and Lyke[5] of 0.68×10^{-9} s), together with the predicted D, gives a $D\tau_0 = 2.3 \times 10^{-14}$ cm^2, which also is compatible with our value of $(D\tau_0)_{av} = 2.0 \times 10^{-14}$ cm^2.

Acknowledgment. This research was supported in part by the U.S. Department of Energy, Division of Chemical Sciences, Office of Basic Energy Sciences. We are also grateful to Professor C. L. Braun for comments generated by his careful reading of this manuscript and to Mr. D. B. Johnston for his technical assistance.

Reaction between NO_x and NH_3 on Iron Oxide–Titanium Oxide Catalyst

Akira Kato,* Shimpei Matsuda, Tomoichi Kamo, Fumito Nakajima, Hiroshi Kuroda, and Tsuneo Narita

Hitachi Research Laboratory, Hitachi Ltd., Kuji-cho, Hitachi-shi, Ibaraki-ken, 319-12 Japan, and Kure Works, Babcock-Hitachi K.K., Takara-machi, Kure-shi, Hiroshima-ken, 737 Japan *(Received: October 14, 1980; In Final Form: August 24, 1981)*

The reduction of NO_x (NO_2 alone or mixture of NO and NO_2) with NH_3 on iron oxide–titanium oxide catalyst was studied using a flow reactor. The reaction between NO_2 and NH_3 proceeds at 3:4 mole ratio in the presence or absence of oxygen. When the reaction gas mixtures contain equal amounts of NO and NO_2, the reaction consuming equimolal NO and NO_2 proceeds preferentially at a NH_3/NO_x ratio of unity. The rate of the reaction is faster than either the NO–NH_3 or NO_2–NH_3 reaction. The overall reactions between NO_x (NO_2, NO + NO_2) and NH_3 are given as $6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O$ and $NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O$. Reaction mechanisms are proposed to explain the experimental results.

Introduction

It is of practical importance to remove nitrogen oxides (NO_x = NO + NO_2) in a flue gas from the view point of air pollution control. It has been known that NO_x are selectively reduced by ammonia in the presence of large excess of oxygen.[1] The selective catalytic reduction of NO_x by NH_3 has been commercially used in recent years. A catalyst used in a commercial plant must possess high activity and selectivity, since the volume of flue gas to be treated is extraordinarily large. In addition, the catalyst must be resistant to the SO_x poisoning, since sulfur dioxide (SO_2) and sulfur trioxide (SO_3) are usually contained in a fossile fuel fired combustion flue gas. A series of catalysts consisting mainly of titania have been developed as commercial catalysts because they show a high activity, selectivity, and resistance to the SO_x poisoning over a wide range of temperatures, 200–450 °C.[2,3] Mechanisms of the NO–NH_3 reaction have been proposed for various catalysts, such as precious metals,[4,5] metal oxides,[6–10] and zeolites.[11–14]

In a previous paper[15] we have shown that the reaction ratio of NO with NH_3 is unity on iron oxide–titanium oxide catalyst and the reaction is completely inhibitied by the absence of oxygen. Based on the experimental results, a reaction mechanism is proposed, the overall reaction given by eq 1.

$$NO + NH_3 + {}^1/_4O_2 \rightarrow N_2 + {}^3/_2H_2O \quad (1)$$

Previous investigations of the NO_x–NH_3 reaction have dealt almost exclusively with the NO–NH_3 system. Little attention has been paid to the NO_2–NH_3 reaction and the NO–NO_2–NH_3 reaction. However, the reactions can be applied to the treatment of a flue gas from a nitric acid plant and pickling process. The reactions are of considerable interest and importance for a collective understanding of the reaction between NO_x and NH_3.

The purpose of the present investigation is to clarify the reaction between NO_x (NO + NO_2) and NH_3 on iron oxide–titanium oxide catalyst.

Experimental Section

Catalyst. The iron oxide–titanium oxide catalyst which consisted of Fe and Ti at a 1:9 atomic ratio was prepared from iron(II) sulfate and metatitanic acid as described in the previous paper.[15]

Reaction. The reaction of NO_x with NH_3 was carried out in a conventional flow type apparatus. The apparatus and procedure were essentially the same as described earlier, special care being taken for a gas mixture containing NO_2.

When a test gas contained NO_2, both an inlet tubing (after mixing with NH_3) and an outlet tubing (before removing NH_3) were kept above 200 °C to minimize the N_2

(1) H. C. Andersen, W. J. Green, and D. R. Steele, *Ind. Eng. Chem.*, **53**, 199 (1961).
(2) S. Matsuda, M. Takeuchi, Y. Hishinuma, F. Nakajima, T. Narita, Y. Watanabe, and M. Imanari, *J. Air Pollut. Control Assoc.*, **28**, 350 (1978).
(3) F. Nakajima, Y. Hishinuma, T. Kumura, Y. Arikawa, and T. Narita, Symposium on Stack Gas Cleanup, Joint Meeting of ACS and CSJ, Honolulu, HI, 1979.
(4) K. Otto, M. Shelef, and J. T. Kummer, *J. Phys. Chem.*, **74**, 2690 (1970).
(5) K. Otto, M. Shelef, and J. T. Kummer, *J. Phys. Chem.*, **75**, 875 (1971).
(6) K. Otto and M. Shelef, *J. Phys. Chem.*, **76**, 37 (1972).
(7) H. Niiyama, A. Ebitani, E. Echigoya, *J. Catal.*, **48**, 1941 (1977).
(8) M. Takagi, T. Kawai, M. Soma, T. Onishi, and K. Tamaru, *J. Catal.*, **50**, 441 (1977).
(9) M. Inomata, A. Miyamoto, and Y. Murakami, *J. Catal.*, **62**, 140 (1980).
(10) S. Yoshida, A. Ueda, and K. Tarama, *Ind. Eng. Chem. Prod. Res. Dev.*, **18**, 283 (1979).
(11) K. A. Windhorst and J. H. Lunsford, *J. Am. Chem. Soc.*, **97**, 1407 (1975).
(12) T. Seiyama, T. Arakawa, T. Matsuda, Y. Takita, and N. Yamazoe, *J. Catal.*, **48**, 1 (1977).
(13) M. Mizumoto, N. Yamazoe, and T. Seiyama, *J. Catal.*, **55**, 119 (1978).
(14) T. Seiyama, M. Mizumoto, T. Ishihara, and N. Yamazoe, *Ind. Eng. Chem. Prod. Res. Dev.*, **18**, 279 (1971).
(15) A. Kato, S. Matsuda, F. Nakajima, M. Imanari, and Y. Watanabe, *J. Phys. Chem.*, **85**, 1710 (1981).

0022-3654/81/2085-4099$01.25/0

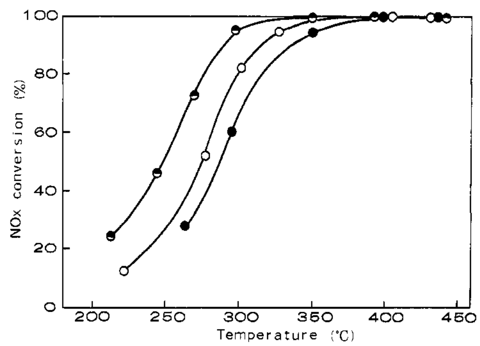

Figure 1. Catalytic activity of iron oxide-titanium oxide catalyst on NO_x-NH_3 reaction. Gas composition: (O), 200 ppm NO, 240 ppm NH_3; (●) 200 ppm NO_2, 320 ppm NH_3; (◐) 100 ppm NO, 100 ppm NO_2, 240 ppm NH_3, and 3% O_2, 10% H_2O, the remainder N_2. Space velocity: 60 000 h^{-1}.

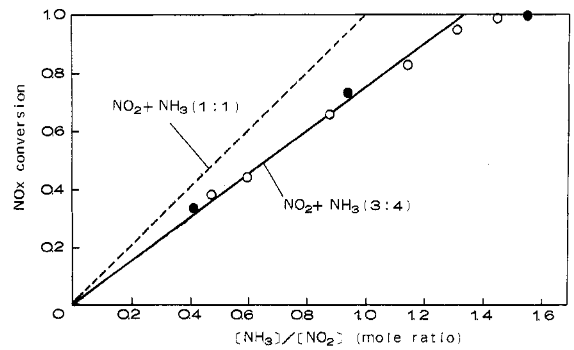

Figure 2. NO_x conversion as a function of $(NH_3)/(NO_2)$ ratio. Effect of temperature. Reaction temperature: (O) 350 °C; (●) 400 °C. Gas composition: 300 ppm NO_2, 0-515 ppm NH_3, 3% O_2, the remainder N_2. Space velocity: 30 000 h^{-1}.

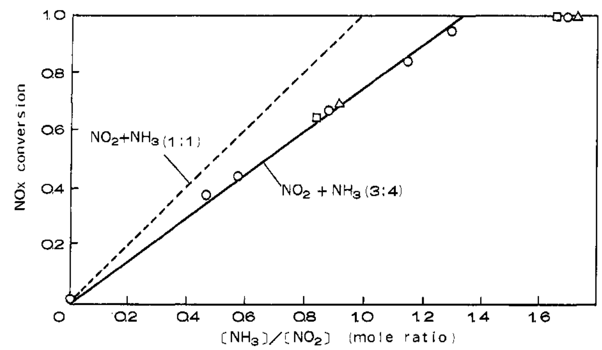

Figure 3. NO_x conversion as a function of $(NH_3)/(NO_2)$ ratio. Effect of O_2 concentration. Reaction temperature: 350 °C. Gas composition: 300 ppm NO_2, 0-515 ppm NH_3, (△) 0% O_2; (O) 3% O_2; (□) 10% O_2, the remainder N_2. Space velocity: 30 000 h^{-1}.

formation by homogeneous reaction. It is known[16] that NO_2 reacts homogeneously with NH_3 forming N_2 and NH_4NO_3 in the range of 150 to 200 °C. The test gas was passed through concentrated H_3PO_4 solution to remove NH_3 and H_2O prior to the NO_x analysis. Then the gas was led to a chemiluminescence analyzer to measure the concentration of NO and NO_2. The analyzer (Horiba Ltd., Model MEXA-C1) works on the basis of the chemiluminescence between NO and O_3. When a test gas contained NO_2, it was passed through the NO_2 converter, which was attached to the analyzer, where NO_2 was decomposed to NO. The formation of N_2O was measured by gas chromatography using Porapak Q as a column packing after condensation of N_2O in a liquid N_2 trap at −195 °C. For the measurement of the concentration of NH_3, the gas mixture was passed through 0.5 wt % boric acid solution. The concentration of NH_3 in the solution was determined by the Nessler method.

The NO_x conversion is calculated on the basis of the concentration of NO_x ($NO + NO_2$) and defined as follows.

$$NO_x \text{ conversion} = \left(1 - \frac{\text{outlet } (NO + NO_2)}{\text{inlet } (NO + NO_2)}\right) \times 100\ (\%)$$

N_2O was not counted in the calculation of NO_x conversion, since the formation of N_2O was very small in all experiments.

Results and Discussion

Catalytic Activity on NO_x-NH_3 Reaction. Catalytic activity of the iron oxide-titanium oxide catalyst on the NO_x-NH_3 reaction was first examined. In Figure 1 the NO_x conversion vs. temperature for gas mixtures containing various NO_x compositions, i.e., NO alone, equimolal mixture of NO and NO_2, and NO_2 alone. It is seen that the catalyst possesses high activity and selectivity over a temperature range of 300-440 °C, considering a high space velocity (60 000 h^{-1}) and low NH_3/NO_x mole ratios (1.2 or 1.6) employed in the present experiment. The rate of NO_x reduction is found to be depend on the inlet compositions of NO_x. The reaction rate decreases in the order of NO-NO_2-NH_3 > NO-NH_3 > NO_2-NH_3.

Reaction Ratio of NO_2 with NH_3. To clarify the overall reaction equation of NO_2 with NH_3, it is of importance to determine the reaction ratio of NO_2 with NH_3. Therefore the NO_x conversion as a function of the NH_3/NO_2 ratio was studied under a variety of conditions. Gas mixtures containing 300 ppm NO_2, 0-515 ppm NH_3, 3% O_2, and the remainder N_2 were used in the experiments. The gas was passed through the catalyst bed at a space velocity of 30 000 h^{-1} (NTP). Under these conditions the reaction proceeds completely in such a way that either of the two reactants, NO_2 or NH_3, is consumed entirely. Figure 2 shows the NO_x conversion as a function of the NH_3/NO_2 ratio at 350 and 400 °C. It is clearly seen that the NO_2 conversion is $^3/_4$ of the NH_3/NO_2 ratio at 350 and 400 °C. Ammonia was not observed in the gas mixture leaving the catalyst bed at the NH_3/NO_2 ratio less than $^4/_3$. The formation of small amounts of N_2O, 5-10 ppm, was observed in the experiments. The N_2O formation did not substantially affect the reaction ratio of NO_2 with NH_3, because the amount was so small compared with that of the reacted NO_2.

The formation of NO was observed in the experiments. In the exit gas approximately 10% of the total NO_x was found to be present as NO at the inlet NH_3/NO_2 ratio 0.46. As the NH_3/NO_2 ratio was increased, the formation of NO was decreased. As is seen in Figure 2, the reaction of NO_2 with NH_3 proceeds at a 3:4 mole ratio. It seemed that the deviation from the 3:4 mole ratio caused by the formation of NO and N_2O was very small.

An effect of O_2 on the NO_2-NH_3 reaction was studied using a test gas containing 300 ppm NO_2, 0-515 ppm NH_3 and 0, 3, or 10% O_2, the result being shown in Figure 3.

It was found that the NO_x conversion was not affected by the absence of O_2. The NO_x conversion was $^3/_4$ of the NH_3/NO_2 ratio over an O_2 concentration up to 10%. It is clearly seen that the reaction of NO_2 with NH_3 proceeds at 3 to 4 mole ratio in the presence or absence of oxygen. It was also observed the NO_x conversion in the NO_2-NH_3 reaction remained constant for more than 10 h in the presence or absence of O_2 over the NH_3/NO_2 region of the

(16) F. Falk and R. N. Pease, *Ind. Eng. Chem.*, 76, 4746 (1954).

TABLE I: Results in the Reaction of $NO-NO_2-NH_3$

expt no.	temp, °C	inlet gas, ppm NO	inlet gas, ppm NO_2	inlet gas, ppm NH_3	NH_3/NO_x	outlet gas, ppm NO	outlet gas, ppm NO_2	NO_x conv, %
A-1	359	453	150	600	0.995	1	1	99.7
A-2	359	453	150	509	0.84	87	3	85.1
A-3	359	453	150	250	0.41	320	25	42.8
B-1	345	300	300	0	0.0	292	300	1.4
B-2	345	300	300	116	0.193	235	237	21.4
B-3	345	300	300	260	0.434	172	170	43.0
B-4	348	300	300	329	0.549	137	136	54.5
B-5	348	300	300	448	0.737	82	66	75.3
B-6	348	300	300	560	0.90	28	23	91.5
C-1	355	151	459	0	0.00	147	456	1.1
C-2	355	151	459	125	0.209	90	390	21.3
C-3	355	151	459	217	0.356	48	335	37.2
C-4	355	151	459	305	0.501	12	289	50.7
C-5	355	151	446	357	0.598	5	246	58.0
C-6	355	151	446	437	0.731	1	180	69.7
C-7	355	151	446	525	0.879	1	117	80.2
C-8	355	151	446	634	1.06	<1	32	94.5
C-9	355	151	446	700	1.17	<1	4	99.2

present experiment. It has been reported by us and others that oxygen is involved in the $NO-NH_3$ reaction. Therefore, the NO_2-NH_3 reaction differs greatly from the $NO-NH_3$ reaction concerning the involvement of O_2.

Reaction Ratio of NO_x ($NO + NO_2$) with NH_3. In the NO and NO_2 coexisting system, the reactions are found to be rather complicated. Three gas mixtures containing different NO/NO_2 ratio were used: (1) NO (450 ppm) and NO_2 (150 ppm) ($NO > NO_2$); (2) NO (300 ppm) and NO_2 (300 ppm) ($NO = NO_2$); (3) NO (150 ppm) and NO_2 (450 ppm) ($NO_2 > NO$).

In Figure 4, the NO_x conversion as a function of the NH_3/NO_x ratio is shown. In the NO and NO_2 coexisting system, the reaction ratio of NH_3 to NO_x changes according to the NO/NO_2 ratio in the gas mixture. In case that the concentration of NO was equal to or larger than that of NO_2, the NO_x conversion was equal to the NH_3/NO_x ratio. In Table I, the compositions of the inlet NO_x and the outlet NO_x are summarized. From the analysis of the composition of the outlet NO_x, it was found that the reaction consuming equal amounts of NO and NO_2 proceeds preferentially (A1–A3, B1–B6).

In the gas mixture containing 450 ppm NO and 150 ppm NO_2, a decrease of the NO_x conversion was observed in experiments A-1 and A-2 when O_2 supply was stopped. On the other hand, the reaction proceeded normally for several hours with or without O_2 addition in experiment A-3.

In case that the concentration of NO_2 was larger than that of NO, total NO_x ($NO + NO_2$) reacted with NH_3 at 1 to 1 mole ratio until NO was consumed entirely (see Figure 4). Then the remaining NO_2 reacted with NH_3 at 3:4 mole ratio. Therefore, the line which shows the relation between the NO_x conversion and the NH_3/NO_x ratio bends at halfway as illustrated in Figure 4 (broken line).

In Table II the reaction ratio of NO_x with NH_3, the effect of O_2 on the reaction, and the ratio of reacted NO/NO_2 are summarized. In the NO system (case 1), the reaction

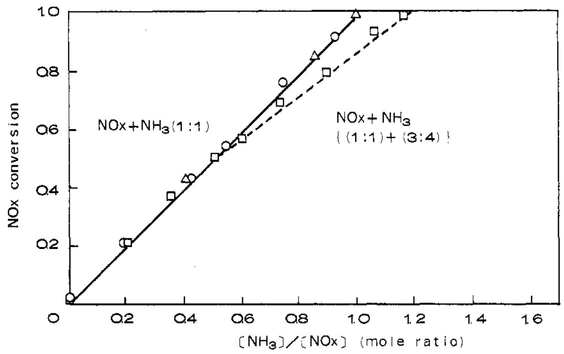

Figure 4. NO_x conversion as a function of $(NH_3)/(NO_x)$ ratio. Effect of $(NO)/(NO_2)$ ratio in $NO-NO_2-NH_3$ reaction. Reaction temperature: 350 °C. Gas composition: (△) 450 ppm NO, 150 ppm NO_2; (○) 300 ppm NO, 300 ppm NO_2; (□) 150 ppm NO, 450 ppm NO_2, 3% O_2, the remainder N_2. Space velocity: 30 000 h^{-1}.

ratio of NO with NH_3 is unity. The effect of O_2 is present, the reaction being completely inhibited by the absence of O_2.[2,15] In the NO_2 system (case 5), the reaction of NO_2 with NH_3 proceed at 3 to 4 mole ratio in the presence or absence of O_2. In the equimolal $NO-NO_2$ system (case 3), the overall reaction ratio NH_3/NO_x is unity, and the ratio of reacted NO/NO_2 is unity in the presence or absence of O_2. The rate of the reaction is faster than either $NO-NH_3$ or NO_2-NH_3 reaction. In the $NO > NO_2$ system (case 2), the reaction consuming equal amounts of NO and NO_2 proceeds preferentially and the remainder NO reacts with NH_3 as in case 1. The effect of O_2 is, therefore, present at the high NH_3/NO_x ratio. In the $NO_2 > NO$ system (case 4), the reaction consuming equal amounts of NO and NO_2 proceeds preferentially and the remainder NO_2 reacts with NH_3 as in case 5. The effect of O_2 is not present and the overall NH_3/NO_x ratio changes at the high NH_3/NO_x ratio.

Overall Reaction Equation. In the previous paper, we reported the reaction equation of NO with NH_3 in the presence of oxygen on iron oxide–titanium oxide catalyst. It has been shown that NO reacts with NH_3 at a 1:1 mole ratio over a wide range of temperature and O_2 concentration and the reaction is completely retarded by the absence of O_2. The overall reaction equation is shown by reaction 1.

$$NO + NH_3 + {}^1/_4O_2 \rightarrow N_2 + {}^3/_2H_2O \qquad (1)$$

In the NO_2 system, the reaction between NO_2 and NH_3 proceeds at 3:4 mole ratio and oxygen is not involved in the reaction. The reaction proceeds normally in the presence or absence of O_2. Therefore, overall reaction is given by eq 2.

$$3NO_2 + 4NH_3 \rightarrow {}^7/_2N_2 + 6H_2O \qquad (2)$$

In the equimolal NO and NO_2 coexisting system, the reaction consuming an equal amount of NO and NO_2 proceeds in the presence or absence of O_2, and the reaction ratio of NH_3/NO_x is unity. Therefore, overall reaction is given by

$$NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O \qquad (3)$$

TABLE II: Reaction Ratio of NO_x with NH_3

case	gas composition NO, ppm	gas composition NO_2, ppm	effect of O_2	$NO:NO_2$ (reacted)	$NO_x:NH_3$ (reacted)
1	300		present		1:1
2	450	150	$[NH_3] \leqslant 2[NO_2]$:none $[NH_3] > 2[NO_2]$:present	$[NH_3] \leqslant 2[NO_2]$:1:1	1:1
3	300	300	none	1:1	1:1
4	150	450	none	$[NH_3] \leqslant 2[NO]$:1:1	$[NH_3] \leqslant 2[NO]$:1:1
5		300	none		3:4

Kasaoka et al.[17] have studied the reaction between NO, NO_2, and equimolal mixtures of NO and NO_2 with NH_3 on V_2O_5–TiO_2, V_2O_5–Al_2O_3, $Fe_2(SO_4)_3$–TiO_2, $Fe_2(SO_4)_3$–Fe_2O_3, $CuSO_4$–TiO_2 and Cu(II) ion-exchanged Y-type zeolite catalysts. The overall equations obtained here are in good agreement with those reported by Kasaoka.

Reaction Mechanism. NO–NH_3–O_2 System. It has been reported in our previous papers that NO reacts with NH_3 at a 1:1 mole ratio in the presence of O_2 and the reaction is completely inhibited by the absence of O_2 on iron oxide–titanium oxide catalyst. The following reaction mechanism for NO with NH_3 in the presence of excess O_2 has been presented.

$$NH_3(ads) + NO(ads) \rightarrow N_2 + H_2O + H(ads) \quad (4)$$

$$2H(ads) + O \rightarrow H_2O + \square \quad (5)$$

$$O_2 + 2\square \rightarrow 2O \quad (6)$$

O = adsorbed oxygen or lattice oxygen; $\square$ = oxygen adsorption site or lattice site; (ads) = adsorbed state.

The reaction (4) + $^1/_2$(5) + $^1/_4$(6) gives reaction 1.

$$NO + NH_3 + {}^1/_4O_2 \rightarrow N_2 + {}^3/_2H_2O \quad (1)$$

NO–NO_2 Equimolal System. It is important to take into consideration the following experimental observation. (1) The reaction consuming equal amounts of NO and NO_2 proceeds preferentially. (2) The reaction ratio of NO_x with NH_3 is unity. (3) Oxygen is not involved in the reaction.

We examined the oxidation of NO by O_2 in the temperature range of 300–450 °C on the iron oxide–titanium oxide catalyst. The reaction gas mixture containing 200 ppm NO and 3% O_2 was used in the experiment. It was found that the conversion of NO to NO_2 was less than 1%. Therefore it is unlikely that NO reacts with NH_3 after being oxidized to NO_2. The following reaction mechanism for NO–NO_2 equimolal system is proposed.

$$NO(ads) + NH_3(ads) \rightarrow N_2 + H_2O + H(ads) \quad (4)$$

$$NO_2(ads) + 2H(ads) \rightarrow NO(ads) + H_2O \quad (7)$$

The reaction (4) × 2 + (7) gives reaction 3. NO_2(ads) reacts with H(ads) preferentially in the presence of oxygen. Reaction 7 must be much faster than reaction 5. The overall reaction 3 proceeds faster than reaction 1.

NO_2–NH_3 System. It is important to take into consideration the following experimental observation. (1) NO_2 reacts with NH_3 at 3:4 mole ratio. (2) The principal product containing nitrogen is N_2. (3) Oxygen is not involved in the reaction. (4) NH_3 reacts with NO_2 preferentially in the presence of oxygen. (5) NH_3 reacts with oxygen in the absence of NO_2.

We examined the decomposition of NO_2 in the temperature range of 300–400 °C on the iron oxide–titanium oxide catalyst. The reaction gas mixture containing 200 ppm NO_2 and 3% O_2 was used in the experiment. It was found that the formation of NO was less than 0.5% of the inlet NO_2. Considering the above result, extraction of oxygen species from NO_2 should be brought by NH_3 at first. Kasaoka et al.[17,18] have studied NO_2–NH_3 reaction and NO–NO_2–NH_3 reaction on various metal oxide catalysts supported on TiO_2 and suggested that the reduction of NO_2 with NH_3 to NO was important at the beginning of the reduction. It seems that the NO_2–NH_3 reaction is a complex reaction proceeding by several routes. It is very useful to investigate the proposed reaction mechanisms of NH_3–O_2, since the NO_2–NH_3 reaction may be considered to be an oxidation of NH_3 with NO_2.

Bodenstein[19] studied the oxidation of NH_3 on platinum wire. The NH_3 oxidation mechanism proposed by Bodenstein which appears to be most acceptable is as follows.[20]

$$NH_3 + O = NH_3O\ (NH_2OH) \quad (8)$$

$$NH_3O + O_2 = HNO_2 + H_2O \xrightarrow{+O_2} HNO_3 \quad (9)$$

This mechanism is known as the hydroxylamine mechanism. Bodenstein observed the formation of NH_2OH and HNO_2 in the reaction. He concluded that hydroxylamine, NH_3O, is a primary product of the surface reaction. Krauss[21] studied the oxidation of NH_3 on the oxides of Mn, Ni, Co, Cu, and Fe. He concluded that the adsorbed oxygen or lattice oxygen reacts with NH_3 or NH_3O

$$NH_3 + O \rightarrow NH_3O \quad (10)$$

or

$$NH_3O + O \rightarrow HNO + H_2O \quad (11)$$

which in turn reacts as follows with HNO

$$NH_3O + HNO \rightarrow N_2 + 2H_2O \quad (12)$$

$$HNO + HNO \rightarrow N_2O + H_2O \quad (13)$$

From the above information, it is most likely that NO_2 reacts with NH_3 forming NH_3O species as a first step of surface reaction in the NO_2–NH_3 reaction.

$$NO_2(ads) + NH_3(ads) \rightarrow NO(ads) + NH_3O(ads) \quad (14)$$

It is probable that NH_3O species react with NO_2 successively. We did not observe NH_3O species nor other intermediates. Therefore we cannot discuss the reaction mechanism in more detail at present.

The NO_2–NH_3 reaction must be a complex reaction proceeding by many elementary steps as the overall reaction 2 has a complex stoichiometry.

$$6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O \quad (2)$$

Considerable additional work is required before a detailed discussion on the NO_2–NH_3 reaction mechanism can be presented.

Conclusion

The reaction between NO_2 and NH_3 proceeds at 3:4 mole ratio in the presence or absence of oxygen on iron oxide–titanium oxide catalyst. When the reaction gas mixtures contain equal amounts of NO and NO_2, the reaction consuming equimolal NO and NO_2 proceeds preferentially at a NH_3/NO_x ratio of unity. The reaction rate of the reaction is faster than either the NO–NH_3 or NO_2–NH_3 reaction.

(17) S. Kasaoka, E. Sasaoka, T. Yamanaka, and M. Ono, *Nippon Kagaku Kaishi*, 874 (1978).

(18) S. Kasaoka, T. Yamanaka, and E. Sasaoka, *Nenryo Kyokaishi*, **56**, 834 (1977).

(19) M. Bodenstein and G. Buttner, *Angew. Chem.*, **47**, 364 (1934).

(20) J. K. Dixon and J. E. Longfield, in "Catalysis", P. H. Emmett, Ed., Vol. 7, Reinhold, New York, 1960, Chapter 4, p 281.

(21) W. Krauss, *Z. Elektrochem.*, **53**, 320 (1949); **54**, 264 (1950).