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Intermediate Species and Reaction Pathways for the Oxidation of Ammonia on Powdered Catalysts

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Ammonia oxidation reaction pathways on high surface area silver powder have been studied by TPD, temperature programmed reaction FT-Raman, and transient as well as steady-state ammonia oxidation experiments. NO was found to be the main reaction intermediate yielding N_2O as well as N_2. NO could be formed even at room temperature and when oxidized to NO_x became adsorbed to the silver surface, thus blocking the active sites for oxygen dissociation. The dissociation of oxygen is thus believed to be the rate-controlling step for ammonia oxidation. The selectivity for N_2, N_2O, and NO is mainly determined by the surface oxygen coverage and by reaction temperature. The adsorbed NO_x and N_2O_x species are actually inhibitors for ammonia oxidation but these adsorbed species lower the surface oxygen coverage. Hence the selectivity for nitrogen is improved with increasing amounts of these adsorbed species. © 2001 Academic Press

Key Words: **ammonia; oxidation; silver; silver catalysts; reaction mechanism.**

1. INTRODUCTION

The selective catalytic oxidation of ammonia to nitrogen and water (SCO process) has been proposed as an effective ammonia abatement process (1–3). Among the catalysts published in the open literature, noble metals such as Pt and Ir are the most active catalysts at low temperatures. However the selectivity of these metal catalysts is not satisfying, especially under the condition of very high O_2/NH_3 ratios. Silver was also found in our laboratory to be one of the most active ammonia oxidation catalysts but also showed a poor selectivity to nitrogen, also forming N_2O as a main product. In order to improve the selectivity of these catalysts it is essential to develop a clear understanding of the reaction pathways for ammonia oxidation on these catalysts.

The majority of mechanistic studies on ammonia oxidation have been done on platinum catalysts. Three reaction mechanisms have been proposed in earlier studies. The nitroxyl (HNO) mechanism suggests that the first step is the formation of a nitroxyl species that will further react to give out N_2, N_2O, and NO (4). Bodenstein (5, 6) extended this mechanism by suggesting that the formation of hydroxylamine (NH_2OH) was the first step. This NH_2OH is converted to HNO in a next reaction step. An imide mechanism in which the first step yields imide (NH) was postulated by Raschig (7) and Zawadzki (8). Based on the data of secondary ion mass spectrometry (SIMS) Fogel *et al.* concluded that the intermediate species HNO, NH_2OH, HNO_2, and N_2O were not formed during ammonia oxidation at partial pressures of 10^{-4} Torr (9). The only intermediate specie was NO. The formation of N_2 was proposed to be a result of the NO reacting with NH_3.

New insights into the reaction mechanism of ammonia oxidation were obtained from surface science experiments (10–13). Single crystals of platinum were used in these experiments and the reaction was carried out under high vacuum conditions. The first step of ammonia oxidation was believed to be the formation of NH_x species through oxydehydrogenation of ammonia. Mieher and Ho (11) concluded that NO and N_2 were formed by the combination of nitrogen atoms with adsorbed oxygen atoms or with two nitrogen atoms, respectively. However Bradley *et al.* (13) suggested that NO was directly produced by reacting NH_a with O_a. The formation of N_2 resulted from the consecutive dissociation of NO. Since only NO and N_2 were produced under the reaction conditions of these studies, the formation of N_2O is not discussed. The recent study of Van den Broek and van Santen (14, 15) showed that NH and OH were the main surface species adsorbed on Pt and Ir sponge catalysts after ammonia oxidation. The reaction of NH and OH was thought to be the rate-determining step under their reaction conditions. They argued that N_2O was produced by NO reacting with adsorbed N. The STM technique was used by the group of M. W. Roberts (16–18) to study ammonia oxidation on copper surfaces. They observed that at very low temperatures ammonia could be oxidized to adsorbed NH_2 and NH species. At higher temperatures NO formation was also observed. On metal oxide catalysts a mechanism based on the recombination of two NH_x species giving rise to a hydrazinium intermediate was also proposed (19–21).

Ammonia adsorption on Ag(110) has been studied previously by TPD, TPRS, and EELS with and without

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coadsorption of molecular and atomic oxygen (22). It was concluded that a diffusing nitrogen adatom was the reactive intermediate in NO and N_2 formation. On the basis of a combination of XPS and VEEL spectra a dioxygen–NH_3 complex has been suggested to be a key intermediate in the oxidation of ammonia on Ag(111) surfaces (35, 36). No report has been published to date on the intermediate species and reaction mechanisms on polycrystalline silver at atmospheric pressure. In this study the ammonia reaction pathways were studied by TPD, temperature programmed reaction (TPR), FT-Raman, and pulsed ammonia reactions on high surface area silver powder at high O_2/NH_3 ratios.

2. EXPERIMENTAL

Polycrystalline silver was prepared from Ag_2O (>99.99%) powder. The powder was first reduced in flowing H_2/He overnight at 400°C and then oxidized in flowing O_2/He at 400°C for 2 h. This process was repeated three times to remove any carbon species and to maintain a stable surface area. Catalytic activity measurements were carried out in a quartz, fixed-bed reactor (4 mm in internal diameter). The amount of silver powder catalyst was about 0.2 g. Ammonia, oxygen, and helium flow rates were controlled by mass flow meters. NH_3, NO, and NO_2 were analyzed by a ThIs Analytical Model 17C Chemiluminescence NH_3 Analyzer, in which a high temperature converter oxidized NH_3 to NO_x by O_2. Other substances such as N_2O, N_2, and H_2O were analyzed by a quadruple mass spectrometer (Baltzers OmniStar). The nitrogen mass balance was calculated based on a combination of these two analysis techniques. It attained a balance of 90 ± 10% for all the measurements.

NH_3 TPD and TPR experiments were performed using a fixed-bed flow reactor system equipped with a computer-interfaced quadruple mass spectrometer. After adsorption of NH_3 at room temperature the TPD or TPR data were recorded by mass spectrometer while the temperature was increased from 50 to 500°C at a heating rate of 10°C/min. FT-Raman spectra were obtained with a Bruker FRA 106 Raman Spectrometer equipped with an *in situ* reaction chamber. The standard laser was an air-cooled, diode-pumped Nd:YAG operating at 1.064 μm with a maximum laser power of 500 mW. Usually a laser power of 150 mW was used for measures under atmospheric conditions. Detection was performed by a liquid-nitrogen-cooled InGaAs detector. One hundred scans were co-added at a resolution of 2 cm^{-1}.

3. RESULTS

3.1. NH_3 Oxidation on Silver Powder at High O_2/NH_3 Ratios

Ammonia oxidation at high O_2/NH_3 ratios was carried out on silver powder at temperatures below 400°C. Figure 1 shows the results of NH_3 conversion and products' selectivity versus reaction temperatures. It can be seen that silver is very active for ammonia oxidation and shows high conversion even below 160°C. At low ammonia conversion the N_2 selectivity decreases with increasing temperature. At high ammonia conversion the N_2 selectivity increases with increasing temperature. When the temperature is over 300°C the N_2 selectivity decreases again because of the formation of NO.

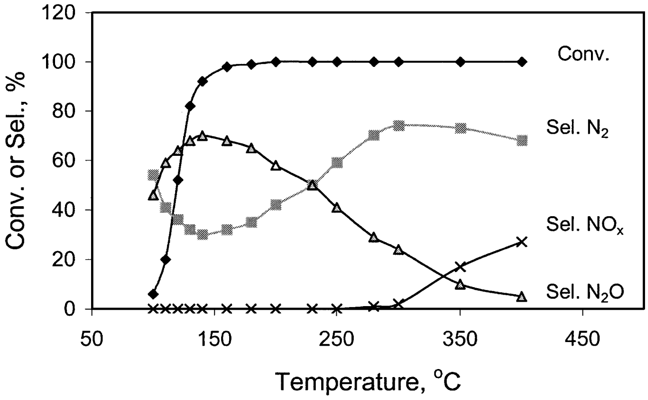

FIG. 1. Ammonia oxidation on silver powder at various temperatures. Reaction conditions: $NH_3 = 1000$ ppm; $O_2 = 10$ vol%; total flow rate = 50 Nml/min; catalyst weight = 0.1 g.

3.2. TPD and TPR of Ammonia on Reduced and on Oxygen-Covered Silver Powder

Figure 2 shows the NH_3 TPD profile measured on completely reduced silver powder. Apparently a small amount of water in the helium or in the ammonia can be adsorbed on Ag and is desorbed at about 150°C. Trace ammonia also desorbs at this temperature. This is mostly from water-coupled ammonia. This result shows that a clean silver surface cannot adsorb ammonia above room temperature. This is in accordance with the literature (22). Figure 3 shows the NH_3 TPD profile measured on oxygen precovered silver powder.

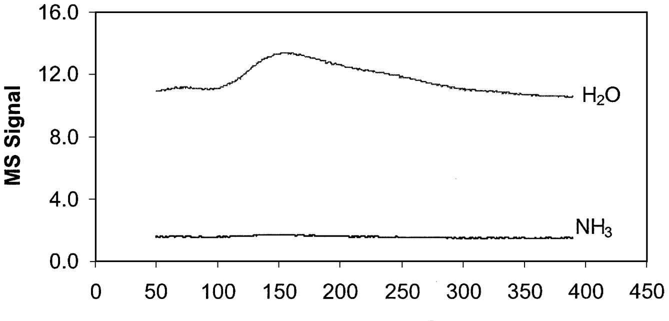

FIG. 2. NH_3 TPD on reduced silver powder. Silver powder was reduced at 400°C for 2 h and then in NH_3/He flow for 0.5 h at 50°C. TPD was performed in He = 20 Nml/min flow. Temperature was increased from 50 to 400°C at a rate of 10°C/min.

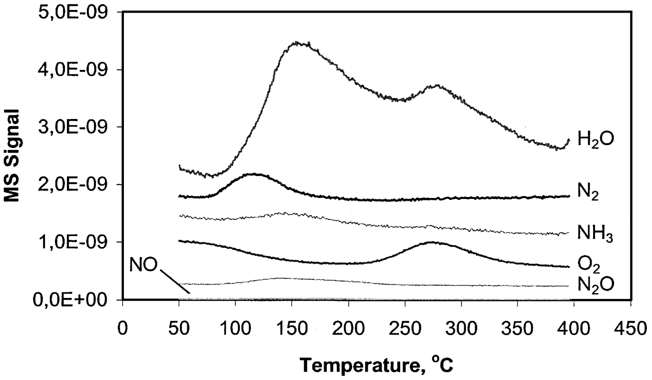

FIG. 3. NH_3 TPD on oxygen-covered silver powder. The reduced silver was first oxidized at 200°C for 10 min in flowing O_2 (10%)/He followed by NH_3 adsorption and TPD as described in Fig. 2.

There are two water production peaks at 150 and 280°C, respectively. The peak at 150°C is similar to the water desorption peak shown in Fig. 2. The peak at 280°C can be caused by the reaction of adsorbed OH species according to the following reactions:

$$OH + OH \rightarrow H_2O + O \qquad [1]$$

$$O + O \rightarrow O_2. \qquad [2]$$

The oxygen peak appears at the same position as the water peak. This strongly suggests that reaction step [1] is rate-limiting. There is still a trace of NH_3 desorbed at 150°C. Significantly more N_2 is produced at a temperature of 120°C. This N_2 production must come from adsorbed nitrogenous species on the silver surface. On Ag(111) surfaces a dioxygen–NH_3 complex has been detected by XPS and VEEL at 80 K which is suggested to be a key intermediate in the oxidation of ammonia (35). When temperature is increased to 210 K the dioxygens are not present and NH species appear. The study on Ag(110) surfaces for ammonia oxidation shows that NH groups persist on the surface at temperatures well into the water desorption peak at 310 K and possibly to significantly higher temperatures (22). Thus the adsorbed nitrogen species may be NH_x produced by oxygen abstraction of hydrogen from NH_3:

$$NH_3 + O \rightarrow NH_2 + OH \qquad [3]$$

$$NH_2 + O \rightarrow NH + OH. \qquad [4]$$

Besides N_2 there is also some N_2O produced. The maximum production temperature for N_2O production is higher than that of N_2. This indicates that the selectivity of ammonia oxidation depends on the surface N/O ratio. With the production of N_2 the amount of NH_x decreases and the O/N increases, leading to increased N_2O production to maximum.

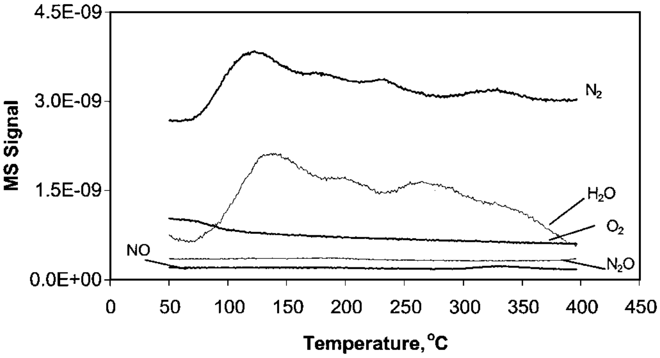

FIG. 4. NH_3 TPR profiles on oxygen-covered silver powder. Silver pretreatment was as in Fig. 3. TPR performed in NH_3/He = 20 Nml/min flow with NH_3 concentration of 1000 ppm from 50 to 400°C at 10°C/min.

Figure 4 shows the NH_3 temperature programmed reaction (TPR) profiles on an oxygen precovered Ag powder. The NH_3/He was flowing constantly over the silver powder during the increase in temperature. With increasing temperature the rates of reactions [3] and [4] are greatly increased and the surface N/O ratio increases accordingly. Now over the entire temperature range the only product is nitrogen. There are four N_2 production maxima at 120, 170, 240, and 300°C, respectively. The first one is apparently caused by adsorbed surface atomic oxygen. The later two appear coincidentally after water production has reached a minimum. It is possible that water inhibits the migration of subsurface oxygen onto the surface. When water desorbs, more subsurface oxygen may become accessible for the ammonia oxidation reaction. It also can be seen from the water production profile that a new peak at about 200°C appears in addition to the two already mentioned. This peak surely is not the result of reaction [1]. It must originate from the following reactions:

$$OH + NH_3 \rightarrow H_2O + NH_2 \qquad [5]$$

$$OH + NH_2 \rightarrow H_2O + NH \qquad [6]$$

$$OH + NH \rightarrow H_2O + N. \qquad [7]$$

The possibility of reactions [5]–[7] cannot be excluded at low temperature but at least one of these reactions, most probably reaction [7], will probably occur only at higher temperatures (>150°C). There is also a new feature at about 300°C in the H_2O profile which is in the same position as the fourth N_2 peak in the N_2 profile. This may be caused by the ammonia oxidation by bulk dissolved oxygen that is migrated onto the silver surface at high temperature.

3.3. *Ammonia Pulse Reaction Studies*

To further clarify the reaction mechanism, pulse reactions were carried out at different temperatures. Pulses of NH_3

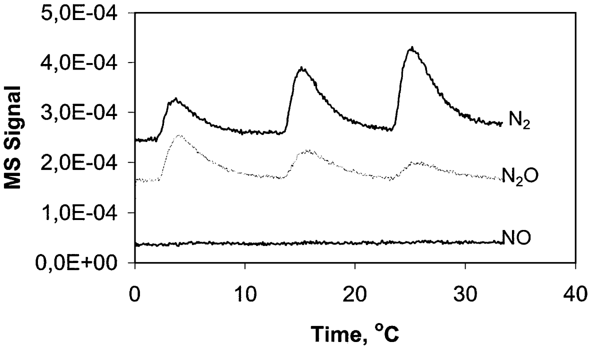

FIG. 5. NH_3 pulse reaction profiles on silver powder at 200°C. Silver first reduced at 400°C in flowing H_2 (10%)/He = 40 Nml/min for 2 h and then in flowing O_2 (10%)/He = 20 Nml/min at 200°C. Each pulse contained 5 μl NH_3.

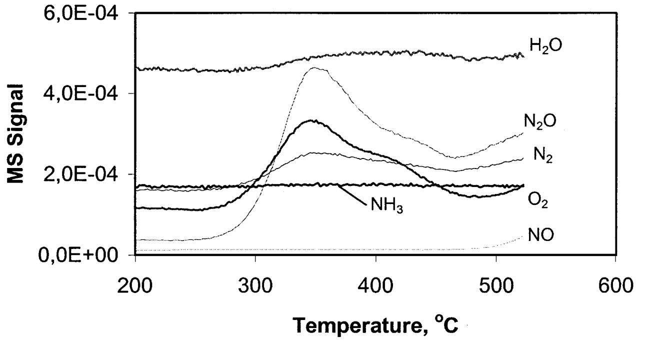

FIG. 7. TPD profiles after NH_3 oxidation reaction at 200°C on silver powder. Reaction conditions: NH_3 = 1000 ppm; O_2 = 10%; flow rate = 50 Nml/min; catalyst weight = 0.1 g. TPD was performed in flowing He = 20 Nml/min from 200 to 550°C at 10°C/min.

(aica 0.22 μmol) were made into a flow of O_2(10 vol%)/He. It can be seen from Fig. 5 that during the first ammonia pulse large amounts of N_2O were produced simultaneously with N_2 production. During the following ammonia pulse the amount of N_2O production was greatly reduced while N_2 production increased. When the reaction temperature was raised from 200 to 400°C the situation changed completely. Large amounts of NO were produced during the NH_3 pulse but the N_2 selectivity changed little (see Fig. 6). These results indicate that some adsorbed nitrogen species were produced during the first NH_3 pulse that greatly changed the reaction selectivity of the following NH_3 pulse reaction.

3.4. Reaction Intermediates

To clarify the nature of the adsorbed species TPD experiments were done on a silver powder catalyst after reaction under different conditions. Figure 7 shows the TPD profiles measured on a Ag powder catalyst after reaction for 1 h in excess oxygen at 200°C. It can be seen that the production profile patterns for N_2O, N_2, and O_2 are almost same. This may indicate that these products originate from the same species. It is well known that NO can react to give N_2O, N_2, and O_2 according to the following reactions (23, 24):

$$NO + NO \rightarrow N_2O + O \qquad [8]$$

$$NO + NO \rightarrow N_2 + O_2 \qquad [9]$$

$$O + O \rightarrow O_2. \qquad [10]$$

To assess the importance of NO adsorption on Ag powder TPD experiments were carried out. When NO was coadsorbed with O_2 on reduced silver powder at 200°C the TPD profiles were exactly the same as those obtained after NH_3 oxidation reaction (see Fig. 8). This strongly indicates that the adsorbed intermediate nitrogen species are mainly NO-induced species.

It also can be seen from Fig. 7 that there is some water produced. This may indicate the presence of some OH or NH_x species but the quantity is small. The fact that there is a trend to desorb N_2, NO, N_2O, and O_2 at higher temperature (>500°C) suggests the existence of more than one NO-induced species. This species may be NO_3 since it is the most stable species on the silver surface.

When the reaction was carried out at low O_2/NH_3 ratios (e.g.,1/1) the TPD profile after reaction was totally different

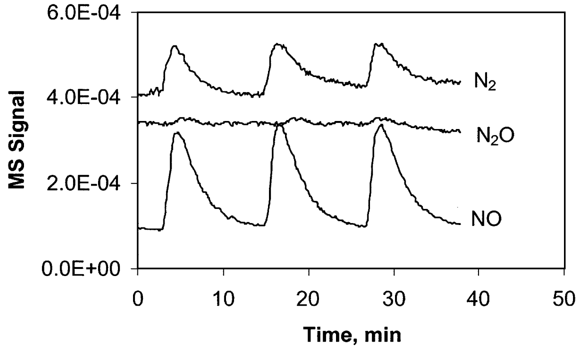

FIG. 6. NH_3 pulse reaction profiles on silver powder at 400°C. Reaction conditions were the same as those in Fig. 5.

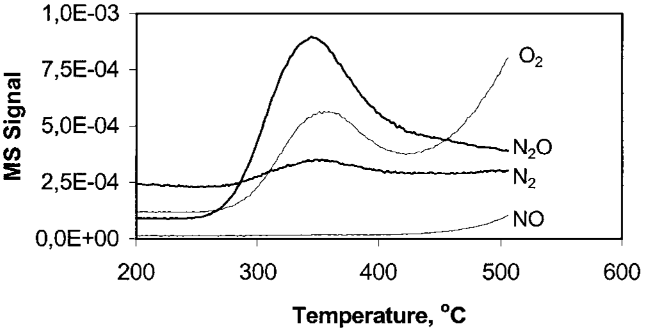

FIG. 8. TPD profiles after NO + O_2 adsorption at 200°C for 5 min. NO = 1000 ppm; O_2 = 10%; NO/O_2/He = 20 Nml/min. TPD performed in flowing He = 20 Nml/min from 200 to 550°C at 10°C/min.

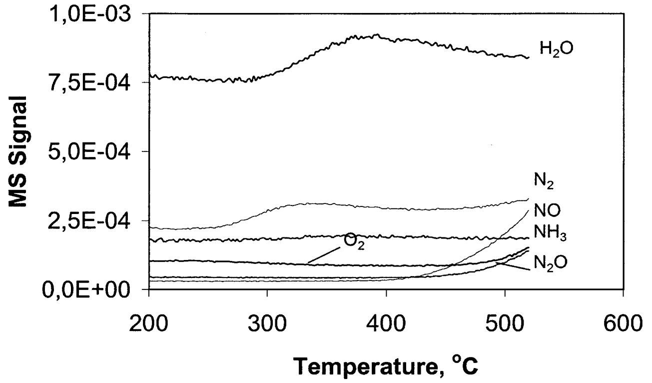

FIG. 9. TPD profiles after NH_3 oxidation at 200°C on silver powder. Reaction conditions: $NH_3 = 1\%$; $O_2 = 1\%$; flow rate = 50 Nml/min; catalyst weight = 0.1 g. TPD performed in flowing He = 20 Nml/min from 200 to 550°C at 10°C/min.

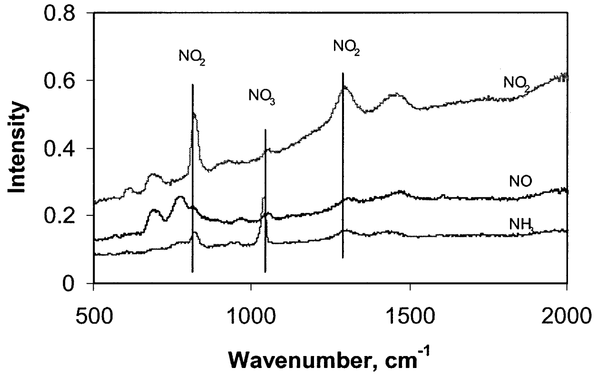

FIG. 10. Raman spectra for NO, NO_2, and NH_3 adsorbed on silver powder. NO and NO_2 adsorption at 50°C on reduced silver powder; NH_3 adsorption at 50°C on oxygen-covered silver powder.

(see Fig. 9). Much more water was produced and only N_2 desorbs at low temperature. As most of the OH species can be desorbed as H_2O at 280°C, according to reaction [1], the comparatively large amount of water must come from NH_x species. Most probably N_2 and H_2O result from the following reaction:

$$NH_x + NO_x \rightarrow N_2 + OH_x. \qquad [11]$$

Thus, apparently there are more NH_x species on the surface when the O_2/NH_3 ratio decreases.

3.5. *FT-Raman Spectroscopy*

FT-Raman measurements were carried out on a silver powder with preadsorbed NO, NO_2, or NH_3. For NO or NO_2 adsorption a completely reduced silver powder was used and the adsorption temperature was 50°C. For NH_3 adsorption the reduced silver powder was first oxidized in O_2 at 200°C for 1 h and then NH_3 was adsorbed at 100°C to increase the Raman signal. All of the measurements were done at room temperature to avoid the heating effects. The resulting spectra are shown in Fig. 10. Bao *et al.* have studied NO adsorption on Ag(110) by Raman and XPS (25). They concluded that NO was not stable on silver surface. NO was quickly oxidized to NO_2 and NO_3, which were strongly adsorbed on silver surface. The SERS spectra of NO_2 adsorbed on the silver powder were also reported in the literature (26, 27). Peaks at 815, 1045, and 1285 cm^{-1} after exposure of silver powder to several nitrogen dioxide pulses added into the He gas stream were observed. They assigned the peaks at 815 and 1285 cm^{-1} to adsorbed NO_2^- and the peak at 1045 cm^{-1} to adsorbed NO_3^- on silver surface. Comparing the Raman spectrum of NH_3 adsorption with NO and NO_2 adsorption spectra in Fig. 10, it is obvious that a spectrum similar to that of NO and NO_2 adsorption appears upon adsorption of NH_3 on oxygen-covered silver powder. This strongly indicates that NH_3 can be quickly oxidized to NO which will consequently be oxidized to NO_2^- and NO_3^- species. The remaining peaks in Fig. 10, such as in the positions of 615, 670, and 985 cm^{-1}, are assigned to the different oxygen species on the silver surface (29).

Raman measurements were carried out on silver powder at different temperatures following *in situ* ammonia oxidation to observe the changes of surface species. The resulting spectra are shown in Fig. 11. Based on previously published Raman data on the silver–oxygen interaction (28, 29) and on Raman and IR measurements of adsorbed N_2O_x(30–33), the peak at 245 cm^{-1} is assigned to surface adsorbed atomic oxygen and the peaks at 266 and 1540 cm^{-1} are assigned to the N–N stretching Raman band of N_2O_x. The x can be 2, 3, 4, or 5. Unambiguous determination of x is difficult since these N_2O_x species often show intensities at nearly the same positions in Raman and IR spectra. It can be seen from Fig. 11 that the intensity of surface atomic oxygen decreases with increasing temperature. The intensity of the N_2O_x peaks increased slightly as heating began but stayed unchanged afterward. The NO_2 peak intensity

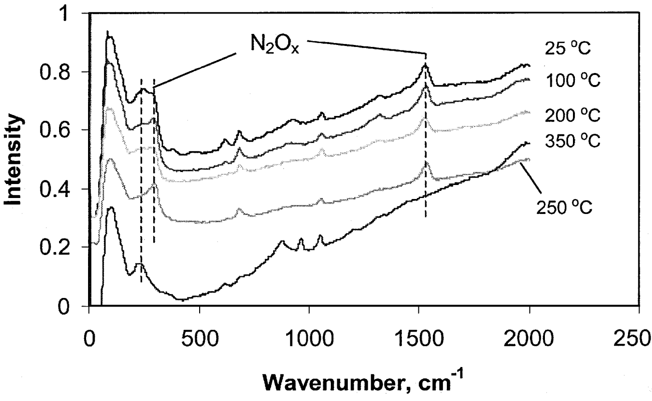

FIG. 11. Raman spectra measured at RT after ammonia oxidation on silver powder at different temperatures. Reaction conditions: $NH_3 =$ 1000 ppm; $O_2 = 10\%$; $NH_3/O_2/He = 50$ Nml/min.

decreased but NO_3^- adsorption signal stayed unchanged as the temperature increased. When the temperature was increased to 300°C the signals of N_2O_x disappeared and the surface atomic oxygen adsorption signal recovered again.

4. DISCUSSION

NH_3 TPD and TPR results show that NH_3 does not adsorb on clean silver surface above room temperature. On an oxygen precovered silver surface NH_3 dissociatively adsorbs only as NH_x with one or two hydrogen abstracted by oxygen according to reactions [3] and [4]. This is considered to be the initial step for ammonia oxidation. Reactions [3] and [4] can be enhanced by either increasing the temperature or by increasing the oxygen coverage on the silver surface (17, 18).

NH_x species can consecutively react with either O or OH according to reaction [7] to give N:

$$NH_x + O \rightarrow N + OH_x. \qquad [12]$$

The N is very reactive and gives NO or N_2 according to

$$N + O \rightarrow NO \qquad [13]$$

$$N + N \rightarrow N_2. \qquad [14]$$

When there is preadsorbed oxygen on the silver surface the probability of reaction [14] occurring is low due to the high rate of reaction [13]. The Raman experimental results clearly showed that NO_x species appeared even at room temperature upon ammonia adsorption. There was no evidence for the formation of molecular nitrogen at room temperature on silver powder. The fact that reactions [12] and [13] can take place at room temperature indicates that reaction [12] is not the rate-controlling step for gas phase NO formation as suggested by many authors (11, 15, 21). Actually the NO formed cannot desorb at low temperatures and quickly reacts with other adsorbed oxygen to produce NO_x which will strongly adsorb on the silver surface and block the active sites for oxygen dissociation. Since reaction [14] is not significant at high O_2/NH_3 ratio conditions, the formation of nitrogen may occur as follows:

$$NH_x + NO \rightarrow N_2 + OH_x \qquad [15]$$

$$NO + NO \rightarrow N_2 + O_2. \qquad [16]$$

Reaction [16] actually involves the same NO dissociation and atomic nitrogen combination as in reaction [14]. This occurs only at low temperatures on reduced silver and oxygen is a strong inhibitor of this reaction.

The mechanism of N_2O formation from ammonia is not very clear. In low pressure ammonia oxidation studies on Pt and Ag single crystals, no N_2O formation was found over a large temperature interval and a large range of NH_3/O_2 ratios (13, 22). On Pt and Ag polycrystals, however, large amounts of N_2O were produced at low temperatures. At higher temperatures NO, instead of N_2O, was produced. The possible N_2O formation pathways proposed in the literature are as follows (4, 15, 23, 34):

$$N + NO \rightarrow N_2O \qquad [17]$$

$$NO + NO \rightarrow N_2O + O \qquad [18]$$

$$HNO + HNO \rightarrow N_2O + H_2O \qquad [19]$$

$$HNO_3 + NH_3 \rightarrow NH_4NO_3 \rightarrow N_2O + 2H_2O. \qquad [20]$$

Reactions [19] and [20] involve the intermediate HNO and HNO_3 species that were not observed on the silver surface. Thus, these two reactions are unlikely to occur on silver catalysts. The difference between reactions [17] and [18] is that the dissociation of NO is required in order that reaction [18] can proceed. This can only happen at very low surface oxygen coverage. The chemisorption of nitric oxide at a Ag(111) surface has been reported to form N_2O at 80 K. However at 295 K this surface is unreactive to NO(g) under the same condition (37). Our experiments on silver powder also show that N_2O can be produced only on reduced silver at the initial stage of NO adsorption. When NO is introduced continuously to a reduced silver powder catalyst at temperatures from 50 to 400°C no N_2O is produced except for at the initial time. Hence reaction [17] is the most likely reaction candidate for the formation of N_2O. To give further evidence for this theory, the SCR reaction was also carried out on reduced silver powder. The results are shown in Figs. 12 and 13. It can be seen from Fig. 12 that the production of N_2O is not significant when NO reacts with NH_3 alone on the silver catalyst. In the presence of oxygen NO can react quickly with NH_3 to give rise to N_2O and N_2 (see Fig. 13). These experiments clearly indicate that N_2 and N_2O are not formed mainly from NO alone. NO cannot react directly with NH_3 on silver either. The role of O_2 is actually

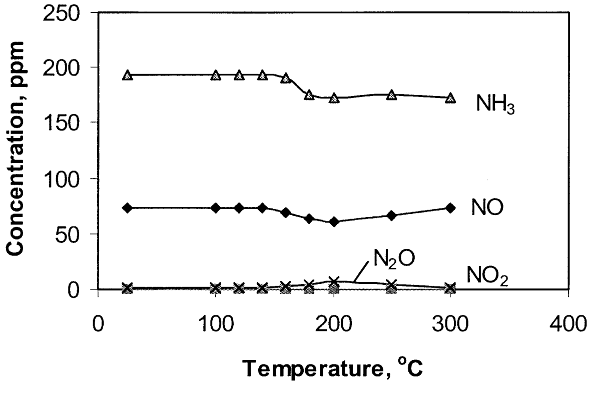

FIG. 12. NO + NH_3 SCR reaction on reduced silver powder. Reaction conditions: $NH_3 = 194$ ppm; NO = 74 ppm; catalyst weight = 0.1 g; NH_3/NO/He = 100 Nml/min.

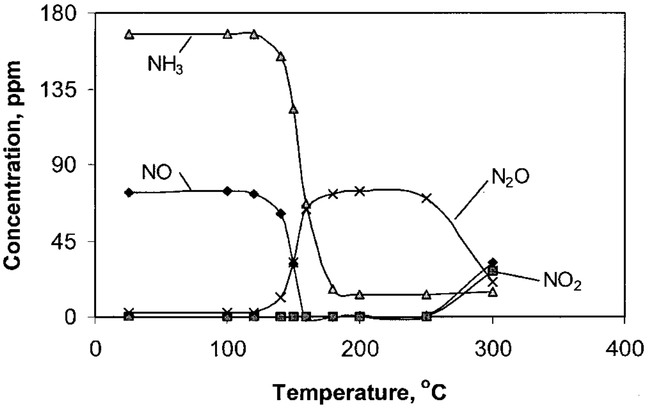

FIG. 13. $NH_3 + NO + O_2$ SCR reaction on reduced silver powder. Reaction conditions: $NH_3 = 168$ ppm; $NO = 74$ ppm; $O_2 = 10\%$; catalyst weight $= 0.1$ g; $NH_3/NO/O_2/He = 100$ Nml/min.

to produce adsorbed NH_x and N species that can then react readily with NO to produce N_2 and N_2O.

Apparently NO_2, NO_3^-, and N_2O_x species are produced by NO reacted with O or O_2:

$$NO + O \rightarrow NO_2 \qquad [21]$$

$$NO + 2O \rightarrow NO_3^- \qquad [22]$$

$$NO + NO_x \rightarrow N_2O_x. \qquad [23]$$

Thus the overall ammonia reaction pathway on silver powder in an oxygen-rich atmosphere can be described schematically as in Fig. 14. It can be seen clearly from this scheme that NO is the key intermediate. Even at room temperature the NO can be quickly produced. Since NO cannot desorb at low temperature, it blocks the active sites for oxygen dissociation. So the reaction can continue only when the adsorbed NO is removed. At moderate temperatures (below 300°C) the NO can only be removed either as N_2O or N_2 through surface reaction [17] and reaction [15], respectively. At even higher temperatures NO can directly desorb as one of the products. The rate-controlling step is thus the oxygen dissociation rate which is determined by the rate of NO removal. The selectivities to N_2 and to N_2O are also controlled by the relative rates of reactions [15] and [17]. Actually, the relative rates of these two reactions are controlled by the surface oxygen coverage. At high surface oxygen coverage the reaction from NH_x to NO and N is very fast so that the surface NH_x concentration decreases and the rate of reaction [15] decreases accordingly. The selectivity is thus mainly toward N_2O. On the contrary the reaction becomes more selective to nitrogen when the surface oxygen coverage decreases.

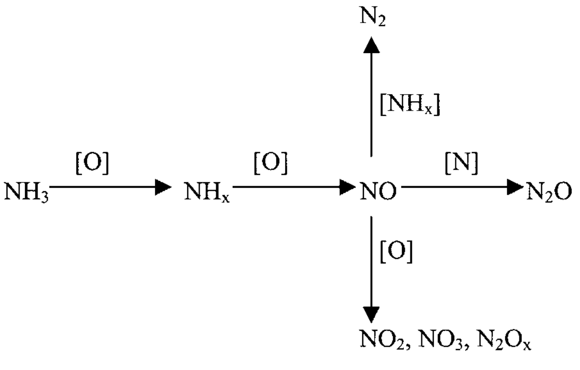

FIG. 14. Scheme illustrating the pathways of NH_3–O_2 reactions.

As the surface NO_2, NO_3, and N_2O_x species block some of the active sites for oxygen dissociation, they become inhibitors for ammonia oxidation. However the adsorption of these species on the silver surface decreases the oxygen coverage. So the selectivity to nitrogen increases with increasing amounts of these adsorbed species. The Raman spectra for ammonia oxidation clearly showed that atomic surface oxygen intensity decreased with increasing temperature from 50°C up to 300°C. This is due to the fact that the amount of adsorbed N_2O_x species increases with increasing temperature. At a temperature higher than 350°C N_2O_x decomposes and is removed from the surface so the oxygen coverage again increases. The steady-state tests for ammonia oxidation on silver powder at different temperatures (Fig. 1) also show that the nitrogen selectivity increases with increasing temperature up to 300°C. With further increase of temperature, the selectivity to nitrogen decreases due to the increasing rate of NO desorption. Ammonia pulse reactions again indicated the effect of adsorbed NO_x and N_2O_x species on the product selectivity. After the first ammonia pulse at 200°C some adsorbed NO_x and N_2O_x species were produced that partially blocked the surface and decreased the surface oxygen coverage. In subsequent ammonia pulse reactions the selectivity to nitrogen was improved due to the lower surface O/N ratio. At higher temperature (400°C) the desorption rate of NO became rapid so that the NO was formed instead of N_2O. Since little NO_x can be adsorbed on the silver surface at this temperature there is almost no selectivity difference among three consecutive ammonia pulses.

5. CONCLUSIONS

Silver is a very active catalyst for ammonia oxidation. At low temperatures (below 300°C) mainly N_2 and N_2O are produced. At higher temperatures NO instead of N_2O becomes one of the products. NO is an important reaction intermediate for this reaction. Even at room temperature the NO can be produced and adsorbed on the silver surface in the form of NO_x. Since NO cannot desorb at low temperature it blocks the active sites for oxygen dissociation. The dissociation of oxygen is thus believed to be the rate-controlling step for ammonia oxidation. The selectivity to N_2, N_2O, and NO is determined by surface oxygen coverage and temperature. Low surface oxygen coverage favors nitrogen formation. Adsorbed NO_x and N_2O_x species are actually inhibitors for ammonia oxidation but they also lower the surface oxygen coverage. Hence, the selectivity to nitrogen is improved by increasing the amount of these adsorbed species on silver surface.

Generally speaking, silver alone, like Pt, is not a good catalyst for selective ammonia oxidation to nitrogen because too much N_2O is produced. It follows from the above conclusions that blocking of the sites for oxygen dissociation is an effective way to improve the nitrogen selectivity, but also would result in a loss of catalyst activity.

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