Catalytic Reductions of NO with H₂, CO or NH₃ over Supported Metal Oxide Catalysts*

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Summary: The roles of reducing agents such as H₂, CO and NH₃ in catalytic reduction of NO over supported metal oxide catalysts were studied from the viewpoint of reaction mechanisms. The reaction of NO with H₂ or CO was proved to proceed through the redox cycles of the catalyst, that is, catalyst was oxidized by NO and then was reduced, to complete the catalytic sequence by the reducing agents. On the other hand, it was confirmed that NH₃ or fragments of NH₃ directly reacted with the adsorbed NO.

These differences of the roles of reducing agents in the reaction mechanism satisfactorily explain some features of catalytic removal of NO in the practical process containing oxygen.

1 Introduction

The catalytic reduction of NO with H₂^{1)~3)}, CO^{1),4)} or NH₃^{1),5),6)} has been studied by many investigators. The roles of these reducing agents have been independently discussed both from theoretical and practical points of view. There are significant differences in several aspects among the reactions of NO with H₂, CO and NH₃. First, it is said¹⁾ that the reduction of NO in the presence of O₂ with H₂ or CO is "non-selective" reduction, because O₂ reacts simultaneously or predominantly with these reducing agents and then the main reaction is greatly retarded by it. On the other hand, the reduction of NO with NH₃ in the presence of O₂ is called "selective" reduction, since O₂ is not consumed or does not retard the main reaction even if it is consumed. Anderson⁶⁾ reported that the reduction of NO with NH₃ is rather enhanced by O₂. Secondly, both reactants contain nitrogen atom in the case of NO reaction with NH₃ while NO is the sole source of nitrogen in the other case.

One of the most important problems in these systems is whether the reaction proceeds through redox cycles of the catalyst or not. In the former scheme, catalyst was oxidized by NO and then it was reduced to complete the catalytic sequence by reducing agents. In the latter scheme, reactants or fragments of these were directly coupled on the surface. Oxidation state of the

surface did not change during one catalytic sequence. With these considerations in mind, the roles of reducing agents in these reaction systems were respectively studied here from viewpoints of reaction mechanisms.

2 Experimental

Catalyst: Fe₂O₃-γ-Al₂O₃ was prepared by impregnating γ-alumina which was obtained from commercially available alumina sol-200 (Nissan Chem. Co.) with ferric nitrate. The atomic ratio of Fe/Al was 5/95. It was calcined at 650°C for 1 hr. Prereduction of catalyst with H₂ was done at 500°C for 1 hr just before use. CuO-γ-Al₂O₃ was prepared and pretreated by the similar way.

NO+H₂ Reaction: Activity test was done using a conventional flow method. Special attention was paid for eliminating impurities in He or H₂, carrier gas in the pulse reactions. This was established by using two molecular sieve traps in series cooled with liquid N₂. The apparatus was made of glass in order to avoid leakage from junctions. Effluents were first trapped in a column of Porapak Q for 10 min and then was analyzed by taking off the liquid N₂ bath.

A reduction rate of the catalyst and also the rate of reaction (NO+H₂) which was compared with the former were measured in a closed gas recycling apparatus.

NO+CO Reaction: The reaction was done in a flow method.

Numbers of sites being available was evaluated by oxygen titration as follows. The reaction

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under steady state was interrupted by replacing reactants mixture with purified He. A fixed amount of O₂ was then introduced at the same temperature and the consumption of it was determined by a thermal conductivity detector.

NO + NH₃ Reaction: The reaction was done in a closed gas recycling apparatus. Liberated H₂O was eliminated by KOH-packed column. The rate of reaction was calculated from gas chromatographic analysis of produced N₂ and N₂O and also pressure decrease as well.

3 Results and Discussion

3.1 Reaction of Nitric Oxide with Hydrogen²⁾

Plots of the yields of N₂ and N₂O against contact times showed the characteristic feature of consecutive reaction, that is, NO → N₂O → N₂. This was especially emphasized here because quite different feature was found in the reaction of NO with NH₃.

When NO was introduced as a pulse in stream of He over a prereduced catalyst, N₂ and N₂O were produced. The yields decreased as numbers of pulses increased. From integrated amount of produced N₂ and N₂O, the numbers of reduced sites which were available to react with NO was calculated as 0.36 mmol/g.

If the reaction proceed through the redox scheme, the yield of N₂ and/or N₂O should be the same when either inert gas, He, or reducing agent, H₂, is used as a carrier gas. The results were given in **Table 1**. Practically the same yield was obtained in both atmosphere. It should be noted that inlet pulse is far smaller than the number of available sites. The reduction rate of the catalyst and the rate of reaction were given in **Fig. 1**. The initial rate of reaction over prereduced catalyst was higher but it reached a steady value after 15 min. The catalyst after 15 min of reaction was found to be completely oxidized.

The rate equation based on redox scheme, which will be discussed in the latter section, hold well. These observations suggest that the reaction

proceed through the redox scheme.

3.2 Reaction of Nitric Oxide with Carbon Monoxide

The rate of reaction of NO with CO depended on both partial pressures of NO and CO. The number of reduced sites as measured by oxygen titration was also dependent on them. The typical example was given in **Fig. 2**.

The rate equation was derived based on the following set of elementary steps.

Temperature : 300°C, Catalyst : Wt. 1 g
Pressures : NO 85 torr, H₂ 85 torr

Fig. 1 Reaction of NO + H₂ over Fe₂O₃-γ-Al₂O₃ and Reduction of the Catalyst with H₂

Catalyst : Fe₂O₃-Al₂O₃ (0.3g)
Reaction temperature : 380°C
W/F : 1.12 g·hr/mol
NO partial pressure : 0.03 atm

Fig. 2 Correlations of NO Conversion or the Amount of O₂ Absorbed by the Catalyst with Gaseous Pressure of CO

Table 1 Effects of Carrier Gas on the Pulse Reaction of NO or N₂O over Fe₂O₃-γ-Al₂O₃ at 250°C

Reactants	Conversion(%) in		W/F (g·min/ml)	Pulse Size (ml)
	He	H ₂		
NO	26	29	1.0 × 10 ⁻³	0.14
N ₂ O	65	68	2.0 × 10 ⁻³	0.7

Reaction temperature : 380°C
NO partial pressure : 0.03 atm
Catalyst : Fe₂O₃-γ-Al₂O₃

Fig. 3 Verification of Eq. (5) and (6)

Table 2 Kinetic Parameters Defined in Eq. (1)~(6) for the Fe₂O₃-γ-Al₂O₃ and the CuO-γ-Al₂O₃ Catalysts

Catalyst	Fe ₂ O ₃ -Al ₂ O ₃ ^{a)}	CuO-Al ₂ O ₃ ^{b)}
$2k_1k_2/(k_1+k_2)$ [atm ⁻¹ ·hr ⁻¹]	2.22×10^3	2.54×10^3
k_4 [atm ⁻¹ ·hr ⁻¹]	2.86×10^3	6.66×10^3
N_R/N_O ^{c)}	1.3	2.6
N	104 μmol	143 μmol

a) at 350°C

b) at 250°C

c) N_O is number of oxidized sites, N_O=N-N_R.

$$r = \frac{2N \frac{k_1k_2}{k_1+k_2} k_4 P_{\text{NO}} P_{\text{CO}}}{\frac{2k_1k_2}{k_1+k_2} P_{\text{NO}} + k_4 P_{\text{CO}}} \quad (5)$$

$$N_R = \frac{Nk_1P_{\text{CO}}}{\frac{2k_1k_2}{k_1+k_2} P_{\text{NO}} + k_4 P_{\text{CO}}} \quad (6)$$

herein N_R is number of reduced sites and N is total number of sites. The validity of these equations were tested in **Fig. 3**. The similar analysis was also done for the same reaction over CuO-γ-Al₂O₃, which showed the highest activity in our studies. The kinetic parameters obtained from both catalytic reactions were listed in **Table 2**. These values were quite reasonable when redox properties of the catalysts were taken into consideration. The comparison confirms indirectly the validity of these analysis.

The rate of reduction of the catalyst with CO measured by the same method as given in **Fig. 3** was again in the same order of magnitude as the

Fig. 4 Conversion of NO or Fraction of N₂ in the Products against Time at Various Temperature

rate of reaction.

3.3 Reaction of Nitric Oxide with Ammonia

The reaction of NO with NH₃ took place at far lower temperature than the others did. The activity of the prereduced catalyst was extremely high, however, it showed a steady activity after the second run. The catalyst was oxidized by NO in the first run. This indicates that non-catalytic reaction of NO with reduced surface took place besides catalytic reaction of NO with NH₃. The catalyst showed the constant activity after the second run. The catalyst which had been used at least one run was thus called "stationary catalyst". When either NO or NH₃ was introduced over the stationary catalyst, the formation of N₂ and/or N₂O was hardly found. Followingly, the redox scheme which was valid in both NO+H₂ and NO+CO reaction is improbable in this case.

The selectivity defined as N₂/(N₂+N₂O) in the gas phase was high in the initial stage and then approached to 0.67 at any conditions as shown in **Fig. 4**. This phenomena are contrary to that observed in the reactions of NO+H₂ and NO+CO. This showed that further reduction of N₂O to N₂ hardly took place even at highest temperature. These findings were satisfactorily explained based on the following schemes which have been proposed by Otto and shelef⁵⁾.

Fig. 5 Verification of Eq. (12) and (13)

Eq. (7) may be divided into two elementary steps as given in the bracket. Eq. (10) shows the total stoichiometry. The total stoichiometry clearly showed why the selectivity approached to 0.67. The formation of N₂O in the initial stage is small because surface concentration of HNO is small. The following probable Langmuir-Hinshelwood rate equation was applied to the rate of N₂ formation, based on the assumption that surface reaction of NO with NH₃ is the rate determining step.

$$r = \frac{kK_{\text{NO}}K_{\text{NH}_3}P_{\text{NO}}P_{\text{NH}_3}}{(1 + K_{\text{NO}}P_{\text{NO}} + K_{\text{NH}_3}P_{\text{NH}_3})^2} \quad (11)$$

Eq. (11) is transformed to the following equations.

$$\left(\frac{P_{\text{NO}}}{r}\right)^{1/2} = \frac{1 + K_{\text{NH}_3}P_{\text{NH}_3} + K_{\text{NO}}P_{\text{NO}}}{(kK_{\text{NO}}K_{\text{NH}_3}P_{\text{NH}_3})^{1/2}} \quad (12)$$

$$\left(\frac{P_{\text{NH}_3}}{r}\right)^{1/2} = \frac{1 + K_{\text{NH}_3}P_{\text{NH}_3} + K_{\text{NO}}P_{\text{NO}}}{(kK_{\text{NO}}K_{\text{NH}_3}P_{\text{NO}})^{1/2}} \quad (13)$$

Linear relationships between $(P_{\text{NO}}/r)^{1/2}$ and P_{NO} at constant P_{NH_3} , and between $(P_{\text{NH}_3}/r)^{1/2}$ and P_{NH_3} at constant P_{NO} were obtained, as shown in **Fig. 5**. Heats of adsorption of NO and NH₃ and real activation energy were obtained to be 11.3 kcal/mol, 12.8 kcal/mol and 13.5 kcal/mol, respectively.

4 Conclusion

The roles of reducing agents in the catalytic reduction of NO were summarized in **Table 3**. The roles of H₂ or CO are to reduce the catalyst which has been preoxidized by NO. On the other hand, the roles of NH₃ are to couple directly with and abstract O-atom from NO.

As has been pointed out by many investigators, the reaction of NO with NH₃ proceeds at lower

Table 3 Reaction Mechanisms of NO Reduction with Various Reducing Agents over Fe- γ -Al₂O₃ Catalyst

Reducing Agents	Effect of O ₂ on the Reduction of NO	Reaction Mechanism	Reaction Temperature Range
H ₂	Non selective	Redox type	300~450°C
CO	Non selective	Redox type	300~450°C
NH ₃	Selective	L-H mechanism	150~200°C

temperature than the others do although, generally speaking, NH₃ is milder reducing agent than H₂ or CO. This fact explains here that the roles of NH₃ are different from those of H₂ or CO.

Roughly speaking, it is expected that the reducibility of the catalyst is a probable measure of catalytic activity in the reaction of NO with H₂ or CO. This was confirmed and reported elsewhere. On the other hand, catalytic activity in the reaction of NO with NH₃ showed no good relation with the reducibility of the catalysts. The activities of three partially reduced metal oxides, Fe₂O₃, CuO and NiO supported on Al₂O₃ are in the following order: Fe₂O₃ > CuO > NiO. It is contrary to the order of reducibility. The activity is probably related to the ability of dissociative adsorption of NH₃. This is reasonable considering the fact that Fe-Al₂O₃ is the active catalyst in NH₃ synthesis.

One of the probable explanations for the differences of selective and non selective reduction could be proposed here based on the differences in the reaction mechanisms. That is, oxidation step in the redox scheme (1)~(3) can be replaced by the oxidation of the catalyst with O₂ instead of NO or N₂O. This makes the reaction non-selective.

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