NOx reduction over Pd/La0.9Ba0.1AlO3-δ at low temperature under exhaust gas condition

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Abstract: NOx reduction by propylene over Ba-substituted LaAlO3 supported Pd catalyst (Pd/La0.9Ba0.1AlO3-δ) was investigated. Pd/La0.9Ba0.1AlO3-δ revealed higher activity than other Pd catalysts at low temperatures (≤ 573 K) for NOx reduction by propylene. Comparison with Ba-impregnated LaAlO3 supported Pd catalyst (Pd/Ba/LaAlO3) indicated that Pd/La0.9Ba0.1AlO3-δ showed higher activity than Pd/Ba/LaAlO3. From this result, substitution of La site in the LaAlO3 support with Ba was more effective for NOx reduction than Pd/Ba/LaAlO3 on which Ba was sequentially impregnated.

Keywords: NOx reduction, Perovskite oxides, Pd catalyst.

1. Introduction
Vehicle exhaust gas contains harmful pollutants such as carbon monoxide (CO), unburned hydrocarbons (HC) and nitrogen oxides (NOx).1 Automotive catalysts convert these pollutants into CO2, N2 and H2O.2 However, automotive catalysts are faced with problems of lower exhaust gas temperature with improvement of fuel efficiency, less activity of conventional catalysts at low temperature, and severe regulations against automotive emissions. To solve these problems, development of catalysts which show higher activity than conventional catalysts are required. Then, the present study assessed catalytic activity for NOx reduction by propylene at low temperatures.

2. Experimental
Perovskite-type oxides were prepared using a citric acid complex method. Catalysts were prepared using an impregnation method. The Pd loading amount was 0.5 wt%.

Catalytic activity tests for NOx reduction were conducted in a fixed bed quartz reactor at atmospheric pressure. Tests were performed with 50 mg of catalyst. The reaction gas composition consisted of 1000 ppm of NO, 500 ppm of C3H6, 2000 ppm of O2, 7 vol% of H2O, and Ar as a balance gas, simulating the exhaust gas of λ = 1.14. The total gas flow rate of the reaction gas was 200 cc min⁻¹. Pre-treatment of the catalyst was conducted for oxidation (5 % O2, Ar balanced at 773 K for 15 min) and reduction (5 % H2, Ar balanced at 773 K for 15 min). Catalytic activities were measured at 673, 623, 573, 523 and 473 K. NO conversion was analyzed using an online GC-TCD (GC-8A; Shimadzu Corp.). N2 yield was analyzed using a chemiluminescent method NOx analyzer (NOA-7000; Shimadzu Corp.).

3. Results and discussion
First, we conducted NOx reduction by propylene as a model of unburned hydrocarbon in an exhaust gas on Pd/La0.9Ba0.1AlO3-δ and Pd/Al2O3 for comparison as a reference catalyst. Catalytic activities on Pd/La0.9Ba0.1AlO3-δ are shown in Fig. 1. Catalytic activities on Pd/Al2O3 are shown in Fig. 2. Pd/La0.9Ba0.1AlO3-δ showed higher performance for NOx reduction reaction than Pd/Al2O3 at 473, 523, 573 K. These results suggested that the partial substitution with a different cation (especially Ba) for La site in Pd/LaAlO3 brought high performance for NOx reduction reaction.

Alkaline earth metal, particularly Ba, is a component in a lean NOx trap catalyst (LNT) for NOx storage. LNT catalysts can convert NOx to N2 via nitrate formed by the reaction between surface Ba.
species and gaseous NOx under a lean condition, followed by reduction of nitrate to N$_2$ under a fuel rich condition.

Therefore, to clarify the effect of substitution of La site in the LaAlO$_3$ support with Ba, we evaluated the catalytic activity of sequentially impregnated Pd/Ba/LaAlO$_3$ catalyst. Ba loading amount is 6.4wt% which is equal to Ba amount of Pd/La$_{0.9}$Ba$_{0.1}$AlO$_{3.5}$. Catalytic activities of Pd/La$_{0.9}$Ba$_{0.1}$AlO$_{3.5}$, Pd/Ba/LaAlO$_3$ and Pd/LaAlO$_3$ are presented in Fig.3. Pd/Ba/LaAlO$_3$ catalyst shows slight increase in NO conversion at 523, 573 K. However, compared to Pd/La$_{0.9}$Ba$_{0.1}$AlO$_{3.5}$, the catalytic activity of Pd/Ba/LaAlO$_3$ is inferior to that of Pd/La$_{0.9}$Ba$_{0.1}$AlO$_{3.5}$ at 473 K to 623 K.

According to the above results, La$_{0.9}$Ba$_{0.1}$AlO$_{3.5}$ was found to be superior support of Pd catalyst for NOx reduction. We investigated the role of La$_{0.9}$Ba$_{0.1}$AlO$_{3.5}$ support compared to LaAlO$_3$, Ba/LaAlO$_3$ and Al$_2$O$_3$ support.

4. Conclusions

We conducted the reduction of NO by C$_3$H$_6$ under wet and slightly lean conditions. Pd/La$_{0.9}$Ba$_{0.1}$AlO$_{3.5}$ catalyst showed higher catalytic activity than Pd/Ba/LaAlO$_3$ and Pd/Al$_2$O$_3$ at low temperatures of 523, 573 K. Substitution of La site in LaAlO$_3$ support with Ba was more effective for NOx reduction.

References