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The Mechanism of the Reaction of Nitrogen Oxide with Ammonia over Cr_2O_3–Al_2O_3 and Cr_2O_3 Catalysts

II. Isotope Labeling Studies[1]

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The reaction of NO with $^{15}NH_3$ was studied over 9.3% Cr_2O_3–Al_2O_3 and Cr_2O_3 as catalyst; relevant properties characterizing these oxides are described in Part I (preceding paper). The main isotope species in the products, nitrogen and nitrous oxide, were ^{15}NN and NNO when the reaction proceeds in a stationary state. A noncatalytic reaction of NO with prereduced surface to give NN was also significant, especially in the beginning. When the catalyst was preoxidized, the reaction was greatly enhanced and a large amount of ^{15}NNO was found. It is concluded that the reaction takes place on surface oxygens.

INTRODUCTION

Attention has recently been focused on the reaction of NO + NH_3 from both theoretical and practical points of view. Otto *et al.* (*1*) studied the reaction mechanism by means of the isotope labeling technique. The main isotopic species in the nitrogen-containing products were $\bar{N}N$ and NNO, although considerable amounts of $\bar{N}NO$ and NN were also produced ($\bar{N}$ denotes the isotope-labeled nitrogen atom from ammonia, $^{15}NH_3$). They explained the results on the basis of the relative amounts of surface fragments derived from $\bar{N}H_3$, i.e., $\bar{N}H_3$, $\bar{N}H_2$, $\bar{N}H$, and $\bar{N}$. The catalysts employed in their studies were mainly noble metals on which dissociative adsorption of NH_3 was readily expected.

Generally speaking, the decomposition of NH_3 hardly takes place on metal oxides, indicating that no dissociative adsorption occurs. Thus the study of the reaction mechanism for NO + NH_3 over metal oxide catalysts will give a new light on general understanding of the reaction. Takagi *et al.* (*2*) suggested from their ir studies that the reaction over V_2O_5 catalyst in the presence of O_2 proceeds through the coupling of NO_2-like species with the ammonium ion. The view is, however, limited to but one of the elementary steps.

The following scheme was proposed in our preceding study on the reaction of NO + NH_3 over Fe_2O_3–Al_2O_3 catalyst (*3*):

$$NO + \bar{N}H_3 \rightarrow \bar{N}N + H_2O + H, \qquad (a)$$

$$2H + 2NO \rightarrow 2HNO \rightarrow N_2O + H_2O. \qquad (b)$$

Combining Eqs. (a) and (b) yields total stoichiometry:

$$4NO + 2\bar{N}H_3 = 2\bar{N}N + N_2O + 3H_2O.$$

The nitrogen atom which comes from ammonia is written here as $\bar{N}$ in order to distinguish it from that which comes from nitrogen oxide. The proposed scheme was based upon the following findings: (i) The ratio of nitrogen/nitrous oxide in gas phase products was 2 and was independent of

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[1] For Part I, see Ref. (*4*).

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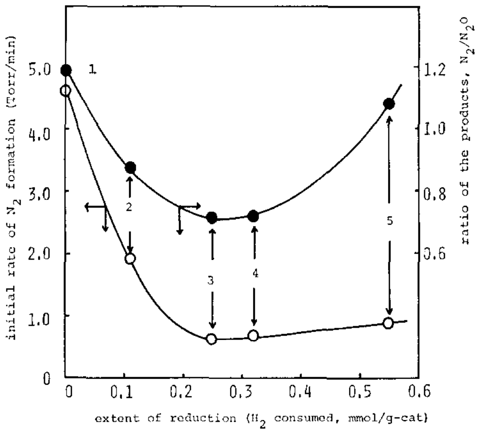


FIG. 1. Correlations of the initial rate of N_2 formation or N_2/N_2O ratio with the change in the extent of reduction: (1) fully oxidized catalyst; treated with 300 Torr of O_2 at 300°C for 1 hr; (2) treated with 26 Torr of H_2 for 10 min after full oxidation; (3) treated with 120 Torr of H_2 for 2 min after full oxidation; (4) treated with 150 Torr of H_2 for 5 min after full oxidation; (5) treated with 300 Torr of H_2 for 1 hr after full oxidation.

reaction temperature. The ratio of 2 is readily explained in terms of total stoichiometry. (ii) The main products of the $NO + \bar{N}H_3$ reaction were $\bar{N}N$ and NNO where $\bar{N}$ is isotopically labeled nitrogen, ^{15}N.

The purpose of the present study is to confirm the above scheme over Cr_2O_3-Al_2O_3 and Cr_2O_3 catalysts and to elucidate the nature of the active sites and the role of oxygen on the surface. These catalysts were suitable for the latter purpose because they are sensitive to reductive and oxidative pretreatments. In Part I (*4*) the activities of various Cr_2O_3-Al_2O_3 catalysts were studied. The activity pattern showed two maxima when plotted against Cr content, at 9.3% Cr and 100% Cr. Based on these results, the reaction mechanism has now been studied using these oxides as characteristic catalysts. 9.3% Cr_2O_3-Al_2O_3 is reducible, whereas Cr_2O_3 is irreducible (*4*).

EXPERIMENTAL METHODS

The reaction was carried out in a conventional gas circulation system, the total volume of which was 274 cm^3. Except for the experiment of Fig. 1, the catalysts were pretreated in the following way, viz, pumping at 200°C for 1 hr under 10^{-4} Torr, prereduction with 300 Torr of H_2 at 300°C and pumping at 300°C for 1 hr under 10^{-4} Torr. Reaction runs were repeated several times between which no treatment other than pumping at the reaction temperature was done. Stationary activity was established after several runs, indicating that no further change in oxidation state of the surface occurs. Such a surface is hereafter termed "stationary surface." The reaction was carried out at 200°C where mass transfer from the bulk gas stream to the surface of the catalyst did not affect the global rate.

$^{15}NH_3$ was obtained from the reaction of $(^{15}NH_4)_2SO_4$ with KOH. An aqueous solution of KOH was poured on ^{15}N-ammonium sulfate powder first at room temperature and afterwards at 50–60°C. The liberated $^{15}NH_3$ was trapped and then was subjected to the same treatments for the purification as described in Part I (*4*). The stated value for the isotope concentration of ^{15}N in ammonium sulfate was 96%.

Other experimental details are given in Part I (*4*).

RESULTS AND DISCUSSION

Rate Equation

The effects of initial pressure on the initial rate of reaction at 200°C were studied for the two catalysts over the range of $P_{NO} = 50$–300 Torr and $P_{NH_3} = 50$–300 Torr. These results established power rate expressions as follows:

$$r = kP_{NO}^{1.0}P_{NH_3}^{0} \quad \text{for 9.3\% } Cr_2O_3\text{-}Al_2O_3,$$

$$r = k'P_{NO}^{0.7}P_{NH_3}^{0.2} \quad \text{for } Cr_2O_3.$$

Isotope-Labeling Studies over Prereduced Catalyst

Isotope distributions in the products, nitrogen and nitrous oxide, as a function of

TABLE 1

Isotope Distributions in Nitrogen-Containing Products in the Reaction of $NO + \bar{N}H_3$ over Prereduced 9.3% Cr_2O_3–Al_2O_3[a]

Run No.	Time (min)	Product distribution (%)				$\frac{3[\bar{N}NO] + [\bar{N}N]}{2[NN] + [NNO]}$
		$\bar{N}N$	NN	NNO	$\bar{N}NO$	
1	10	39.1	39.4	21.4	0.0	0.39
	20	42.9	35.9	21.2	0.0	0.46
	40	45.6	31.8	22.6	0.0	0.52
	60	47.1	29.7	23.2	0.0	0.57
2	10	56.2	20.6	23.2	0.0	0.92
	20	59.0	18.2	22.8	0.0	1.00
	40	62.2	14.8	23.0	0.0	1.18
	60	64.0	12.2	23.8	0.0	1.33
3	10	56.3	21.3	22.4	0.0	0.87
	40	64.3	13.0	22.7	0.0	1.32
	60	65.3	11.4	23.3	0.0	1.42
4	10	64.7	15.3	20.0	0.0	1.28
	20	64.2	14.6	21.2	0.0	1.27
	40	70.7	12.2	17.1	0.0	1.70
	60	68.7	9.5	21.8	0.0	1.68

[a] Reaction temperature, 200°C; catalyst: 9.3% Cr_2O_3–Al_2O_3, 1.0 g, prereduced with 300 Torr of H_2 at 300°C for 1 hr; initial pressures: $P_{NO} = 100$ Torr, $P_{\bar{N}H_3} = 50$ Torr.

reaction time and of run number are listed in Table 1 for Cr_2O_3–Al_2O_3 and in Table 2 for Cr_2O_3, respectively.

The key features of the results for 9.3% Cr_2O_3–Al_2O_3 are as follows. (i) The main products are $\bar{N}N$ and NNO. $\bar{N}\bar{N}$, $\bar{N}NO$, or $\bar{N}\bar{N}O$ is hardly found. NN was also found, especially in the first run. (ii) The isotopic composition of the products is affected by the oxidation state, i.e., the composition is dependent on the number of runs as well as on reaction time. These qualitative features are similar to those found for Fe_2O_3–Al_2O_3 catalyst (*3*).

While the ratio, $\bar{N}N$/NNO, was found to be equal to 2 for the reaction over the stationary surface of Fe_2O_3–Al_2O_3 (*3*), this ratio was higher than 2 over Cr_2O_3–Al_2O_3. It was confirmed from separate experiments that N_2 was produced from the decomposition of N_2O or the reaction of $N_2O + NH_3$, although the extent to which the reaction occurs over the stationary surface was rather small. The reaction of N_2O with a reduced surface was also confirmed to be significant. Since reduction of the surface was expected to take place during the pumping, this reaction may influence the ratio, $\bar{N}N$/NNO. Hence, the ratio is not a decisive parameter in theis case. The amount of NN was largest for the first run for which the catalyst was pretreated with H_2.

The results for Cr_2O_3 are given in Table 2. The general feature is similar in that the main products are $\bar{N}N$ and NNO. Nevertheless, there are some significant differences between the results for 9.3% Cr_2O_3–Al_2O_3 and Cr_2O_3. No NN was found, indicating that the decomposition of NNO hardly occurs over Cr_2O_3. On the other hand, $\bar{N}NO$, which was not produced over 9.3% Cr_2O_3–Al_2O_3, was observed to a considerable extent. These results were not

TABLE 2

Isotope Distributions in Nitrogen-Containing Products in the Reaction of NO + $\bar{\mathrm{N}}\mathrm{H}_3$ over Prereduced $\mathrm{Cr_2O_3}$[a]

Run No.	Time (min)	Product distribution (%)				$\frac{[\bar{\mathrm{N}}\mathrm{N}]}{2[\mathrm{NNO}] - 3[\bar{\mathrm{N}}\mathrm{NO}]}$	$\frac{3[\bar{\mathrm{N}}\mathrm{NO}] + [\bar{\mathrm{N}}\mathrm{N}]}{2[\mathrm{NN}] + [\mathrm{NNO}]}$
		$\bar{\mathrm{N}}\mathrm{N}$	NN	NNO	$\bar{\mathrm{N}}\mathrm{NO}$		
1	10	59.0	0.0	35.3	5.7	1.10	2.16
	20	59.3	0.0	34.8	5.9	1.14	2.21
	40	59.1	0.0	35.2	5.7	1.11	2.16
	60	57.9	0.0	36.4	5.7	1.04	2.06
2	10	60.1	0.0	35.8	4.1	1.01	2.02
	20	57.6	0.0	37.7	4.7	0.94	1.90
	40	61.8	0.0	33.0	5.2	1.02	2.35
	60	59.6	0.0	34.9	5.5	0.94	2.18

[a] Reaction temperature, 200°C; catalyst; $\mathrm{Cr_2O_3}$, 1.0 g, prereduced with 300 Torr of $\mathrm{H_2}$ at 300°C for 1 hr; initial pressures:; $P_{\mathrm{NO}} = 100$ Torr, $P_{\bar{\mathrm{N}}\mathrm{H}_3} = 50$ Torr.

dependent on the number of runs or reaction time.

The ratio, $(3\bar{\mathrm{N}}\mathrm{NO}+\bar{\mathrm{N}}\mathrm{N})/(2\mathrm{NN}+\mathrm{NNO})$ listed in Tables 1 and 2 gives the balance of reductant (H) and oxidant (O). The formulation is derived from the following considerations. Stoichiometric equations can be written as (c)–(f), but note that these are not elementary reaction steps from the kinetic point of view.

$$\mathrm{NO} + \mathrm{NH_3} = \bar{\mathrm{N}}\mathrm{NO} + 3\mathrm{H}, \qquad \text{(c)}$$

$$\mathrm{NO} + \bar{\mathrm{N}}\mathrm{H_3} = \bar{\mathrm{N}}\mathrm{N} + \mathrm{H} + \mathrm{H_2O}, \qquad \text{(d)}$$

$$\mathrm{NO} + \mathrm{NO} = \mathrm{NNO} + \mathrm{O}, \qquad \text{(e)}$$

$$\mathrm{NO} + \mathrm{NO} = \mathrm{NN} + 2\mathrm{O}. \qquad \text{(f)}$$

The formation of one $\bar{\mathrm{N}}\mathrm{NO}$ molecule, which comes from one NO and one $\bar{\mathrm{N}}\mathrm{H_3}$ molecule, requires three hydrogen atoms to be removed. In other words, 3 × [amount of $\bar{\mathrm{N}}\mathrm{NO}$ produced] corresponds to the amount of hydrogen atoms to be removed away. Only one hydrogen atom is produced in the formation of $\bar{\mathrm{N}}\mathrm{N}$, because the two other hydrogen atoms from $\bar{\mathrm{N}}\mathrm{H_3}$ couple with the oxygen atom from NO to produce $\mathrm{H_2O}$. Thus the numerator, $3\bar{\mathrm{N}}\mathrm{NO} + \bar{\mathrm{N}}\mathrm{N}$, means the net amount of H atoms. In the same way the denominator, $2\mathrm{NN} + \mathrm{NNO}$, gives the net amount of O atoms on the formation of NN and NNO.

If the ratio is equal to 2, no change in surface oxidation state takes place, because hydrogen and oxygen atoms combine with each other to form $\mathrm{H_2O}$. This is the situation taking place over the stationary surface. If, on the other hand, the value is smaller than 2, the amount of the oxidant is larger than that corresponding to stoichiometry and an excess amount of O atoms has been consumed for the oxidation of the surface. Note that no $\mathrm{H_2}$ or $\mathrm{O_2}$ was found in the product under any reaction conditions. As a matter of fact, the ratio for 9.3% $\mathrm{Cr_2O_3}$–$\mathrm{Al_2O_3}$ is far lower than 2 in the first run but it increases with the number of runs. It becomes closer to 2 in the fourth run, indicating that no further change in oxidation state occurs. It should be noted that the ratio is always lower in the first measurement of a run than in the final measurement of the preceding run (refer to run 2 row 4 vs run 3 row 1 and run 3 row 3 vs run 4 row 1), except for the comparison between the first and the second runs (run 1 row 4 vs run 2 row 1). This indicates that some reduction or desorption of oxygen occurs during the pumping. Since the values listed in Table 1 are integrated ones, it never becomes equal to 2 even if stationary surface is established after several minutes of reaction. This is the reason why the ratio was not exactly equal to but slightly less than 2. This ratio is, on the other hand, close to 2 for Cr_2O_3 from the very beginning. This corresponds to the finding (*4*) that Cr_2O_3 is hardly reduced under the condition given in (*4*, Fig. 3).

In summary, schemes (a) and (b) which were proposed before (*3*) are approximately valid for the reaction over the stationary surface of the catalysts. Over a prereduced 9.3% Cr_2O_3–Al_2O_3 catalyst, the reaction of NO is accompanied by oxidation of the surface. No such reaction takes place on a Cr_2O_3 catalyst.

Effect of Preoxidation

As described in Part I (*4*), either prereduction or preoxidation caused marked improvements in the catalytic activity. A detailed study on Cr_2O_3 catalyst is described here in order to clarify the nature of active sites. The procedure of the experiments was as follows. The catalyst was preoxidized with 300 Torr of O_2 at 300°C for 1 hr. After pumping for 30 min at the same temperature it was reduced with a known amount of H_2 for various lengths of time. The amount of H_2 reacted with the catalyst was determined from the decrease of the pressure. The system was evacuated again at 300°C for 30 min. Then, 150 Torr of NO and NH_3 were introduced and were subjected to reaction at 200°C. The rate of reaction was determined from the initial slope of conversion vs time plots.

Figure 1 illustrates the rate of N_2 formation or the initial N_2/N_2O ratio versus the amount of H_2 consumed during the pretreatments. The latter value is an index of the extent to which the catalyst is reduced from the fully oxidized state (hereafter termed "the extent of reduction").

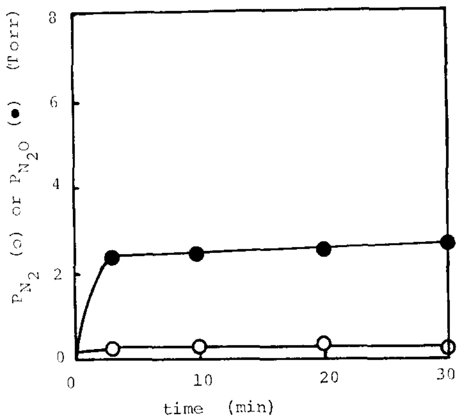


FIG. 2. The reaction of NO with the Cr_2O_3 surface. Reaction temperature, 200°C; catalyst: Cr_2O_3, 1.0 g; pretreatment of the catalyst: pumping for 1 hr after several reaction runs to establish a stationary surface.

The initial activity of the fully oxidized catalyst was so large that we could hardly determine the slope. As an illustration in Fig. 1, the slope was determined from the origin and first experimental point (3 min after the reaction was started). The catalytic activity reaches a stationary value after 5 min.

The initial activity decreased with the amount of consumed H_2 until the latter value reached 0.25 mmol/g-cat. Then it increased again, but slightly in the case of Cr_2O_3, with the extent of reduction. The value, 0.25 mmol/g-cat, might have some physical meaning, because the number of Cr_2O_3 "molecules" which are exposed on the surface is roughly estimated to be 0.28 mmol/g-cat. The estimated value was established from the density of Cr_2O_3, 5.2 g/cm^3 and an experimentally determined BET area, 23.5 m^2/g-cat (*4*). Since we do not know the crystallographic plane or number of oxygen atoms per unit lattice which is exposed on the surface, we could not put much emphasis on the rough coincidence, 0.25 vs 0.28 mmol/g-cat. What we can say with some certainty is that the oxidation–reduction considered here is regarded as a surface phenomenon: oxidation–reduction in the bulk solid is immaterial.

TABLE 3

Isotope Distributions in Nitrogen-Containing Products in the Reaction of NO + $\bar{\mathrm{N}}\mathrm{H}_3$ over Preoxidized $\mathrm{Cr_2O_3}$[a]

Time (min)	Product distribution (%)				$\frac{3[\bar{\mathrm{N}}\mathrm{NO}] + [\bar{\mathrm{N}}\mathrm{N}]}{2[\mathrm{NN}] + [\mathrm{NNO}]}$
	$\bar{\mathrm{N}}\mathrm{N}$	NN	NNO	$\bar{\mathrm{N}}\mathrm{NO}$	
5	91.1	0.0	1.2	7.7	95.2
30	72.5	0.0	15.0	12.5	7.3
60	67.3	0.0	20.0	12.6	5.3

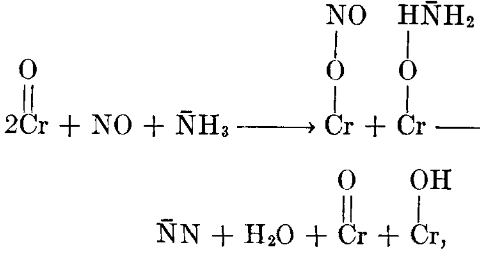
[a] Reaction temperature, 200°C; catalyst: $\mathrm{Cr_2O_3}$, 1.0 g, preoxidized with 300 Torr of $\mathrm{O_2}$ at 300°C for 1 hr; initial pressures: $P_{\mathrm{NO}} = 100$ Torr, $P_{\mathrm{NH_3}} = 50$ Torr.

The isotope labeling technique was applied for the reaction over the fully oxidized catalyst. It is apparent from the results listed in Table 3 that $\bar{\mathrm{N}}\mathrm{NO}$ is the major product, especially in the beginning. The initial products ratio, $\bar{\mathrm{N}}\mathrm{NO}/\mathrm{NNO}$, over the preoxidized catalyst, was as much as 6.4 while the value over the stationary catalyst was 0.16 (Table 2, run 2). The oxidant–reductant balance, $(3[\bar{\mathrm{N}}\mathrm{NO}] + [\bar{\mathrm{N}}\mathrm{N}])/(2[\mathrm{NN}] + [\mathrm{NNO}])$, was as much as 95, indicating the surface was reduced during the reaction.

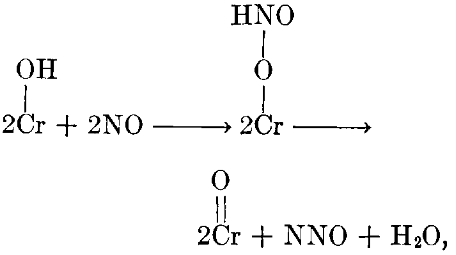
DISCUSSION

The significant improvement in the catalytic activity by preoxidation suggests that the active sites are surface oxygen. Additional evidence for this is the finding that a similar activity vs Cr content pattern was observed for both NO + $\mathrm{NH_3}$ and NO + CO reaction (*4*). The NO + CO reaction consists of at least two elementary steps (*3*, *5*): two NO molecules combine to form $\mathrm{N_2O}$ and/or $\mathrm{N_2}$ as a result of which one or more oxygen atoms are left on the surface (surface is oxidized). The oxidized surface is again reduced by CO and the catalytic sequence is completed. The rate determining step is considered (*5*) to be the second step, the reduction of the oxidized surface. Then, the rate is proportional to the amount of surface oxygen. If we assume the active sites in the NO + $\mathrm{NH_3}$ reaction are surface oxygen, the similarity in both reactions is acceptable because such a reaction rate is proportional to the number of active sites. This view also explains the findings reported by Markvard and Pour (*6*) that the existence of $\mathrm{O_2}$ enhances catalytic activity in the NO + $\mathrm{NH_3}$ reaction.

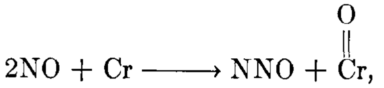
Hence, reaction schemes can be written in which the roles of the active sites are involved:



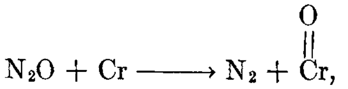
$$2\overset{\mathrm{O}}{\overset{\|}{\mathrm{Cr}}} + \mathrm{NO} + \bar{\mathrm{N}}\mathrm{H_3} \longrightarrow \overset{\mathrm{NO}}{\overset{|}{\overset{\mathrm{O}}{\overset{|}{\mathrm{Cr}}}}} + \overset{\mathrm{H\bar{N}H_2}}{\overset{|}{\overset{\mathrm{O}}{\overset{|}{\mathrm{Cr}}}}} \longrightarrow \bar{\mathrm{N}}\mathrm{N} + \mathrm{H_2O} + \overset{\mathrm{O}}{\overset{\|}{\mathrm{Cr}}} + \overset{\mathrm{OH}}{\overset{|}{\mathrm{Cr}}}, \quad (1)$$



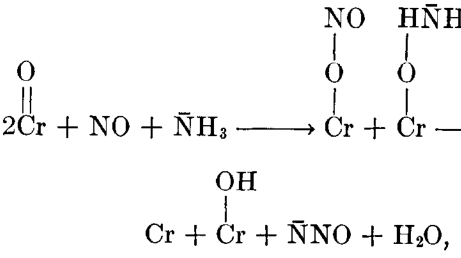
$$2\overset{\mathrm{OH}}{\overset{|}{\mathrm{Cr}}} + 2\mathrm{NO} \longrightarrow 2\overset{\mathrm{HNO}}{\overset{|}{\overset{\mathrm{O}}{\overset{|}{\mathrm{Cr}}}}} \longrightarrow 2\overset{\mathrm{O}}{\overset{\|}{\mathrm{Cr}}} + \mathrm{NNO} + \mathrm{H_2O}, \quad (2)$$



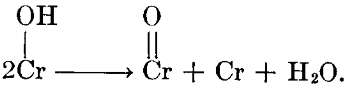
$$2\mathrm{NO} + \mathrm{Cr} \longrightarrow \mathrm{NNO} + \overset{\mathrm{O}}{\overset{\|}{\mathrm{Cr}}}, \quad (3)$$



$$\mathrm{N_2O} + \mathrm{Cr} \longrightarrow \mathrm{N_2} + \overset{\mathrm{O}}{\overset{\|}{\mathrm{Cr}}}, \quad (4)$$



$$2\overset{\mathrm{O}}{\overset{\|}{\mathrm{Cr}}} + \mathrm{NO} + \bar{\mathrm{N}}\mathrm{H_3} \longrightarrow \overset{\mathrm{NO}}{\overset{|}{\overset{\mathrm{O}}{\overset{|}{\mathrm{Cr}}}}} + \overset{\mathrm{H\bar{N}H_2}}{\overset{|}{\overset{\mathrm{O}}{\overset{|}{\mathrm{Cr}}}}} \longrightarrow \mathrm{Cr} + \overset{\mathrm{OH}}{\overset{|}{\mathrm{Cr}}} + \bar{\mathrm{N}}\mathrm{NO} + \mathrm{H_2O}, \quad (5)$$



$$2\overset{\mathrm{OH}}{\overset{|}{\mathrm{Cr}}} \longrightarrow \overset{\mathrm{O}}{\overset{\|}{\mathrm{Cr}}} + \mathrm{Cr} + \mathrm{H_2O}. \quad (6)$$

Here, surface oxygen is tentatively written as a double-bond type because such oxygen was considered to be a probable intermediate in the reaction of NO + CO (*7*).

If the catalytic reaction proceeds through Eqs. (*1*) and (*2*), the products are $\bar{N}N$ and NNO in which the ratio of $\bar{N}N$/NNO is equal to 2. This may be the case for the reaction over the stationary surface of 9.3% Cr_2O_3–Al_2O_3. However, another possibility should also be pointed out, namely that the combination of reactions (1), (3) and (6) also explains the above results. Applying the steady state condition to the surface, the ratio, $\bar{N}N$/NNO, should be equal to 2. Although the intermediate, HNO, was found over Pt–Al_2O_3 catalyst (*8*), no such information has yet been available for this system.

Over a prereduced surface, reactions (3) and (4) occur and the surface is gradually oxidized until a stationary state is established.

Over a preoxidized catalyst, reactions (5) and (6) take place predominantly. Either reaction (5) or the combination of (1) and (6), or both of them, is the mechanism by which the surface is reduced. These reactions are responsible for the large enhancement of rate which occurred in the first few minutes of the reaction.

As given in Table 2, such changes in the oxidation state of prereduced Cr_2O_3 are immaterial, because isotopic distribution of the products does not change with the number of runs and the hydrogen–oxygen balance was established from the very beginning. Nevertheless, $\bar{N}NO$ was found to a considerable extent, and is independent of reaction time as well as the number of runs. Since $\bar{N}NO$ formation is accompanied by a reduction of the surface, the surface oxidation process (3) should also take place in order to account for such stationary formation of $\bar{N}NO$. Figure 2 shows the results when NO alone was contacted with a stationary catalyst. The formation of N_2O was found in the beginning. Since there is no NH_3 in the system, the surface was completely oxidized after several minutes and the reaction ceased to occur.

In the steady state of the reaction, the surface concentrations of Cr=O, Cr–OH and Cr are constant, that is,

$$\frac{d[\mathrm{Cr{=}O}]}{dt} = -r_1 + 2r_2 + r_3 - 2r_5 + r_6 = 0, \tag{7}$$

$$\frac{d[\mathrm{Cr{-}OH}]}{dt} = r_1 - 2r_2 + r_5 - 2r_6 = 0, \tag{8}$$

$$\frac{d[\mathrm{Cr}]}{dt} = -r_3 + r_5 + r_6 = 0, \tag{9}$$

where r is the rate of reaction and the subscripts 1 to 6 refer to the reactions (1) to (6). Reaction (4) was neglected in this derivation because no formation of NN was observed. The combination of Eqs. (7) and (9) yields

$$\frac{r_1}{2(r_2 + r_3) - 3r_5} = 1. \tag{10}$$

The rates of the reactions are approximately related to the integral amounts of products.

$$[\bar{N}N] \simeq r_1, \tag{11}$$

$$[\mathrm{NNO}] \simeq r_2 + r_3, \tag{12}$$

$$[\bar{N}\mathrm{NO}] \simeq r_5. \tag{13}$$

Substituting r by the integral amounts of products,

$$\frac{[\bar{N}N]}{2[\mathrm{NNO}] - 3[\bar{N}\mathrm{NO}]} = 1. \tag{14}$$

Values are listed in Table 2 and are apparently close to unity.

The adsorbed species of NO and NH_3 in reactions (1) and (5) are tentatively written in the formulas. Figure 1 in Part I (*4*) shows that the inflection of the N_2 and N_2O formation vs reaction time occurred at the same point. This suggests that the active sites for the reaction (1) and (5) are the same and the selectivity, $\bar{N}N/\bar{N}NO$, is determined "by chance." This, however, is not a stringent test to clarify it, because the rate of reaction was so high that we could not determine the inflection point with good accuracy. Some possibility remains that the nature of oxygen atoms required to promote Eqs. (1) and (5) is different from each other.

Several uncertainties for the scheme remain: for instance (i) whether the surface oxygen responsible for the stationary activity is the same as or different from that for the initial high activity, and (ii) whether both reactants, NO and NH_3, or only one of them is activated on the surface oxygen. Studies to distinguish such possibilities are now in progress and will be presented in a forthcoming paper.

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