

Highly Selective NH₃ Formation in a NO–CO–H₂O Reaction over Pt/TiO₂

Tetsuya Nanba,* Shouichi Masukawa, Junko Uchisawa, and Akira Obuchi
*National Institute of Advanced Industrial Science and Technology (AIST),
 Research Center for New Fuels and Vehicle Technology, 16-1 Onogawa, Tsukuba 305-8569*

(Received April 9, 2008; CL-080367; E-mail: tty-namba@aist.go.jp)

Pt/TiO₂ showed high selectivity toward NH₃ formation in the conversion of NO and CO in the presence of H₂O, higher than that observed for the reaction of NO with H₂.

A promising catalytic system for low-temperature nitrogen oxides abatement, de-NO_x, is selective catalytic reduction (SCR) by H₂, referred to herein as H₂-SCR. Platinum catalysts are known to exhibit activity at low temperatures in the presence of excess oxygen.¹ H₂-SCR could be used in de-NO_x of diesel exhaust, but the practical application of H₂-SCR is hindered because the H₂ content in diesel exhaust is very low, and providing an on-board hydrogen supply is not feasible in such cases. Recently, Nakatsuji et al. proposed a de-NO_x system that combines several catalytic reactions and the switching of engine operation between lean-burn and rich-burn conditions while simultaneously generating an on-board H₂ supply.² In this system, NO_x is first stored on platinum catalyst supports under lean-burn engine operation conditions. The stored NO_x then reacts with H₂ generated from the reaction of CO and H₂O (i.e., the water-gas shift (WGS) reaction: CO + H₂O → CO₂ + H₂) under rich-burn operation conditions. In this study, we investigated the role of the WGS reaction in the conversion of NO and CO in the presence of H₂O, a reaction referred to herein as the NO–CO–H₂O reaction. We demonstrate that Pt/TiO₂ exhibited high activity and extremely high NH₃ selectivity when used as a catalyst support in this reaction.

The catalysts used were 1 wt % Pt supported on transition-metal oxides, and catalysts were prepared by means of the incipient wetness method. H₂PtCl₆ (Kishida Chemical) was used as the precursor of Pt. The oxides used as supports were TiO₂ (P-25; Nippon-Aerosil), ZrO₂ (RSC-H; Daiichi-Kigenso), CeO₂ (Nacalai Tesque), SiO₂ (Wakogel C-100; Wako Pure Chemical Industries), and Al₂O₃ (KHS-46; Sumitomo Chemical). After Pt loading, the samples were calcined at 773 K for 4 h. Catalytic activity was measured by a conventional plug flow reactor. The weight of the catalysts was 0.1 g. To study the NO–CO–H₂O reaction, He feed gas containing 1100 ppm NO, 900–3100 ppm CO, and 0 or 1% H₂O was used at a flow rate of 100 mL·min^{−1}. Catalysts were treated in 10% H₂ at 573 K for 1 h before they were subjected to reactions. Product selectivity was calculated

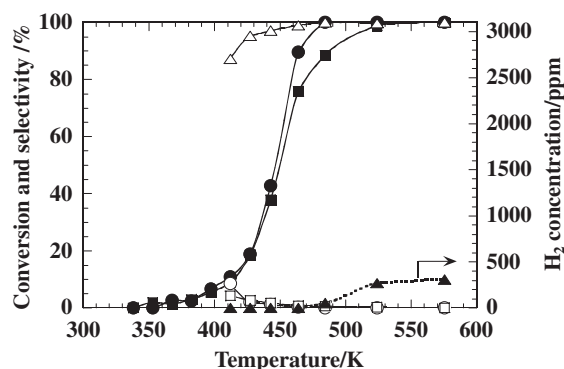


Figure 1. Temperature dependence of NO–CO–H₂O reaction over Pt/TiO₂. Catalyst weight was 0.1 g. Feed gas composition was 1100 ppm NO, 3100 ppm CO, and 1% H₂O. Total flow rate was 100 mL·min^{−1}. Symbols indicate NO (●) and CO (■) conversions, N₂ (○), N₂O (□), and NH₃ (△) selectivity, and H₂ concentration (---▲---).

at the temperature at which NO conversion was more than 10%. The details of this analysis were described previously.³

Figure 1 shows the extent of NO and CO conversion over Pt/TiO₂ as a function of temperature. The selectivity toward N₂, N₂O, and NH₃ formation as a function of temperature and the concentration of generated H₂ are also plotted in Figure 1. As shown in Figure 1, light-off temperature of NO and CO conversion was at 400 K, and NO conversion reached 100% at 483 K. It is noted that CO₂ formation was equivalent to the amount of CO converted. NH₃ was formed with very high selectivity, whereas the selectivities of N₂ and N₂O were lower than 10% at all measured temperatures. Furthermore, H₂ formation was observed at temperatures above 493 K, suggesting that the WGS reaction occurred simultaneously with the conversion of NO.

We confirmed that the conversion of NO and CO in the absence of H₂O (i.e., the NO–CO reaction) over Pt/TiO₂ was negligible at all temperatures investigated. CO conversions in the WGS reaction in the absence of NO were 52, 86, and 98% at 473, 523, and 573 K, respectively, and we confirmed that the amount of H₂ formed was equivalent to the amount of CO

Table 1. Activities of Pt/TiO₂ for NO–CO–H₂O and NH₃ selectivity in NO–H₂ reaction^a

CO conc. /ppm	NO conversion/%			CO conversion/%			NH ₃ selectivity/% ^b		
	373 K	423 K	473 K	373 K	423 K	473 K	373 K	423 K	473 K
3100	3	17	90	2	16	76	— (71)	94 (94)	99 (99)
1900	7	75	100	8	83	100	— (55)	90 (67)	77 (64)
900	17	75	100	33	100	100	82 (21)	45 (24)	17 (2)

^aFeed: 1100 ppm NO, 900–3100 ppm CO, 1% H₂O, Catalyst weight: 0.1 g, Flow rate: 100 mL·min^{−1}. ^bParenthetical values are NH₃ selectivities for the NO–H₂ reaction in which H₂ and CO concentrations were equal.

Table 2. Activities of Pt catalysts supported on various materials for NO–CO–H₂O reaction^a

Catalyst	NO conversion/%			CO conversion/%			NH ₃ selectivity/%		
	473 K	523 K	573 K	473 K	523 K	573 K	473 K	523 K	573 K
Pt/TiO ₂	90	100	100	76	88	99	99	100	100
Pt/ZrO ₂	48	100	100	38	97	100	85	99	98
Pt/CeO ₂	38	93	100	30	78	94	90	98	96
Pt/Al ₂ O ₃	2	20	98	2	16	73	—	83	82
Pt/SiO ₂	9	52	100	5	36	88	—	71	92

^aFeed gas: 1100 ppm NO, 3100 ppm CO, 1% H₂O, Catalyst weight: 0.1 g, Flow rate: 100 mL·min.

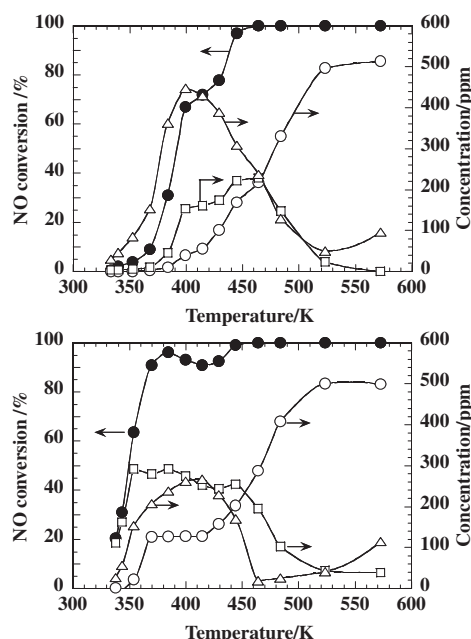


Figure 2. Temperature dependence of NO–CO–H₂O reaction (a) and NO–H₂ reaction (b) over Pt/TiO₂. Catalyst weight was 0.1 g. Feed gas composition was 1100-ppm NO, 900-ppm CO, and 1% H₂O for the NO–CO–H₂O reaction, and 1100-ppm NO, 1000-ppm H₂, and 1% H₂O for the NO–H₂ reaction. The flow rate for both feed gases was 100 mL·min^{−1}. Symbols indicate NO conversion (●) and N₂ (○), N₂O (□), and NH₃ (△) selectivity.

converted in all three cases. The data suggest that the reaction rate of CO with H₂O was much faster than that with NO. Table 1 lists NO and CO conversions at the temperatures at which NO conversion was lower than 100%. Comparing the NO and CO conversions at 3100 ppm CO, the amounts of CO converted at 423 and 473 K were 496 and 2355 ppm, and the amounts of NO converted were 187 and 990 ppm. The amount of CO converted was roughly 2.5 times higher than the amount of NO converted. The balanced reaction for NH₃ formation from NO and H₂ (i.e., the NO–H₂ reaction) is NO + 5/2H₂ → NH₃ + H₂O. It is noted that the amounts of NH₃ formation for NO–CO–H₂O and NO–H₂ reaction above 473 K were in good agreement with each other. The extent of H₂ formation shown in Figure 1 corresponds to complete consumption of NO. We suspect that NO was converted to NH₃ by H₂ formed in the WGS reaction.

Table 1 also lists the NO–CO–H₂O activity over Pt/TiO₂ at

1900 and 900 ppm of CO concentrations. NO and CO conversions increased with decreasing CO concentration. The self-poisoning of CO caused by its strong adsorption on Pt is well-known,⁴ so a decreasing concentration of CO should relate to enhancement of NO and CO conversion. The selectivity of NH₃ formation for the NO–H₂ reaction with 3000 ppm H₂ was close to 100% (Table 1) and was almost the same as that observed for the NO–CO–H₂O reaction. As the CO concentration decreased, the selectivity toward NH₃ in the NO–CO–H₂O reaction became higher than that in the NO–H₂ reaction at corresponding H₂ concentrations. Figure 2 shows activities of the NO–CO–H₂O reaction with 900-ppm CO and of the NO–H₂ reaction with 1000-ppm H₂. The formation of NH₃ was higher in the NO–CO–H₂O reaction than in the NO–H₂ reaction. N₂ and N₂O formation below 450 K in the NO–CO–H₂O reaction were lower than those in the NO–H₂ reaction. The results suggest that the reaction of NO with H₂ formed in the WGS reaction produced much more NH₃ than the amount produced by the NO–H₂ reaction.

We tested the NO–CO–H₂O reaction over Pt/ZrO₂ and Pt/CeO₂, two other catalysts that are highly active for the WGS reaction^{5,6} (Table 2). Pt/ZrO₂ and Pt/CeO₂ exhibited high NO conversion and NH₃ selectivity, but Pt/TiO₂ had the highest activity. For comparison, Pt/Al₂O₃ and Pt/SiO₂, which have lower activity for the WGS reaction than Pt/ZrO₂ and Pt/CeO₂ and are known to form NH₃ through the formation and hydrolysis of isocyanate,⁷ were tested. The light-off temperatures of NO and CO conversions were above 473 K and NH₃ selectivity was lower for these two catalysts than for the other catalysts. These results, as well as the results for Pt/TiO₂ discussed above, suggest that the catalysts with a lower light-off temperature for the WGS reaction exhibit selective NH₃ formation in the NO–CO–H₂O reaction at low temperatures. We are currently investigating mechanisms of the reaction of NO with H₂ formed from the WGS reaction.

References

- 1 R. Burch, M. D. Coleman, *Appl. Catal., B* **1999**, 23, 115.
- 2 T. Nakatsuji, M. Matsubara, J. Rouistenmäki, N. Sato, H. Ohno, *Appl. Catal., B* **2007**, 77, 190.
- 3 T. Nanba, K. Sugawara, S. Masukawa, J. Uchisawa, A. Obuchi, *Ind. Eng. Chem. Res.* **2005**, 44, 3426.
- 4 K. Arnby, A. Törnroona, B. Andersson, M. Skoglundh, *J. Catal.* **2004**, 221, 252.
- 5 A. Luengnaruemitchai, S. Osuwan, E. Gulari, *Catal. Commun.* **2003**, 4, 215.
- 6 D. Tibiletti, F. C. Meunier, A. Goguet, D. Reid, R. Burch, M. Boaro, M. Vicario, *J. Catal.* **2006**, 244, 183.
- 7 N. W. Cant, D. C. Chambers, I. O. Y. Liu, *J. Catal.* **2005**, 231, 201.