Highly Selective NH_3 Formation in a NO–CO–H_2O Reaction over Pt/TiO_2

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/TiO_2 showed high selectivity toward NH_3 formation in the conversion of NO and CO in the presence of H_2O, higher than that observed for the reaction of NO with H_2.

A promising catalytic system for low-temperature nitrogen oxides abatement, de-NO_x, is selective catalytic reduction (SCR) by H_2, referred to herein as H_2-SCR. Platinum catalysts are known to exhibit activity at low temperatures in the presence of excess oxygen.[1] H_2-SCR could be used in de-NO_x of diesel exhaust, but the practical application of H_2-SCR is hindered because the H_2 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 H_2 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 H_2 generated from the reaction of CO and H_2O (i.e., the water–gas shift (WGS) reaction: $CO + H_2O \rightarrow CO_2 + H_2$) 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 H_2O, a reaction referred to herein as the NO–CO–H_2O reaction. We demonstrate that Pt/TiO_2 exhibited high activity and extremely high NH_3 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. H_2PtCl_6 (Kishida Chemical) was used as the precursor of Pt. The oxides used as supports were TiO_2 (P-25; Nippon-Aerosil), ZrO_2 (RSC-H; Daiichi-Kigenso), CeO_2 (Nacalai Tesque), SiO_2 (Wakogel C-100; Wako Pure Chemical Industries), and Al_2O_3 (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–H_2O reaction, He feed gas containing 1100 ppm NO, 900–3100 ppm CO, and 0 or 1% H_2O was used at a flow rate of 100 mL·min^{-1}. Catalysts were treated in 10% H_2 at 573 K for 1 h before they were subjected to reactions. Product selectivity was calculated at the temperature at which NO conversion was more than 10%. The details of this analysis were described previously.[3]

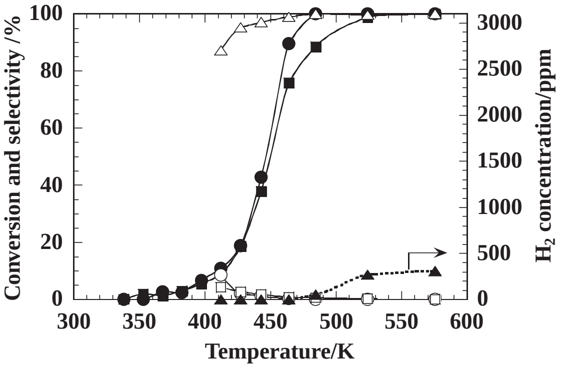

Figure 1. Temperature dependence of NO–CO–H_2O reaction over Pt/TiO_2. Catalyst weight was 0.1 g. Feed gas composition was 1100 ppm NO, 3100 ppm CO, and 1% H_2O. Total flow rate was 100 mL·min^{-1}. Symbols indicate NO (●) and CO (■) conversions, N_2 (○), N_2O (□), and NH_3 (△) selectivity, and H_2 concentration (- -▲- -).

Figure 1 shows the extent of NO and CO conversion over Pt/TiO_2 as a function of temperature. The selectivity toward N_2, N_2O, and NH_3 formation as a function of temperature and the concentration of generated H_2 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 CO_2 formation was equivalent to the amount of CO converted. NH_3 was formed with very high selectivity, whereas the selectivities of N_2 and N_2O were lower than 10% at all measured temperatures. Furthermore, H_2 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 H_2O (i.e., the NO–CO reaction) over Pt/TiO_2 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 H_2 formed was equivalent to the amount of CO

Table 1. Activities of Pt/TiO_2 for NO–CO–H_2O and NH_3 selectivity in NO–H_2 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)

[a]Feed: 1100 ppm NO, 900–3100 ppm CO, 1% H_2O, Catalyst weight: 0.1 g, Flow rate: 100 mL·min^{-1}. [b]Parenthetical values are NH_3 selectivities for the NO–H_2 reaction in which H_2 and CO concentrations were equal.

Table 2. Activities of Pt catalysts supported on various materials for NO–CO–H_2O 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_2O_3	2	20	98	2	16	73	—	83	82
Pt/SiO_2	9	52	100	5	36	88	—	71	92

[a]Feed gas: 1100 ppm NO, 3100 ppm CO, 1% H_2O, Catalyst weight: 0.1 g, Flow rate: 100 mL·min.

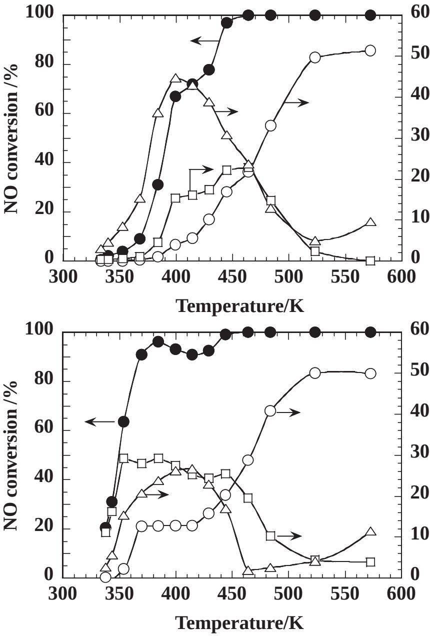

Figure 2. Temperature dependence of NO–CO–H_2O reaction (a) and NO–H_2 reaction (b) over Pt/TiO_2. Catalyst weight was 0.1 g. Feed gas composition was 1100-ppm NO, 900-ppm CO, and 1% H_2O for the NO–CO–H_2O reaction, and 1100-ppm NO, 1000-ppm H_2, and 1% H_2O for the NO–H_2 reaction. The flow rate for both feed gases was 100 mL·min^{-1}. Symbols indicate NO conversion (●) and N_2 (○), N_2O (□), and NH_3 (△) selectivity.

converted in all three cases. The data suggest that the reaction rate of CO with H_2O 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 NH_3 formation from NO and H_2 (i.e., the NO–H_2 reaction) is $NO + 5/2H_2 \rightarrow NH_3 + H_2O$. It is noted that the amounts of NH_3 formation for NO–CO–H_2O and NO–H_2 reaction above 473 K were in good agreement with each other. The extent of H_2 formation shown in Figure 1 corresponds to complete consumption of NO. We suspect that NO was converted to NH_3 by H_2 formed in the WGS reaction.

Table 1 also lists the NO–CO–H_2O activity over Pt/TiO_2 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 NH_3 formation for the NO–H_2 reaction with 3000 ppm H_2 was close to 100% (Table 1) and was almost the same as that observed for the NO–CO–H_2O reaction. As the CO concentration decreased, the selectivity toward NH_3 in the NO–CO–H_2O reaction became higher than that in the NO–H_2 reaction at corresponding H_2 concentrations. Figure 2 shows activities of the NO–CO–H_2O reaction with 900-ppm CO and of the NO–H_2 reaction with 1000-ppm H_2. The formation of NH_3 was higher in the NO–CO–H_2O reaction than in the NO–H_2 reaction. N_2 and N_2O formation below 450 K in the NO–CO–H_2O reaction were lower than those in the NO–H_2 reaction. The results suggest that the reaction of NO with H_2 formed in the WGS reaction produced much more NH_3 than the amount produced by the NO–H_2 reaction.

We tested the NO–CO–H_2O reaction over Pt/ZrO_2 and Pt/CeO_2, two other catalysts that are highly active for the WGS reaction[5,6] (Table 2). Pt/ZrO_2 and Pt/CeO_2 exhibited high NO conversion and NH_3 selectivity, but Pt/TiO_2 had the highest activity. For comparison, Pt/Al_2O_3 and Pt/SiO_2, which have lower activity for the WGS reaction than Pt/ZrO_2 and Pt/CeO_2 and are known to form NH_3 through the formation and hydrolysis of isocyanate,[7] were tested. The light-off temperatures of NO and CO conversions were above 473 K and NH_3 selectivity was lower for these two catalysts than for the other catalysts. These results, as well as the results for Pt/TiO_2 discussed above, suggest that the catalysts with a lower light-off temperature for the WGS reaction exhibit selective NH_3 formation in the NO–CO–H_2O reaction at low temperatures. We are currently investigating mechanisms of the reaction of NO with H_2 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. Törncrona, 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.