Two Reaction Paths at Different Temperatures in the Reduction of Nitrogen Monoxide with Hydrogen over Supported Palladium Catalysts

Atsushi Ueda,* Takayuki Nakao,† Masashi Azuma,† and Tetsuhiko Kobayashi
Osaka National Research Institute, AIST, Midorigaoka 1, Ikeda, Osaka 563
†*Department of Applied Chemistry, Osaka Institute of Technology, Omiya 5, Asahi-ku, Osaka 535*

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Two conversion maxima at 373K and 573K have been found to appear in the NO reduction with H_2 over metal oxides supporting Pd, when O_2 is present in the stream of reactants. At the lower temperature, NO directly reacts with H_2, but primarily produced NO_2 on the catalyst can successively react with H_2 in preference to the simple combustion of H_2 at the higher temperature.

Removal of nitrogen oxides (NOx) from the exhaust gases has been attractive interests for the prevention of the acid rain as well as the prevention of the photochemical air pollution. Usually, ammonia and hydrocarbons are used as reductants of NOx.[1] This is because these reductants can be active even in the presence of oxygen.[2,3] The exhaust gases often contain hydrogen as a reducing component. However, since hydrogen is easily consumed in the reaction with oxygen, it had been considered that hydrogen was difficult to be used as a reductant of NOx in the presence of oxygen. Recently, it has been shown that zeolite supporting Pt can catalyze the NO-H_2 reaction even when oxygen is present in the system.[4] Therefore, it is worthy to explore other catalysts for the selective reduction of NOx with hydrogen. In this letter, we will report that two conversion maxima appear at different temperatures in the NO reduction with hydrogen over supporting Pd catalysts when oxygen is present in the system.

The metal oxides used as supports were titania (Japan Aerosil Ltd., P-25, anatase with a specific surface area of 50 m^2g^{-1}), alumina (JRC-ALO7, a reference catalyst of the Catalysis Society of Japan, γ -Al_2O_3 with a specific surface area of 174 m^2g^{-1}), silica (silica gel 60 extra pure, Merk, with a specific surface area of 400 m^2g^{-1}), and magnesia (Ube Industries Ltd., MgO with a specific surface area of c. a. 100 m^2g^{-1}). The reagent grade $Pd(NO_3)_2$ and platinum acetylacetonate (Kishida Chemicals Ltd.) 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^3min^{-1}, and then was kept at 573K 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^3min^{-1}. 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 NOx 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 NOx meter (Yanaco CLS-88US). Calibration was done with a standard gas containing known concentrations of the components.

Figure 1 shows that the conversion of NO to N_2 and N_2O over supported Pt and Pd catalysts as a function of temperature. Over the Pt catalyst, conversion maxima appears at 373K. Higher reaction temperatures bring about a sudden decrease of the NO conversion. This behaviour of the Pt catalyst qualitatively coincids with that for the Pt-ZSM-5 catalyst.[4] At temperatures higher than 423K, the conversion of H_2 reached almost 100%. Consumption of hydrogen by a simple combustion with oxygen might be the reason of such a sudden decrease in the NO conversion at these temperatures.

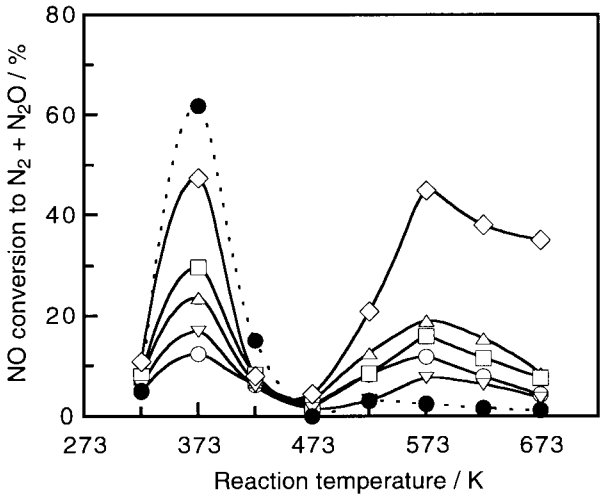

Figure 1. Conversion of NO to N_2 and N_2O as a function of reaction temperature in the reduction of NO with hydrogen over Pd supported on several metal oxides and Pt/Al_2O_3. ○, Pd/MgO ; △, Pd/BaO ; □, Pd/Mn_2O_3 ; ▽, Pd/CeO_2 ; ◇, Pd/TiO_2 ; ●, Pt/Al_2O_3. The loading amounts of Pd and Pt were 1wt%. Reaction gas; 1000ppm NO, 3000ppm H_2, 5vol% O_2, and 10vol% H_2O with the balance He at a space velocity of 20,000 h^{-1}ml/g-catalyst.

In the case of Pd catalysts, two conversion maxima of NO are clearly observed at 373K and 573K. Among the Pd catalysts

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Table 1. Conversions of NO to N_2 and N_2O in the reduction of NO with H_2 over Pd and Pt catalysts[a]

Catalyst	Conversion of NO at 373K			Conversion of NO at 573K		
	to N_2/%	to N_2O/%	to N_2+N_2O/%	to N_2/%	to N_2O/%	to N_2+N_2O/%
Pd/TiO_2	21.7	25.8	47.5	27.4	17.5	44.9
Pd/Al_2O_3	2.7	0	2.7	2.1	0	2.1
Pd/SiO_2	4.5	2.3	6.8	10.2	5.4	15.6
Pd/ZrO_2	6.5	9.3	15.8	10.2	8.0	18.2
Pd/MgO	7.8	5.4	12.4	8.1	3.7	11.8
Pd/SrO	7.4	6.4	13.8	12.1	5.4	17.5
Pd/BaO	13.5	10.1	23.6	14.5	4.5	19.0
Pd/SnO_2	17.2	12.5	29.7	10.5	5.4	15.9
Pd/La_2O_3	4.5	3.5	8.0	7.2	3.4	10.6
Pd/CeO_2	11.2	5.7	16.9	5.4	2.1	7.5
Pt/TiO_2	10.5	40.1	50.6	0.6	0	0.6
Pt/Al_2O_3	6.6	55.6	62.2	2.8	0	2.8
Pt/MgO	5.4	38.2	43.6	1.4	0	1.4
Pt/ZrO_2	4.8	29.4	34.2	2.5	0	2.5

[a]The loading amount of Pd or Pt was 1wt%. Reaction gas; 1000ppm NO, 3000ppm H_2, 5vol.% O_2, and 10vol.% H_2O with the balance He at a space velocity of 20,000 h^{-1}ml/g-catalyst.

tested, TiO_2 supporting Pd shows the highest conversion of NO. Table 1 summarizes the reaction selectivity to N_2 and N_2O. The formation of N_2O tends to be higher at the lower temperature. The Pd catalysts look more selective to the N_2 formation than the Pt catalysts.

At around 573K, NO is known to be oxidized to NO_2 by oxygen over noble metal catalysts.[5, 6] It was confirmed that NO_2 was formed both on the Pt and Pd catalysts and that the maximum of the NO_2 yield appeared at 550K under the present reaction condition (Table 2). The thermodynamic limitation of the NO_2 formation[5, 6] should be the lower NO_2 yield at higher temperatures. Thus, the reduction of NO_2, instead of NO, by H_2 was compared on the TiO_2 supporting Pd and the Al_2O_3 supporting Pt at 573K. The conversion of NO_2 to N_2 and N_2O on the Pd/TiO_2 catalyst was proved to be almost equal to that of NO. However, the conversion of NO_2 on the Pt/Al_2O_3 catalyst was less than 4%. This suggests that NO_2 can react with H_2 on the Pd catalysts in preference to the H_2 combustion but not on the Pt catalysts, though NO_2 is formed on both Pt and Pd catalysts at 573K. Appearance of the two conversion maxima at 373K and 573K over the Pd catalysts should be due to a switch of the reaction path between the direct reduction of NO by H_2 and the reduction of in-situ generated NO_2 by H_2.

Table 2. Conversions of NO to NO_2 in the oxidation of NO with O_2 over Pt/Al_2O_3 and Pd/TiO_2[a]

Reaction Temperature /K	Conversion of NO to NO_2		
	Pt/Al_2O_3	Pd/TiO_2	Eq.[b]
400	5.3	1.2	100
450	30.2	18.8	99.2
500	60.8	48.2	96.6
550	80.3	72.0	88.7
600	72.8	71.2	72.7
650	52.9	52.8	53.1

[a]The loading amount of Pd or Pt was 1wt%. [b] Equilibrium conversion to NO_2. Reaction gas; 1000ppm NO, 5vol.% O_2, and 10vol.% H_2O with the balance He at a space velocity of 20,000 h^{-1}ml/g-catalyst.

Palladium oxide, PdO, was detected in the Pd/TiO_2 catalyst by the XRD measurements before and after reaction. In the case of the Pt/Al_2O_3 catalyst, metallic Pt was confimed to exist after the reaction. Kinetic details of the elemental reaction steps have been currently studied and will be reported in a separate paper. Effects of the support oxides on the chemical state of Pd and hence on the reaction selectivity are also our concern.

References and Notes

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