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Bifunctional Oxidation of Ammonia with Metal Oxide–Pt/Al_2O_3 Mechanical Mixtures

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Selectivity to N_2 in the reaction of NH_3 with metal oxides has been markedly increased by the addition of Pt/Al_2O_3 to the metal oxides, whereas the activity of the metal oxides has not been changed. The metal oxides on their own have oxidized NH_3 to NO, NO_2, and N_2O as well as N_2, and furthermore, the selectivities in the reaction with metal oxides have depended markedly on the reaction temperature and inlet concentration of NH_3 in the pulse. In the oxidation of NH_3 with metal oxide–Pt/Al_2O_3 mechanical mixtures, N_2 has been selectively produced irrespective of the reaction temperature and the inlet concentration of NH_3 in the pulse. The activity of the mixtures has been shown, on the other hand, to be the same as that of the metal oxides. All of the experimental data have been explained in terms of the following scheme: In the oxidation of NH_3 with metal oxide–Pt/Al_2O_3 mixtures, NH_3 is at first oxidized by metal oxides to form NO_x(NO, NO_2, and N_2O) and N_2, then the NO_x components is transfered through the gas phase from the metal oxides to Pt particles on Al_2O_3, and finally the NO_x components react with NH_3 on Pt particles to form N_2 selectively.

Attention is focused on reactions on multi-component solid catalysts, because of their interesting catalyses which cannot be obtained for reactions on individual components. Synergistic effects appearing in their catalyses provide an important subject of investigation in heterogeneous catalytic chemistry. In other words, it is highly desirable to find new types of synergistic effects for various kinds of multi-components' catalysts and various types of reactions, and to reveal their mechanisms. Much research has been done on the synergistic effects involved in the multi-components' metal oxide catalysts, multi-components' precious metal catalysts (or alloy catalysts), and supported precious metal–metal oxide mixed catalysts. Furthermore, it has been suggested that these synergistic effects are brought about by various mechanisms including (i) the dispersion of the primary component, (ii) the control of the oxidation state or the electronic state of the primary component, (iii) the formation of a new active site by the chemical interaction of individual components, and (iv) the cooperation of different kinds of active sites by the transfer of intermediate species or reactive species from one component to another through the gas phase, surface, or bulk.[1)] However, the synergistic effects appearing in the reactions on precious metal–metal oxide mixed catalysts have been not well investigated except the bifunctional catalyses involved in the reactions of hydrocarbons on Pt/Al_2O_3,[2)] Pt/SiO_2–Al_2O_3,[3)] and Pt–WO_3[4)] catalysts, and the oxidation of H_2 with precious metal–metal oxide mixtures.[5)] The precious metal–metal oxide catalysts have received increasing attention as catalysts for the automotive exhaust gas control,[6–11)] selective oxidations of hydrocarbons,[12,13)] and steam reforming reactions.[14,15)]

In the present study, the synergistic effect in the oxidation of NH_3 with metal oxide–Pt/Al_2O_3 mixed catalysts was investigated using the pulse reaction technique. The oxidation of NH_3 was used as a test reaction for the following reasons: (i) The selective oxidation of NH_3 to N_2 is highly desirable from the environmental point of view. (ii) Since the mechanism of the oxidation of NH_3 is markedly different from that of hydrocarbons or H_2,[16)] the metal oxide–Pt/Al_2O_3 is expected to show interesting synergistic effects which are significantly different from those in the oxidations of hydrocarbons or H_2. The enhanced activity of metal oxide caused by the addition of precious metal is considered to be brought about by the "hydrogen spillover" for the oxidation of H_2,[5)] and by the migration of oxygen through the oxide lattice to react with hydrocarbon or hydrocarbon residues adsorbed at sites on or near precious metal additives for the oxidation of hydrocarbons.[17)] Metal oxide–Pt/Al_2O_3 mixed catalysts were used for the following reasons: (i) Pt is one of the least active metals for the decomposition of NH_3. This would make it possible to propose a detailed mechanism of the synergistic effect in the oxidation of NH_3. Although a mixture of a metal oxide and a precious metal such as Ru or Rh—highly active for the decomposition of NH_3[18)]—may cause an interesting synergistic effect, this system would be too complex, as a first step of investigation, to reveal a detailed mechanism of the synergistic effect. (ii) For the metal oxide–Pt/Al_2O_3 mechanical mixtures, most of the Pt particles can be considered to be separated from the metal oxides by Al_2O_3. Therefore, the migration of oxygen from the metal oxide to Pt particles on Al_2O_3 is not expected to proceed rapidly. The hydrogen spillover from Pt to the metal oxide, on the other hand, can proceed readily in the mixtures.[5)] Pulse reaction technique was used for the following reasons: (i) It is considered that this technique is effective for the investigation of the behaviour of reactions on multi-components' catalysts. (ii) Since catalytic oxidations usually proceed by the redox mechanism, the stoichiometric oxidation of the reactant with the preoxidized catalyst often gives important information about their mechanisms. The stoichiometric reaction—in this study, the oxidation of NH_3 with the metal oxide–Pt/Al_2O_3 mixed catalysts—can be more easily investigated using the pulse reaction technique than using the flow reaction technique.

Experimental

Catalysts and Reagents. The method of preparation of metal oxides has been described previously.[16)] Pt/Al_2O_3

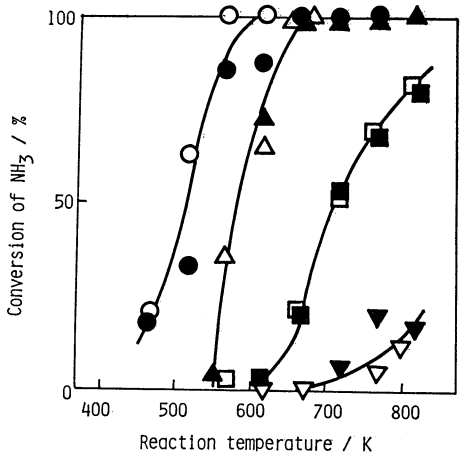

Fig. 1. Conversion of NH_3 in the oxidation of NH_3 with metal oxide–Pt/Al_2O_3 mixtures and with metal oxides.
Pluse size: 18.2 cm^3; concentration of NH_3 in pulse: 2.65%. Carrier gas (He) flow rate: 86 cm^3 min^{-1}.
●: MnO_2–Pt/Al_2O_3, ○: MnO_2, ▲: V_2O_5–Pt/Al_2O_3, △: V_2O_5, ■: Co_3O_4–Pt/Al_2O_3, □: Co_3O_4, ▼: Fe_2O_3–Pt/Al_2O_3, ▽: Fe_2O_3.

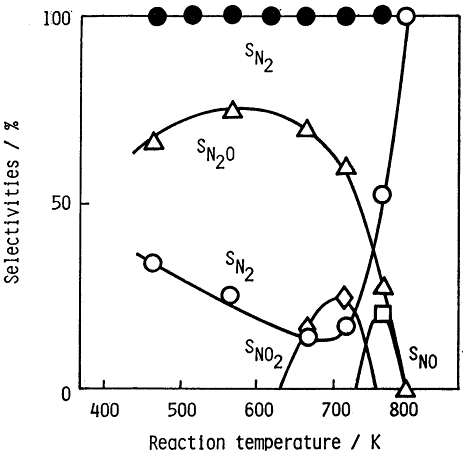

Fig. 2. Selectivities in the oxidation of NH_3 with MnO_2 and with MnO_2–Pt/Al_2O_3 mixture.
Pulse size: 18.2 cm^3; concentration of NH_3 in pulse: 2.65%. Carrier gas (He) flow rate: 86 cm^3 min^{-1}.
○, ●: Selectivity to N_2, △: selectivity to N_2O, □: selectivity to NO, ◇: selectivity to NO_2.
Open symbols: MnO_2, closed symbol: MnO_2–Pt/Al_2O_3 mixture.

(Pt loading of 0.5 wt%) was purchased from Nippon Engelhard. Unless otherwise specified, a metal oxide–Pt/Al_2O_3 mechanical mixture was prepared by mixing a powder of both components in an agate mortar for 20 min without water (this mixture is hereafter referred to as *Mixing* if it is necessary to discriminate it from other mixtures with different states of mixing). The weights of samples were 0.1 g for a metal oxide and 0.2 g (0.1 g of a metal oxide and 0.1 g of Pt/Al_2O_3) for a metal oxide–Pt/Al_2O_3 mixture. The weight of metal oxide (0.1 g) was common for both samples. The metal oxides and the mixtures were then pressed and granulated to be used as samples. The size of the sample granules ranged from 0.3 mm to 0.6 mm. Commercial ammonia (99.9% purity) and hydrogen (99.99% purity) were used as reactants without further purification.

Apparatus and Procedures. Experiments were conducted using a pulse apparatus. The reactant and product components were analyzed by gas chromatography with thermal conductivity detectors at room temperature. Columns used were tetraethylenepentamine on Difron for NH_3, silica gel for N_2O, and Molecular Sieve type 13X for H_2, N_2, and NO and they were connected in the intermediate cell system.[19] The confirmation of NO_2 as a product was made with the phenol disulfonic acid method. Helium or argon as carrier gas was purified with titanium metal sponge heated at 1023 K. Pulses of ammonia at various concentrations were supplied to the reactor by a 6-way valve.

Results and Discussion

Activity of Metal Oxide–Pt/Al_2O_3 Mixtures for the Oxidation of Ammonia. The Pt/Al_2O_3 catalyst was inactive for the decomposition of NH_3 under the experimental condition in the present work. On the other hand, the metal oxides have been shown to be active for the reaction with NH_3.[20] The conversion of NH_3 (X_{NH_3}) in the oxidation of NH_3 with various metal oxides is shown in Fig. 1 together with that in the reaction with the metal oxide–Pt/Al_2O_3 mixtures. It should be noted in Fig. 1 that the conversion of NH_3 in the oxidation of NH_3 with a metal oxide–Pt/Al_2O_3 mixture is almost the same as that with the metal oxide, indicating that no synergistic effect exists in the activity of the mixtures for the oxidation of NH_3.

Selectivity in the Oxidation of Ammonia with Metal Oxide–Pt/Al_2O_3 Mixtures. Oxidation of NH_3 with the metal oxides forms various products, such as N_2, N_2O, NO, and NO_2, depending on the reaction temperature and concentration of NH_3 in the pulse.[20] The selectivities to these products in the oxidation of NH_3 with the metal oxide–Pt/Al_2O_3 mixtures and the metal oxides are shown in Figs. 2 and 3. S_{NO}, S_{NO_2}, S_{N_2O}, and S_{N_2} represent the selectivities to NO, NO_2, N_2O, and N_2, respectively. Figure 2 shows the selectivities for MnO_2 and MnO_2–Pt/Al_2O_3 mixture at various temperatures. In the oxidation of NH_3 with MnO_2, N_2, N_2O, NO, and NO_2 were all produced, although the selectivities to individual products varied markedly with reaction temperature. On the other hand, in the oxidation of NH_3 with MnO_2–Pt/Al_2O_3 mixture, only N_2 was obtained as a product irrespective of the reaction temperature indicated in Fig. 2. Similarly, N_2 was selectively produced in the oxidation of NH_3 with V_2O_5–Pt/Al_2O_3 and Co_3O_4–Pt/Al_2O_3 mixtures irrespective of the reaction temperature. In the oxidation of NH_3 with V_2O_5 or Co_3O_4 alone, N_2, N_2O, and NO were produced and the selectivities to these products varied with reaction temperature. The most remarkable feature of the synergistic effect on the oxidation of NH_3 with the metal oxide–Pt/Al_2O_3 mixtures can be seen in the selectivities at various concentrations of NH_3 in the pulse. As shown in Fig. 3, in the oxidation of NH_3 with Co_3O_4 at 793 K, the conversion of NH_3 (X_{NH_3}) was 100% and all of NO, N_2O, and N_2 were formed irrespective of the inlet concentration of NH_3. Also, as the concentration of NH_3 in the pulse decreased, the selectivity

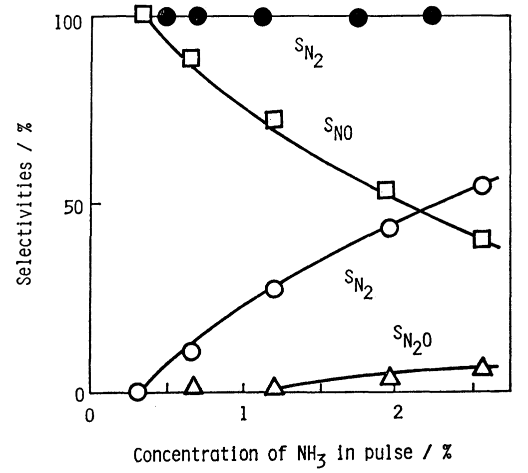

Fig. 3. Selectivities in the oxidation of NH_3 by Co_3O_4 and Co_3O_4–Pt/Al_2O_3 mixture with various concentrations of NH_3 in pluse.
Reaction temperature: 793 K; pulse size: 7.4 cm^3. Carrier gas (He) flow rate: 116 cm^3 min^{-1}.
○, ●: Selectivity to N_2, △: selectivity to N_2O, □: selectivity to NO.
Open symbols: Co_3O_4; closed symbol: Co_3O_4–Pt/Al_2O_3 mixture.

to NO (S_{NO}) increased to 100%, whereas, the selectivities to N_2O (S_{N_2O}) and N_2 (S_{N_2}) decreased to 0%. This means that when the inlet concentration of NH_3 is low, NH_3 is oxidized almost selectively to NO by Co_3O_4. On the other hand, in the oxidation of NH_3 with Co_3O_4–Pt/Al_2O_3 mixture, the selectivity of the reaction was completely changed; N_2 was selectively formed even if the inlet concentration of NH_3 in the pulse was low. Similar phenomena were also observed for the MnO_2–Pt/Al_2O_3 and V_2O_5–Pt/Al_2O_3 mixtures. Thus, it can be said that the selectivity of the oxidation of NH_3 with the metal oxides was significantly changed by the mixing of Pt/Al_2O_3 with the metal oxides; N_2 was selectively produced irrespective of the concentration of NH_3 in pulse.

Oxidation of NH_3 by MnO_2–Pt/Al_2O_3 Mixtures under Various States of Mixing. Since, according to the previous studies,[4,21,22] the degree of mixing of a precious metal and a metal oxide can give a significant effect on the synergy between both components, it seems interesting to investigate the effect of the degree of mixing on the oxidation of NH_3 with the metal oxide–Pt/Al_2O_3 mixtures. The results for the mixtures of MnO_2 and Pt/Al_2O_3 are indicated in Fig. 4. In accordance with the data shown in Fig. 1, the conversion of NH_3 in the reactions with these mixtures was almost the same as that with MnO_2 for all kinds of mixtures. The mixing of MnO_2 and Pt/Al_2O_3 is considered to become closer as the number of state increases, *i.e.* from Mixture II to Mixture VI. As shown in Fig. 4, the selectivity of the reaction of NH_3 with the mixtures has varied significantly with the degree of mixing of both components. That is, both Mixtures V and VI have oxidized NH_3 selectively to N_2 at any of the temperatures indicated in Fig. 4. Mixture IV, which is coarser than Mixtures V and VI, also showed significant synergistic effect at 673 and 723 K. Mixtures II and III, the coarsest mixtures, exhibited little synergistic effect in the selectivity. It is worth noting in Fig. 4 that the incomplete mixing of Pt/Al_2O_3 particles (0.3—0.6 mm) with MnO_2 particles (0.3—0.6 mm), *i.e.* Mixture V (this is hereafter denoted as *Shaking*), was sufficient to oxidize NH_3 selectively to N_2, and furthermore very rough mixing, *e.g.* Mixture IV, exhibited a significant synergistic effect in the selectivity. Similar data to those shown in Fig. 4 were also obtained for V_2O_5–Pt/Al_2O_3 mixtures with various states of mixing (Table 1).

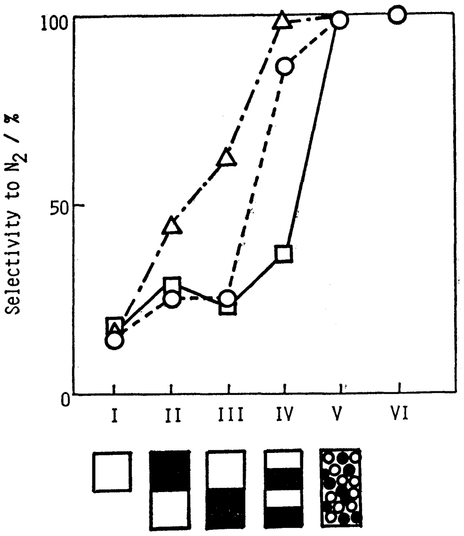

Fig. 4. Effect of the degree of mixing on the selectivity to N_2 in the oxidation of NH_3 with MnO_2–Pt/Al_2O_3.
Reaction temperature: □; 623 K, ○; 673 K, △; 723 K. Pulse size: 18.2 cm^3; concentration of NH_3 in pulse: 2.65%.
Carrier gas (He) flow rate: 86 cm^3 min^{-1}.
I: MnO_2, II: Pt/Al_2O_3 (upper layer)+MnO_2 (lower layer), III: MnO_2 (upper layer)+Pt/Al_2O_3 (lower layer), IV: MnO_2 (lst layer)+Pt/Al_2O_3 (2nd layer)+MnO_2 (3rd layer)+Pt/Al_2O_3 (4th layer), V: Roughly mixed sample of MnO_2 particles (0.3—0.6 mm) and Pt/Al_2O_3 particles (0.3—0.6 mm), VI: Throughly mixed sample in agate mortar.

Contribution of Hydrogen Spillover or Migration of Oxygen to the Synergistic Effect. The hydrogen spillover plays an essential role in the oxidation of H_2 with the metal oxide–precious metal mixtures.[5] It is considered that the hydrogen spillover plays no role in the synergistic effect in the selectivity of the oxidation of NH_3 with the metal oxide–Pt/Al_2O_3 mixtures on the basis of the following reasons: In Table 1, the results of the oxidations of H_2 and NH_3 are shown for various samples, such as V_2O_5, Pt/Al_2O_3, V_2O_5–Pt/Al_2O_3(*Shaking*), and V_2O_5–Pt/Al_2O_3(*Mixing*).[23] X_{H_2} is the conversion of H_2 in the oxidation of H_2 with the samples, and it can be used as a measure of the extent of the hydrogen spillover. The inlet concentration of H_2 was nearly 1.5 times that of NH_3, which corresponds to the ratio of the number of hydrogen atoms in NH_3 to that in H_2. As shown in Table 1, the oxidation of H_2 takes place readily for V_2O_5–Pt/Al_2O_3(*Mixing*), whereas it hardly proceeds for

TABLE 1. RESULTS OF THE NH_3 PULSE REACTION AND THE HYDROGEN SPILLOVER AT 823 K

Sample	The reaction of H_2 with sample[a,b]	The reaction of NH_3 with sample[c,d]			
	$X_{H_2}/\%$	$X_{NH_3}/\%$	$S_{N_2}/\%$	$S_{N_2O}/\%$	$S_{NO}/\%$
V_2O_5	3	100	83	2	15
Pt/Al_2O_3	0	4	100	0	0
V_2O_5–Pt/Al_2O_3 (*Shaking*)	6	100	100	0	0
V_2O_5–Pt/Al_2O_3 (*Mixing*)	100	100	100	0	0

Pulse size: 18.2 cm^3.

a) Concentration of H_2 in pulse: 3.7%. b) Carrier gas (Ar) flow rate: 86 $cm^3\ min^{-1}$. c) Concentration of NH_3 in pulse: 2.65%. d) Carrier gas (He) flow rate: 86 $cm^3\ min^{-1}$.

X_{H_2} and X_{NH_3} are the conversions of H_2 and NH_3, respectively. S_{N_2}, S_{N_2O}, and S_{NO} are the selectivities to N_2, N_2O, and NO, respectively.

V_2O_5–Pt/Al_2O_3(*Shaking*). This means that the hydrogen spillover cannot take place for V_2O_5–Pt/Al_2O_3 (*Shaking*) but it can take place readily for V_2O_5–Pt/Al_2O_3(*Mixing*). If the hydrogen spillover played a significant role in the oxidation of NH_3 with the metal oxide–Pt/Al_2O_3 mixtures, the selectivity of the reaction should differ considerably between V_2O_5–Pt/Al_2O_3(*Shaking*) and V_2O_5–Pt/Al_2O_3(*Mixing*). The selectivity to N_2 for V_2O_5–Pt/Al_2O_3(*Shaking*), however, was the same as that for V_2O_5–Pt/Al_2O_3(*Mixing*) and reached 100%; neither N_2O nor NO was produced for both V_2O_5–Pt/Al_2O_3(*Shaking*) and V_2O_5–Pt/Al_2O_3 (*Mixing*), in contrast to the products' distribution for V_2O_5. Furthermore, a considerable synergistic effect was observed for the Mixture IV in Fig. 4 in the selectivity of the oxidation of NH_3, while the hydrogen spillover did not take place for the mixture.

Moreover, it has been suggested that, in the oxidation of hydrocarbons with V_2O_5–precious metal systems, the migration of oxygen through the bulk oxide takes place so as to react with hydrocarbons at or near the metal additives; thereby the reaction is much enhanced by the addition of precious metals to V_2O_5.[17] Similarly, if the migration of oxygen through the bulk oxide to Pt particles takes place easily in the oxidation of NH_3 with the metal oxide–Pt/Al_2O_3 mixtures, the reaction has to be much enhanced by the addition of Pt/Al_2O_3 to the metal oxides because of the high activity of Pt/Al_2O_3 for the oxidation of NH_3 with oxygen. The migration of oxygen from the metal oxides to Pt particles on Al_2O_3, however, hardly occurs in the metal oxide–Pt/Al_2O_3 mixtures, since most of the Pt particles are expected to be separated from the particles of the metal oxide by Al_2O_3 in the metal oxide–Pt/Al_2O_3 mixtures. This inference is in accord with the experimental data; the activity of the metal oxide–Pt/Al_2O_3 mixtures for the oxidation of NH_3 is almost the same as that of the metal oxides as shown in Fig. 1. Consequently it is noted that neither the hydrogen spillover from Pt to metal oxides nor the migration of oxygen from metal oxides to Pt plays a significant role in the oxidation of NH_3 with metal oxide–Pt/Al_2O_3 mixtures.

Recently, Il'chenko[24] reported that the addition of $Pt/BaSO_4$ to metal oxides substantially increases the activity of the metal oxides for the oxidation of NH_3, while the selectivity in the reaction slightly changes. This is in marked contrast to the present results for the metal oxide–Pt/Al_2O_3 mixtures. Since Pt particles in the metal oxide–$Pt/BaSO_4$ mixtures are considered to be in contact with the grains of the metal oxide,[24] the difference may be brought about by the migration of adsorbed ammonia activated on Pt to the metal oxides or by the migration of oxygen of the metal oxides to Pt in the oxidation of NH_3 with the metal oxide–$Pt/BaSO_4$ mixtures. According to our preliminary experiments on the oxidation of NH_3 with V_2O_5–Pt black mixtures and V_2O_5–Pt mixtures supported on Al_2O_3, in fact, the activity of the metal oxide for the oxidation of NH_3 was significantly enhanced by the presence of Pt contacting with the metal oxide. The details of the results will be reported in a subsequent paper with additional data to reveal the mechanism.

It should be noted here that such mechanisms of the synergistic effects as (i) the dispersion of the primary component, (ii) the control of the oxidation state or the electronic state of the primary component, or (ii) the formation of a new active site by the chemical interaction of individual components are not important in the oxidation of NH_3 with the metal oxide–Pt/Al_2O_3 mixtures. This is because most of the Pt particles are not in contact with the metal oxides for the mixtures and a considerable synergistic effect appears even for the reaction with the V_2O_5–Pt/Al_2O_3 (*Shaking*) and the Mixture IV shown in Fig. 4.

Mechanism of the Synergistic Effect in the Oxidation of NH_3 with Metal Oxide–Pt/Al_2O_3 Mixtures. NO has been regarded to play an important role as an intermediate in the catalytic oxidation of NH_3.[18,25,26] In the preceding work,[20] it has been found that the oxidation of NH_3 with the metal oxides proceeds by a similar scheme as follows:

$$NH_3 \xrightarrow[\text{I}]{\text{lattice oxygen}} NO \xrightarrow[\text{II}]{NH_3} N_2,\ N_2O, \qquad (1)$$

where NH_3 is first oxidized by the lattice oxygen of a metal oxide to NO (Step I), which then reacts with NH_3 (the NO–NH_3 reaction) to form N_2 and N_2O (Step II). The NO–NH_3 reaction (Step II) takes place catalytically. According to this scheme, the activity in the oxidation of NH_3 with a metal oxide is determined by Step I, whereas the selectivity is limited by the relative rate of Step II to that of Step I.

This scheme is now applied to the oxidation of NH_3 with the metal oxide–Pt/Al_2O_3 mixtures in

Table 2. Relation between NO/NH_3 ratio and the selectivities of $NO-NH_3$ reaction on Pt/Al_2O_3 catalyst at 773 K

NO/NH_3 ratio	$X_{NO}/\%$	$X_{NH_3}/\%$	$S_{N_2}/\%$	$S_{N_2O}/\%$
0.49	100	61	100	0
0.53	98	77	97	3
0.73	97	85	96	4

Catalyst weight: 0.1 g. Concentration of NO in pulse: 2.0%. Pulse size: 18.2 cm^3. Carrier gas (He) flow rate: 86 $cm^3 min^{-1}$.
X_{NO} and X_{NH_3} are the conversions of NO and NH_3, respectively. S_{N_2} and S_{N_2O} are the selectivities to N_2 and N_2O, respectively.

order to interpret the synergistic effect involved in the oxidation of NH_3 with the metal oxide–Pt/Al_2O_3 mixtures. According to the scheme, the activity of the sample is limited by Step I. Since Pt/Al_2O_3 is not active for the decomposition of NH_3, the agreement of the conversion of NH_3 for a metal oxide–Pt/Al_2O_3 mixture with that for the metal oxide means that the activity of the metal oxide for the oxidation of NH_3 is not enhanced by its mixing with Pt/Al_2O_3. In accordance with the above-mentioned discussion either the hydrogen spillover or the migration of oxygen hardly takes place in the oxidation of NH_3 with the mixtures. The activity of the metal oxide–Pt/Al_2O_3 mixtures for the oxidation of NH_3 is therefore determined only by that of the metal oxides. On the other hand, the selectivity of the reaction is determined, according to this scheme, by the rate of the $NO-NH_3$ reaction (Step II), since the rate of Step I is not changed by the addition of Pt/Al_2O_3 to the metal oxides. The metal oxides employed in this study were all active for the $NO-NH_3$ reaction. However, the activity of the metal oxides is considered insufficient to form N_2 selectively, since considerable amounts of NO, N_2O, and NO_2 were produced in the oxidation of NH_3 with the metal oxides, especially when the inlet concentration of NH_3 was decreased as shown in Fig. 3. As it is well known, Pt/Al_2O_3 catalyst is highly active for the $NO-NH_3$ reaction,[27,28] indicating that the activity of the metal oxide–Pt/Al_2O_3 mixtures for the $NO-NH_3$ reaction is much higher than that of the metal oxides. Furthermore, as shown in Table 2, the selectivity to N_2 in the $NO-NH_3$ reaction on Pt/Al_2O_3 catalyst increased as the ratio of the concentration of NO to that of NH_3 decreased, and attained 100% when the NO/NH_3 ratio was smaller than 0.5. Thus, if it can be assumed that the NO/NH_3 ratio is small enough under the condition of the oxidation of NH_3 with metal oxide–Pt/Al_2O_3 mixtures, the high selectivity to N_2 can be explained in terms of the scheme of Reaction 1. This assumption seems to be valid, since the activity of Pt/Al_2O_3 catalyst for the $NO-NH_3$ reaction has been shown to be very high and, therefore, the concentration of NO can be considered to be kept at a low level under the reaction condition.

Since most of the Pt particles in the mixtures are separated from the metal oxides by Al_2O_3, the NO produced by the oxidation of NH_3 should transfer from the metal oxides to Pt particles in order to react with NH_3 on Pt to form N_2 selectively. The migration of NO on the surface of Al_2O_3, however, does not seem to take place, since the migration of either oxygen or hydrogen cannot occur in the oxidations of NH_3 and H_2 with V_2O_5–Pt/Al_2O_3(*Shaking*). Consequently the migration of adsorbed NO species, which is heavier than hydrogen or oxygen, cannot be expected. Therefore, NO is considered to transfer from the metal oxides to Pt through the gas phase.

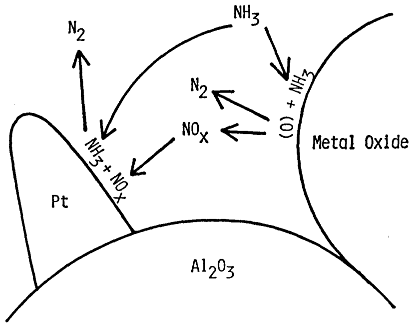

Fig. 5. Mechanism of the oxidation of NH_3 with a metal oxide–Pt/Al_2O_3 mixture.

Taking into consideration that both N_2O and NO_2 can also react with NH_3 on Pt/Al_2O_3 catalyst to form N_2, the scheme shown in Fig. 5 can be proposed for the reaction of NH_3 with the metal oxide–Pt/Al_2O_3 mixtures. That is, in the oxidation of NH_3 with the metal oxide–Pt/Al_2O_3 mixtures, NH_3 is, at first, oxidized by the metal oxides to form NO_x (NO, NO_2, and N_2O) and N_2 (Step I), then NO_x components transfer through the gas phase from the metal oxides to the Pt particles on Al_2O_3, and finally NO_x components react readily with NH_3 on Pt to form N_2 selectively (Step II). The significantly high selectivity to N_2 for the incomplete mixtures, such as Mixtures IV and V in Fig. 4 and V_2O_5–Pt/Al_2O_3(*Shaking*) in Table 1, can be understood in terms of the scheme shown in Fig. 5, since the gas-phase transfer can proceed more readily than the surface migration because of the absence of the activation energy in the transfer through the gas phase.[29] It should be emphasized that the rate of the gas-phase transfer of NO_x components is much faster than the rate of Step I. This assures the selective oxidation of NH_3 to N_2 with the metal oxide–Pt/Al_2O_3 mixtures even under conditions where the yield of NO is 100% in the oxidation of NH_3 with the metal oxides (Fig. 3).

It is interesting to investigate whether metal oxide–Pt/Al_2O_3 mixtures are also effective for the selective oxidation of NH_3 to N_2 by gaseous O_2. According to our preliminary continuous flow experiments under the dilute gas condition, the yield of NO and NO_2 in the oxidation of NH_3 with gaseous O_2 on Pt/Al_2O_3 was significantly decreased by the addition of MoO_3 or WO_3 to Pt/Al_2O_3. Details of the results and mechanisms will be reported in a subsequent paper.

As mentioned above, the synergistic effect in the oxidation of NH_3 differs considerably from that of the oxidation of hydrocarbons. The difference in the synergistic effect may be due to the difference in the schemes of both reactions, especially in the activity of deep oxidation products. In the oxidation of NH_3, the deep oxidation products, such as NO and NO_2, are produced first and then they react with NH_3 to form the mild oxidation products, such as N_2 and N_2O, while, in the oxidation of hydrocarbons, the deep oxidation products, such as CO and CO_2, do not convert to the mild oxidation products.

Conclusion

The selective oxidation of NH_3 to N_2 with the metal oxide–Pt/Al_2O_3 mixtures has been found to involve two kinds of active sites—one is the site on the metal oxide for the oxidation of NH_3 to NO_x and N_2, and the other is the site on Pt metal for the reaction of NO_x with NH_3 to form N_2. Although these two kinds of active sites are considerably separated from each other, a rapid gas-phase transfer of the reactive intermediate (NO_x) from the metal oxide to Pt assures cooperation between both sites. In other words, this kind of synergistic effect can take place even if the different kinds of active sites are considerably separated from one another. A heterogeneous catalytic reaction usually involves two or more steps; furthermore, reactive intermediates sometimes desorb from the surface to the gas phase during the reaction. Therefore, the mechanism described in this study could be applied to various types of catalytic reactions and give important suggestion on the design of multi-component catalysts.

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29) Selectivity to N_2 at 723 K in the oxidation of NH_3 with Mixture II was slightly higher than that with MnO_2 alone (Fig. 4). This may be due to the adhesion of a part of MnO_2 to the inner wall of the reactor above the Pt/Al_2O_3–MnO_2 interface of Mixture II, which causes the synergistic effect by the scheme shown in Fig. 5.