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THE EFFECTS OF SUPPORTS ON THE REACTION OF NO WITH NH_3 CATALYZED BY V_2O_5

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The reaction mechanism of the catalytic reduction of NO by NH_3 was studied using V_2O_5-Al_2O_3 and V_2O_5-SiO_2 catalysts. On V_2O_5-Al_2O_3 the reaction rate was enhanced by the presence of oxygen and the reaction was found to proceed through the formation of NO_2 adsorbed on the catalyst surface. While on V_2O_5-SiO_2 no effects of oxygen were observed and the reaction seems to proceed through the formation of HNO adsorbed on the catalyst, since N_2O, which may be produced by the decomposition of HNO adsorbed, was detected during the reaction.

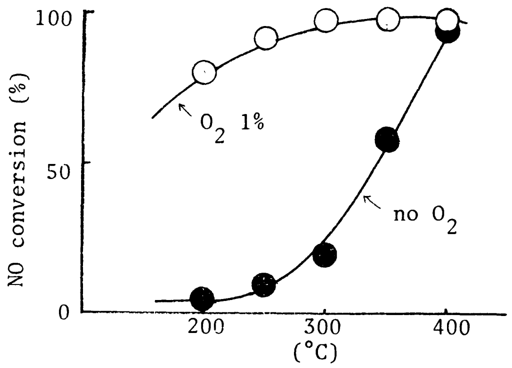
Of all the reagents employed for the catalytic removal of NO in flue gases, ammonia has been considered as the most effective one for practical use. This is due to the fact that the reaction rate is enhanced by the presence of oxygen$^{1)}$, which is an usual component in flue gases. A lot of papers have been published on catalytic activities$^{2,3)}$ and mechanisms$^{4,5)}$ for the present reaction. Most of them, however, focused on the catalysis of oxides supported on Al_2O_3, which are actually much more active than the oxides supported on SiO_2.

Our attempt is to show the difference of the reaction mechanisms of the reduction of NO by NH_3 on V_2O_5-Al_2O_3 from those on V_2O_5-SiO_2 catalysts, and to understand the effects of catalyst carrieres on the present reaction.

The experiments were made using a conventional flow reactor under the following conditions; the space velocity is $1\times10^4 \sim 3\times10^4 hr^{-1}$ with 5 ml of catalysts crushed to 1 mm in diameters and the reaction temperatures are in the range of 200~400°C. The gases were obtained directly from cylinders to make mixtures of desired concentrations of NO, NH_3 and O_2. N_2 or He was used as a balance gas. The concentrations of NO and NO_2 were measured by an analyser of chemiluminescence type and that of NH_3 by a conventional chemical analysis with absorption and titration (JIS 099). Oxygen and the products (N_2 and N_2O) were analysed by a gas-chromatography using columns packed with molecular sieve 5A and active carbon. The concentrations higher than 5ppm of these gases can be detected quantitatively. The catalysts studied were 10 wt% of V_2O_5 supported on Al_2O_3 and SiO_2, respectively. They were prepared by impregnating Al_2O_3 or SiO_2 bead in an aqueous vanadyl oxalate solution and by drying and calcinating in air at 550°C.

Fig.1 shows the catalytic activity of V_2O_5-Al_2O_3 catalyst in the presence or absence of oxygen. The presence of oxygen accelarated the reaction rate of NO with

Fig.1 Catalytic activity of V_2O_5-Al_2O_3 $SV=15,000hr^{-1}$



Inlet gas contents; NO~200ppm, NH_3~300ppm, SO_2~500ppm, H_2O~10%, N_2 balance

NH_3, as was first observed by Markvart on Pt-Al_2O_3 catalyst1). They suggested that oxygen would sweep one of ammonia fragments adsorbed on the catalyst surface so as to regenerate the sites for a successive adsorption of ammonia. This means the following scheme(I) for the reaction;

$$NH_3(g) \longrightarrow NH_2(ad) + H(ad) \tag{1}$$

$$NH_2(ad) + NO \longrightarrow N_2 + H_2O \tag{2}$$

$$H(ad) + 1/4\ O_2 \longrightarrow 1/2\ H_2O \tag{3}$$

Recently, Tamaru et al. proposed an another scheme(II) by means of infrared spectroscopy that the reaction proceeds through the formation of NO_2(ad) on the catalyst surface as is shown below4):

$$NH_3(g) + HO(ad) \longrightarrow NH_4O(ad) \tag{4}$$

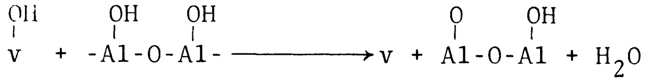
$$1/2\ O_2(g) \longrightarrow O(ad) \tag{5}$$

$$NO(ad) + O(ad) \longrightarrow NO_2(ad) \tag{6}$$

$$NH_4O(ad) + NO_2(ad) \longrightarrow N_2 + 2H_2O + O(ad) \tag{7}$$

$$H_2O + O(ad) + v \longrightarrow 2OH(ad) \tag{8}$$

After this sequence, OH(ad) would react with OH(ad) on the surface of Al_2O_3:

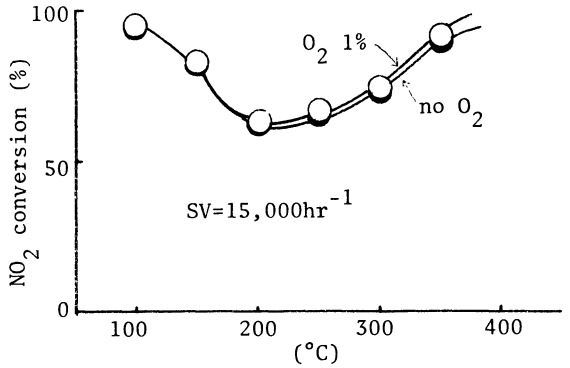


$$\overset{OH}{\underset{}{v}} + -\overset{OH}{Al}-O-\overset{OH}{Al}- \longrightarrow v + \overset{O}{Al}-O-\overset{OH}{Al} + H_2O \tag{9}$$

where "v" represents a reaction site on the catalyst. The oxygen remained on the surface of the carrier may diffuse into an oxygen vacancy in the bulk of Al_2O_3. This seems to crystalise the carrier and to reduce the surface area of the catalyst for a long time of the reaction.

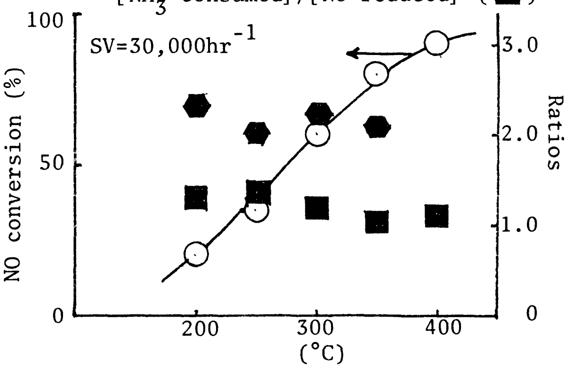
One of the differences between these two mechanisms is the adsorbed species on the catalysts with which oxygen reacts. In the scheme(I), oxygen attacks H(ad) to form H_2O, while in the scheme(II), it reacts with NO(ad) to produce NO_2(ad).

Fig.2 Reaction of NO_2 with NH_3 on V_2O_5-Al_2O_3



Inlet gas contents; NO_2~ 400ppm, NH_3~ 500ppm, H_2O ~ 10%, N_2 balance

Fig.3 Ratios of [NH_3 consumed]/[O_2 reacted] (⬢) and of [NH_3 consumed]/[NO reduced] (■)



Inlet gas contents are same to those in Fig.1.

Accordingly, if the scheme(II) will be probable for the present reaction, the reaction of NO_2 with NH_3 will not be affected by the presence of oxygen. The results obtained for the reaction of NO_2 and NH_3 on V_2O_5-Al_2O_3 catalyst were shown in Fig.2, and will support the scheme(II).

The ratios of the amount of NH_3 consumed to that of oxygen reacted(X) and to that of NO reduced(Y) during the reaction are characteristic to the schemes, respectively. For the scheme(I), X and Y should be 4.0 and 1.0, respectively, while for the scheme(II) they should become 2.0 and 1.0. The experiments to measure these ratios were done under a high space velocity of $3\times10^4 hr^{-1}$ so as to minimize ammonia combustion. The resulting values of X and Y were very close to 2.0 and 1.0, respectively(Fig.3). This also supports the scheme(II) for the present reaction on V_2O_5-Al_2O_3 catalyst.

The catalytic activity of V_2O_5-SiO_2 is shown in Fig.4 and it was not affected by the presence of oxygen. The products contained a small amount of N_2O both in the presence and absence of oxygen. The concentration of N_2O formed was less than 10ppm at the temperatures lower than 300°C and around 15ppm at 300∿350°C. At the temperatures higher than 350°C, the amount of N_2O produced decreased to zero. The formation of N_2O was never observed on V_2O_5-Al_2O_3 catalyst when oxygen existed. Otto and Shelef reported that N_2O formation was observed during the reaction of NO with NH_3 on Pt-Al_2O_3 and CuO-Al_2O_3 catalysts when oxygen was absent in the reactants(6) They suggested that N_2O would be produced by the scheme(III) shown below:

$$NH_3(g) \longrightarrow NH_2(ad) + H(ad) \qquad (10)$$

$$NH_2(ad) + NO \longrightarrow N_2 + H_2O \qquad (11)$$

$$H(ad) + NO \longrightarrow HNO(ad) \qquad (12)$$

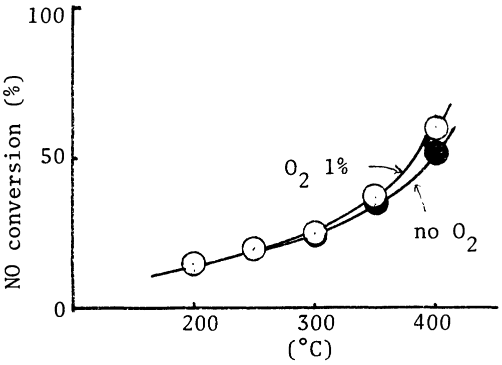
$$HNO(ad) \longrightarrow 1/2\ N_2O + 1/2\ H_2O \qquad (13)$$

$$N_2O \longrightarrow N_2 + 1/2\ O_2 \qquad (14).$$

This scheme(III) can explain the present results of no effects of oxygen on the reaction rate over V_2O_5-SiO_2 catalyst. In order to know if the scheme(III) can be available for the present reaction on V_2O_5-SiO_2 even in the presence of oxygen, the ratio of the amount of ammonia consumed to that of NO reduced was measured during the course of the reaction. The ratios obtained for various concentrations of oxygen

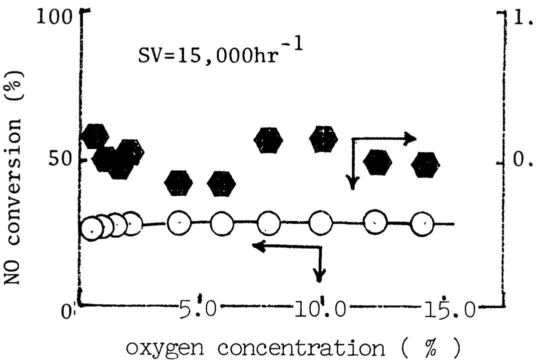
Fig.4 Catalytic activity of V_2O_5-SiO_2

$SV=15,000hr^{-1}$



Inlet gas contents are same to those in Fig.1.

Fig.5 Ratios of [NH_3 consumed]/[NO reduced] on V_2O_5-SiO_2 catalyst



Inlet gas contents are same to those in Fig.1.

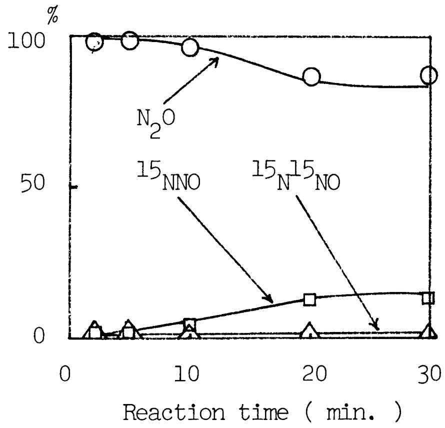
co-existed were around 0.5 as is shown in Fig.5.

Another evidence to support the scheme(III) was obtained by an isotopic reaction of NO and $^{15}NH_3$ (more than 95% of ^{15}N was contained) on V_2O_5-SiO_2. The reaction was carried out at 150°C in a conventional circulating reactor with 0.350gr of catalyst. The catalyst was enough treated with oxygen at 400°C after an evacuation at the same temperature so as to avoide a formation of N_2O by the following reaction:

$$2\ NO + \text{reduced catalyst} \xrightarrow{\qquad} N_2O + \text{oxidized catalyst.}$$

The distributions of N_2O, ^{15}NNO and $^{15}N^{15}NO$ produced by the present reaction were measured by means of mass spectroscopy. As is shown in Fig.6, N_2O was formed predominantly, while little or no ^{15}NNO and $^{15}N^{15}NO$ were observed. This means that the nitrogen atoms in N_2O formed come from NO but scarcely from $^{15}NH_3$, hence, probably, N_2O is mainly produced by the step(13) in the scheme(III).

Fig.6 Distribution of N_2O, ^{15}NNO and $^{15}N^{15}NO$



These observation led us to the conclusion that the reaction of NO and NH_3 on V_2O_5-SiO_2 catalyst passes through the formation of N_2O according to the scheme(III).

On the basis of these results, the difference of the activities between V_2O_5-Al_2O_3 and V_2O_5-SiO_2 catalysts can be ascribed to the activated states of oxygen adsorbed on the catalysts. Tamaru et al. said from the shifts of the infrared spectra of NH_4^+(ad) on catalysts that the oxidation states of vanadium ions in V_2O_5-SiO_2 catalyst are lower than those in V_2O_5-Al_2O_3[7]. Therefore, oxygen will stick to the sites on V_2O_5-SiO_2 and will become too stable in the catalyst to react with other species adsorbed on the catalyst surface. This would be a reason why NO, instead of oxygen, reacts with H(ad) to form HNO(ad) on V_2O_5-SiO_2 catalyst and why its activity is lower than V_2O_5-Al_2O_3 catalyst.

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