



## Preparation and screening of various multi-component catalysts for NO<sub>x</sub> conversion under lean-burn conditions: An active and heat-resistant RhPt–NaMn–Ce/Al<sub>2</sub>O<sub>3</sub> catalyst

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### ABSTRACT

The present work has been undertaken to improve the thermal stability of an RhPt–NaTi/Al<sub>2</sub>O<sub>3</sub> catalyst, which is one of promising lean NO<sub>x</sub> trap catalysts for practical NO<sub>x</sub> conversion. For this purpose, we mainly directed our attention to the component of Na that acts as NO<sub>x</sub> trapping sites and intended to improve the thermal stability of this Na species by using various additives. After screening of various RhPt–Na $\alpha$ /Al<sub>2</sub>O<sub>3</sub> ( $\alpha$  = Ti, Si, Mg, Ca, Mn, Co, Ni, La, and Nd) catalysts, Mn addition was found to be effective for improving thermal stability of the catalyst. Moreover, the modification of Al<sub>2</sub>O<sub>3</sub> support with Ce additive was indicated to be effective, and the most active and thermally stable catalyst was RhPt–NaMn–Ce/Al<sub>2</sub>O<sub>3</sub>, which was able to function actively even after a severe heat treatment at 800 °C. The reasons for the high thermal stability of this catalyst were examined by evaluating NO oxidation activity of a model catalyst including Mn and characterizing features of the RhPt–NaMn–Ce/Al<sub>2</sub>O<sub>3</sub> catalyst with FTIR of adsorbed NO and chemisorption of CO and CO<sub>2</sub>. An important factor is that the addition of Mn prevents the Na species from undesired sintering during heat treatments, resulting in a larger surface area of exposed Na species, namely NO<sub>x</sub> trapping sites. This catalyst can also function in a commercial vehicle engine under lean-burn conditions and should be a promising catalyst for practical use.

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### 1. Introduction

Both the reduction of CO<sub>2</sub> emission and the purification of exhaust gas for cars are desirable for environmental protection. The lean combustion methods for gasoline engines and for diesel engines are effective for fuel cost improvement. But because of a large amount of oxygen in the exhaust gas in the lean combustion method, nitrogen oxide (NO<sub>x</sub>) in the exhaust gas cannot be efficiently removed by a traditional three-way catalyst. Therefore, new approaches are needed for treating this important issue. Lean NO<sub>x</sub> trap catalyst technology is one of the useful solutions, in which NO<sub>x</sub> is trapped by the catalyst during relatively long lean periods. The lean period is interrupted for a shorter time by a rich spike and during the rich periods the NO<sub>x</sub> stored in the lean periods is decomposed and subsequently reduced to inert nitrogen. Typical

effective catalysts are composed of alkali and alkaline earth metals such as K, Na and Ba species for trapping NO<sub>x</sub> and precious metals such as Pt, Pd, and Rh for oxidizing and reducing NO<sub>x</sub> [1–10]. These catalysts have been reported to show high performance of NO<sub>x</sub> purification.

For practical application in vehicle exhaust systems, however, higher thermal stability is still required; the catalysts should function actively even at high temperatures such as 800 °C [11,12]. It was reported that thermal stability of Pt was improved by Pd addition [13] and Ce oxide could stabilize the precious metals [14–16]. The NO<sub>x</sub> trap materials was also reported to have improved thermal stability by using mixed oxides composed of Na and Ti on Al<sub>2</sub>O<sub>3</sub> support [7], and the lean NO<sub>x</sub> trap RhPt–NaTi–Ce/Al<sub>2</sub>O<sub>3</sub> catalyst showed good thermal stability. Na oxides acted as NO<sub>x</sub> trap materials and Ti oxides were further added to prevent the sintering of Na oxides. In the literature, however, there are fewer reports on the lean NO<sub>x</sub> trap catalysts containing Na species compared to those with Ba or K species. In the present work, the authors have studied further improvement of the thermal stability of an RhPt–NaTi/Al<sub>2</sub>O<sub>3</sub> catalyst, which is one of promising catalysts for practical NO<sub>x</sub> conversion. This paper will report the effectiveness

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of addition of Mn species and discuss possible reasons for this improvement of the thermal stability observed.

## 2. Experimental

### 2.1. Catalyst preparation

The catalyst samples including Rh, Pt and Na were prepared by the following method. First,  $\text{Al}_2\text{O}_3$  slurry was prepared by adding an  $\text{Al}_2\text{O}_3$  (surface area  $200\text{ m}^2/\text{g}$ ) to 5 wt%  $\text{HNO}_3$  solution, followed by milling with vibration. This  $\text{Al}_2\text{O}_3$  slurry was poured into cordierite honeycomb cells (Nihon Gaisi, 400 cells/in.<sup>2</sup>) and dispersed on their surface. The volume of the honeycomb used was 0.62 L ( $\varnothing 86\text{ mm} \times 107\text{ mm}$ ). The  $\text{Al}_2\text{O}_3$ -coated honeycomb was dried in air at  $150^\circ\text{C}$  for 2 h and calcined in air at  $600^\circ\text{C}$  for 1 h. For laboratory scale activity test, it was cut into a small piece of  $6\text{ cm}^3$  ( $17\text{ mm} \times 17\text{ mm} \times 21\text{ mm}$ ) and used as a starting support material. The amount of  $\text{Al}_2\text{O}_3$  loaded was found to be 150 g per 1 L of the honeycomb within  $\pm 8\text{ g}$ . It was confirmed by SEM (Hitachi S-4100) that  $\text{Al}_2\text{O}_3$  was uniformly dispersed over the surface of the honeycomb, giving an average thickness of  $\text{Al}_2\text{O}_3$  coating of  $100\ \mu\text{m}$ .

Then, this  $\text{Al}_2\text{O}_3$ -coated support was loaded with several active components by impregnation methods, including such species as Na, Ti, Si, Mg, Ca, Mn, Co, Ni, La, Nd, and Ce from  $\text{NaNO}_3$  (Wako),  $\text{TiO}_2$  sol (Isihara Sangyo),  $\text{SiO}_2$  sol (Nissan Kagaku),  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ca}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , and  $\text{Ce}(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$  (Wako), respectively. After the impregnation of a single component or multi-components, the honeycomb was dried and calcined in air under the same conditions as used for the  $\text{Al}_2\text{O}_3$  coating. The loadings of Na, Ti, and the others were 0.8, 0.1, and 0.2 mol per 1 L of the  $\text{Al}_2\text{O}_3$ -coated honeycomb, respectively. Finally, Rh and Pt were co-impregnated using an aqueous solution of  $\text{Rh}(\text{NO}_3)_3$  and  $\text{Pt}(\text{NH}_3)_2(\text{NO}_3)_2$  (Tanaka Kikinzoku) to the  $\text{Al}_2\text{O}_3$ -coated honeycomb loaded already with some additives, followed by drying and calcination in air under the same conditions as described above. The loadings of Rh and Pt were adjusted to be 0.002 and 0.015 mol per 1 L of the  $\text{Al}_2\text{O}_3$ -coated honeycomb, respectively, according to the previous work [7], which had examined the optimization of the precious metal loadings. The catalyst samples prepared will be expressed with, for example,  $\text{RhPt-NaMn-Ce/Al}_2\text{O}_3$ , in which the  $\text{Al}_2\text{O}_3$ -coated honeycomb was impregnated first with Ce, co-impregnated next with Na and Mn, and then with Rh and Pt. This catalyst contained 0.002 mol (0.2 g) Rh, 0.015 mol (3 g) Pt, 0.8 mol (18 g) Na, 0.2 mol (11 g) Mn, and 0.2 mol (28 g) Ce per 1 L of the  $\text{Al}_2\text{O}_3$ -coated honeycomb, in which  $\text{Al}_2\text{O}_3$  was 150 g. The spatial distribution of active species on the  $\text{Al}_2\text{O}_3$ -loaded honeycomb support was examined by cutting across the 0.62 L honeycomb into three pieces of the same size and measuring the amounts of active species in these three pieces by atomic absorption spectroscopy (Hitachi Z-8100) for Na and ICP (Horiba Jobin Yvon ULTIMA2) for the other components. The amounts of those active species were found to be within relative errors of  $\pm 5\%$  of the nominal values for the three pieces, indicating their uniform dispersion on the support under the preparation procedures and conditions used.

### 2.2. NOx purification test

An ordinary fixed-bed flow reactor was used to examine the NOx purification activity of the catalysts prepared. A tubular reactor of 27 mm in diameter was vertically fixed within a vertical electric furnace, and the honeycomb catalyst ( $6\text{ cm}^3$ ) was placed inside the reactor. The catalyst inlet temperature was adjusted to the desired value between 300 and  $500^\circ\text{C}$ . Before the activity test, the cata-

lyst sample was pretreated in stream of a rich gas of 1000 ppm NO, 600 ppm  $\text{C}_3\text{H}_6$ , 0.6% CO, 12%  $\text{CO}_2$ , 0.5%  $\text{O}_2$ , 3300 ppm  $\text{H}_2$ , 10%  $\text{H}_2\text{O}$  diluted with  $\text{N}_2$  at  $500^\circ\text{C}$  for 30 min. Then, a lean gas of 600 ppm NO, 500 ppm  $\text{C}_3\text{H}_6$ , 0.1% CO, 10%  $\text{CO}_2$ , 5%  $\text{O}_2$ , 10%  $\text{H}_2\text{O}$  diluted with  $\text{N}_2$  and the rich gas were alternately passed at  $3000\text{ cm}^3\text{ min}^{-1}$  (space velocity  $30,000\text{ h}^{-1}$ ) through the catalyst every 3 min. The NOx concentration at the outlet of reactor was measured in 1 min after switching to the lean gas with a NOx (NO,  $\text{NO}_2$ ) meter (Horiba CLA-510) and the NOx conversion was calculated by:

NOx conversion

$$= \frac{\text{NO conc. at the inlet} - \text{NOx conc. at the outlet}}{\text{NO conc. at the inlet}}$$

For examining thermal stability of various catalysts, they were subjected to heat treatments in air at 700, 800, and  $900^\circ\text{C}$  for 5 h before the above-mentioned activity test. Some selected catalysts prepared separately under the same procedures and conditions were tested and the errors of the conversion values obtained were found to be within  $\pm 3\%$ .

### 2.3. NO oxidation test

The catalytic activity for NO oxidation was also tested for a few selected catalysts using the same apparatus and procedures as used in the NOx purification. The catalyst inlet temperature was adjusted to the desired value between 200 and  $550^\circ\text{C}$ . After the catalyst pretreatment with the rich gas at  $500^\circ\text{C}$  for 30 min, a gaseous mixture containing 600 ppm NO and 5%  $\text{O}_2$  diluted with  $\text{N}_2$  was passed through the catalyst at a flow rate of  $3000\text{ cm}^3\text{ min}^{-1}$ . After the NO concentration at the reactor outlet was stable, the conversion of NO oxidation was calculated by:

NO oxidation conversion

$$= \frac{\text{NO conc. at the inlet} - \text{NO conc. at the outlet}}{\text{NO conc. at the inlet}}$$

### 2.4. Catalyst characterization

The catalyst samples prepared were characterized by FTIR and adsorption of CO and  $\text{CO}_2$ . *In situ* FTIR (Horiba FT-210) was used to examine the state of NOx species adsorbed and trapped on the catalysts. The powdered catalyst sample was pretreated in a stream of 1% CO diluted with He at  $500^\circ\text{C}$  for 30 min, cooled down to  $300^\circ\text{C}$  in a stream of He, and kept at this temperature. After that, a mixture of 600 ppm NO and 5%  $\text{O}_2$  diluted with He was passed over the catalyst sample for 3 min. The FTIR spectra were collected by using the spectrum measured before the NO adsorption as a background.

The chemisorption of CO and  $\text{CO}_2$  was used to determine the amount of noble metals and base sites exposed on the catalyst surface. Prior to the chemisorption, the granulated catalyst sample was pretreated in a stream of 10% CO diluted with He at  $400^\circ\text{C}$  for 30 min and further in He stream at  $450^\circ\text{C}$  for 2 h. The CO and  $\text{CO}_2$  adsorption was made by pulse method; after the catalyst temperature was lowered to  $100^\circ\text{C}$  in He stream,  $0.5\text{ cm}^3$  of 10% CO or  $10\text{ cm}^3$  of 4%  $\text{CO}_2$  diluted with He was introduced into the reactor until no further change occurred in the amount of CO or  $\text{CO}_2$  detected at the outlet. The amount of CO and  $\text{CO}_2$  in the effluent gas was measured with a thermal conductivity detector (Shimadzu GC-8A).

## 3. Results and discussion

### 3.1. Screening of various promoters

To improve thermal stability of  $\text{RhPt-NaTi/Al}_2\text{O}_3$  catalyst, Na species were modified by using various additives ( $\alpha$ ) instead of Ti species, as listed in Table 1, which were loaded with Na to the  $\text{Al}_2\text{O}_3$

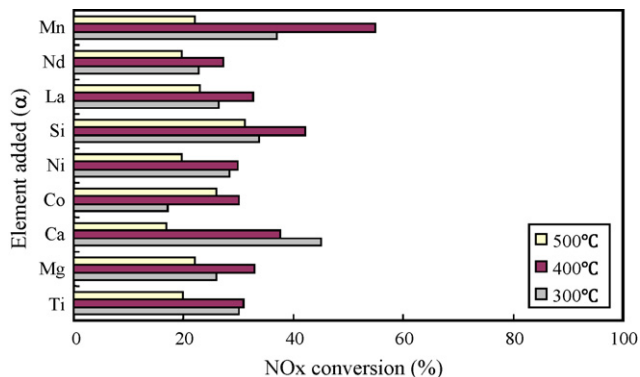
**Table 1**List of elements added as promoters to RhPt–Na/Al<sub>2</sub>O<sub>3</sub> catalyst.

Element ( $\alpha$ )	Ionic radius (Å) and comparison to Na <sup>+</sup> (0.97 Å)
Ti (standard)	Ti <sup>4+</sup> (0.68) < Na <sup>+</sup>
Mg	Mg <sup>2+</sup> (0.66) < Na <sup>+</sup>
Ca	Ca <sup>2+</sup> (0.99) > Na <sup>+</sup>
Mn	Mn <sup>2+</sup> (0.70) < Na <sup>+</sup>
Co	Co <sup>3+</sup> (0.72) < Na <sup>+</sup>
Ni	Ni <sup>2+</sup> (0.69) < Na <sup>+</sup>
Si	Si <sup>4+</sup> (0.40) < Na <sup>+</sup>
La	La <sup>3+</sup> (1.18) > Na <sup>+</sup>
Nd	Nd <sup>3+</sup> (1.12) > Na <sup>+</sup>

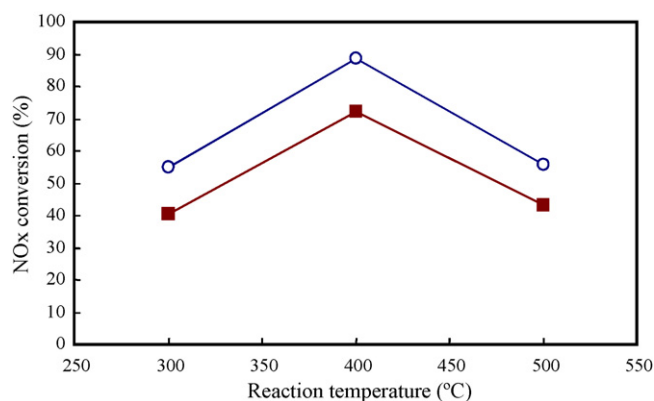
before the impregnation of RhPt. Our intention was to improve the thermal stability of supported Na species acting as NO trap sites. We expected that a certain additive could form a mixed oxide with Na and this could prevent the undesired sintering of Na species from taking place at high temperatures.

The effectiveness of those additives given in Table 1 was studied. Yanagida proposed a theory of solid solutions and discussed the possibility of forming mixed metal oxides from a couple of metal species from the viewpoint of ion filling [17]. In the case of Na<sub>2</sub>O, the coordination number is 6 and so the ideal ion radius is thought to be 0.58 Å. Since the radius of Na<sup>+</sup> is 0.97 Å, smaller ion species would be favorable for the formation of a mixed oxide although the resulting mixed oxide is not of ideal crystal structure. Among the additives listed in Table 1, the addition of Ti (standard), Mg, Mn, Co, Ni, and Si would be positive but not for Ca, La and Nd. The latter three elements were also used for comparison.

Various Al<sub>2</sub>O<sub>3</sub> supported catalysts were prepared by loading RhPt on Na $\alpha$ /Al<sub>2</sub>O<sub>3</sub>. Fig. 1 shows the activities for NOx conversion at 300, 400, and 500 °C for those catalysts after heat treatment at a high temperature of 900 °C for 5 h. At a reaction temperature of 300 °C, the catalyst modified with Ca was the most active, followed by those modified with Mn and Si. Those catalysts, in particular, the Mn-modified one, were also more active at 400 °C than the others. This was the same at 500 °C but the differences in the activity among all the catalysts were not so large as compared to the results at 300 and 400 °C. The addition of Mn, Si, and Ca was turned out to be effective for improving heat resistance of the catalyst. For the Mn, Si added catalysts, the results agreed with the expectation from Yanagida's consideration (Table 1). In contrast, this was not the case for Ca addition. Alkaline earth Ca species can trap NOx and would improve the catalytic performance. Moreover, the close ionic radius between Na<sup>+</sup> and Ca<sup>2+</sup> may favor the interaction between them in the oxide. NOx conversion at 400 °C of Mn added catalyst was remarkably high. Therefore, we selected the Mn-modified catalyst, RhPt–NaMn/Al<sub>2</sub>O<sub>3</sub>, for further efforts to prepare catalysts of higher thermal stability.



**Fig. 1.** NO conversion at different temperatures for RhPt–Na/Al<sub>2</sub>O<sub>3</sub> catalysts modified with various elements after heat treatment at 900 °C for 5 h in air.



**Fig. 2.** NO conversion activities of RhPt–NaMn/Al<sub>2</sub>O<sub>3</sub> catalysts modified with and without Ce after heat treatment at 800 °C for 5 h in air. (■) RhPt–NaMn/Al<sub>2</sub>O<sub>3</sub> and (○) RhPt–NaMn–Ce/Al<sub>2</sub>O<sub>3</sub>.

Furthermore, the effectiveness of modification of Al<sub>2</sub>O<sub>3</sub> support with Ce species was examined. The support was loaded consequently with Ce, (Mn, Na), and then (Rh, Pt). In conventional three-way catalysts, Ce was used to control NOx conversion for stoichiometric exhaust gas even if air–fuel ratio of the gas slightly changed [18–20]. The lean NOx trap catalyst was also required to keep high NOx conversion under stoichiometric exhaust gas conditions. It was previously reported that the addition of Ce species improved the thermal stability of lean NOx trap catalyst; the additives acted to stabilize the precious metals and trap NOx under lean conditions [14].

Thus, we attempted to use Ce additive to improve the performance of our highly active RhPt–NaMn/Al<sub>2</sub>O<sub>3</sub> catalyst. Fig. 2 shows the NOx conversion of Ce-modified and unmodified catalysts after heat treatment at 800 °C for 5 h. The former catalyst was more active than the latter at reaction temperatures of 300, 400, and 500 °C. The presence of Ce improved the conversion by an amount well above 10% under the conditions used. Namely, it was confirmed that the Ce additive was effective in improving the catalytic performance of RhPt–NaMn/Al<sub>2</sub>O<sub>3</sub>.

The thermal stability of RhPt–NaMn–Ce/Al<sub>2</sub>O<sub>3</sub> catalyst was further examined, which was heat-treated at 700, 800, and 900 °C. We thought that heat treatment at 800 °C was sufficient to test the catalyst stability for practical use but a higher temperature of 900 °C was also used for comparison. Fig. 3 shows the results of NOx conversion with this catalyst and RhPt–NaTi–Ce/Al<sub>2</sub>O<sub>3</sub> as a reference catalyst. The RhPt–NaTi–Ce/Al<sub>2</sub>O<sub>3</sub> was used as a control because it was indicated to be an active and thermally stable lean NOx trap catalyst [7]. When these two catalysts were not heat-treated (fresh; the maximum temperature of catalyst preparation was 600 °C), they showed similar NO conversion levels at 300, 400, and 500 °C. The catalytic activities tended to decrease on the heat treatments but the results at 400 °C showed that our RhPt–NaMn–Ce/Al<sub>2</sub>O<sub>3</sub> catalyst was more effective for NOx conversion than the RhPt–NaTi–Ce/Al<sub>2</sub>O<sub>3</sub> one after heat treatments at 700 and 800 °C. The former catalyst showed NO conversion levels >90% even when it was heat-treated at 700 and 800 °C. After the most severe treatment at 900 °C, unfortunately, the activities of these two catalysts were similar. This might be caused by decomposition of Na–Ti and Na–Mn mixed oxides, followed by reaction between Na and Ce species. Those results demonstrate that the addition of Mn to Na species can improve the thermal durability of the catalyst even after a severe heat treatment at 800 °C.

It is known that K-modified lean NOx trap catalysts show better performance at temperatures >350 °C than Ba-modified ones [9]. This was thought to be caused by the weak basicity of Ba species. As indicated in Fig. 3, the activity of RhPt–NaMn–Ce/Al<sub>2</sub>O<sub>3</sub> catalyst

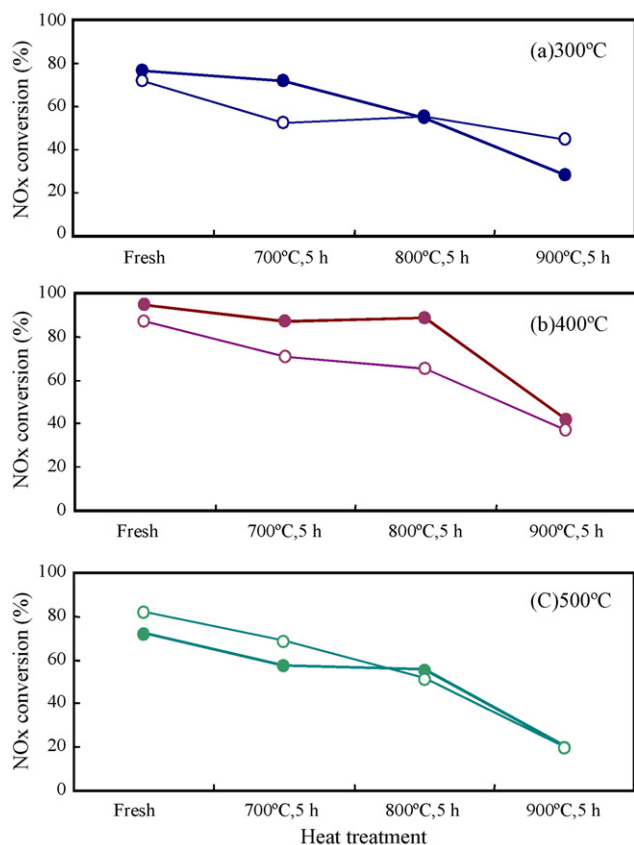


Fig. 3. NO conversion at 300, 400, and 500 °C for RhPt–NaTi–Ce/Al<sub>2</sub>O<sub>3</sub> (○) and RhPt–NaMn–Ce/Al<sub>2</sub>O<sub>3</sub> (●) catalysts after various heat treatments in air.

at 400 °C was very high, which seemed to originate from the strong basicity of Na species similar to K species. Therefore, this catalyst was thought to be effective for applying to practical vehicle in which exhaust gas temperature was high. Moreover, in Ref. [7], the NOx trap catalyst loaded with Na showed better performance than the one with K after heat treatment. Thus, Na species is a good candidate for NOx trap material with high heat resistance. As a result, the Na loaded RhPt–NaMn–Ce/Al<sub>2</sub>O<sub>3</sub> catalyst has both high activity and thermal stability for NOx conversion above 400 °C.

### 3.2. Effects of Mn addition

#### 3.2.1. NO oxidation test

Next, possible reasons for the improvement of the catalyst thermal stability by the addition of Mn species were investigated. In the lean period, NO is oxidized by precious metals and then oxidized NOx is trapped by base materials on the catalyst. In our RhPt–NaMn–Ce/Al<sub>2</sub>O<sub>3</sub> catalyst, the addition of Mn may contribute to the promotion of NO oxidation reaction ( $\text{NO} + (1/2)\text{O}_2 \rightarrow \text{NO}_2$ ) and/or the trap of NO<sub>2</sub> formed.

It was reported in the literature that Mn oxide had the activity for NO oxidation [21,22]. First, we examined the possibility of Mn addition to promote the NO oxidation using two model catalysts of RhPt/Al<sub>2</sub>O<sub>3</sub> and RhPtMn/Al<sub>2</sub>O<sub>3</sub>, in which all the metal components were simultaneously impregnated onto the support. The activities of these catalysts for NO oxidation were tested after heat treatment at 800 °C for 5 h. The Mn-modified catalyst was observed to be more active than the unmodified one at temperatures <400 °C (data not shown.). At 400 °C or higher, the NO conversion was limited by chemical equilibrium under the conditions used. These results indicate that the addition of Mn can improve the catalytic performance for NO oxidation but not so significantly. Therefore, the marginal

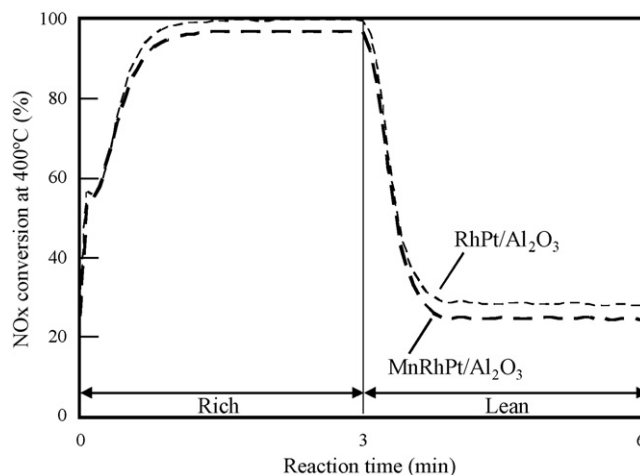


Fig. 4. The change of NO conversion under rich and lean conditions against reaction time for Mn-promoted and unpromoted RhPt/Al<sub>2</sub>O<sub>3</sub> catalysts after heat treatment at 800 °C for 5 h in air. Rich gas: 1000 ppm NO, 600 ppm C<sub>3</sub>H<sub>6</sub>, 0.6% CO, 12% CO<sub>2</sub>, 0.5% O<sub>2</sub>, 3300 ppm H<sub>2</sub>, 10% H<sub>2</sub>O diluted with N<sub>2</sub>. Lean gas: 600 ppm NO, 500 ppm C<sub>3</sub>H<sub>6</sub>, 0.1% CO, 10% CO<sub>2</sub>, 5% O<sub>2</sub>, and 10% H<sub>2</sub>O diluted with N<sub>2</sub>.

improvement of NO oxidation activity cannot be the main reason for the enhancement of NO conversion activity on the addition of Mn (Fig. 3). Next, the influence of Mn addition on the trapping of NOx was studied. The two model catalysts were used for NOx conversion under rich and lean gas conditions. Fig. 4 shows the NOx conversion at 400 °C for these catalysts after heat treatment at 800 °C for 5 h. The catalysts indicated very similar conversion levels, so the addition of Mn was unlikely to affect the ability of NOx trapping.

#### 3.2.2. FTIR

The influence of Mn addition was further studied with FTIR measurements of NO trapped on the surface of catalysts. Fig. 5 gives the FTIR spectra for the most effective RhPt–NaMn–Ce/Al<sub>2</sub>O<sub>3</sub> catalyst, the above-mentioned two model catalysts RhPt/Al<sub>2</sub>O<sub>3</sub> and MnRhPt/Al<sub>2</sub>O<sub>3</sub>, and an additional sample of Mn/Al<sub>2</sub>O<sub>3</sub> after the exposure to a mixture of 600 ppm NO, 5% O<sub>2</sub>, and He at 300 °C for 3 min. For RhPt–NaMn–Ce/Al<sub>2</sub>O<sub>3</sub> catalyst, two absorption bands were detected with large and shoulder peaks located at 1411 and 1319 cm<sup>-1</sup>, which might be assigned to NO<sub>2</sub> adsorbed on Na

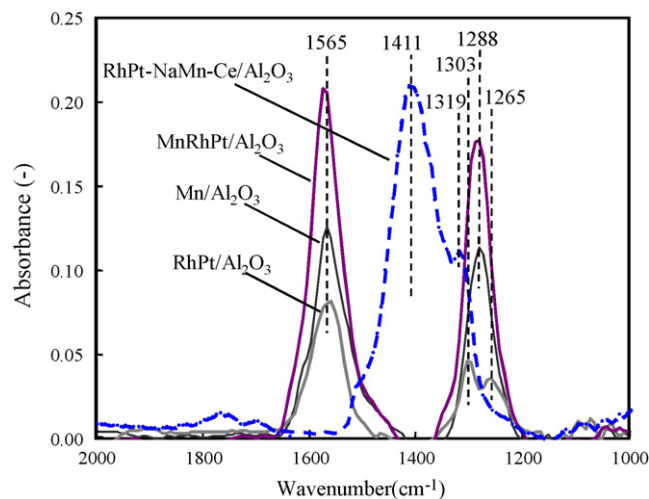
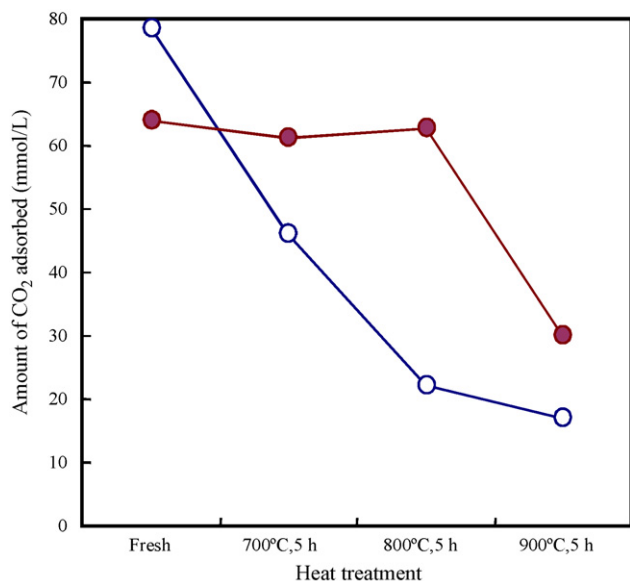


Fig. 5. FTIR spectra of NO adsorbed on RhPt–NaMn–Ce/Al<sub>2</sub>O<sub>3</sub>, MnRhPt/Al<sub>2</sub>O<sub>3</sub>, Mn/Al<sub>2</sub>O<sub>3</sub> and RhPt/Al<sub>2</sub>O<sub>3</sub> after the exposure of 600 ppm NO–5% O<sub>2</sub>–He at 300 °C for 3 min.





**Fig. 6.** The amount of CO<sub>2</sub> adsorbed on RhPt–NaTi–Ce/Al<sub>2</sub>O<sub>3</sub> (○) and RhPt–NaMn–Ce/Al<sub>2</sub>O<sub>3</sub> (●) catalysts after various heat treatments in air.

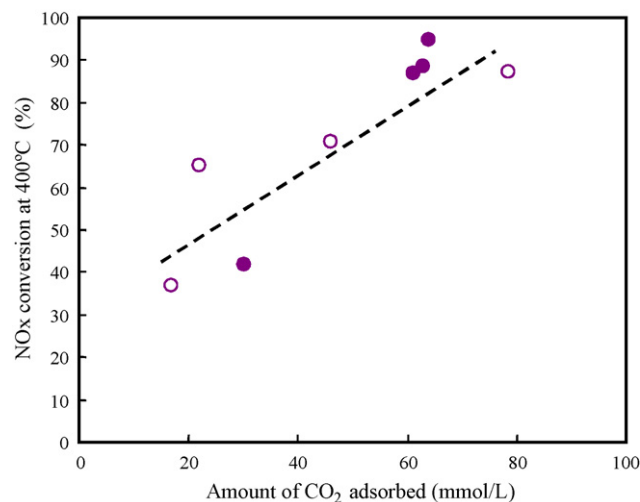
base sites and NaNO<sub>3</sub>, respectively [23,24]. On the other hand, for RhPt/Al<sub>2</sub>O<sub>3</sub>, three peaks were observed at 1265, 1303, and 1565 cm<sup>-1</sup>. Two peaks at 1265 and 1565 cm<sup>-1</sup> and the peak at 1303 cm<sup>-1</sup> were thought to be assigned to NO<sub>3</sub><sup>-</sup> species on Al<sub>2</sub>O<sub>3</sub> support and on noble metals, respectively [24]. The MnRhPt/Al<sub>2</sub>O<sub>3</sub> and Mn/Al<sub>2</sub>O<sub>3</sub> samples gave two absorption peaks at 1288 and 1565 cm<sup>-1</sup>, which might be assigned to NO<sub>3</sub><sup>-</sup> species on the Mn oxide and on Al<sub>2</sub>O<sub>3</sub> support, respectively [24]. These peak positions were different from those observed for RhPt–NaMn–Ce/Al<sub>2</sub>O<sub>3</sub>. This indicates, therefore, that NO<sub>x</sub> should not be trapped on Mn species but on Na species in the RhPt–NaMn–Ce/Al<sub>2</sub>O<sub>3</sub> catalyst, in accordance with the results of Fig. 4 that very similar NO conversion levels were obtained for RhPt/Al<sub>2</sub>O<sub>3</sub> and RhPtMn/Al<sub>2</sub>O<sub>3</sub> catalysts that do not include Na.

### 3.2.3. CO and CO<sub>2</sub> adsorption

The adsorption of CO and CO<sub>2</sub> was studied for the two active catalysts of RhPt–NaMn–Ce/Al<sub>2</sub>O<sub>3</sub> and RhPt–NaTi–Ce/Al<sub>2</sub>O<sub>3</sub> in order to determine the amounts of noble metals and base sites exposed on the catalysts.

The fresh RhPt–NaTi–Ce/Al<sub>2</sub>O<sub>3</sub> catalyst was observed to adsorb more than four times larger amount of CO compared to the fresh RhPt–NaMn–Ce/Al<sub>2</sub>O<sub>3</sub> one (data not shown.). After severe heat treatments at 700, 800, and 900 °C, however, the amount of CO adsorbed on our RhPt–NaMn–Ce/Al<sub>2</sub>O<sub>3</sub> was a little larger than that of RhPt–NaTi–Ce/Al<sub>2</sub>O<sub>3</sub>. These results indicate that the presence of Mn additive is not effective to improve the surface area of exposed RhPt species in the former compared to the latter.

Fig. 6 gives the results of CO<sub>2</sub> adsorption. The amount of CO<sub>2</sub> adsorbed on the fresh RhPt–NaTi–Ce/Al<sub>2</sub>O<sub>3</sub> catalyst was larger than that on our RhPt–NaMn–Ce/Al<sub>2</sub>O<sub>3</sub> catalyst. It should be noted that for RhPt–NaMn–Ce/Al<sub>2</sub>O<sub>3</sub>, the amount of CO<sub>2</sub> did not decrease on heat treatments at 700 and 800 °C, in contrast to RhPt–NaTi–Ce/Al<sub>2</sub>O<sub>3</sub> catalyst, which showed a significant decrease. The most severe treatment at 900 °C caused a decrease of the CO<sub>2</sub> adsorption for RhPt–NaMn–Ce/Al<sub>2</sub>O<sub>3</sub> as well but it was still able to adsorb a larger amount of CO<sub>2</sub> by a factor of about 2 than RhPt–NaTi–Ce/Al<sub>2</sub>O<sub>3</sub>. Na species can adsorb CO<sub>2</sub> but Mn is unlikely to be an adsorption site for CO<sub>2</sub>. Fig. 6 shows, therefore, that the number of basic Na sites effective for CO<sub>2</sub> adsorption is larger for RhPt–NaMn–Ce/Al<sub>2</sub>O<sub>3</sub> after severe heat treatments at tempera-



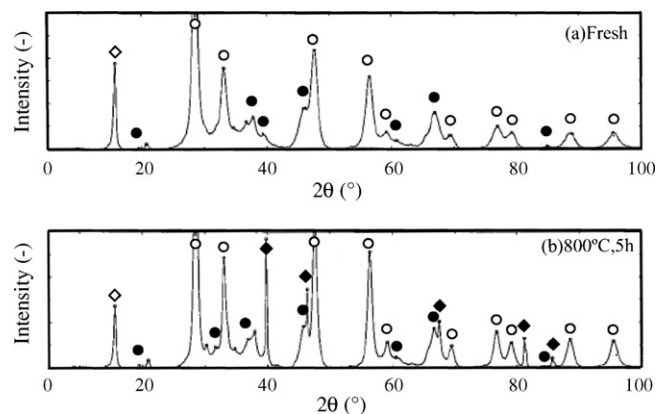
**Fig. 7.** The relationship between NO conversion at 400 °C and amount of CO<sub>2</sub> adsorbed for RhPt–NaTi–Ce/Al<sub>2</sub>O<sub>3</sub> (○) and RhPt–NaMn–Ce/Al<sub>2</sub>O<sub>3</sub> (●) catalysts.

tures up to 900 °C than for RhPt–NaTi–Ce/Al<sub>2</sub>O<sub>3</sub>. The presence of Mn should effectively suppress the sintering of Na species at high temperatures, resulting in the large surface area of exposed Na species. Fig. 7 shows a good correlation of the NO<sub>x</sub> conversion with the amount of CO<sub>2</sub> adsorbed for the two catalysts after several heat treatments.

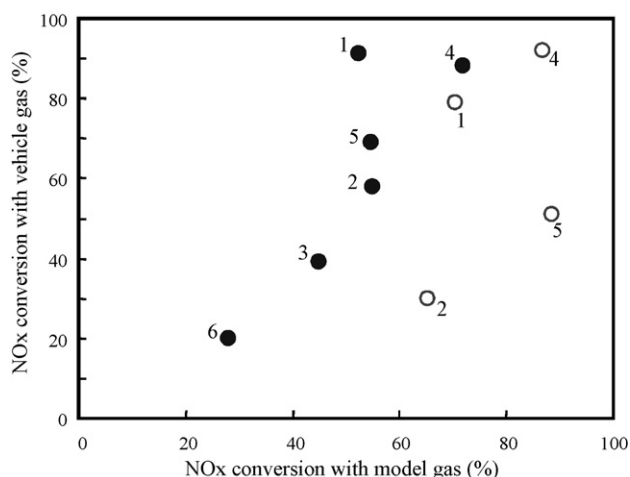
### 3.2.4. XRD measurement

Fig. 8 shows the XRD patterns of fresh and 800 °C heat-treated RhPt–NaMn–Ce/Al<sub>2</sub>O<sub>3</sub> catalysts. The fresh sample indicated the diffraction peaks originating from CeO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Na–Mn mixed oxides. Namely, the mixed oxides were produced from Na and Mn species in this catalyst. No diffraction peaks due to the precious metals were observed. The precious metals were likely to be highly dispersed on the surface of Al<sub>2</sub>O<sub>3</sub>. On the other hand, for the catalyst after heat-treated at 800 °C, Pt was detected besides CeO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Na–Mn mixed oxides, indicating the sintering of Pt. The sizes of Na–Mn mixed oxides calculated from XRD results were 20 and 21 nm for the fresh and heat-treated samples, respectively. It was thus indicated that Na–Mn mixed oxide did not sinter by heat treatment, which agreed with the results obtained from the CO<sub>2</sub> adsorption measurements (Fig. 6).

In conclusion, the present results show the RhPt–NaMn–Ce/Al<sub>2</sub>O<sub>3</sub> catalyst to be highly effective for NO<sub>x</sub> conversion. The positive effects of Mn additive are likely to result



**Fig. 8.** The XRD patterns of RhPt–NaMn–Ce/Al<sub>2</sub>O<sub>3</sub> catalysts for (a) fresh and (b) after heat-treated at 800 °C for 5 h in air. (○) CeO<sub>2</sub>, (●) Al<sub>2</sub>O<sub>3</sub>, (◇) Na<sub>0.7</sub>MnO<sub>2</sub>, and (◆) Pt.



**Fig. 9.** Comparison in the catalytic performance for NO conversion between for model gas and for vehicle gas with RhPt–NaTi–Ce/Al<sub>2</sub>O<sub>3</sub> and RhPt–NaMn–Ce/Al<sub>2</sub>O<sub>3</sub> catalysts after various heat treatments. Reaction temperature: 300 °C (●), 400 °C (○). Catalysts: (1), (2), (3) RhPt–NaTi–Ce/Al<sub>2</sub>O<sub>3</sub> after heat treatment at 700, 800, 900 °C for 5 h each in air. (4), (5), (6) RhPt–NaMn–Ce/Al<sub>2</sub>O<sub>3</sub> after heat treatment at 700, 800, 900 °C for 5 h each in air.

from its action for suppressing the sintering of Na species during heat treatment and then keeping the high surface area of exposed Na species, which act as NOx trapping sites. Although a part of Na species may exist in carbonate or hydroxide form, the mixed oxides were produced from Na and Mn species, these were highly dispersed on the surface of Al<sub>2</sub>O<sub>3</sub>, and the sintering of Na species was suppressed. The Mn additive is unlikely to change the ability of NOx trapping and to effectively act as NO oxidation sites.

### 3.3. Performance under practical conditions

The present results indicate that our RhPt–NaMn–Ce/Al<sub>2</sub>O<sub>3</sub> catalyst is most effective for NO conversion under the laboratory conditions. So, it is interesting and significant to test its performance under practical vehicle operation conditions. For this purpose, we used a 1.8 L engine, which was practically loaded in a lean-burn vehicle. Two catalyst honeycombs of 0.62 L each were connected in series and tested; the engine was operated with a lean gas for about 1 min and the gas was switched to a rich gas for 0.2 s every about 1 min. The concentration of NOx was measured at the inlet and outlet of the catalyst just before the switch from the lean gas to the rich gas, and the NOx conversion was determined. The concentration of NOx at the inlet of the catalyst was changing between 100 and 200 ppm in this test. After driving more than 10 min, the concentration of NOx was measured. The activity for NOx conversion was measured at catalyst inlet temperatures of 300 and 400 °C for the RhPt–NaMn–Ce/Al<sub>2</sub>O<sub>3</sub> and RhPt–NaTi–Ce/Al<sub>2</sub>O<sub>3</sub> catalysts after heat treatments at 700, 800, 900 °C for 5 h each. Fig. 9 presents the results of NOx conversion with a model laboratory gas and a practical vehicle gas. The NOx conversion with vehicle gas at 400 °C for the RhPt–NaMn–Ce/Al<sub>2</sub>O<sub>3</sub> and RhPt–NaTi–Ce/Al<sub>2</sub>O<sub>3</sub> catalysts after heat treatments at 900 °C

for 5 h was not measured. There is scatter in Fig. 9, mainly due to difficulty of the control of reaction conditions for the vehicle test. After considering these circumstances, one may say that Fig. 9 indicates that the evaluation with a model laboratory gas can estimate the performance under practical vehicle operation conditions. Moreover, compared with the catalytic performance for vehicle gas with RhPt–NaMn–Ce/Al<sub>2</sub>O<sub>3</sub> and RhPt–NaTi–Ce/Al<sub>2</sub>O<sub>3</sub> catalysts after heat treatment at 800 °C for 5 h, the RhPt–NaMn–Ce/Al<sub>2</sub>O<sub>3</sub> catalyst is more active under the vehicle gas conditions. Namely, our RhPt–NaMn–Ce/Al<sub>2</sub>O<sub>3</sub> catalyst is one of promising catalysts for NOx conversion under practical conditions.

## 4. Conclusions

The present results demonstrate that the RhPt–NaMn–Ce/Al<sub>2</sub>O<sub>3</sub> is a promising catalyst for NOx conversion under practical vehicle conditions. The high thermal stability can be achieved by the presence of Ce and Mn species. The Mn additive contributes to improve the catalytic activity for NO oxidation but this is less important. It can prevent the Na species from sintering even after a severe heat treatment at 800 °C, resulting in the larger surface area of exposed Na species on Al<sub>2</sub>O<sub>3</sub>, which acts as sites for trapping NOx. The high performance of our catalyst is confirmed for NOx conversion in a vehicle engine under lean-burn conditions.

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