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Role of Surface Oxygen in the Reaction of NO with NH_3 over Chromia Catalyst

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The role of surface oxygen on chromia for the reaction of nitrogen oxide (NO) with ammonia (NH_3) was investigated. The activity of preoxidized catalyst was initially very high but settled to a stationary value in a few minutes after the surface oxygen had been consumed. There are two kinds of surface oxygen, of high and low oxidizing power. The former is that of chromate and is responsible for the initial high activity. Both NO and NH_3 are activated by the oxygen of surface chromate, NO as a nitrito-type species and NH_3 as the dissociatively adsorbed state. Second, surface hydroxyl plays a role for the activation of ammonia. Two reaction paths are present for the formation of nitrogens, namely, nitrito species with a fragment of dissociatively adsorbed ammonia and nitrito species with ammonium ion.

INTRODUCTION

In our previous studies, the reaction of NO with NH_3 over Fe_2O_3–Al_2O_3 (*1*), Cr_2O_3–Al_2O_3 (*2, 3*), and Cr_2O_3 (*3*) catalyst was studied, mainly by the isotope-labeling technique. From the viewpoint of environmental chemistry, the mechanism of the reaction in the presence of oxygen is of primary concern. This is not only because actual exhaust gases contain a considerable amount of oxygen but also because such oxygen enhances the catalytic activity to a considerable extent (*4*). However, the study of the three-reactant system, NO, NH_3, and O_2, is accompanied by experimental difficulty. Unless an extremely low pressure of NO is employed, NO and O_2 react homogeneously to form NO_2 and subsequent interaction with NH_3 finally gives some adduct which makes reaction studies impossible.

Instead, our approach is to clarify the reaction mechanism over preoxidized catalyst. It was already pointed out (*3*) that preoxidation showed a pronounced effect on activity, which is similar to the effect of gaseous oxygen. Several suggestions have already been made in order to account for the effect of gaseous or surface oxygen. For example, Takagi *et al.* (*5*) suggested from their ir studies that NO is oxidized by gaseous oxygen to form NO_2 which then reacts with surface ammonium ion (NH_4^+). Several other investigators considered that surface oxygen promotes dissociative adsorption of NH_3 (*4, 6*).

The main problems to be answered in this report are the following: (i) whether or not the surface oxygen is consumed during the reaction or, in other words, whether oxygen takes a part in the stoichiometry of the reaction; (ii) what kind of oxygen species are responsible for the enhancement of the activity; and (iii) how the oxygen species take part in the elementary steps of the reaction.

Chromia catalyst is suitable for this kind of study because the behavior of surface oxygen on chromia has been extensively studied (*7–10*).

EXPERIMENTAL

Catalyst. Chromia was prepared as follows. Chromium nitrate was hydrolyzed with aqueous ammonia at room temperature. The resulting slurry was washed with ion-exchanged water several times, dried at

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100°C for 1 day, and calcined in an air flow at 600°C for 3 hr. The method is the same as reported previously (*2*). The BET area of the catalyst was 24 m^2/g. X-Ray examination revealed that it was α-chromia.

Reaction. The reaction was carried out in a conventional vacuum-gas circulation apparatus, the details of which are given elsewhere (*2*). Before the activity tests were made, the following pretreatments were performed *in situ;* 1-hr reduction with hydrogen at 300°C, 1-hr oxidation with 300 Torr of O_2 at a defined temperature, and 1-hr pumping at 150°C.

Oxidation power distribution. The oxidation power distribution was measured by the method proposed by Uchijima *et al.* (*11*). The method consists of oxidation–reduction titration by iodometry in several media of different pH. When a medium of high pH is used, only strong sites are able to oxidize KI. On the contrary, when a medium of low pH is employed, weaker sites also play a role for the oxidation. Then the oxidation power distribution is determined in an integral form.

Temperature-programmed desorption (TPD) studies. The TPD apparatus was of the vacuum type, equipped with a mass spectrometer (Shimazu, MASPEQ 070) for analysis of desorbed products and with a Pirani gauge for measuring pressure. The system was continuously pumped through a capillary during the measurement; when desorption takes place, the pressure of the system increases and when the desorption ceases to occur the pressure returns to a stationary value, thus giving rise to a TPD profile.

Preoxidation of the catalyst was effected by the same sequential procedure as that for reaction studies.

Adsorption of nitrogen oxide and ammonia, or a mixture of the two, was carried out at room temperature for 30 min. The mixture, [NO + NH_3], had been well mixed and stored in a gas holder, in order to ensure that both reactants contacted with the catalyst at the same time. If the adsorptions of the two reactants were done sequentially, the obtained TPD profiles were affected by the sequence of the contact.

TPD profiles of desorbed gases are illustrated in the following figures by plotting heights of parent peaks of each desorbed species in the mass spectrometer. Scanning over the range, m/e = 4 to 80, was done within 1 min. TPD profiles were also recorded with a Pirani gauge connected to a recorder. Since this gives a continuous curve, the shoulders of peaks, if they exist, can be found with better accuracy.

Gases. NO and NH_3 were obtained from commercial cylinders. They were purified by vacuum distillation before use. $^{18}O_2$ (^{18}O fraction, 99.5%) was supplied by the Japan Isotope Association and was given no further treatment. $^{15}NH_3$ was obtained by the same procedure as described elsewhere (*3*). The atomic fraction of ^{15}N was 96%. Throughout the paper, isotopically labeled atoms are written as $\bar{N}$ or $\bar{O}$. Chemical formulas are generally used to distinguish isotope species. When the name of a compound appears, it is for the general description of the behavior of the compound.

RESULTS

Preliminary Studies

When the mixture of nitrogen oxide and ammonia was contacted with the preoxidized catalyst at 150°C, a very rapid formation of both nitrogen and nitrous oxide occurred in the first few minutes. Then a slow but steady formation of N_2 and N_2O was observed until either one of the reactants was depleted. The latter stage of the reaction is the catalytic reaction, the mechanism of which had already been proposed. Steady formation was observed from the very beginning if the catalyst, which had been used for such a reaction study with a subsequent pumping at the same temperature, was employed for the second reaction run (*3*). Our primary concern in this paper is to clarify the reaction mechanism which is predominant in the first stages of the reaction.

N_2 and N_2O produced in the first 20 min are termed "products from nonstationary reaction" in the sense that the surface is not stationary but changes in its oxidation state as the reaction proceeds.

When the single reactant, ammonia, was contacted with the catalyst at 150°C, the formation of the two products was also observed, but to a lesser extent. The contact of NO alone resulted in no appreciable change in gas-phase composition.

The Effects of Preoxidation Temperature

The amounts of the two products from the nonstationary reaction are plotted in Fig. 1 against preoxidizing temperatures. They increased with the temperature until 250–300°C, but further increase of the latter had no effect. The amounts of both products showed a similar dependence on preoxidizing temperature, indicating that active sites for the formation of N_2 and N_2O are closely related to each other.

When CO was contacted at 150°C with preoxidized catalyst, CO_2 was produced. The experiment was done with a closed gas-circulation apparatus, equipped with a KOH-packed column by which the produced CO_2 was trapped. Since disproportionation of CO ($2CO \rightarrow CO_2 + C$) did not occur under these conditions, the amount of produced CO_2 was an exact measure of the amount of reactive oxygen on the surface. Figure 1 also shows the plots of produced CO_2 against preoxidation temperatures. A similar dependence on the temperature to that for N_2, N_2O formation is apparent. The similarity is physically acceptable if we consider that the nonstationary reaction of NO with NH_3 accompanies the consumption of surface oxygen.

It is possible to estimate the amount of surface oxygen consumed during the reaction of nitrogen oxide with ammonia if we use isotope-labeled ammonia, $\bar{N}H_3$, as one of the reactants (*3*). The stoichiometry of the reaction gives the following equation (1):

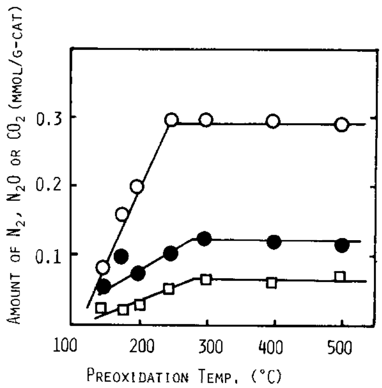


FIG. 1. Effect of preoxidation temperature on the amount of N_2 (○) and N_2O (□) produced by the "nonstationary reaction" of [NO + NH_3] and on the amount of CO_2 (●) formed upon contact of CO with the preoxidized catalyst. Preoxidation: with 300 Torr of O_2 for 1 hr, reaction of [NO + NH_3]; at 150°C with $P_{NO} = P_{NH_3} = 150$ Torr, reaction of CO; at 150°C with 150 Torr of CO.

$$\text{Consumed O-atom on the surface} = \tfrac{1}{2}\{[\bar{N}N] + 3[\bar{N}NO]\} - 2[NN] - [NNO], \quad (1)$$

where the bracket means the amount of individual species produced. If, contrary to experimental finding, the formation of $\bar{N}\bar{N}$ or $\bar{N}\bar{N}O$ had occurred, a different formulation should be encountered. Table 1 shows the results of NO with $\bar{N}H_3$, in which corrections were not applied for the presence of unlabeled ammonia in the reactant. The value of Eq. (1), after the correction, was 0.13 mg-atom/g-cat., which is in good accordance with the amount of CO_2 produced (0.12 mg-atom/g-cat.).

TABLE 1

The Amount of Isotopically Labeled Products from Nonstationary Reaction[a]

Products (mmol/g cat.)				
$\bar{N}N$	NN	$\bar{N}NO$	NNO	Value of Eq. (1)[b]
0.259	0.0406	0.0466	0.0174	0.13 mg-atom/g-cat.

[a] Reaction conditions: at 150°C with the mixture, 150 Torr of NH_3 (96% $\bar{N}$) and of NO; pretreatment with 300 Torr of O_2 at 300°C for 1 hr.

[b] Corrections were applied for the presence of NH_3 in the reactants.

Oxidizing Power Distribution of Surface Oxygen

The oxidizing power distribution, as measured by Uchijima's method, is given in Fig. 2. It seems that there are two types of oxygen, of high and low oxidizing power, on the surface, although a distinct difference is not so clear in the integral form. Differentiation with respect to pH reveals minimum at pH = 9.0. Oxygen of high oxidizing power (pH > 9.0) amounted to 0.1 mg-atom/g-cat., which roughly corresponded to the amount of oxygen consumed during the reactions, NO + NH_3 and CO + preoxidized catalyst.

No strong site (of high oxidizing power) was found on "used" catalyst which had been subjected to a reaction NO + NH_3, but a weaker site (of low oxidizing power) still remained.

TPD Studies of Oxygen

TPD profiles of surface oxygen on catalysts which had been treated at various temperatures are given in Fig. 3. Two peaks appeared, at 380 and at ca. 550°C. The maximum of the latter peak was uncertain because the temperature rise was stopped at 550°C. Both peaks were due to oxygen, as revealed by mass spectrometry.

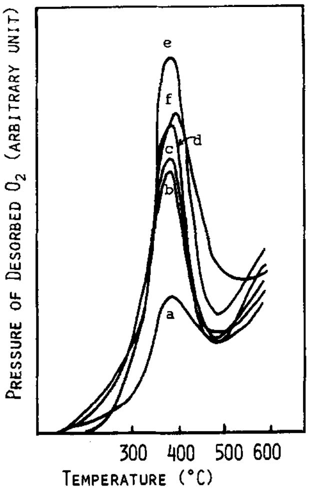


FIG. 3. TPD profiles of oxygen. Pretreatment of the catalyst: with 100 Torr of O_2 for 1 hr at (a) 100°, (b) 150°, (c) 200°, (d) 250°, (e) 300°, and (f) 400°C followed by pumping at 150°C, temperature rise 20°C/min.

Areas of the peak at 380°C (integrated between 150 and 500°C), which shows the relative amounts of oxygen desorbed in the temperature range, showed a similar dependence on the preoxidization temperatures. This fact indicates that the reactive oxygen so far discussed gives the peak at 380°C. It

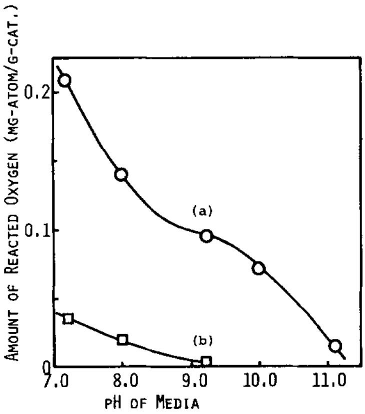


FIG. 2. Oxidation power distribution. Amount of surface oxygen consumed for oxidation of KI as a function of pH of media. Curve (a), "fresh catalyst" which was preoxidized with 300 Torr at O_2 at 300°C for 1 hr; curve (b), "used catalyst" which was subjected to the reaction of NO + NH_3, the reaction conditions being the same as for Fig. 1.

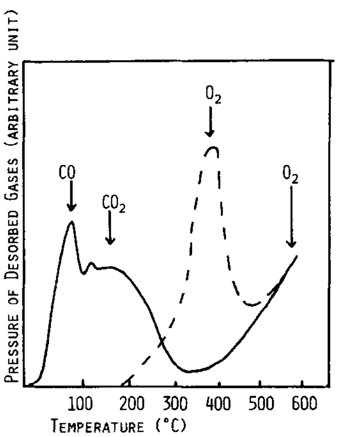


FIG. 4. TPD profiles of CO adsorbed on preoxidized catalyst (solid line). Broken line shows TPD of oxygen, which is the same as that given in Fig. 3(c). Preoxidation with 300 Torr of O_2 at 200°C for 1 hr; adsorption of CO, with 100 Torr of CO at room temperature for 30 min.

is supported by the finding given in Fig. 4, in which the TPD profile of CO adsorbed on oxidized catalyst is shown. The peak at 380°C disappeared and CO_2 was produced. On the other hand, the peak at 550°C did not change at all.

The TPD profile of NO adsorbed on $\bar{O}_2$-preoxidized surface is given in Fig. 5. There are two species which have a mass number of 32, N$\bar{O}$ and O_2. However, it was easy to distinguish the two possibilities. N$\bar{O}$ or O_2, when Fig. 5 was compared with the same experiment but in which the preoxidation was done with O_2. It was found that desorption of nitrogen oxide did not occur at temperatures higher than 300°C.

The three isotope species O_2, O$\bar{O}$, and $\bar{O}_2$ desorbed in the same temperature range with similar TPD profiles. Integration of the three peaks gave the relative amounts of the three isotopic oxygens (because of identical sensitivity to mass spectrometry), from which the atomic fraction of $\bar{O}$ (θ) in the desorbed oxygen was calculated to be 0.34. Suppose that the desorption of oxygen occurs by random pairing, then the relative amount of O_2, O$\bar{O}$, and $\bar{O}_2$ can be expected from the knowledge of the averaged $\bar{O}$ fraction, $\theta = 0.34$. The expected ratio of the three isotopic species is in good accordance with the expected ratio, as given in Fig. 6. This clearly shows that all the oxygen molecules lost their molecular identity on the surface. Also, all the resultant species were equivalent.

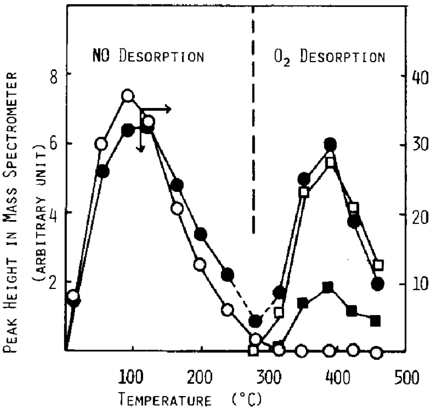


FIG. 5. TPD of NO adsorbed on $\bar{O}_2$-preoxidized catalyst. Pretreatment: 300°C, 1 hr with 100 Torr of $\bar{O}_2$, following by pumping at 150°C. NO adsorption: 0°C, 30 min with 100 Torr of NO followed by pumping for 30 min. ○, $m/e = 30$ (NO); ●, $m/e = 32$ (N$\bar{O}$ < 300°C or O_2 > 300°C); □, $m/e = 34$ (O$\bar{O}$); ■, $m/e = 36$ ($\bar{O}_2$).

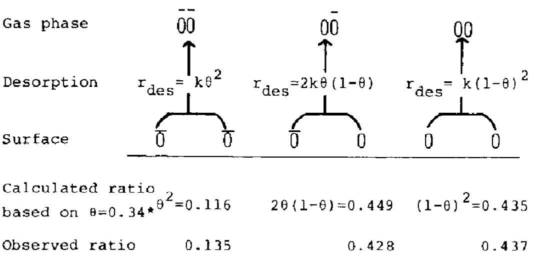
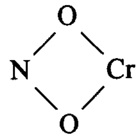


FIG. 6. Scheme for oxygen desorption. θ, atomic fraction of $\bar{O}$ on the surface.

It is noteworthy that the value of θ, 0.34, is that for the surface at 300°C. A higher value is expected for the initial surface, because nitrogen oxide which had desorbed at the lower temperature had taken off a part of $\bar{O}$ from the surface. θ for initial surface can roughly be estimated to be 0.54, from a knowledge of the amount of desorbed N$\bar{O}$. One might be afraid that NO adsorption–desorption phenomena may affect oxygen desorption. However, we have also measured the TPD of $\bar{O}_2$-oxidized catalyst, on which no NO adsorption was done. Completely the same conclusion was obtained, except that θ was different.

Nitrogen Oxide Desorption

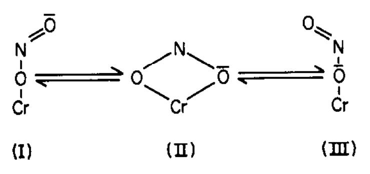
A peak of nitrogen oxide appeared at around 100°C (see also Fig. 5). No other peak was found, indicating that only one kind of adsorbed species is present on the oxidized surface. This was also confirmed from the TPD profile obtained with a Pirani gauge, which affords a better criterion for the absence of any other peak. Desorption of N$\bar{O}$ also occurred at the same temperature range as did NO. Little N$\bar{O}$ appeared in gas phase during the contact of gaseous NO with $\bar{O}_2$-oxidized surface. The findings suggest that nitrogen oxide adsorption occurs on a surface oxygen giving nitrogen dioxide-like species, one of whose oxygen is left on the surface upon desorption. Interaction of NO with surface oxygen has already been postulated by one of the present authors (*16*).

If we first assume the free nitrogen dioxide ion (NO_2^- or $NO\bar{O}^-$) or chelate-type structure  as an adsorbed state, we can anticipate the ratio $NO/N\bar{O}$ by the use of Eq. (2), since the two oxygen atoms in these species are equivalent.

$$\frac{NO}{N\bar{O}} = \frac{1 - \theta + \theta/2}{\theta/2} = \frac{2 - \theta}{\theta}. \quad (2)$$

With the knowledge of $\theta = 0.54$, the ratio becomes 2.7 which is smaller than the observed values, 5.7 at 100°C, 3.6 at 200°C, and 2.7 at 240°C. Furthermore, the observed ratio was not constant throughout the temperature range as would be expected for free nitrogen dioxide or chelate-type structure, but decreased with temperature.

These findings are satisfactorily explained by assuming a nitrito-type species (**I** or **III** in Eq. (3)). In the recent review by Arai (*13*), such a species is considered as a probable adsorbed state of nitrogen oxide on oxidized surface.


(3)

Exchange of O with Ō may take place through a chelate structure (**II**). The extent to which such exchange occurs, increases and approaches to equilibrium with temperature. Kugler *et al.* (*14*) suggested the chelate-type structure (**II**) as an adsorbed species while our view is that it is an intermediate (or an activated complex, in other words) for exchange of oxygen. The main difference between that work and ours is that Kugler *et al.* prereduced their catalyst on which coordinatively unsaturated chromium ions may be present, while we preoxidized the catalyst.

TPD of NH_3

Figure 7 illustrates TPD profiles when NH_3 was adsorbed on the preoxidized surface. Decomposition of NH_3 to N_2 and N_2O occurred at 240°C. The important finding for our present purpose is that the peak at 380°C disappeared, indicating reactive oxygens were consumed during the decomposition of ammonia. Unreacted NH_3 and produced H_2O was also found in the gas phase at around 200°C or higher; however, quantitative analysis was impossible because of the restrictions of the mass spectrometer.

TPD of [NO + $\bar{N}H_3$] Mixture

TPD profiles for [NO + $\bar{N}H_3$] mixture are given in Fig. 8. Desorption of oxygen at 380°C disappeared. Formation of $\bar{N}N$ which is a major product in reaction studies (*1*) occurred with two maxima, 120 and 240°C (peaks A and B, respectively), indicating that two reaction paths are present. The characteristic of peak B is that is accompanies simultaneous formation of $\bar{N}\bar{N}$, $\bar{N}\bar{N}O$, etc. These findings as well as that given in Fig. 6 strongly suggest that oxida-

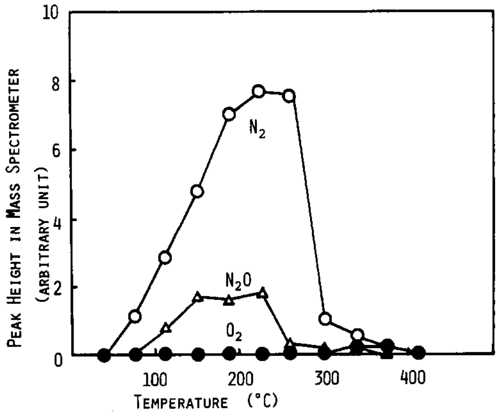


FIG. 7. TPD of NH_3 adsorbed on preoxidized catalyst. Pretreatment the same as that given in Fig. 5 except that O_2 was used instead of $\bar{O}_2$. NH_3 adsorption at room temperature for 30 min with 10 Torr of NH_3.

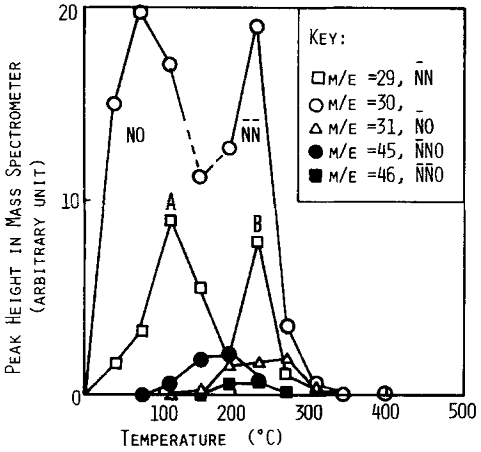


FIG. 8. TPD of [NO + $\bar{N}H_3$] mixture adsorbed on preoxidized catalyst. Pretreatment the same as that given in Fig. 7. Adsorption at room temperature with equimolal mixture of [NO + $\bar{N}H_3$], 20 Torr.

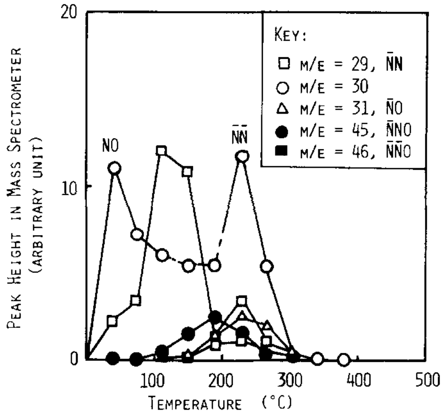


FIG. 9. TPD of [NO + $\bar{N}H_3$] mixture adsorbed on preoxidized–hydrated catalyst. Pretreatment the same as that given in Fig. 7, followed by contact with 20 Torr of H_2O for 30 min with subsequent pumping at room temperature for 30 min. Adsorption the same as that given in Fig. 8.

tive decomposition of ammonia occurs in the temperature range 200 ~ 300°C, and a resulting fragment is an intermediate for the formation of $\bar{N}N$. In other words, as soon as a fragment of ammonia is produced, it reacts with neighboring species by all means. It gives $\bar{N}N$ when nitrogen oxide (or most likely nitrito-type species as described in the previous section) is present as a nearest neighbor. If there is no such species but another fragment as neighbor, it gives $\bar{N}\bar{N}$, $\bar{N}\bar{N}O$, etc. This view explains why $\bar{N}\bar{N}$ or $\bar{N}\bar{N}O$ appears in the TPD experiment while they do not in the reaction studies. In reaction circumstances, there are sufficient amounts of nitrogen oxide in the gas phase. When nitrogen oxide on the surface is depleted, it is supplied from the gas phase. Thus, any surface fragments have chances to interact with the most favorite opponent, which makes the reaction selective. In the TPD experiment, however, the relative amount of NO and $\bar{N}H_3$ on the surface is different from stoichiometry, and the excess amount of $\bar{N}H_3$ has no other chance than coupling with itself.

The characteristic feature of peak A, formation of $\bar{N}N$ at about 120°C, is that $\bar{N}N$ uniquely appeared at this temperature. In order to obtain further information on peak A, the following experiments were done. Figure 9 shows the TPD profile of the mixture adsorbed on oxidized–hydrated surface. Peak A became larger and B smaller. Figure 10 shows the same experiment for the catalyst which had been subjected to oxidation–pumping at 400°C followed by the standard preoxidation

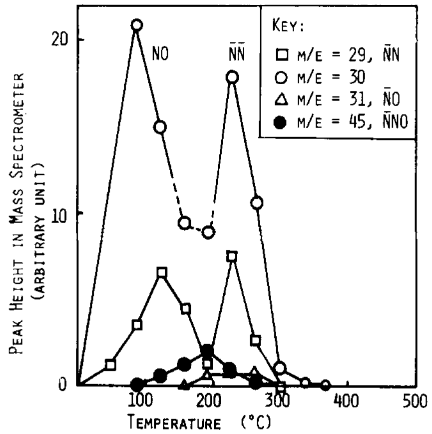


FIG. 10. TPD of [NO + $\bar{N}H_3$] mixture adsorbed on highly dehydrated–oxidized catalyst. Pretreatments: 400°C for 1 hr with 100 Torr of O_2 and pumping at 400°C for 1 hr, followed by the same preoxidation procedure (see Fig. 7). Adsorption the same as that given in Fig. 7. The peaks of m/e = 46 were small and thus omitted.

procedure. Peak A became smaller and peak B remained unchanged. In the situation given in Fig. 9, one could expect an increase in the number of surface hydroxyls and, in the situation of Fig. 10, a decrease. These facts suggest the participation of surface hydroxyl. Zecchina *et al.* (*15*) suggested that surface hydroxyl on chromia is very difficult to remove even by pumping at a temperature higher than 400°C. Accordingly, it is not unreasonable that peak A still remained in TPD of Fig. 10. In connection with these findings, we recall the reaction mechanism proposed by Takagi *et al.* (*5*), who suggested that ammonium ion reacts with nitrogen dioxide on the surface of V_2O_5.

DISCUSSION

Reactive Oxygen Species

It is known that the phase change in chromia (amorphous to α-form) occurs at 400°C and that this is promoted by the presence of gaseous or surface oxygen (*7–9*). It is supposed by Zecchina *et al.* (*8*) that the phase change occurs through surface migration of chromate ion $[CrO_4]^{2-}$. They also stated that oxygen atoms adsorbed on coordinatively unsaturated Cr^{3+} (Cr^{3+}_{cus}) do not desorb even at 400°C. Weller and Voltz (*10*) showed that "islands" of chromate structure were formed when chromia was heated with O_2 at high temperature. Bukaneva *et al.* (*12*) suggested that chromium ions of intermediate valency, e.g., Cr^{5+}, which are common on Al_2O_3-supported chromia catalysts, are not stable on unsupported chromia. Based on these views, the reactive oxygen which is of high oxidizing power (Fig. 2), which desorbs at 380°C (Fig. 3) and which readily reacts with CO at low temperatures (Figs. 1 and 4) is that of surface chromate. We have also confirmed the presence of hexavalent chromium ions when preoxidized catalyst was subjected to water extraction.

The results given in Fig. 5 (oxygen desorption) also support the view, because the oxygens in chromate are all equivalent and are atomic. Upon decomposition, half of the oxygen atoms in chromate couple with each other to form oxygen molecules. That is,

$$Cr_2O_3 + \tfrac{3}{2}\bar{O}_2 \rightarrow 2Cr(O, \bar{O})_3 \tag{4}$$

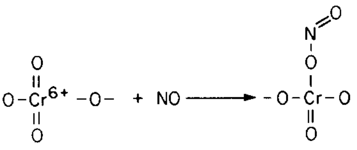
$$2Cr(O, \bar{O})_3 \rightarrow Cr_2(O, \bar{O})_3 + \tfrac{3}{2}(O_2, O\bar{O}, \bar{O}_2). \tag{5}$$

Mechanism of Nonstationary Reaction

We shall discuss here the mechanism of the reaction, especially the formation of $\bar{N}N$ which was the major product in the reaction studies. The findings which are taken into consideration are as follows. (1) Oxygen of surface chromate plays a part in the stoichiometry of the reaction. (2) NO is adsorbed on surface chromate as an oxidized form (Fig. 5). (3) Oxidative decomposition of ammonia occurs at around 240°C and the resultant fragment is a probable intermediate. (4) Surface hydroxyl also plays a role, which affords an additional (alternative) path for $\bar{N}N$ formation.

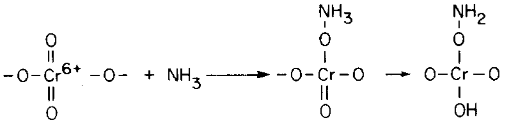
In addition, the following are also taken into account. Zecchina *et al.* (*15*) suggested that hydroxyl bonded to coordinatively unsaturated Cr^{3+} (Cr^{3+}_{cus}) is hardly removed even by pumping at 400°C, while oxidation–pumping cycles results in a remarkable decrease of it. The latter treatment corresponds to chromate formation and its decomposition. Based on this view, surface hydroxyl, which exists initially and on which ammonia is adsorbed, is bonded to Cr^{3+}_{cus} rather than to Cr^{6+}. Ammonium ions may migrate on the surface and couple with nitrito-type species on chromate. This, however, does not exclude the possibility that hydroxyl on chromate structure produced during the reaction also plays a role for the formation of ammonium ions.

The details of the dissociative adsorption of ammonia are not clear. Tentatively, we consider that the adsorption at room temperature occurs through hydrogen bonding with oxygen on chromate. The oxidative decomposition of such species occurs at around 200°C and the resulting fragments (most likely NH$_2$) interact with neighboring species. Based on these findings and considerations, the following schemes may be written:



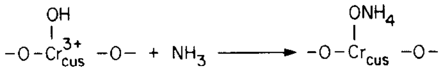
$$O{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Cr^{6+}}}{-}O{-} + NO \longrightarrow -O{-}\overset{\overset{\overset{N=O}{|}}{O}}{\underset{\underset{O}{\|}}{Cr}}{-}O \qquad (6)$$

(I)



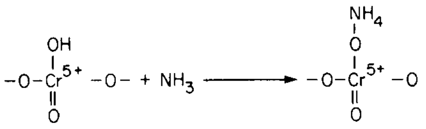
$$-O{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Cr^{6+}}}{-}O{-} + NH_3 \longrightarrow -O{-}\overset{\overset{NH_3}{O}}{\underset{\underset{O}{\|}}{Cr}}{-}O \rightarrow O{-}\overset{\overset{NH_2}{O}}{\underset{\underset{OH}{|}}{Cr}}{-}O \qquad (7)$$

(II)



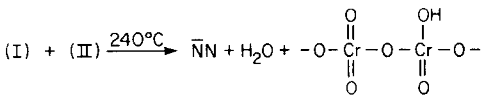
$$-O{-}\overset{\overset{OH}{|}}{Cr^{3+}_{cus}}{-}O{-} + NH_3 \longrightarrow -O{-}\overset{\overset{ONH_4}{|}}{Cr_{cus}}{-}O{-} \qquad (8)$$

(III)

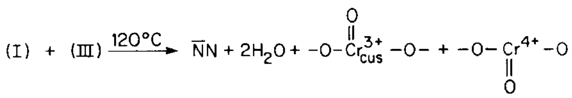


$$-O{-}\overset{\overset{OH}{|}}{\underset{\underset{O}{\|}}{Cr^{5+}}}{-}O{-} + NH_3 \longrightarrow -O{-}\overset{\overset{NH_4}{O}}{\underset{\underset{O}{\|}}{Cr^{5+}}}{-}O \qquad (9)$$

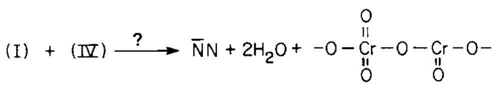
(IV)



$$(I) + (II) \xrightarrow{240°C} \overline{N}N + H_2O + -O{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Cr}}{-}O{-}\overset{\overset{OH}{|}}{\underset{\underset{O}{\|}}{Cr}}{-}O{-} \qquad (10)$$



$$(I) + (III) \xrightarrow{120°C} \overline{N}N + 2H_2O + -O{-}\overset{\overset{O}{\|}}{Cr^{3+}_{cus}}{-}O{-} + -O{-}\underset{\underset{O}{\|}}{Cr^{4+}}{-}O \qquad (11)$$



$$(I) + (IV) \xrightarrow{?} \overline{N}N + 2H_2O + -O{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Cr}}{-}O{-}\underset{\underset{O}{\|}}{Cr}{-}O{-} \qquad (12)$$

Surface chromate thus loses its oxygen as the reaction proceeds and finally becomes α-chromia.

Strictly speaking, the mechanism given here is not for the "catalytic reaction" but for the stoichiometric reaction of NO + NH$_3$ with surface oxygen. It is probable, however, that the catalytic sequence may be completed by the reoxidation of surface by gaseous oxygen. In usual circumstances, exhaust gas contains a large excess of oxygen and the temperature is high enough to oxidize Cr^{3+}.

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