CHEMISTRY LETTERS, pp. 935-938, 1979. Published by the Chemical Society of Japan

EFFECTS OF THE ADDITION OF METAL OXIDES ON THE REDUCTION OF NITRIC OXIDE WITH HYDROGEN ON Pt/Al_2O_3 CATALYST

Yukio KOSAKI, Akira MIYAMOTO, and Yuichi MURAKAMI
(Department of Synthetic Chemistry, Faculty of Engineering,
Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464)

The selectivity to NH_3 in the NO-H_2 reaction on Pt/Al_2O_3 has been markedly decreased by the addition of metal oxides. This effect has been found to be brought by the hydrogen spillover from Pt to metal oxides, and by a successive reaction of NH_3(the NO-NH_3 reaction) as an intermediate of the NO-H_2 reaction.

Attention is focused on the three-way catalyst system for the control of automotive exhaust emissions. This technique brings about the simultaneous removal of nitric oxide, carbon monoxide, and hydrocarbons in a single bed of supported metal catalyst by the use of an oxygen sensor in order to hold the air/fuel ratio at the stoichiometric point.[1)] However, unavoidable dynamic fluctuation of the air/fuel ratio around the stoichiometric point prevents a successful operation of the technique. In order to solve this problem, it is desired to give an oxygen storage ability to a supported metal catalyst.[2)] In this work, the effects of the addition of metal oxides on the reduction of NO by H_2 on Pt/Al_2O_3 catalyst have been investigated at the reducing inlet composition, since reactions involved in the real three-way catalyst consist of many complex ones and, among those, the reaction of NO with H_2(one of main reducing components at the reducing inlet composition of exhaust gas) is considered to be one of the most important reactions.

Method of preparation of metal oxides(V_2O_5, MoO_3, WO_3, and SnO_2) was described previously.[3)] Pt/Al_2O_3(Pt loading of 0.5 wt %) was purchased from Nippon Engelhard. Pt/Al_2O_3-metal oxide mechanical mixtures were prepared by mixing powder of equal amounts of both components in an agate mortar for 20 min without water(this is hereafter denoted as Mixing), or by shaking particles of both components(28 - 48 mesh)(this is denoted as Shaking). Experiments were carried out by an ordinary pulse apparatus. Helium or argon as carrier gas was purified with the titanium metal sponge heated at 750 °C, and a Molecular Sieve trap. The reaction temperature was 297 °C. Pulse size was 18.22 cm^3 and the inlet concentration of NO in pulse was 2.3 %. Carrier gas flow rate was 87 cm^3/min.

The metal oxides employed in this work were all found to be inactive for the NO-H_2 reaction, and not to be treated by H_2. Figure 1 shows the results of the NO-H_2 reaction on both Pt/Al_2O_3 and Pt/Al_2O_3-V_2O_5(Mixing). On Pt/Al_2O_3, when the ratio of the inlet concentration of H_2($C^\circ_{H_2}$) to that of NO(C°_{NO}) was larger than unity, i.e. at the reducing inlet composition, NH_3 was produced as a product, while NO was completely

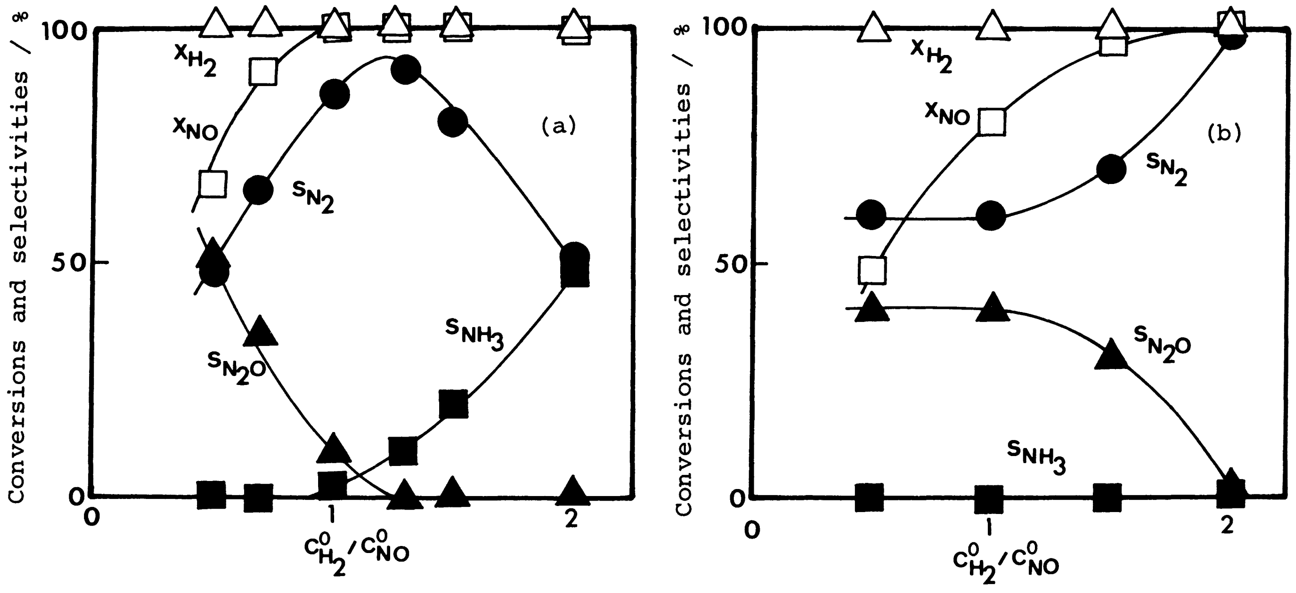


Figure 1. Conversions and selectivities in the NO-H_2 reaction on Pt/Al_2O_3 and Pt/Al_2O_3-V_2O_5(Mixing).
(a), Pt/Al_2O_3 = 0.1 g; (b), Pt/Al_2O_3-V_2O_5(Mixing) = 0.2 g.

removed. As $C^o_{H_2}/C^o_{NO}$ increased, the selectivity to NH_3(S_{NH_3}) increased and attained as high as 50 % at $C^o_{H_2}/C^o_{NO}$ = 2.0. These behaviors of each component are similar to those in the NO-H_2-O_2 reaction near the stoichiometric point.[4] On the other hand, on Pt/Al_2O_3-V_2O_5(Mixing), NH_3 was not produced in the whole range of the inlet composition indicated in Fig. 1, while the conversion of NO(X_{NO}) decreased slightly. It is therefore evident that the addition of V_2O_5 to Pt/Al_2O_3 is an effective way to control the formation of NH_3 in the "rich" region, i.e. $C^o_{H_2}/C^o_{NO} > 1$.

In order to study the mechanism of the effects of metal oxides on the reaction, following experiments were made: In Table 1, results of both the reaction of H_2 with mixing catalysts and the NO-H_2 reaction at the reducing inlet composition($C^o_{H_2}/C^o_{NO}$ = 2.0) are shown for various states of mixing. Since the enhanced rate of the reduction of a metal oxide by H_2 in a precious metal-metal oxide mixture is well documented in terms of the hydrogen spillover,[5] the conversion of H_2(X_{H_2}) in the reaction of H_2 with

Table 1. Relationship between the reaction of H_2 with mixtures and the NO-H_2 reaction

	The reaction of H_2 with catalyst[a]	The NO-H_2 reaction[b]			
Catalyst	X_{H_2}(%)	X_{NO}(%)	S_{NH_3}(%)	S_{N_2}(%)	S_{N_2O}(%)
V_2O_5(0.1 g)	0	0	-	-	-
Pt/Al_2O_3(0.1 g)	0	100	49	51	0
Pt/Al_2O_3-V_2O_5(Shaking) (0.2 g)	0	100	46	54	0
Pt/Al_2O_3-V_2O_5(Mixing) (0.2 g)	70	100	0	97	3

a), Conc. of H_2 in pulse = 3.7 %; b), Conc. of NO in pulse = 2.3 %($C^o_{H_2}/C^o_{NO}$ = 2.0).

the mixing catalysts can be used as a measure of the extent of the hydrogen spillover. From Table 1, it is noted that the hydrogen spillover did not occur in Pt/Al_2O_3-V_2O_5(Shaking), whereas, it did occur in Pt/Al_2O_3-V_2O_5(Mixing). In conformity with the behaviors of the hydrogen spillover, S_{NH_3} in the NO-H_2 reaction on Pt/Al_2O_3-V_2O_5(Shaking) was almost the same as that on Pt/Al_2O_3, while that on Pt/Al_2O_3-V_2O_5(Mixing) was completely decreased. Furthermore, as shown in Fig. 2, S_{NH_3} in the NO-H_2 reaction on Pt/Al_2O_3-metal oxide(V_2O_5, MoO_3, WO_3, or SnO_2)(Mixing) decreased with increasing X_{H_2} in the reaction of H_2 with the mixing catalysts, that is, the extent of the hydrogen spillover. These results indicate that the extent of the hydrogen spillover from Pt to metal oxides influences the selectivity to NH_3 in the NO-H_2 reaction on Pt in Pt/Al_2O_3-metal oxide mixing catalysts.

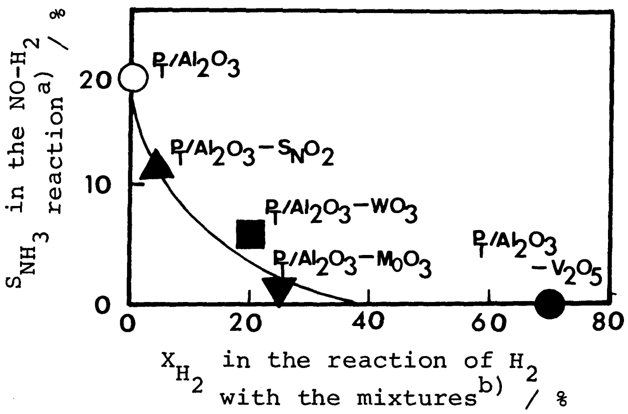
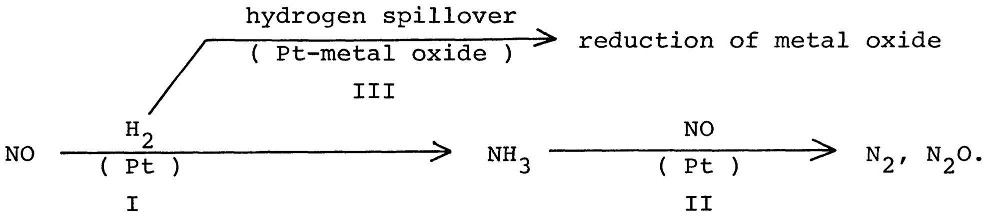


Figure 2. Relationship between X_{H_2} in the reaction of H_2 with Pt/Al_2O_3-metal oxide (Mixing) and S_{NH_3} in the NO-H_2 reaction.
Pt/Al_2O_3 = 0.1 g.
Pt/Al_2O_3-metal oxide(Mixing) = 0.2 g.
a), $C^\circ_{H_2}/C^\circ_{NO}$ = 1.5.
b), Concentration of H_2 in pulse = 3.7 %.

Figure 3 shows results of the NO-H_2 reaction on different amounts of catalyst for both Pt/Al_2O_3 and Pt/Al_2O_3-V_2O_5(Mixing). The data can be explained in terms of the following scheme:



According to this scheme, NO is first reduced by H_2 to NH_3(Step I) on Pt and NH_3 then reacts with NO(Step II; the NO-NH_3 reaction) on Pt to form N_2 and N_2O. This is in accordance with experiments, since the selectivity of the reaction to NH_3(S_{NH_3}) increases with decreasing catalyst weight(Fig. 3(a)). In the presence of metal oxide, Step III(that is, hydrogen spillover) takes place in addition of Steps I and II, and Step I and Step III proceed competitively. Near the inlet of catalyst bed($W < 0.01$ g), as shown in Fig. 3(b), the formation of NH_3 by Step I occurs readily and H_2 is markedly removed by both Steps I and III. At the following part of catalyst bed($W > 0.01$ g), Steps I and III scarcely take place because of the considerable decrease of H_2 concentration and the reaction of NO with NH_3(Step II) causes the complete removal of both NO and NH_3. In other words, when Pt/Al_2O_3 is mechanically mixed with the metal oxide, the hydrogen spillover(Step III) proceeds as fast as the formation of NH_3(Step I). This brings about a significant decrease of the selectivity to NH_3, while the conversion of NO is little decreased.

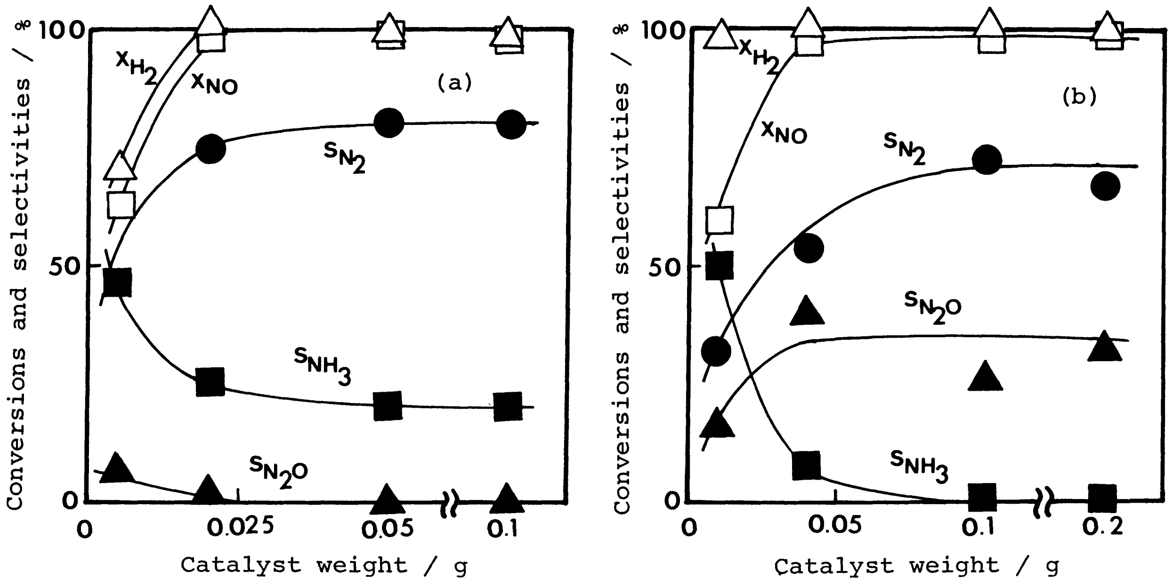


Figure 3. Conversions and selectivities in the NO-H_2 reaction on Pt/Al_2O_3 and Pt/Al_2O_3-V_2O_5(Mixing). (a), Pt/Al_2O_3; (b), Pt/Al_2O_3-V_2O_5(Mixing). $C^{\circ}_{H_2}/C^{\circ}_{NO} = 1.5$.

As mentioned above, the metal oxide in Pt/Al_2O_3-metal oxide(Mixing) is reduced at the reducing inlet composition to treat NO without the formation of NH_3 at the outlet of reactor. The reduced metal oxide in the mixing catalyst was then confirmed to be reoxidized by O_2 pulse. Similarly, the reduced metal oxide is considered to be readily oxidized by O_2 in the oxidizing composition of exhaust gas.2) In other words, the metal oxide in the mixing catalyst is reduced to remove excess H_2 by hydrogen spillover at the reducing inlet composition and is reoxidized to remove excess O_2 at the oxidizing inlet composition. Therefore, the oxidation state of the metal oxide in the Pt/Al_2O_3-metal oxide mixing catalyst is expected to be maintained after the whole cycle of the dynamic fluctuation of the inlet gas between reducing and oxidizing compositions. This means that the whole process can proceed catalytically with the redox cycle of the metal oxide according to the dynamic fluctuation of the composition of the inlet gas, suggesting that the addition of the metal oxide to supported metal catalyst is a promising way to deal with the dynamic fluctuation of the composition of exhaust gas.

REFERENCES

1) M. Shelef, Catal. Rev. 11, 1 (1975).
2) H. S. Gandhi, A. G. Piken, M. Shelef, and R. G. Delosh, SAE paper 760201 (1976).
3) Y. Murakami, Y. Kosaki, M. Motokawa, Y. Ooyabu, and A. Miyamoto, Nippon Kagaku Kaishi, 1977, 612.
4) A. Miyamoto, B. Inoue, and Y. Murakami, Ind. Eng. Chem. Prod. Res. Dev. (in press).
5) P. A. Sermon and G. C. Bond, Catal. Rev. 8, 211 (1973).

(Received May 1, 1979)