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# Two conversion maxima at 373 and 573 K in the reduction of nitrogen monoxide with hydrogen over $Pd/TiO_2$ catalyst

Atsushi Ueda[a,*], Takayuki Nakao[b], Masashi Azuma[b], Tetsuhiko Kobayashi[a]

[a]*Osaka National Research Institute, AIST, Midorigaoka 1-8-31, Ikeda, Osaka 563-8577, Japan*
[b]*Department of Applied Chemistry, Osaka Institute of Technology, Omiya 5, Asahi-ku, Osaka 535-1855, Japan*

## Abstract

Supporting Pt and Pd catalysts have been examined for the reduction of NO with $H_2$ in the presence of oxygen and moisture. All catalysts showed a conversion maximum in the NO reduction at around 373 K. An additional conversion maximum was found to appear at around 573 K over several metal oxides supporting Pd, and $Pd/TiO_2$ gave the highest conversion at around 573 K among the catalysts tested. In the reaction at 373 K, NO might be reduced directly by $H_2$ both on Pt and Pd catalysts to give $N_2$ and $N_2O$. At the conversion maximum of the $Pd/TiO_2$ catalyst at 575 K, however, in situ generated $NO_2$ seems to react with $H_2$. © 1998 Elsevier Science B.V. All rights reserved.

*Keywords:* Nitrogen monoxide; Reduction; Hydrogen; Palladium; Titania

## 1. Introduction

Ammonia and light hydrocarbons have been intensively studied as reductants for the catalytic removal of NO from exhaust gases. This is because these reductants can selectively react with NO even in the presence of $O_2$. Hydrogen can act as a reductant of NO on noble metal catalysts if the concentration of $O_2$ is low in the exhaust gases [1–3]. However, only few attempts have been reported for the NO reduction by $H_2$ in oxygen-rich conditions. This is because hydrogen is easily consumed in the simple combustion with $O_2$ [4,5]. Recently, zeolite supporting Pt has been reported to show a catalytic activity to this reaction at around 373 K [6].

Hydrogen, as well as light hydrocarbons and CO, is often contained in exhaust gases. It is, therefore, worthy to explore catalysts for the reduction of NO with $H_2$ in oxygen-rich conditions. In this study, metal oxides supporting Pt and Pd have been examined in the NO reduction with $H_2$ in order to compare the effect of support oxides on the reaction selectivity.

## 2. Experimental

The metal oxides used as supports were titania (Japan Aerosil, P-25, anatase with a specific surface area of $50\ m^2\ g^{-1}$), alumina (JRC-ALO7, a reference catalyst of the Catalysis Society of Japan, $\gamma$-$Al_2O_3$ with a specific surface area of $174\ m^2\ g^{-1}$), silica (silica gel 60 extra pure, Merk, with a specific surface area of $400\ m^2\ g^{-1}$), and magnesia (Ube Industries,

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*Corresponding author. Tel.: +81-727-51-9656; fax: +81-727-51-9630; e-mail: ueda@onri.go.jp

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MgO with a specific surface area of ca. 100 $m^2 g^{-1}$). The reagent grade $Pd(NO_3)_2$ and platinum acetylacetonate (Kishida) were used.

The support oxides were impregnated with aqueous solutions of palladium and platinum using a rotary evaporator. The precursors obtained were dried under vacuum for 18 h, and then calcined in air at 773 K for 5 h. The X-ray diffraction pattern of each sample before and after the reaction was measured using a Rigaku X-ray powder diffractometer (RINT 2000).

Catalytic activity measurements were carried out by using a fixed-bed flow reactor. A sample (300 mg) was placed in a quartz tube, heated to 573 K in 30 min in a stream of He at a rate of 100 $cm^3 min^{-1}$, and then was kept at 573 K for 30 min. The reactant gas mixture containing NO 1000 ppm, $H_2$ 3000 ppm, $O_2$ 5.0 vol%, and $H_2O$ 10 vol% in He background was passed through the catalyst bed at a flow rate of 100 $cm^3 min^{-1}$ unless otherwise stated. The catalyst temperature was monitored with a quartz-tube covered thermocouple contacting with the inlet part of the catalyst bed and was raised stepwise and maintained for 2 h at each temperature.

Reactants and products were analyzed with three gas chromatographs and a $NO_x$ meter. Oxygen and nitrogen were analyzed by a gas chromatograph (GC) (Yanaco G-2800) equipped with a thermal conductivity detector (TCD) and a column of molecular sieve 13X (5 m) kept at 313 K. Nitrous oxide ($N_2O$) was analyzed by a GC (Yanaco G-2800) equipped with TCD and a column of active carbon (3 m) kept at 373 K. Hydrogen was analyzed by a GC (Shimadzu GC-8A) equipped with TCD and a column of molecular sieve 13X (3 m) kept at 313 K. Nitrogen oxides (NO and $NO_2$) were analyzed with a chemiluminescent $NO_x$ meter (Yanaco CLS-88US). Calibration was done with a standard gas containing known concentrations of the components.

## 3. Results and discussion

The reduction of NO by $H_2$ was performed over metal oxides supporting Pt and Pd. Fig. 1 shows typical results of the NO conversion as a function of reaction temperature. The selectivity to the products is summarized in Table 1. Most of the catalysts tested showed the conversion maxima at around 373 K. The $Pt/Al_2O_3$ catalyst brought about the highest conversion of NO at this temperature, where the main product was $N_2O$. In this temperature region, the catalysts supporting Pt afforded higher conversions than those on the Pd catalysts. The conversion of $H_2$ reached 100% at temperatures higher than 423 K on all catalysts tested. Consumption of $H_2$ in the reaction with $O_2$ is one of the plausible explanations to a

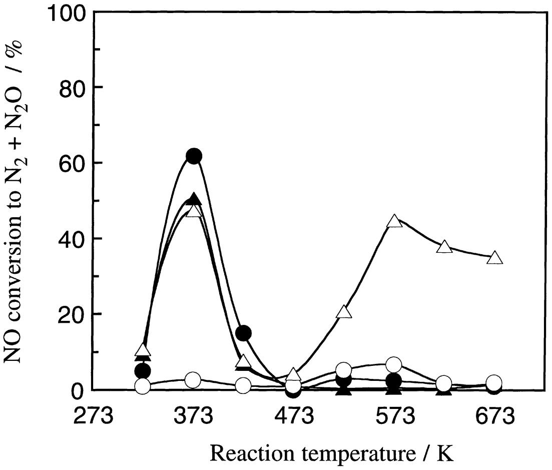

Fig. 1. Conversion of NO to $N_2$+$N_2O$ as a function of reaction temperature in the reduction of NO by $H_2$ over Pd and Pt catalysts. (○) $Pd/Al_2O_3$; (△) $Pd/TiO_2$; (●) $Pt/Al_2O_3$; (▲) $Pt/TiO_2$. The loading amount of Pd or Pt was 1 wt%. Reaction gas: 1000 ppm NO, 3000 ppm $H_2$, 5 vol% $O_2$, 10 vol% $H_2O$ in He background at a space velocity of 20 000 $h^{-1}$ ml g-catalyst$^{-1}$.

Table 1
Conversions of NO to $N_2$ and $N_2O$ in the reduction of NO by $H_2$ over Pd and Pt catalysts (the loading amount of Pt or Pd was 1 wt%; reaction gas: 1000 ppm NO, 3000 ppm $H_2$, 5 vol% $O_2$, and 10 vol% $H_2O$ with the balance He at a space velocity of 20 000 $h^{-1}$ ml g-catalyst$^{-1}$)

| Catalyst | Conversion of NO at 373 K to | | Conversion of NO at 573 K to | |
|---|---|---|---|---|
| | $N_2$ (%) | $N_2O$ (%) | $N_2$ (%) | $N_2O$ (%) |
| $Pd/TiO_2$ | 21.7 | 25.8 | 27.4 | 17.5 |
| $Pd/Al_2O_3$ | 2.7 | 0 | 2.1 | 0 |
| Pd/MgO | 7.8 | 5.4 | 8.1 | 3.7 |
| $Pd/SiO_2$ | 4.5 | 2.3 | 10.2 | 5.4 |
| $Pt/TiO_2$ | 10.5 | 40.1 | 0.6 | 0 |
| $Pt/Al_2O_3$ | 6.6 | 55.6 | 2.8 | 0 |
| Pt/MgO | 5.4 | 38.2 | 1.4 | 0 |

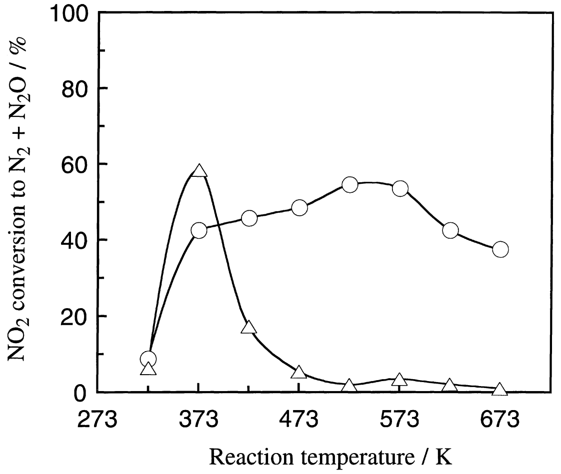

Fig. 2. Conversion of $NO_2$ to $N_2$+$N_2O$ as a function of reaction temperature in the reduction of $NO_2$ by $H_2$ over Pd/$TiO_2$ and Pt/$Al_2O_3$ catalysts. (○) Pd/$TiO_2$; (△) Pt/$Al_2O_3$. The loading amount of Pd or Pt was 1 wt%. Reaction gas: 1000 ppm $NO_2$, 3000 ppm $H_2$, 5 vol% $O_2$, and 10 vol% $H_2O$ in He background at a space velocity of 20 000 $h^{-1}$ ml g-catalyst$^{-1}$.

sudden drop in the NO conversion at temperatures higher than 373 K.

On the catalysts supporting Pd, however, an additional conversion maximum was observed at around 573 K (Fig. 1), showing higher selectivities to $N_2$ than to $N_2O$ (Table 1). The Pd/$TiO_2$ catalyst exhibited the highest activity at 573 K among the supporting Pd catalysts tested.

The reduction of $NO_2$, in place of NO, was compared between the Pd/$TiO_2$ and the Pt/$Al_2O_3$ catalysts. Fig. 2 shows the conversion of $NO_2$ as a function of reaction temperature. Even if $NO_2$ is used, the $H_2$ consumption by $O_2$ on Pt/$Al_2O_3$ seems to take place preferentially at temperatures higher than 373 K. On the other hand, the Pd/$TiO_2$ catalyst afforded a very widened window of the $NO_2$ conversion. This strongly suggests that the reduction of $NO_2$ by $H_2$ can proceed on Pd/$TiO_2$ in competition with the simple combustion of $H_2$ even at high temperatures.

The oxidation of NO by $O_2$ to $NO_2$ was tested on the Pd/$TiO_2$ and the Pt/$Al_2O_3$ catalysts. Results are shown in Fig. 3. Over both catalysts, the formation of $NO_2$ was observed at temperatures higher than 423 K, and the conversion maxima appeared at 573 K. The thermodynamic limitation brought about the lower $NO_2$ yields at higher temperatures. The temperature-dependency of the $NO_2$ formation is similar to that of the NO reduction on Pd/$TiO_2$ at temperatures between 473 and 673 K (Fig. 1).

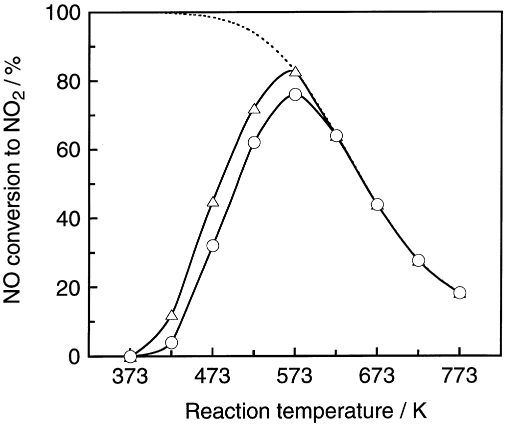

Fig. 3. Conversion of NO to $NO_2$ over Pd/$TiO_2$ and Pt/$Al_2O_3$ catalysts as a function of reaction temperature. (○) Pd/$TiO_2$; (△) Pt/$Al_2O_3$; dotted line denotes the equilibrium curve in the oxidation of NO by $O_2$. The loading amount of Pd or Pt was 1 wt%. Reaction gas: 1000 ppm NO, 5 vol% $O_2$, and 10 vol% $H_2O$ in He background as a space velocity of 20 000 $h^{-1}$ ml g-catalyst$^{-1}$.

Table 2

Rate for NO+$H_2$, $NO_2$+$H_2$, and $O_2$+$H_2$ reaction on Pd/$TiO_2$ and Pt/$Al_2O_3$ catalysts (the loading amount of Pd or Pt was 1 wt%; NO+$H_2$: 1000 ppm NO and 3000 ppm $H_2$ in He background; $NO_2$+$H_2$: 1000 ppm $NO_2$ and 3000 ppm $H_2$ in He background; $O_2$+$H_2$: 5.0 vol% $O_2$ and 3000 ppm $H_2$ in He background)

| Reaction | Rate on Pd/$TiO_2$ at 573 K (mol $s^{-1}$ g-cat$^{-1}$) | Rate on Pt/$Al_2O_3$ at 573 K (mol $s^{-1}$ g-cat$^{-1}$) |
|---|---|---|
| NO+$H_2$ | $6.1\times10^{-6}$ | $2.1\times10^{-5}$ |
| $NO_2$+$H_2$ | $4.1\times10^{-5}$ | $3.2\times10^{-5}$ |
| $O_2$+$H_2$ | $2.5\times10^{-5}$ | $6.4\times10^{-4}$ |

Rates of elementary reactions were measured on the Pd/$TiO_2$ and the Pt/$Al_2O_3$ catalysts at 573 K. The results are summarized in Table 2. On the Pd/$TiO_2$ catalyst, the reduction of $NO_2$ by $H_2$ is faster than the $O_2$+$H_2$ reaction, but the reduction of NO by $H_2$ is slower than the $O_2$+$H_2$ reaction. This indicates that the $NO_2$ formation is indispensable for the selective reduction of $NO_x$ on Pd/$TiO_2$. Appearance of the two conversion maxima at 373 and 573 K over the Pd catalysts should be due to a change of the reaction paths between the direct reduction of NO by $H_2$ and the reduction of in situ generated $NO_2$ by $H_2$. In the case of the $Pt/Al_2O_3$ catalyst, the rate of $NO_2$ reduction by $H_2$ is comparable to that on $Pd/TiO_2$, and is faster than the reduction of NO by $H_2$. However, the combustion of $H_2$ with $O_2$ is much faster than the reaction between $NO_2$ and $H_2$. This must be the reason of the poor selectivity of $Pt/Al_2O_3$ to the $NO_x$ reduction at around 573 K, although $NO_2$ can be formed on this catalyst.

The XRD measurements revealed that Pt exists as metallic state in the Pt catalysts but PdO was observed in the Pd catalysts before and after the reaction. The difference in the oxidation state of Pt and Pd might cause the large difference in the rate of $H_2$ consumption by $O_2$. Further study is needed to clarify the role of $TiO_2$ as a suitable support for PdO.

## 4. Conclusion

It was found that two conversion maxima appeared at 373 and 573 K in the reduction of NO by $H_2$ over supporting Pd catalysts. The $Pd/TiO_2$ catalyst exhibited the highest activity at 573 K among the supporting Pd catalysts tested. The appearance of two conversion maxima on the $Pd/TiO_2$ catalyst can be explained by a switch of the reaction path; a direct reduction of NO by $H_2$ at around 373 K and a reduction of in situ generated $NO_2$ by $H_2$ at around 573 K. Although $NO_2$ is also formed on $Pt/Al_2O_3$ at high temperatures, the reduction of $NO_2$ by $H_2$ is difficult to take place in preference to the $H_2$ combustion on this catalyst.

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