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Selective Reduction of Nitrogen Monoxide with Hydrogen on Pt/Al_2O_3 Containing a Metal Oxide

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By using a three-way catalyst containing a metal oxide, NO can be selectively converted to N_2 and N_2O without the formation of NH_3 even at the "rich" side of the air/fuel ratio. In order to elucidate the mechanism of this action of the added metal oxide, the NO–H_2 reaction on Pt–V_2O_5/Al_2O_3 catalyst was investigated using the pulse reaction technique. In the NO–H_2 reaction on Pt/Al_2O_3 catalyst, a significant amount of NH_3 was formed in the "rich" region of the reactants ($H_2/NO > 1$), although NO was completely removed. In the NO–H_2 reaction on the Pt–V_2O_5/Al_2O_3 catalyst, on the other hand, no NH_3 was formed even in the "rich" region of the reactants; in addition, NO was completely removed. During the NO–H_2 reaction on the Pt–V_2O_5/Al_2O_3 catalyst, the V_2O_5 in the catalyst was found to be reduced from V^{5+} to V^{4+}. The reaction of NO with NH_3 and the reaction of NH_3 or H_2 with Pt–V_2O_5 mixed catalysts for various states of mixing were also investigated. From these results, the NO–H_2 reaction on the Pt–V_2O_5/Al_2O_3 catalyst has been shown to be composed of the following three main steps: Step I, the formation of NH_3 by the reduction of NO with H_2 on Pt; Step II, the NO–NH_3 reaction on Pt to form N_2 or N_2O; and Step III, the reduction of V_2O_5 in the catalyst by H_2 which is accelerated by the "hydrogen spill-over." In the NO–H_2 reaction on Pt/Al_2O_3 catalyst, NO is first reduced to NH_3 in Step I and the NO–NH_3 reaction in Step II follows. In the "rich" region, the formation of NH_3 takes place more readily than the subsequent NO–NH_3 reaction. In the NO–H_2 reaction on the Pt–V_2O_5/Al_2O_3 catalyst, the formation of excess NH_3 is suppressed by the removal of hydrogen from Pt in Step III, and the NH_3 thus produced reacts with NO to form N_2 or N_2O selectively in Step II. The rates of Steps I, II, and III were also discussed in terms of the structure of the catalysts and composition of the reactants.

The three-way catalyst system is used for the simultaneous removal of nitrogen monoxide, carbon monoxide, and hydrocarbons in the automotive exhaust emissions.[1–5] This is done in a single bed of catalyst by controlling the air/fuel ratio within a region near the stoichiometric point, which is called the "window." The width of the "window" is usually very narrow; therefore, in order to control the air/fuel ratio within the "window," a feedback control system of the air/fuel ratio has been developed using an oxygen sensor.[3,6–14] The three-way catalyst coupled with this feedback control system, however, cannot fully control the fluctuation of the air/fuel ratio within the "window," and this brings about the incomplete removal of NO, CO, and hydrocarbons, and also the formation of NH_3. The development of a three-way catalyst with a broad "window" is therefore highly desirable. Although the supported Rh or Rh–Pt catalyst has a "window" with a broader width than the supported Pt or Pd catalyst,[15–19] a large demand for Rh cannot be met by supply because of the limited reserve of the resources.[4,20]

The three-way catalyst containing a metal oxide such as V_2O_5,[21] Re_2O_7,[22,23] MoO_3,[24] or CeO_2[25,26] has been shown to deal effectively with the fluctuation of the air/fuel ratio; thereby, the width of the "window" has been markedly broadened. The role of the added metal oxide has been considered as "oxygen storage."[27–29] However, further details of the mechanism of the action of the metal oxide added to the three-way catalyst have not been clarified. This may be due to the complexity of the system: (i) The automative exhaust gas contains many components, including NO, CO, H_2, hydrocarbons, SO_2, and water, which lead to very complex networks of elementary reactions on the catalyst, and (ii) the three-way catalyst containing the metal oxide has not been well characterized.

As a first step to the investigation of the mechanisms of the reactions involved in the automotive exhaust emissions control using a three-way catalyst containing a metal oxide, the purposes of this study were (i) to investigate whether the action of the added metal oxide for the selective reduction of NO can also be observed in the NO–H_2 reaction on Pt–V_2O_5/Al_2O_3 catalyst—a system which is much simpler than the real three-way catalyst system, and (ii) to reveal the action of the metal oxide in the NO–H_2 reaction on the Pt–V_2O_5/Al_2O_3 catalyst. The NO–H_2 reaction was investigated, since this reaction is one of the most important reactions in the "rich" region for the removal of NO,[30,31] and is mainly responsible for the formation of NH_3.[32] It should be noted that the rate of the reaction in the "rich" region is considered to be much slower than that in the "lean" region.[28] V_2O_5 was chosen as the metal oxide because (i) the structure of V_2O_5 on Al_2O_3 support has been well characterized[33] and (ii) it is one of the metal oxides which have been known to be excellent additives to the three-way catalyst.[21] A pulse reaction technique was employed in this study because this technique is useful for investigating the kinetic behavior of the reduction or oxidation process involved in the redox cycles of a catalyst.[34–36]

Experimental

Catalysts. Pt/Al_2O_3 catalyst (Pt loading was 0.5 wt%) was purchased from Nippon Engelhard Ltd. Pt–V_2O_5/Al_2O_3 catalyst was prepared by impregnating the Pt/Al_2O_3 particles (0.3—0.6 mm) with an oxalic acid solution of ammonium metavanadate, followed by drying and subsequent heating in a stream of O_2 at 773 K for 3 h. Unless otherwise specified, the content of V_2O_5 in the Pt–V_2O_5/Al_2O_3 catalyst was 9 wt%, although Pt–V_2O_5/Al_2O_3 with 36 wt% V_2O_5 loading was also used. A V_2O_5 was prepared by the thermal decomposition of ammonium metavanadate in an O_2 stream at 773 K for 3 h. A Pt/Al_2O_3–metal oxide(M) catalyst (the ratio of Pt/Al_2O_3 to the metal oxide was 1/1 in weight)was prepared by mixing powders of Pt/Al_2O_3 and the metal oxide in a mortar for 20 min without water. A Pt/Al_2O_3–V_2O_5(P) catalyst was obtained by mixing Pt/Al_2O_3 particles (0.3—0.6 mm) with an equal weight of V_2O_5 particles (0.3—0.6 mm) with a spatula, followed by shaking in a pulse reactor.

Reagents. Commercial NO (more than 99.5% purity), H_2 (99.99% purity), and NH_3 (99.9% purity) were used without further purification. He or Ar as a carrier gas was purified with a titanium metal sponge heated at 1023 K and a Molecular Sieve at room temperature.

Apparatus and Procedures. Experiments were conducted using a pulse reaction apparatus, the reactor consisting of a Pyrex glass tube (4 mm i.d.). Unless otherwise specified, experiments were carried out under the following conditions: The carrier gas flow rate was 87 cm^3-STP/min; the reaction temperature was 573 K; the total amount of a single pulse was 5 cm^3-STP; the concentration of NO in pulse was 2.3% which corresponded to the amount of NO 5.1 μmol; the concentration of H_2 was varied over the range 1.15—4.6%, which corresponded to the amounts of H_2 2.25—10.2 μmol; catalyst weights were 5—218 mg. Before introducing the reactant pulse, all catalysts containing a metal oxide were treated with an O_2 stream at 773 K for 30 min. Columns used for gas-chromatographic analysis were tetraethylenepentamine on Difron for NH_3, silica gel for N_2O, and Molecular Sieve type 13X for H_2, N_2, and NO; they were connected in an intermediate cell system.[37] Ar (in the case of He carrier) or N_2 (in the case of Ar carrier) was used as an internal standard.

Converions of NO (X_{NO}) and H_2 (X_{H_2}), yields of NH_3 (Y_{NH_3}), N_2 (Y_{N_2}), and N_2O (Y_{N_2O}), and selectivities to NH_3 (S_{NH_3}), N_2 (S_{N_2}), and N_2O (S_{N_2O}) were calculated from outlet amounts of NO (Q_{NO}), H_2(Q_{H_2}), NH_3 (Q_{NH_3}), N_2 (Q_{N_2}), and N_2O (Q_{N_2O}) as follows:

$$X_{NO} = 1 - Q_{NO}/Q_{NO}^{\circ}, \qquad (1)$$

$$X_{H_2} = 1 - Q_{H_2}/Q_{H_2}^{\circ}, \qquad (2)$$

$$Y_{NH_3} = Q_{NH_3}/Q_{NO}^{\circ}, \qquad (3)$$

$$Y_{N_2} = 2Q_{N_2}/Q_{NO}^{\circ}, \qquad (4)$$

$$Y_{N_2O} = 2Q_{N_2O}/Q_{NO}^{\circ}, \qquad (5)$$

$$S_{NH_3} = Y_{NH_3}/(Y_{NH_3} + Y_{N_2} + Y_{N_2O}), \qquad (6)$$

$$S_{N_2} = Y_{N}/(Y_{NH_3} + Y_{N_2} + Y_{N_2O}), \qquad (7)$$

$$S_{N_2O} = Y_{N_2O}/(Y_{NH_3} + Y_{N_2} + Y_{N_2O}), \qquad (8)$$

where Q°_{NO} and $Q^{\circ}_{N_2}$ are the amounts of NO and H_2 injected into the reactor.

The oxidation state of V_2O_5 in the catalysts before and after the pulse reaction was studied by ESR spectroscopy, using a JEOL ME 1X spectrometer.

Results

Effect of the H_2/NO Ratio on the NO–H_2 Reaction on Pt/Al_2O_3 and Pt–V_2O_5 Mixed Catalysts. Figures 1 and 2 show results of the NO–H_2 reaction on the Pt/Al_2O_3, Pt–V_2O_5/Al_2O_3, Pt–Al_2O_3/V_2O_5(M), and Pt/Al_2O_3–V_2O_5(P) catalysts at various inlet H_2/NO ratios. As is evident from Figs. 1 and 2, the catalytic properties of these catalysts changed significantly depending on the kind of catalysts and composition of the reactants. As shown in Fig. 1, X_{NO} varied with the

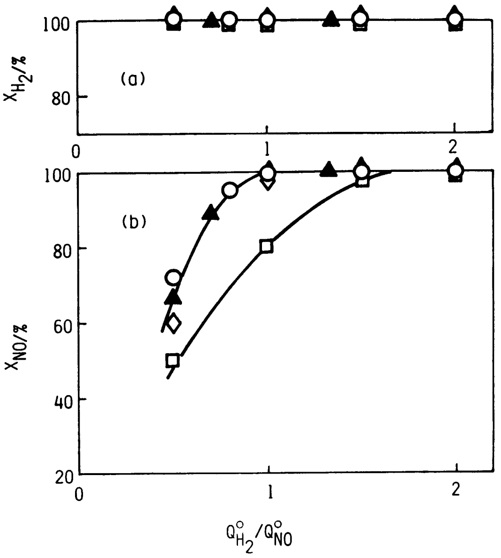


Fig. 1. Effect of the H_2/NO ratio on the conversions of NO (X_{NO}) and H_2 (X_{H_2}) in the NO–H_2 reaction on the Pt/Al_2O_3 and Pt–V_2O_5 mixed catalysts.
Catalyst weight: Pt/Al_2O_3 = 100 mg, Pt–V_2O_5/Al_2O_3 = 109 mg, Pt/Al_2O_3–V_2O_5 (M) = 200 mg, Pt/Al_2O_3–V_2O_5 (P) = 200 mg (Pt weight in catalysts = 500 μg). ▲: Pt/Al_2O_3, ○: Pt–V_2O_5/Al_2O_3, □: Pt/Al_2O_3–V_2O_5 (M), ◇: Pt/Al_2O_3–V_2O_5 (P).

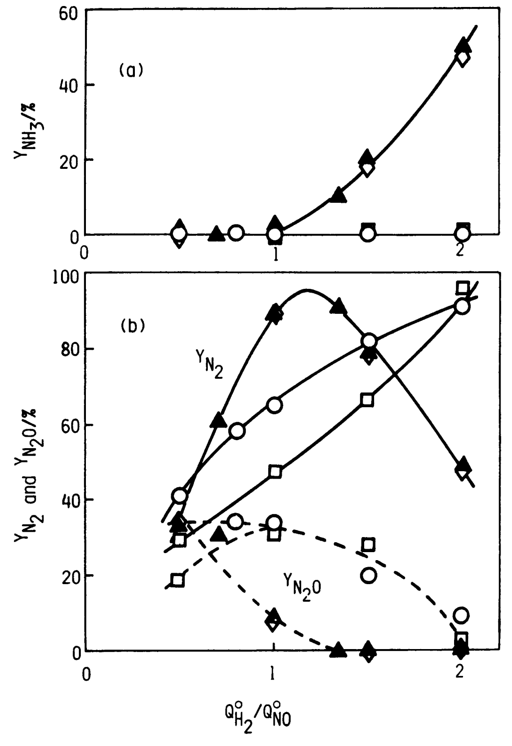


Fig. 2. Effect of the H_2/NO ratio on the yields of NH_3 (Y_{NH_3}), N_2 (Y_{N_2}), and N_2O (Y_{N_2O}) in the NO–H_2 reaction on the Pt/Al_2O_3 and Pt–V_2O_5 mixed catalysts.
Catalyst weight: Pt/Al_2O_3 = 100 mg, Pt–V_2O_5/Al_2O_3 = 109 mg, Pt/Al_2O_3–V_2O_5(M) = 200 mg, Pt/Al_2O_3–V_2O_5-(P) = 200 mg (Pt weight in catalysts = 500 μg). ▲: Pt/Al_2O_3, ○, Pt–V_2O_5/Al_2O_3, □: Pt/Al_2O_3–V_2O_5(M), ◇: Pt/Al_2O_3–V_2O_5(P), —: Y_{N_2}, ···: Y_{N_2O}.

$Q^{\circ}_{H_2}/Q^{\circ}_{NO}$ and the kind of catalysts, while the X_{H_2} was 100% for all of the catalysts indicated. X_{NO} for the Pt/Al_2O_3 catalyst was 100% when $Q^{\circ}_{H_2}/Q^{\circ}_{NO}$ was more than unity; that is, when $Q^{\circ}_{H_2}$ was greater than the stoichiometry ($Q^{\circ}_{H_2}/Q^{\circ}_{NO}=1$, that is, $H_2+NO=H_2O+1/2N_2$). As $Q^{\circ}_{H_2}$ decreased from the stoichiometry, X_{NO} for the Pt/Al_2O_3 catalyst decreased. X_{NO} for the $Pt–V_2O_5/Al_2O_3$ or $Pt/Al_2O_3–V_2O_5(P)$ catalyst was almost equal to X_{NO} for the Pt/Al_2O_3 catalyst at any $Q^{\circ}_{H_2}/Q^{\circ}_{NO}$, while X_{NO} for the $Pt/Al_2O_3–V_2O_5(M)$ catalyst was slightly lower than that for the Pt/Al_2O_3, $Pt/Al_2O_3–V_2O_5(P)$, or $Pt–V_2O_5/Al_2O_3$ catalyst especially in the "lean" region, *i.e.* $Q^{\circ}_{H_2}/Q^{\circ}_{NO}<1$. As shown in Fig. 2, in the "rich" region, *i.e.* $Q^{\circ}_{H_2}/Q^{\circ}_{NO}>1$, a considerable amount of NH_3 was produced in the NO–H_2 reaction on the Pt/Al_2O_3 catalyst, and Y_{NH_3} increased markedly with increasing $Q^{\circ}_{H_2}/Q^{\circ}_{NO}$. In the NO–$H_2$ reaction on the $Pt–V_2O_5/Al_2O_3$ and $Pt/Al_2O_3–V_2O_5(M)$ catalysts, no NH_3 was produced independent of the value of $Q^{\circ}_{H_2}/Q^{\circ}_{NO}$, while NO was almost selectively reduced to N_2 or N_2O as shown in Fig. 2(b). It should be emphasized that no NH_3 was produced even in the "rich" region, *i.e.* $Q^{\circ}_{H_2}/Q^{\circ}_{NO}>1$. Y_{NH_3}, Y_{N_2}, and Y_{N_2O} for the $Pt/Al_2O_3–V_2O_5(P)$ catalyst were almost the same as those for the Pt/Al_2O_3 catalyst. The V_2O_5 alone was not active for the NO–H_2 reaction under the experimental conditions of the present study.

ESR spectra of all the $Pt–V_2O_5$ mixed catalysts were measured before and after the reaction at $Q^{\circ}_{H_2}/Q^{\circ}_{NO}=1.5$ or 2.0. For the $Pt–V_2O_5/Al_2O_3$ and $Pt/Al_2O_3–V_2O_5(M)$ catalysts, the ESR intensity of V^{4+} ions in the used catalyst increased markedly compared with that in the fresh catalyst. For the $Pt/Al_2O_3–V_2O_5(P)$, on the other hand, the ESR intensity of V^{4+} ions in the used catalyst was the same as that in the fresh catalyst. The fresh $Pt–V_2O_5$ mixed catalysts were all yellow in color. The color of the used $Pt–V_2O_5/Al_2O_3$ and $Pt/Al_2O_3–V_2O_5(M)$ catalyst changed to black, but the color of the used $Pt/Al_2O_3–V_2O_5(P)$ catalyst remained yellow. These data indicate that the V_2O_5 in the $Pt–V_2O_5/Al_2O_3$ and $Pt/Al_2O_3–V_2O_5(M)$ catalysts was reduced during the NO–H_2 reaction in the "rich" region, *i.e.* at $Q^{\circ}_{H_2}/Q^{\circ}_{NO}=1.5$ or 2.0, while the V_2O_5 in the $Pt/Al_2O_3–V_2O_5(P)$ catalyst was not reduced.

Effect of the Catalyst Weight on the NO–H_2 Reaction. The NO–H_2 reaction in the "rich" region ($Q^{\circ}_{H_2}/Q^{\circ}_{NO}=1.5$) on the Pt/Al_2O_3, $Pt–V_2O_5/Al_2O_3$, and $Pt/Al_2O_3–V_2O_5(M)$ catalysts was investigated using various amounts of the catalysts. The results are shown in Figs. 3 and 4. Here, the weight of Pt in the catalyst gave the measure of the catalyst weight, since V_2O_5 was not active for the NO–H_2 reaction. Figure 3(a) shows the results of the Pt/Al_2O_3 catalyst. The maximum yield of NH_3 was attained when the Pt weight in the catalysts was *ca.* 25 µg, then Y_{NH_3} decreased gradually up to 50 µg, and it remained unchanged even with further increase of the Pt weight in catalyst. X_{NO} and X_{H_2} increased monotonically with increasing Pt weight in the catalyst, and attained 100% when the Pt weight was 50 µg. Figure 3(b) shows the results of the Pt–

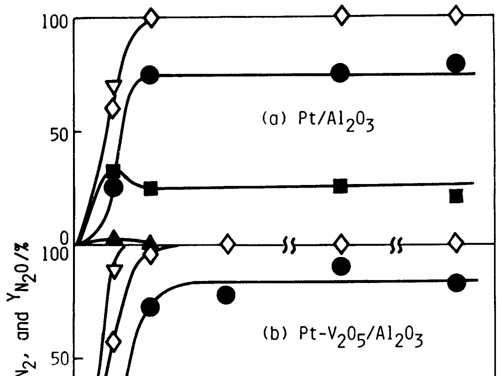


Fig. 3. Relationship between the Pt weight in the Pt/Al_2O_3 and $Pt–V_2O_5$ mixed catalysts and the activities and yields in the NO–H_2 reaction in the "rich" region ($Q^{\circ}_{H_2}/Q^{\circ}_{NO}=1.5$).
◇: X_{NO}, ▽: X_{H_2}, ■: Y_{NH_3}, ●: Y_{N_2}, ▲: Y_{N_2O}.

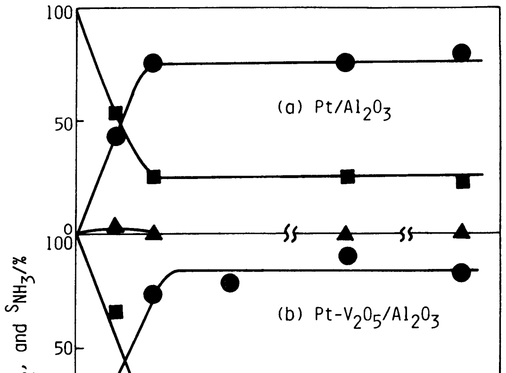


Fig. 4. Relationship between the Pt weight in the Pt/Al_2O_3 and $Pt–V_2O_5$ mixed catalysts and the selectivities in the NO–H_2 reaction in the "rich" region ($Q^{\circ}_{H_2}/Q^{\circ}_{NO}=1.5$).
■: S_{NH_3}, ●: S_{N_2}, ▲: S_{N_2O}.

V_2O_5/Al_2O_3 catalyst. Y_{NH_3} attained its maximum, which was almost the same Y_{NH_3} value as that for the Pt/Al_2O_3 catalyst when the Pt weight in the catalyst was *ca.* 25 μg, then decreased significantly with increasing Pt weight in the catalyst, and finally reached 0% when the Pt weight in the catalyst was 75 μg. The relationship between X_{NO} and the Pt weight was the same as that for the Pt/Al_2O_3 catalyst. However, X_{H_2} for the $Pt–V_2O_5/Al_2O_3$ catalyst was higher than that for the Pt/Al_2O_3 catalyst at the same Pt weight: For example, when the Pt weight in the catalyst was 25 μg, X_{H_2} for the $Pt–V_2O_5/Al_2O_3$ catalyst was about 90%, while X_{H_2} for the Pt/Al_2O_3 catalyst was about 70%. Figure 3(c) shows the results of the $Pt/Al_2O_3–V_2O_5$(M) catalyst. X_{NO}, X_{H_2}, Y_{NH_3}, Y_{N_2}, and Y_{N_2O} for the $Pt/Al_2O_3–V_2O_5$(M) were respectively in accord with those for the $Pt–V_2O_5/Al_2O_3$ catalyst. Figure 4 shows the results of S_{NH_3}, S_{N_2}, and S_{N_2O} at various catalyst weights. It is interesting to note that S_{NH_3} increased markedly with decreasing Pt weight in the catalyst in the region of low Pt weight (50 μg) and it was extrapolated to almost 100% when the Pt weight decreased to 0 μg. A similar relationship was also observed for the reaction in the "lean" region, while S_{NH_3} became 0 when the Pt weight in the catalyst was 50 μg.

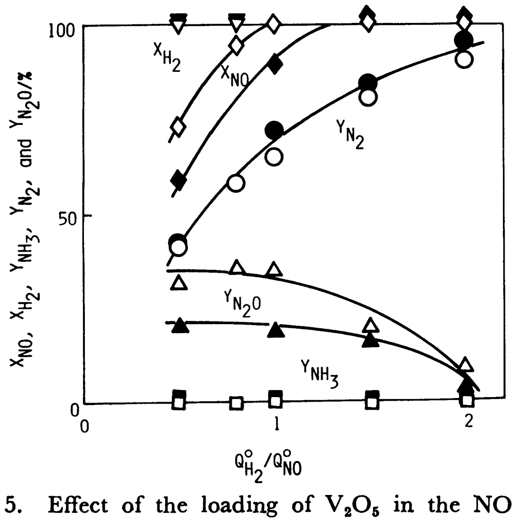


Fig. 5. Effect of the loading of V_2O_5 in the $NO–H_2$ reaction on various $Pt–V_2O_5/Al_2O_3$ catalysts.
Catalyst weight: $Pt–V_2O_5/Al_2O_3$ (9 wt% V_2O_5) = 109 mg, $Pt–V_2O_5/Al_2O_3$ (36 wt% V_2O_5) = 136 mg (Pt weight in catalysts = 500 μg). ◇, ◆: X_{NO}, ▽, ▼: X_{H_2}, □, ■: Y_{NH_3}, ○, ●: Y_{N_2}, △, ▲: Y_{N_2O}. Open symbols: $Pt–V_2O_5/Al_2O_3$ (9 wt% V_2O_5); closed symbols: $Pt–V_2O_5/Al_2O_3$ (36 wt% V_2O_5).

Effect of V_2O_5 Loading on the $NO–H_2$ Reaction on the $Pt–V_2O_5/Al_2O_3$ Catalyst. Figure 5 shows the results of the $NO–H_2$ reaction on the $Pt–V_2O_5/Al_2O_3$ catalysts with two different loadings of V_2O_5, 9 and 36 wt%. X_{H_2} was 100% irrespective of the V_2O_5 loading. X_{NO} for the $Pt–V_2O_5/Al_2O_3$ (36 wt% V_2O_5) was slightly lower than that for the $Pt–V_2O_5/Al_2O_3$ (9 wt% V_2O_5) when $Q^\circ_{H_2}/Q^\circ_{NO}$ was less than 1.5. NH_3 was not produced with either of the catalysts. Y_{N_2} was not significantly changed with the V_2O_5 loading, while Y_{N_2O} for the $Pt–V_2O_5/Al_2O_3$ (36 wt% V_2O_5) was slightly lower than that for the $Pt–V_2O_5/Al_2O_3$ (9 wt% V_2O_5).

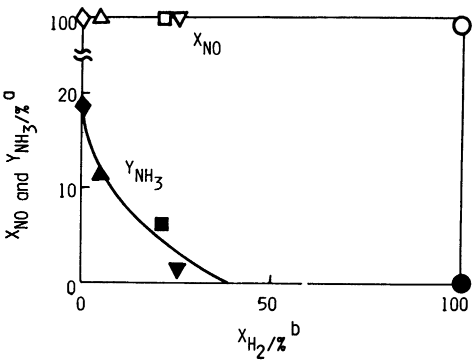


Fig. 6. Relationship between the conversion of NO (X_{NO}) and the yield of NH_3 (Y_{NH_3}) in the $NO–H_2$ reaction on various Pt–metal oxide(M) catalysts and the conversion of H_2 (X_{H_2}) in the reaction of H_2 with catalysts.
a: The $NO–H_2$ reaction, $Q^\circ_{H_2}/Q^\circ_{NO} = 1.5$, b: the reaction of H_2 with catalysts, concentration of H_2 in pulse = 3.7%. Catalyst weight; Pt/Al_2O_3 = 100 mg, Pt/Al_2O_3–metal oxide(M) = 200 mg (Pt weight in catalysts = 500 μg). ◇, ◆: Pt/Al_2O_3, △, ▲: $Pt/Al_2O_3–SnO_2$(M), □, ■: $Pt/Al_2O_3–WO_3$(M), ▽, ▼: $Pt/Al_2O_3–MoO_3$(M), ○, ●: $Pt/Al_2O_3–V_2O_5$(M). Open symbols: X_{NO}, closed symbols: Y_{NH_3}.

The $NO–H_2$ Reaction on Various Pt/Al_2O_3–Metal Oxide(M) Catalysts. Figure 6 shows the results of the $NO–H_2$ reaction on various Pt/Al_2O_3–metal oxide(M) catalysts at $Q^\circ_{H_2}/Q^\circ_{NO} = 1.5$; under this condition, X_{NO} was 100% for all of the catalysts and the metal oxide itself was inactive for either the $NO–H_2$ reaction or the reaction of H_2 (or NH_3) with the catalyst. Here, the results are represented as a relationship between Y_{NH_3} in the $NO–H_2$ reaction and X_{H_2} for the reaction of H_2 with the catalyst. As shown, Y_{NH_3} for the $NO–H_2$ reaction decreased monotonically with increasing X_{H_2} for the reaction of H_2 with the catalyst and it was 0% for the $Pt/Al_2O_3–V_2O_5$(M) catalyst.

The $NO–NH_3$ Reaction, and the Reaction of H_2 or NH_3 with the Catalysts. Table 1 shows the results of the $NO–NH_3$ reaction and those of the reaction of H_2 or NH_3 with the catalysts. These experiments were

Table 1. Activities of $Pt–V_2O_5$ mixed catalysts for various reactions at 573 K

Catalyst	Weight mg	Reaction $NO–NH_3$ b) X_{NO}/%	 H_2-catal c) X_{H_2}/%	 NH_3-catal d) X_{NH_3}/%
Pt/Al_2O_3	100 a)	89	0	0
$Pt–V_2O_5/Al_2O_3$	109 a)	88	100	57
$Pt/Al_2O_3–V_2O_5$(M)	200 a)	87	100	2
$Pt/Al_2O_3–V_2O_5$(P)	200 a)	85	0	2
V_2O_5	100	57	0	2

a) Pt weight in catalyst = 500 μg. b) The inlet NO/NH_3 ratio = 1/1 (the inlet concentration of NO in pulse = 2.5%). c) The reaction of H_2 with the catalyst; the inlet concentration of H_2 in pulse = 3.7%. d) The reaction of NH_3 with the catalyst; the inlet concentration of NH_3 in pulse = 2.5%.

Table 2. Conversion of H_2 in the reaction of H_2 with various Pt-V_2O_5 mixed catalysts at 573 K

Catalyst	Pt weight	V_2O_5 weight	X_{H_2}[a]
	μg	mg	%
Pt-V_2O_5/Al_2O_3(9 wt%V_2O_5)	25	0.5	12
Pt-V_2O_5/Al_2O_3(36 wt%V_2O_5)	25	1.8	14
Pt/Al_2O_3-V_2O_5(M)	25	5.0	19

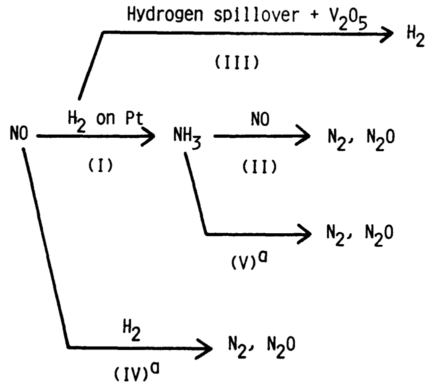
a) The concentration of H_2 in pulse=10% (22 μmol).

made because these reactions are considered to be important steps in the NO–H_2 reaction. As shown in Table 1, X_{NO} in the NO–NH_3 reaction was almost constant for the Pt/Al_2O_3, Pt-V_2O_5/Al_2O_3, Pt/Al_2O_3-V_2O_5(M), and Pt/Al_2O_3-V_2O_5(P) catalysts, while X_{NO} for the V_2O_5 was considerably lower than those for the former catalysts. This indicates that the activity of the Pt/Al_2O_3 catalyst for the NO–NH_3 reaction is not markedly increased by the addition of V_2O_5. X_{H_2} in the reaction of H_2 with the catalyst was 100% for both the Pt-V_2O_5/Al_2O_3 and Pt/Al_2O_3-V_2O_5(M) catalysts, while it was 0% with the Pt/Al_2O_3, Pt/Al_2O_3-V_2O_5(P), or V_2O_5 catalyst. Table 2 also shows the results of X_{H_2} in the reaction of H_2 with the catalyst; the catalyst weight was considerably decreased in order to decrease the value of X_{H_2}. As shown, X_{H_2} was almost constant for the Pt-V_2O_5/Al_2O_3 (9 wt% V_2O_5), Pt-V_2O_5/Al_2O_3 (36 wt% V_2O_5), and Pt/Al_2O_3-V_2O_5(M) catalysts. These data indicate that the V_2O_5 in the Pt-V_2O_5/Al_2O_3 and Pt/Al_2O_3-V_2O_5(M) catalysts was reduced by H_2, while the V_2O_5 in the Pt/Al_2O_3-V_2O_5(P) or V_2O_5 catalyst was not reduced. The data of X_{NH_3} for the reaction of NH_3 with the catalyst (Table 1) indicate that this reaction occurred with the Pt-V_2O_5/Al_2O_3 catalyst, but NH_3 was not decomposed very much on the Pt/Al_2O_3, Pt/Al_2O_3-V_2O_5(M), Pt/Al_2O_3-V_2O_5(P), or V_2O_5 catalyst.

Discussion

Selective Reduction of NO with H_2 on the Pt-V_2O_5/Al_2O_3 Catalyst. A large amount of NH_3 is formed in the NO–H_2 reaction on Pt/Al_2O_3 catalyst.[32] The production of a large amount of NH_3 has also been confirmed in the NO–H_2–O_2 reaction on Pt/Al_2O_3 catalyst in the "rich" region.[31] These results are undesirable from the viewpoint of the selective reduction of NO to N_2 or N_2O. As shown in Fig. 2, for the NO–H_2 reaction on the Pt/Al_2O_3 catalyst, also, a significant amount of NH_3 was produced in the "rich" region of the reactant ($Q^\circ_{H_2}/Q^\circ_{NO}>1$), and the yield of NH_3 increased significantly with increasing $Q^\circ_{H_2}/Q^\circ_{NO}$. This is in accordance with the behavior in the NO–H_2 reaction[32] and in the NO–H_2–O_2 reaction[31] on Pt-Al_2O_3 catalyst. It is interesting that no NH_3 was produced in the NO–H_2 reaction on the Pt-V_2O_5/Al_2O_3 catalyst even in the "rich" region of the reactants; in addition, the conversion of NO was 100%. This behavior of the NO–H_2 reaction on the Pt-V_2O_5/Al_2O_3 catalyst is similar to that of the reaction of the synthetic exhaust gas on a three-way catalyst containing a metal oxide.[28] This indicates that the action of the added metal oxide for the selective reduction of NO to N_2 or N_2O can also be observed in the NO–H_2 reaction on Pt/Al_2O_3 catalyst containing V_2O_5—a system which is much simpler than the real three-way catalyst system.

Reaction Scheme. Although the scheme of the NO–H_2 reaction on the Pt/Al_2O_3 or Pt-V_2O_5/Al_2O_3 has not been well established, the previous data of the NO–H_2 reaction and NO–NH_3 reaction on Pt/Al_2O_3 and metal oxide catalysts lead to the reaction steps shown in Scheme I. Here, Step I is a process where NH_3 is produced by the NO–H_2 reaction on Pt.[32] Step II is a process where N_2 or N_2O is formed by the NO–NH_3 reaction on Pt/Al_2O_3[38,39] and V_2O_5.[40,41] Step III is a process where V_2O_5 is reduced by the reaction with hydrogen spilled over from Pt.[42–44] Step IV is a process where NO is directly reduced to N_2 or N_2O without the formation of NH_3 as an intermediate, and it is observed in the NO–H_2 reaction on some metal oxides.[41,45–47] Step V is a process where NH_3 is decomposed to N_2 on Pt or is oxidized by V_2O_5 to N_2 or N_2O and the latter is observed on Pt-V_2O_5/$BaSO_4$[48] and metal oxides.[49] Scheme 1 merely indicates some possible steps for the NO–H_2 reaction on the Pt/Al_2O_3, and Pt-V_2O_5/Al_2O_3 catalysts; therefore, it is necessary to investigate which of these Steps I—V play the main role in the NO–H_2 reaction on the Pt/Al_2O_3 and Pt-V_2O_5/Al_2O_3 catalysts.



Scheme 1. Mechanism of the NO–H_2 reaction on the Pt/Al_2O_3 and Pt-V_2O_5/Al_2O_3 catalysts. a: Step IV or V does not play an important role in the NO–H_2 reaction under the conditions of this study.

First, the scheme of the NO–H_2 reaction on the Pt/Al_2O_3 catalyst is discussed: Step III cannot play an important role on the Pt/Al_2O_3 catalyst because of the absence of the metal oxide. Step V is also negligible, since the decomposition of NH_3 did not occur on the Pt/Al_2O_3 (Table 1). According to Scheme 1, the primary products of the NO–H_2 reaction are determined by the relative rate of Step I to that of Step IV. From the results of S_{NH_3}, S_{N_2}, and S_{N_2O} shown in Fig. 4(a), Step IV is not considered to play a significant role in the NO–H_2 reaction on the Pt/Al_2O_3 catalyst. This is because S_{NH_3} is extrapolated to almost 100% when the Pt weight is decreased to 0. In other words, NH_3 formed by Step I is the main primary product of the NO–H_2 reaction on the Pt/Al_2O_3 catalyst. The formation of NH_3 for the reaction even in the "lean" region supports the validity of this conclusion. As the catalyst weight increases, Y_{NO} and S_{N_2} increase, while S_{NH_3} decreases [Fig. 4(a)]. According to Scheme 1, this is ascribable to the formation of N_2 by the reaction of the unreacted NO with the formed NH_3, that is, Step II. It is therefore considered that Steps I and II proceed successively in the NO–H_2 reaction on the Pt/Al_2O_3 catalyst. This agrees with the previous inference that NH_3 is an important intermediate for the reduction of NO in the synthetic exhaust emissions[50] or for the NO–H_2–O_2 reaction[31] on the Pt/Al_2O_3 catalyst.

Next, the scheme of the NO–H_2 reaction on the Pt–V_2O_5/Al_2O_3 catalyst is discussed. As mentioned above, the V_2O_5 in the Pt–V_2O_5/Al_2O_3 and Pt/Al_2O_3–V_2O_5(M) catalysts was reduced from V^{5+} to V^{4+} during the NO–H_2 reaction in the "rich" region; and these catalysts were effective for the selective reduction of NO to N_2 or N_2O in the "rich" region. On the other hand, the V_2O_5 in the Pt/Al_2O_3–V_2O_5(P) was not reduced during the NO–H_2 reaction; and this catalyst was not effective for the selective reduction of NO. From these results coupled with the data of the reaction of H_2 with the catalyst (Table 1), Step III is considered to proceed readily in the NO–H_2 reaction on the Pt–V_2O_5/Al_2O_3 and Pt/Al_2O_3–V_2O_5(M) catalysts. Similar to the case of the Pt/Al_2O_3 catalyst, S_{NH_3} for the Pt–V_2O_5/Al_2O_3 and Pt/Al_2O_3–V_2O_5(M) catalysts is extrapolated to almost 100% when the catalyst weight decreases to 0. This indicates that Step IV does not play an important role in the NO–H_2 reaction on the Pt–V_2O_5/Al_2O_3 or Pt/Al_2O_3–V_2O_5(M) catalyst; in other words, NH_3 is the main primary product of the NO–H_2 reaction. From the data of the reaction of NH_3 with the catalyst (Table 1), Step V can take place for the Pt–V_2O_5/Al_2O_3, but it proceeds on neither the Pt/Al_2O_3–V_2O_5(M) nor Pt/Al_2O_3–V_2O_5(P) catalyst. However, Step V also does not play an important role in the selective reduction of NO to N_2 or N_2O.[51]

Rates of Steps I and III. As mentioned above, the NO–H_2 reaction on the Pt–V_2O_5/Al_2O_3 catalyst is composed of Steps I, II, and III, and the consumption of hydrogen by Step III proceeding competitively with Step I at the upper part of the catalyst bed is the main factor for the selective reduction of NO in the "rich" region. According to Scheme 1, if the rate of Step III is much slower than that of Step 1, an excess amount of NH_3 is formed in Step I. Even if a part of the excess NH_3 is converted to N_2 or N_2O in Step II, a considerable amount of NH_3 is exhausted from the catalyst bed. According to Scheme 1, also, if the rate of Step III is much faster than that of Step I, the amount of NH_3 produced in Step I is not enough to convert NO completely to N_2 or N_2O in Step II; therefore, the unreacted NO is emitted from the outlet of the catalyst bed. If the rate of formation of NH_3 in Step I is successfully controlled by Step III, the NH_3 produced in Step I reacts with the unreacted NO to form N_2 or N_2O selectively (Step II). Therefore, it is important to investigate the rates of Steps I and III in terms of the composition of the reactants and structures of the catalysts. Although we have not conducted experiments to determine the rates of Steps I and III, $Q_{H_2}(I)$ and $Q_{H_2}(III)$ defined by Eqs. 9 and 10 would be useful as measures of the rates of Steps I and III.

$$Q_{H_2}(I) = Q^{\circ}_{NO}(5/2\ Y_{NH_3} + Y_{N_2} + 1/2\ Y_{N_2O}), \qquad (9)$$

$$Q_{H_2}(III) = Q^{\circ}_{H_2} \cdot X_{H_2} - Q_{H_2}(I). \qquad (10)$$

Each coefficient of Y_{NH_3}, Y_{N_2}, or Y_{N_2O} in Eq. 9 is determined by the stoichiometry of the formation of each product. As is evident from Eqs. 9 and 10, $Q_{H_2}(I)$ and $Q_{H_2}(III)$ are respectively the amounts of H_2 consumed by Steps I and III during the NO–H_2 reaction. Under the experimental conditions shown in Figs. 1, 2, and 5, X_{H_2} is 100%; therefore, Eq. 10 leads to Eq. 11 under the stated conditions.

$$Q_{H_2}(III) = Q^{\circ}_{H_2} - Q^{\circ}_{H_2}(I). \qquad (11)$$

$Q_{H_2}(I)$ and $Q_{H_2}(III)$ are calculated from the data of the NO–H_2 reaction shown in Figs. 1, 2, and 5. As shown in Figs. 7 and 8, $Q_{H_2}(I)$ for the Pt/Al_2O_3 is almost equal to $Q^{\circ}_{H_2}$ at any $Q^{\circ}_{H_2}/Q^{\circ}_{NO}$, while $Q_{H_2}(III)$ for the Pt/Al_2O_3 is very small, which means that almost all of the H_2 in the reactants are consumed by Step I. This is reasonable since Step III occurs only very slightly on the Pt/Al_2O_3 catalyst. As for the results of the Pt–V_2O_5/Al_2O_3 catalysts, $Q_{H_2}(I)$ is almost equal to $Q^{\circ}_{H_2}$ in the "lean" region of the reactants ($Q^{\circ}_{H_2}/Q^{\circ}_{NO}<1$). Correspondingly, the value of $Q_{H_2}(III)$ is very small in this region. In other words, in the "lean" region of the reactants, little H_2 is consumed in Step III but most of the H_2 is consumed in Step I. In the "rich" region of the reactants ($Q^{\circ}_{H_2}/Q^{\circ}_{NO}>1$), $Q_{H_2}(I)$ for the Pt–V_2O_5/Al_2O_3 catalyst is almost independent of $Q^{\circ}_{H_2}/Q^{\circ}_{NO}$, while $Q_{H_2}(III)$ increases markedly with increasing $Q^{\circ}_{H_2}/Q^{\circ}_{NO}$. This means that excess H_2 in the "rich" region is almost selectively removed by Step III, and hence the formation of excess NH_3 in Step I is suppressed. Such changes of $Q_{H_2}(I)$ and $Q_{H_2}(III)$ with $Q^{\circ}_{H_2}/Q^{\circ}_{NO}$ for the Pt–V_2O_5/

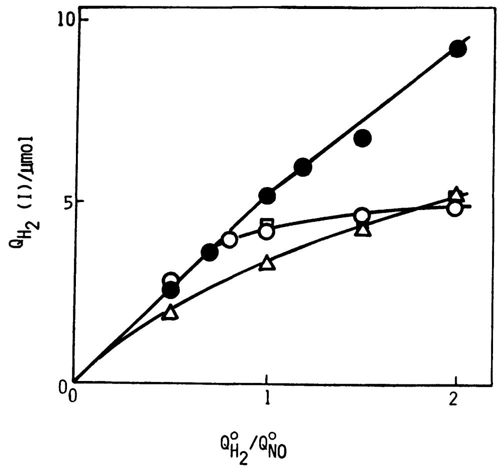


Fig. 7. Consumption of H_2 in Step I in the NO–H_2 reaction on the Pt/Al_2O_3 and various Pt–V_2O_5 mixed catalysts.
Catalyst weight: Pt/Al_2O_3=100 mg, Pt–V_2O_5/Al_2O_3 (9 wt% V_2O_5)=109 mg, Pt–V_2O_5/Al_2O_3 (36 wt% V_2O_5)=136 mg, Pt/Al_2O_3–V_2O_5(M)=200 mg (Pt weight in catalysts=500 µg). ●: Pt/Al_2O_3, ○: Pt–V_2O_5/Al_2O_3 (9 wt% V_2O_5), □: Pt–V_2O_5/Al_2O_3 (36 wt% V_2O_5), △: Pt/Al_2O_3–V_2O_5(M).

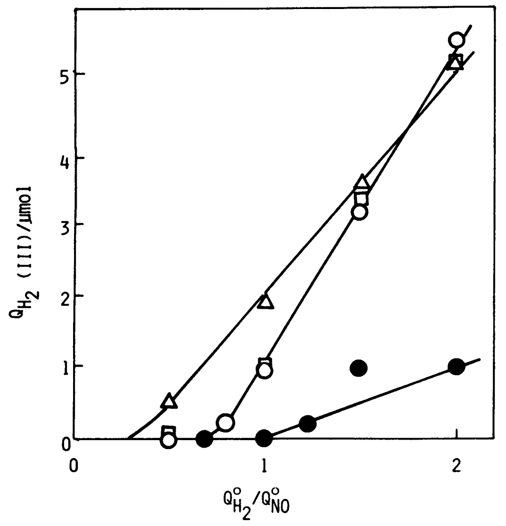


Fig. 8. Consumption of H_2 in Step III in the NO–H_2 reaction on the Pt/Al_2O_3 and various $Pt–V_2O_5$ mixed catalysts.
Catalyst weight: Pt/Al_2O_3 = 100 mg, $Pt–V_2O_5/Al_2O_3$ (9 wt% V_2O_5) = 109 mg, $Pt–V_2O_5/Al_2O_3$ (36 wt% V_2O_5) = 136 mg, $Pt/Al_2O_3–V_2O_5$(M) = 200 mg (Pt weight in catalysts = 500 µg). ●: Pt/Al_2O_3, ○: $Pt–V_2O_5/Al_2O_3$ (9 wt% V_2O_5), □: $Pt–V_2O_5/Al_2O_3$ (36 wt% V_2O_5), △: $Pt/Al_2O_3–V_2O_5$(M).

Al_2O_3 catalyst are desirable from the viewpoint of the selective reduction of NO. The reason for this is that, in the "lean" region, a reducing agent (H_2) is effectively used for the reduction of NO, whereas, in the "rich" region, an excess amount of reducing agent is removed by Step III and the formation of excess NH_3 is suppressed. In this manner, selective reduction of NO to N_2 or N_2O is warranted for a broad composition of the reactants. As shown in Fig. 7, Q_{H_2}(I) for the $Pt–V_2O_5/Al_2O_3$ is almost independent of $Q^{\circ}_{H_2}/Q^{\circ}_{NO}$ in the "rich" region of the reactants. This is in accordance with the behavior of the reduction of NO in the NO–H_2–O_2 reaction on Pt/Al_2O_3 catalyst.[31] According to the computer simulation of the NO–H_2–O_2 reaction on the Pt/Al_2O_3 catalyst,[31] the rate of the reduction of NO with H_2 is only slightly decreased even if the amount of adsorbed hydrogens on Pt surface is decreased by the addition of O_2 to the system.

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