A New SOx Deactivation-Free NOx Reduction System Using Rh/Alumina and Periodical Rich and Lean Conditions

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A SOx deactivation free catalytic NOx reduction system in the presence of excess oxygen has been demonstrated. This system functioned well in the periodical two steps, which consisted of a short operation in oxidizing conditions and a far shorter operation in reducing conditions. In this system, only a Rh catalyst effectively catalyzed NOx reduction. In the presence of 50 ppm SOx, this system did not deteriorate at all.

NOx storage-reduction system can effectively reduce NOx in the periodical two steps, which consists of an operation in oxidizing conditions (NO oxidation and NO_2 adsorption) and a relatively short operation in reducing conditions (NO_2 reduction), and works well for a long period in the absence of SOx.[1-2] However, in the presence of SOx, the system deteriorates drastically due to the irreversible adsorption of SOx on the NO_2 adsorption sites under both lean and rich conditions. There has been many studies to find a solution of the above problem.[3-4] These studies have, to a certain extent, brought the improvement in the durability in the presence of SOx of catalysts and catalytic systems. However, all of them have a poor long-term durability. We tried to find a new NOx reduction system functioning in the above-mentioned two steps (dual-phasic NOx reduction) and catalysts with high long-term durability in the presence of SOx, which can be commercially applied to vehicles with diesel engines and lean burn gasoline engines.

Dual-phasic NOx reduction experiments were conducted over various catalysts in a flow reactor system with simulated gas mixtures. 1.5 wt% metal-loaded powdery catalysts were prepared by immersing γ-alumina in a solution of the catalyst precursor, such as $Pt(NO_2)_2(NH_3)_2$, $Rh(NO_3)_3$ and H_2IrCl_6, followed by drying and calcination in air at 700 ℃ for 3h. A honeycomb-shaped catalyst was prepared by wash-coating cordierite honeycomb with 600 cell per square inch with slurry containing the powdery catalyst. In this experiment, the reaction condition was periodically oscillated between an oxidizing (lean) condition and a reducing (rich) condition (perturbed scan). The time spans of the scan in the lean and rich conditions were 55 and 5 s, respectively. The mixture for the experiments under a rich condition comprised of 500 ppm of NO, 40 ppm of SO_2, 0.4% of O_2, 2% of CO, 2000 ppm of C_3H_6, 9.0% of H_2O, 2% of H_2 and balance of N_2. The gas mixture in the lean condition was prepared by injecting 9.2% oxygen into the gas mixture in the rich condition. We conducted the experiments at a space velocity of 76,000 h^{-1} in the lean condition. NOx conversion was measured from 500 to 200 ℃ with the FT-IR detector (Horiba: MEXA-4300FT). Furthermore, the catalysts were examined also in NOx reduction under the steady lean condition (single-phasic NOx reduction). Rh/alumina only showed a far higher activity in the dual-phasic NOx reduction than in the single-phasic NOx reduction in the wide temperature range from 250 to 450 ℃ as shown in Table 1. In order to clarify the difference in the reaction behaviors, the change of reaction profile due to switching from the lean to the rich condition was observed. A reaction gas in the rich condition was first passed through a flow reactor system for 60 s, and then another reaction gas in the lean condition was flowed for 540 s, while outlet NOx concentration was continuously measured. As shown in Figure 1, the outlet NOx concentration over Rh/alumina in the rich operation was quite low at 300 and 350 ℃ and that on Pt/alumina was quite high at 250 ℃. A short moment after the lean operation started, the concentration over Rh/alumina continued to increase gradually and drastically at 300 ℃ and 350 ℃, respectively and on the contrary, that on Pt/alumina decreased drastically. At 350 s after the lean operation started,

Table 1. Comparison of single and dual-phasic NOx reductions over Rh/alumina, Pt/alumina and Ir/alumina

		NOx conversion (%)					
temperature/℃		200	250	300	350	400	450
single-phasic	Rh	0	9	22	31	10	5
	Pt	38	25	14	11	7	3
	Ir	0	2	9	21	18	12
dual-phasic	Rh	5	29	55	46	34	19
	Pt	32	24	13	10	7	3
	Ir	12	18	28	35	31	25

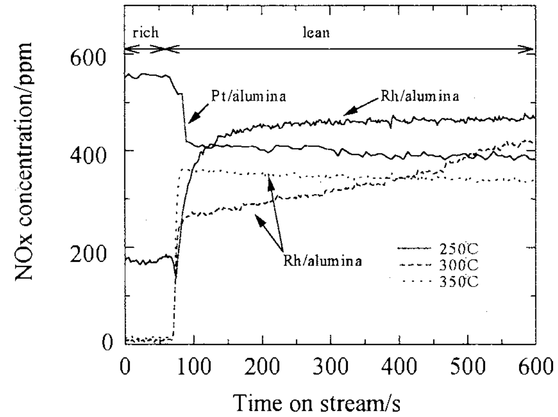

Figure 1. Reaction profile of Rh/alumina on a time course from rich to lean condition.

the outlet concentration over Rh/alumina at 300 exceeded that at 350 °C, and the steady concentration at 350 °C was lower than that at 250 and 300 ℃. From this reaction profile, it is expected that in the dual-phasic NOx reduction over Rh/alumina with the span longer than 350 s under the lean condition, NOx will be most effectively reduced at 350 ℃, and on the span shorter than 350 s, NOx will be most effectively reduced at 300 ℃, and on much shorter span, NOx conversion will be quite high at 300 and 350 ℃. Furthermore, it is implied that in the dual-phasic NOx reduction over Pt/alumina with the much shorter span, NOx will be hardly reduced and NOx conversion will reach the value in the steady lean condition soon after the lean operation starts. Thus, the conversion in the dual-phasic NOx reduction could be attributed to the reaction behavior on the time course from rich to lean conditions. Furthermore, it is expected that Rh/alumina will show a high NOx conversion in the dual-phasic NOx reduction using the periodical short lean and far shorter rich operations at 300 and 350 ℃. From the practical point of view, Rh/alumina and Pt/alumina were examined in the dual-phasic reactions with the various perturbed scans of the same lean to rich time span ratio as shown in Table 2 at 300 and 250℃, respectively. Figure 2 shows the effect of various scans under the same reductant consumption on NOx conversion. The NOx conversions over Rh/alumina and Pt/alumina were the highest on the scans of 0.5 and 0.05 s, and scans longer than 25 and 2.5 s, respectively. With decrease in the scan span of the lean condition, NOx conversion over Rh/alumina increased and drastically increased on the scan of 2 and 0.2 s, and the conversion reached more than 90% on the scans of less than 2 and 0.2 s. Figure 3 shows the change of NOx concentration over the Rh/alumina on the various scans at 300 ℃. On the scans of 5 and 0.5 s, and the longer spans, the outlet NOx concentrations oscillated in response to the perturbation. On the scans of 2 and 0.2 s and the shorter scans, however, the oscillation was hardly observed, and the concentration of outlet NO was very low. NO was effectively reduced with 2% H_2 on the scans of 2 and 0.2 s; 48.9% and 54.2% at 250 ℃ and 300 ℃, respectively. We found an interesting and important behavior of the catalyst. SO_2 was adsorbed on the Rh/alumina in the lean condition, but in the rich condition, it was easily and partially desorbed at 350 ℃ and at 250 –300 ℃, respectively (not shown). Durability test in the dual-phasic NOx reduction for 12 h was then conducted on the Rh/alumina and the conventional NOx storage-reduction catalyst of 0.5wt% Pt/2wt% Rh/5wt % K_2CO_3/30wt% $BaCO_3$ supported on alumina with the time scan of 2 and 0.2, and 55 and 5.5 s, respectively. Although usual NOx storage catalytic system was deactivated drastically at 300 ℃, the Rh/alumina was not deactivated at all, as shown in Figure 4.

Table 2. Various time spans in the dual-phasic NOx reduction with the same lean to rich time span ratio

time spans in rich condition/s	0.05	0.1	0.2	0.5	2.5	5.5	11
time spans in lean condition/s	0.5	1.0	2.0	5.0	25	55	110

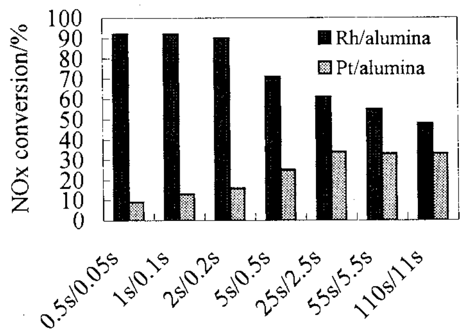

Figure 2. Effect of various perturbated scans under the same reductant consumption on NOx conversion over Rh/alumina and Pt/alumina.

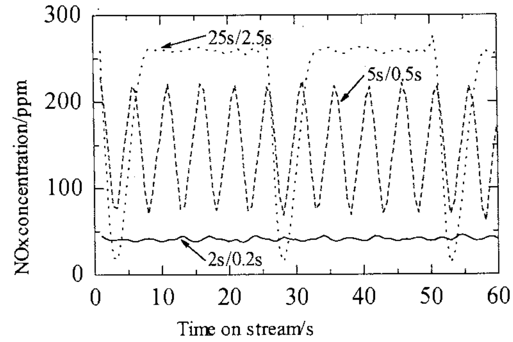

Figure 3. Reaction profile of Rh/alumina in various perturbed scans under the same reduction consumption.

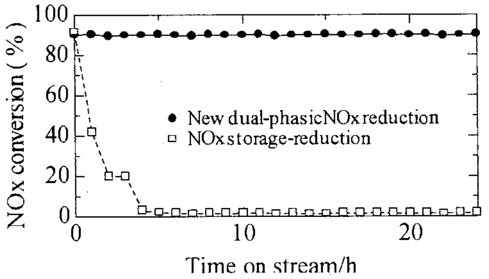

Figure 4. Durability of NOx storage-reduction and new dual-phasic NOx reduction in the presence of 40 ppm.

NOx reduction in this new dual-phasic reaction will be attributed to the transient behavior from rich to lean operation. With decrease in lean span, NOx conversion increased, and on the scans of 2 and 0.2 s and the shorter scans, NOx was effectively reduced over Rh/alumina. Furthermore, this system did not deteriorate at all in a short-term durability test in the presence of 40 ppm SOx. Therefore, the new system is one of the most promising technologies to eliminate NOx in the lean exhaust gases.

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