/T$: (A) 44%-exchanged, (B) 14%-exchanged, (C) 3%-exchanged.

TABLE 1

RATE DATA FOR THE OXIDATION OF AMMONIA OVER Cu(II)Y ZEOLITE IN A CLOSED SYSTEM

% Exchange of Cu^{2+}	Cu^{2+}/unit cell	T(°C)	Rate constant ($hr^{-1}\ g^{-1}$)	E_a (kcal/mol)
0	—	180	0.00	
3	0.8	184	0.242 (0.0047)[a]	
		181.5	0.173 (0.0032)	35.4 ± 2.3
		176.5	0.126 (0.0026)	
		167.5	0.053 (0.0004)	
14	4.0	179	0.602 (0.0052)	
		175	0.343 (0.0036)	
		171.5	0.341 (0.0021)	36.9 ± 3.3
		164.5	0.141 (0.0007)	
		158.5	0.084 (0.0008)	
44	12.8	180	1.109 (0.0076)	
		175	0.635 (0.0069)	37.7 ± 2.3
		169	0.404 (0.0027)	
		164	0.228 (0.0009)	

[a] The numbers in parentheses are standard deviations.

The reaction rate as a function of copper (II) concentration is plotted in Fig. 2 for

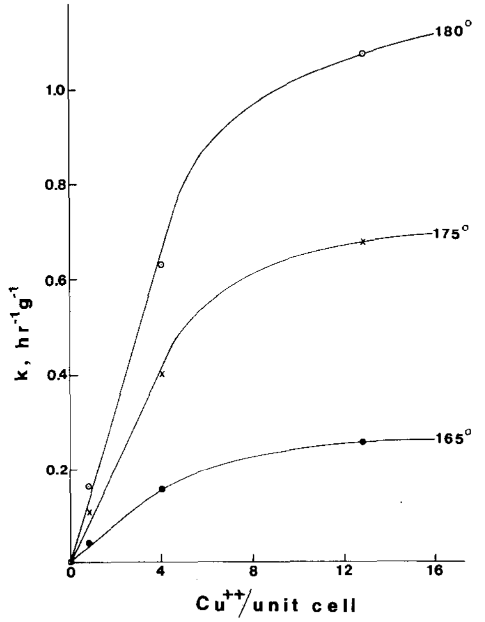

FIG. 2. Rate constants as a function of Cu^{2+} ion concentration at three reaction temperatures.

several reaction temperatures. A nonexchanged NaY sample showed no catalytic activity for ammonia oxidation at 180°C. For the lower exchange levels of 0.8 and 4.0 Cu^{2+} ions/unit cell the reaction rate increased linearly with an increase in copper concentrations, but the activity levels off for the sample with 12.8 Cu^{2+} ions/unit cell.

This deviation from linearity for the 44%-exchanged sample suggested that there may be some loss in crystallinity upon exposure of the dehydrated zeolite to water vapor at elevated temperatures. The gross structural integrity was checked by nitrogen adsorption at −196°C. It was observed that the dehydrated 44% Cu(II)Y zeolite adsorbed 9.31 mmol/g compared with 9.14 mmol/g after the sample had been exposed for 3 hr to 25 Torr of H_2O at 175°C and evacuated at that temperature. A dehydrated 3% Cu(II)Y sample adsorbed 9.96 mmol/g. It appears, therefore, that the more extensive copper exchange and exposure to water did not destroy the zeolite structure. For the more highly exchanged sample it was also determined that the average water desorption rate for the first 4 min was 0.5 molecules/min/Cu^{2+}.

Infrared results. Infrared spectra were recorded in the frequency range of 1200 to 1700 cm^{-1} and 3400 to 3800 cm^{-1} for a 55%-exchanged Cu(II)Y that was pretreated at 400°C with no oxygen treatment. The spectrum of the dehydrated CuY zeolite is shown in Fig. 3, curve 1. After the addition of 10 Torr of ammonia strong peaks were observed at 1615, 1635, 1455, and 1275 cm^{-1} as depicted by curve 2. Curve 3 shows the spectrum 15 min after the addition of oxygen to the CuY-NH_3 system. The peaks at 1635 cm^{-1} became more intense, a decrease in the broad band at 1455 cm^{-1} was noted, and the band at 1275 cm^{-1} appeared to

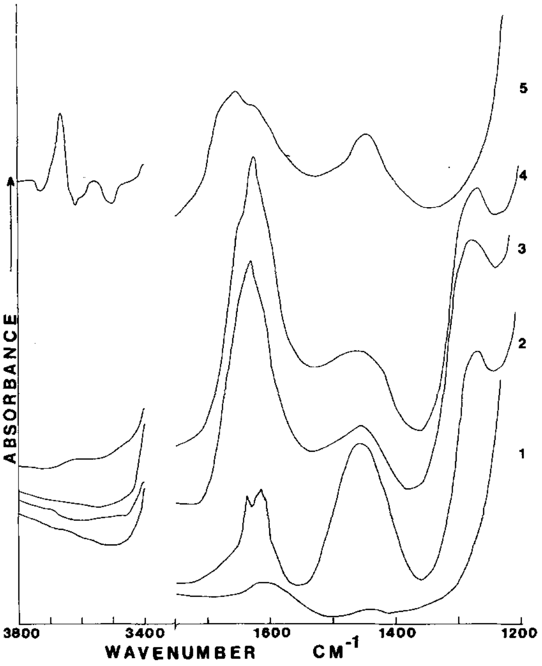

FIG. 3. Infrared spectra in the region of 1200 to 1700 cm^{-1} and 3400 to 3800 cm^{-1} for Cu(II)Y before and after addition of NH_3 and O_2. Spectra were recorded at 170°C: (1) after pretreatment, (2) after addition of 10 Torr of ammonia, (3) 15 min after the addition of oxygen to the system, (4) after reacting 16 hr, (5) after evacuation at 200°C.

increase. Curve 4 shows the spectrum after the reaction was carried out for 16 hr at 170°C. Here the sharp peak at 1635 cm^{-1} has slightly increased and contains a shoulder at 1650 cm^{-1}; whereas, the peak at 1455 cm^{-1} has broadened and the broad band at 1275 cm^{-1} remains. Upon evacuation at 200°C overnight the peaks at 1635 and 1455 cm^{-1} decreased while the peak at 1275 cm^{-1} disappeared as shown in curve 5. Upon evacuation at 200°C peaks occurred in the hydroxyl stretching region at 3660 and 3560 cm^{-1}.

EPR experiments. The EPR spectra of the $[Cu(II)(NH_3)_4]^{2+}$ complex in the CuY (14%) zeolite at −196°C are shown in Fig. 4. Spectrum A is that of the blue $Cu(NH_3)_4^{2+}$ complex formed at room temperature upon addition of 285 Torr of ammonia to the CuY zeolite. Spectrum B occurred after the sample was reduced by NH_3 for 15 hr at 180°C. The sample became white. The extent of reduction of Cu^{2+} to Cu^+ was determined from the $M_I = 3/2$ peak in the parallel region of the spectra of the $Cu(NH_3)_4^{2+}$ complexes. The relative concentration, Δ, was determined by multiplying the height of the peak by the square of the width of the peak at 1/2 the height. The reduction rate was then determined by plotting the Δ versus time and taking the initial slopes as Cu^{2+} reduced/min/Cu^{2+}. The rate for Cu^{2+} reduction and turnover numbers for ammonia oxidation are compared in Table 2 for the three catalysts at 178°C. The non-exchanged NaY zeolite did not show an EPR spectra of the complex in the presence of ammonia. The initial values of Δ for the complex in the 3% and 44% CuY catalysts varied linearly with the Cu^{2+} concentration. The activation energy for reduction was 31.6 ± 4.4 kcal/mol.

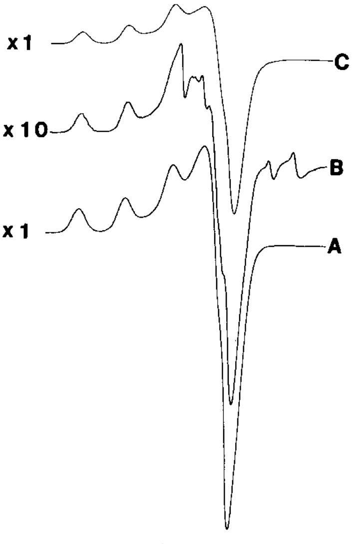

FIG. 4. EPR spectra of Cu(II)–NH_3 complex recorded at −196°C: (A) ammonia adsorbed in 14%-exchanged CuY at 25°C, (B) after reduction for 15 hr at 180°C, (C) after addition of 285 Torr NH_3 and 2 Torr O_2.

TABLE 2

COMPARISON OF TURNOVER NUMBERS FOR Cu^{2+} REDUCTION AND NH_3 OXIDATION AT 178°C

% Exchange of Cu^{2+}	$d[Cu^+]/dt$ (Cu^{2+} reduced/min/Cu^{2+})	$d[NH_3]/dt$ (molecules/min/Cu^{2+})
3	0.29	0.29
14	0.16	0.22
44	0.15	0.12

Regeneration of the reduced catalyst is indicated by the spectrum of Fig. 4C. The addition of 285 Torr of ammonia and 2 Torr of oxygen resulted in spectrum C after the sample remained for several hours at room temperature. The peak intensities are less than those of the original complex even though enough oxygen had been added to completely oxidize the sample back to the original concentration of Cu(II)-ammine complexes. Upon addition of the oxygen the sample immediately turned from white to blue. Other experiments indicate that the complex formation was complete after briefly heating the catalyst at 100°C in an excess of ammonia and oxygen.

DISCUSSION

In the commercial production of nitric oxide via the oxidation of ammonia the formation of N_2 is undesirable; however, in pollution control one attempts to produce N_2 apart from any oxides of nitrogen. The generally accepted mechanism for the oxidation reaction over supported metals involves the formation of NO as the initial oxidation product. This molecule may further react to produce N_2 or N_2O, with varying selectivities from one set of conditions to another. Ostermaier *et al.* (*9*) have recently reported that for NH_3 oxidation over platinum on alumina N_2, N_2O, and H_2O were the only products between 120 and 200°C. Although the mechanism for the reaction on metal oxides is not as firmly established, the results suggest that NO may not be an intermediate. Over doped nickel oxides neither NO nor NO_2 were found in more than trace amounts (*10*). The availability of surface defects or excess oxygen at the surface appears to be the dominant factor in determining the activity for the oxidation reaction.

We propose that the oxidation of NH_3 over CuY zeolites proceeds by a mechanism which has as its rate determining step the reduction of Cu^{2+} to Cu^+ by an ammonia ligand. This is supported by our observations that: (a) the rate and activation energy of Cu^{2+} reduction is essentially the same as the rate of ammonia disappearance, (b) the rate law is first order in complex concentration (at low exchange levels), first order in NH_3 concentration, and zero order in oxygen concentration. The following mechanism is consistent with the experimental data:

$$[Cu(II)(NH_3)_3]^{2+} + NH_3 \rightleftarrows [Cu(II)(NH_3)_4]^{2+}, \quad (5)$$

$$[Cu(II)(NH_3)_4]^{2+} \xrightarrow{\text{slow}} [Cu(I)(NH_3)_3]^+ + NH_2 + H^+, \quad (6)$$

$$[Cu(I)(NH_3)_3]^+ + O_2 \rightarrow [Cu(II)(NH_3)_3]^{2+} + O_2^-, \quad (7)$$

$$2\,NH_2 + O_2 \rightarrow N_2 + 2\,H_2O, \quad (8)$$

$$H^+ + O_l^{2-} \rightarrow O_lH^-, \quad (9)$$

$$O_lH^- + NH_3 \rightarrow O_l^{2-}\;NH_4^+, \quad (10)$$

$$O_l^{2-}\;NH_4^+ + O_2^- \rightarrow O_l^{2-} + NH_3 + HO_2, \quad (11)$$

$$2HO_2 \rightarrow H_2O + \frac{3}{2}\,O_2. \quad (12)$$

Reactions (8) and (12) are not true mechanistic steps, but they indicate reaction pathways for removal of intermediates.

The nitrogen hyperfine structure in the EPR spectrum of the complex in a low-exchanged CuY zeolite provides convincing evidence that at low temperatures there are 4 ammonia molecules/copper ion (*5,11*). A parallel infrared study (*11*) has recently shown that the infrared band at 1275 cm^{-1} is also characteristic of this complex in zeolites as well as in $Cu(NH_3)_4^{2+}$ salts (*12*). Since this band is also observed under reacting conditions at 170°C, one may conclude that the square planar complex is present at these elevated temperatures.

The role of the complex is: (a) to stabilize a large fraction of the copper ions in the supercage where they can readily react with molecular oxygen and (b) to offer a convenient path for the dissociation of ammonia. The role of the ammonia in bringing about the relocation of the cations is very apparent when one observes the EPR spectrum of the 44%-exchanged sample which reflects the formation of spin-exchanged copper pairs within the sodalite cages. Upon exposure to ammonia these pairs are broken up, and the spectrum of the isolated complexes is mainly observed (*11*). Huang and Vansant (*6*) have also pointed out that the complexed Cu^{2+} is much more subject to reduction with CO than the hidden Cu^{2+} ions.

The reduction of the Cu(II) to Cu(I) is apparently accomplished by the formation of a proton which reacts with a lattice oxide ion, yielding a hydroxide ion. In the presence of ammonia this rapidly forms ammonium ions as observed in HY zeolites. The infrared band at 1455 cm^{-1} confirms the presence of these NH_4^+ ions in the CuY zeolite. One should notice that the hydroxyl band at 3660 and 3560 cm^{-1} were only observed after the excess NH_3 had been removed by evacuation of the gas phase at 200°C. The bands in the region of 1615–1635 cm^{-1} were originally due to NH_3 deformation, but later in the reaction the water deformation must also contribute to the ir intensity.

Step 8 in the mechanism is somewhat tenuous since the NH_2 radical would be very unstable at reacting temperatures. This species has been studied independently in zeolites which were γ-irradiated at −196°C after the adsorption of NH_3 (*13*). The NH_2 radical may further dissociate before reacting with O_2, nevertheless, the products are expected to be N_2 and H_2O.

The EPR spectra of Fig. 4, as well as the change in the color of the sample, confirm that the Cu(I) is oxidized to the Cu(II)-ammonia complex upon exposure to molecular oxygen at room temperature. In a somewhat related study it has been demonstrated that the $Co(II)(NH_3)_n$ complex in a zeolite reacts with oxygen at −70°C, forming $[Co(III)(NH_3)_nO_2]^{2+}$ where the unpaired electron, and presumably the negative charge, resides almost completely on the oxygen (*14*). This is a reversible reaction and the oxygen may be removed by brief evacuation of the sample at room temperature. For the copper complex it is imperative that the O_2^- not remain on the complex since the unpaired electrons on the Cu(II) and O_2^- would strongly interact, giving a much different signal than the one which was observed. We conclude that the superoxide ion goes on to react with the NH_4^+ ion as indicated in step 11.

Hildebrandt and Skala (*15*) demonstrated that in zeolites the reaction of ammonium ions with molecular oxygen requires temperatures in excess of 300°C. It is anticipated, however, that the superoxide ion, because of its negative charge, would be much more reactive with the positive ammonium ion. One should note that the NH_4^+ band at 1455 cm^{-1} decreased significantly upon the addition of O_2 to the sample, as indicated in curve 3 of Fig. 3. The products of the reaction are unknown, although it seems likely that the transfer of a proton to form the unstable HO_2 molecule would occur.

The decrease in turnover number for the more highly exchanged sample may be the result of diffusional limitations. Since the turnover numbers for Cu^{2+} reduction and the oxidation of NH_3 are essentially equal for the 44%-exchanged sample, one may conclude that the reaction is limited by the rate at which ammonia reaches the copper ion. A simple model, based only on the diffusion of ammonia suggests that the diffusion rate should be very rapid compared with the reaction rate. The true situation, however, is obviously more complicated because of the presence of water within the zeolite. Undoubtedly this zeolite water would greatly obstruct the movement of ammonia within the crystals.

The mechanism described in Eqs. 5–12 differs considerably from the mechanisms that have been proposed to explain the data obtained for metal and metal oxide catalysts. On Pt catalysts at elevated temperatures the reaction is thought to proceed via the interaction of gas phase NH_3 with chemisorbed oxygen atoms which essentially cover the surface. The rate limiting step is often the diffusion of ammonia to the surface of the catalyst; therefore, true activation energies are difficult to obtain. Over metal catalysts the rate is independent of the oxygen pressure at the elevated temperatures. According to the previously mentioned work of Ostermaier *et al.* (*9*) the rate data at moderate temperatures can best be represented by a Langmuir–Hinshelwood model involving dissociative adsorption of both reactants. In contrast, the reaction rate over Cu_2O is essentially independent of ammonia concentration and first-order in oxygen concentration. Holbrook and Wise (*16*) conclude that the catalytic selectivity for the formation of N_2O or N_2 is related to the surface density of charged oxygen species. Our work focuses attention on the role of the copper–ammonia complex in the zeolite and the importance of the ligand reacting with the metal ion. The zeolite framework is viewed more as a basic solvent than as a catalytic surface.

It is now evident that a number of different transition metal complexes may be formed within the zeolite framework, and many of these contain ligands such as ammonia and oxygen, which may conveniently be reacted with organic molecules. The formation of benzonitrile from toluene and ammonia over Cu-, Zn-, Ag-, and Fe-exchanged X-type zeolites has been reported to occur at 540°C, and the results are interpreted in terms of a metal–ammonia complex (*17*). As demonstrated by the present work these complexes appear to offer new reaction pathways which are in many ways more similar to catalysis by metal complexes in homogeneous media than to conventional heterogeneous catalysis.

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