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Oxidation of Ammonia with Lattice Oxygen of Metal Oxides by Pulse Reaction Technique

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Synopsis. On V_2O_5, MoO_3, and WO_3, lattice oxygen has been found to be the active oxygen species for the *catalytic* oxidation of NH_3, whereas on MnO_2, Co_3O_4, Fe_2O_3, and NiO, adsorbed oxygen also played a significant role in the reaction. NO has been found to be an intermediate in the reaction of NH_3 with lattice oxygen.

Many studies have been reported on the reaction of hydrocarbons with the lattice oxygen of metal oxides in connection with the *catalytic* oxidation of hydrocarbons. On a number of catalysts, lattice oxygen (O^{2-}) has been found to play an important role in the *catalytic* oxidation of hydrocarbons. In a previous paper,$^{1)}$ the authors investigated the *catalytic* oxidation of NH_3 on various metal oxides by a flow technique, and found that NO is an important gas phase intermediate in the oxidation of NH_3. The *catalytic* oxidation of NH_3 was shown to have a specific character, in that NH_3 is first oxidized to NO (deep oxidation product) which then reacts with NH_3 (the NO–NH_3 reaction) to form N_2 and N_2O (partial oxidation products). This is in contrast with the oxidation of hydrocarbons. In the present work, the reaction of NH_3 with the lattice oxygen of metal oxides has been studied to determine the role of lattice oxygen in the oxidation of NH_3 and the importance of NO as an intermediate in the reaction of NH_3 with metal oxides.

Experimental

Materials. The method of preparation of metal oxides has been described previously.$^{1)}$ Commercial ammonia (99.9 % purity) and oxygen (99.8% purity) were used as reactants without further purification.

Apparatus. Experiments were conducted with a pulse apparatus. The reactant and product components (NH_3, N_2, N_2O, and NO) were analyzed using gas chromatography. Helium as a carrier gas (116 ml/min) was purified with titanium metal sponge heated at 750 °C. Pulses of NH_3 with various concentrations were supplied to the reactor by a 6-way valve. 0.1 g of metal oxides were used. Before injection of each sample, the metal oxides were treated with oxygen in a gas stream for 30 min at the reaction temperature in order to regulate the oxidation state of the samples.

Results and Discussion

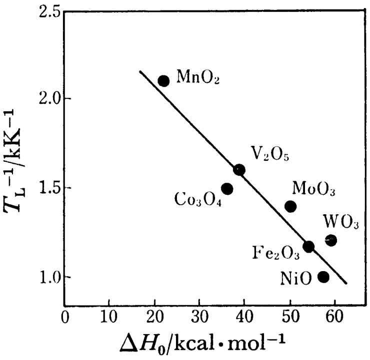

Fig. 1. Relationship between the reactivity of lattice oxygen of a metal oxide (T_L^{-1}) and the enthalpy change (ΔH_0) of the Reaction 1.

Activities of Metal Oxides for the Reaction with Ammonia. The conversion of NH_3 (X_{NH_3}) and the selectivities to N_2, N_2O, and NO (S_{N_2}, S_{N_2O}, and S_{NO}) have been obtained for various metal oxides as functions of the reaction temperature. In order to compare the activities of the metal oxides, the authors have defined T_L^{-1}, where T_L^{-1} represents the reciprocal of the absolute temperature at which X_{NH_3} attains 20% and is a measure of the reactivity of the lattice oxygen of the metal oxide with NH_3. In Fig. 1, the value of T_L^{-1} for a metal oxide is shown against the enthalpy change (ΔH_0) for the following reaction;

$$M_nO_m \longrightarrow M_nO_{m-1} + \frac{1}{2}O_2, \qquad (1)$$

where M_nO_m represents a metal oxide before reaction. As shown in Fig. 1, a correlation was obtained between T_L^{-1} and ΔH_0 indicating that the reactivity of the metal oxide with NH_3 is determined by the enthalpy change of the Reaction 1.

In Fig. 2, the relation between T_L^{-1} and T_C^{-1} is shown, where T_C^{-1} is defined as the reciprocal of the absolute temperature at which the conversion of NH_3 in the *catalytic* oxidation of NH_3 by flow technique attains 20%.$^{1)}$ As shown in Fig. 2, the metal oxides can be divided into two groups. In the first group (V_2O_5, MoO_3, and WO_3), a correlation is obtained between T_L^{-1} and T_C^{-1}, that is, T_L^{-1} is approximately equal to T_C^{-1} within the possible deviations due to the

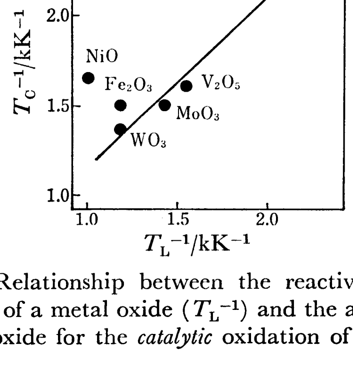

Fig. 2. Relationship between the reactivity of lattice oxygen of a metal oxide (T_L^{-1}) and the activity of the metal oxide for the *catalytic* oxidation of NH_3 (T_C^{-1}).

differences in the reaction technique (pulse or flow technique). The correlation indicates that, on a metal oxide in the first group, the oxygen species responsible for the *catalytic* oxidation of NH_3 is mainly the lattice oxygen of the metal oxide. In the second group (MnO_2, NiO, Fe_2O_3, and Co_3O_4), T_C^{-1} is greater than T_L^{-1} suggesting that on a metal oxide of the second group, in addition to the lattice oxygen, the adsorbed oxygen species such as O_2^- or O^- play a significant role in the *catalytic* oxidation of NH_3. This is in accordance with the results of thermal desorption, that is, the oxygen species, which desorbs at a lower temperature and is assigned to O_2^- or O^- species, was detected for the metal oxide of the second group.[2,3] This classification has been supported by pulse experiments on the effects of gaseous oxygen addition on pulses. The conversion of NH_3 with metal oxides of the second group was enhanced by the addition of O_2 in pulses, whereas X_{NH_3} with the metal oxide of the first group was not changed. Concerning the reaction of NH_3 with metal oxides, the influence of adsorbed oxygen, formed by the treatment with gaseous oxygen before the pulse was negligibly small—the conversion of NH_3 in the first pulse was the same as that in the second pulse measured without the treatment with gaseous oxygen. Furthermore, it is considered that the lowering of the surface lattice oxygen concentration hardly occurred in the reaction of NH_3 with metal oxides at the temperature at which X_{NH_3} attained 20%, since the yield of N_2, the only product at the temperature, was not changed by the increasing concentration of NH_3 in the pulse.

Nitrogen Oxide as an Intermediate in the Oxidation of Ammonia with the Lattice Oxygen of Metal Oxides. As reported in a previous paper,[1] NO plays an important role as a gas phase intermediate in the *catalytic* oxidation of NH_3 on metal oxides. This view agrees with that of Shelef *et al.*[4] and Schmidt *et al.*[5] In the oxidation of NH_3 with lattice oxygen of Co_3O_4 and V_2O_5 at 520 °C and 528 °C respectively, the conversion of NH_3 was 100 % and all of NO, N_2, and N_2O were formed irrespective of the inlet concentration of NH_3. As the concentration of NH_3 in the pulse decreased (Figs. 3 and 4), S_{NO} increased to 100%, and S_{N_2O} and S_{N_2} decreased to 0%. The results can be explained by the following scheme;

$$NH_3 \xrightarrow[\text{I}]{\text{Lattice oxygen}} NO \xrightarrow[\text{II}]{NH_3} N_2,\ N_2O, \qquad (2)$$

where NH_3 is at first oxidized by lattice oxygen to NO 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 under the experimental conditions of the present work.[6] According to the scheme, the activity of a metal oxide is determined by Step I, whereas the selectivities to N_2 and N_2O are limited by the relative rate of Step II to that of Step I. Since Step I and Step II are a monomolecular and a bimolecular reactions respectively, the relative rate of Step II to that of Step I, should increase with an increase in the concentration of NH_3, which is in accord with the experimental results shown in Figs. 3 and 4. Furthermore, in Figs. 3 and 4, the S_{NO} on V_2O_5 decreases more markedly than that on Co_3O_4 with increasing concentration of NH_3, in accordance with the scheme, since the activity of V_2O_5 for the NO–NH_3 reaction is higher than that of Co_3O_4.[6] Thus, it is concluded that NO plays an important role as a gas phase intermediate in the reaction of NH_3 with metal oxides as well as in the *catalytic* oxidation of NH_3.

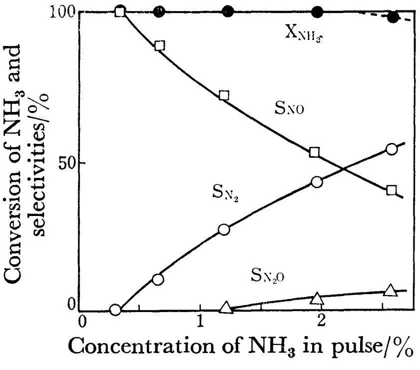

Fig. 3. Oxidation of NH_3 pulse with various NH_3 concentrations by lattice oxygen of Co_3O_4.
Reaction temperature=520 °C. Pulse size=7.42 cm³.

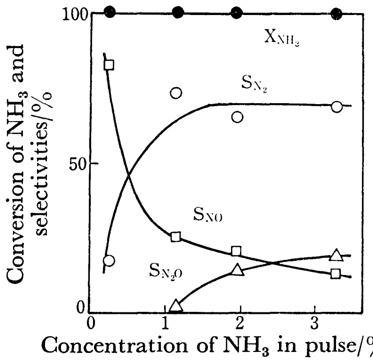

Fig. 4. Oxidation of NH_3 pulse with various NH_3 concentrations by lattice oxygen of V_2O_5.
Reaction temperature=528 °C. Pulse size=7.42 cm³.

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