NO_x reduction over $Pd/La_{0.9}Ba_{0.1}AlO_{3-\delta}$ at low temperature under exhaust gas condition

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Abstract: NOx reduction by propylene over Ba-substituted $LaAlO_3$ supported Pd catalyst ($Pd/La_{0.9}Ba_{0.1}AlO_{3-\delta}$) was investigated. $Pd/La_{0.9}Ba_{0.1}AlO_{3-\delta}$ revealed higher activity than other Pd catalysts at low temperatures (≤ 573 K) for NOx reduction by propylene. Comparison with Ba-impregnated $LaAlO_3$ supported Pd catalyst ($Pd/Ba/LaAlO_3$) indicated that $Pd/La_{0.9}Ba_{0.1}AlO_{3-\delta}$ showed higher activity than $Pd/Ba/LaAlO_3$. From this result, substitution of La site in the $LaAlO_3$ support with Ba was more effective for NOx reduction than $Pd/Ba/LaAlO_3$ 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 CO_2, N_2 and H_2O.[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 quarz 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 C_3H_6, 2000 ppm of O_2, 7 vol% of H_2O, and Ar as a balance gas, simulating the exhaust gas of $\lambda = 1.14$. The total gas flow rate of the reaction gas was 200 cc min^{-1}. Pre-treatment of the catalyst was conducted for oxidation (5 % O_2, Ar balanced at 773 K for 15 min) and reduction (5 % H_2, 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.). N_2 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 $Pd/La_{0.9}Ba_{0.1}AlO_{3-\delta}$ and Pd/Al_2O_3 for comparison as a reference catalyst. Catalytic activities on $Pd/La_{0.9}Ba_{0.1}AlO_{3-\delta}$ are shown in Fig. 1. Catalytic activities on Pd/Al_2O_3 are shown in Fig. 2. $Pd/La_{0.9}Ba_{0.1}AlO_{3-\delta}$ showed higher performance for NOx reduction reaction than Pd/Al_2O_3 at 473, 523, 573 K. These results suggested that the partial substitution with a different cation (especially Ba) for La site in $Pd/LaAlO_3$ 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 N_2 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/$La_{0.9}Ba_{0.1}AlO_{3-\delta}$. Catalytic activities of Pd/$La_{0.9}Ba_{0.1}AlO_{3-\delta}$, 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/$La_{0.9}Ba_{0.1}AlO_{3-\delta}$, the catalytic activity of Pd/Ba/$LaAlO_3$ is inferior to that of Pd/$La_{0.9}Ba_{0.1}AlO_{3-\delta}$ at 473 K to 623 K.

According to the above results, $La_{0.9}Ba_{0.1}AlO_{3-\delta}$ was found to be superior support of Pd catalyst for NOx reduction. We investigated the role of $La_{0.9}Ba_{0.1}AlO_{3-\delta}$ support compared to $LaAlO_3$, Ba/$LaAlO_3$ and Al_2O_3 support.

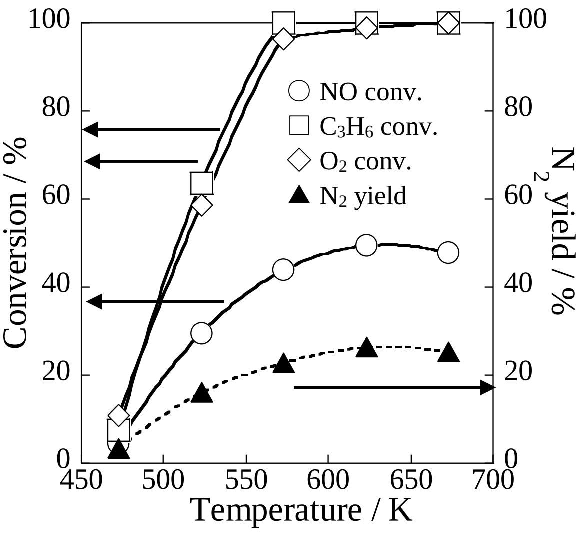

Figure 1. Catalytic activities of Pd/$La_{0.9}Ba_{0.1}AlO_{3-\delta}$.

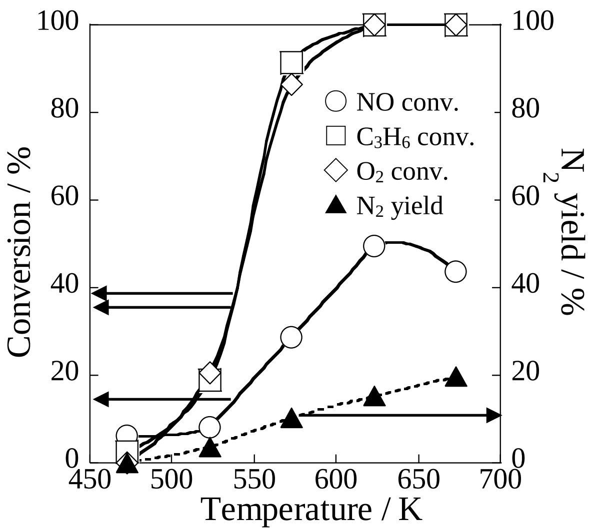

Figure 2. Catalytic activities of Pd/Al_2O_3.

4. Conclusions

We conducted the reduction of NO by C_3H_6 under wet and slightly lean conditions. Pd/$La_{0.9}Ba_{0.1}AlO_{3-\delta}$ catalyst showed higher catalytic activity than Pd/Ba/$LaAlO_3$ and Pd/Al_2O_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

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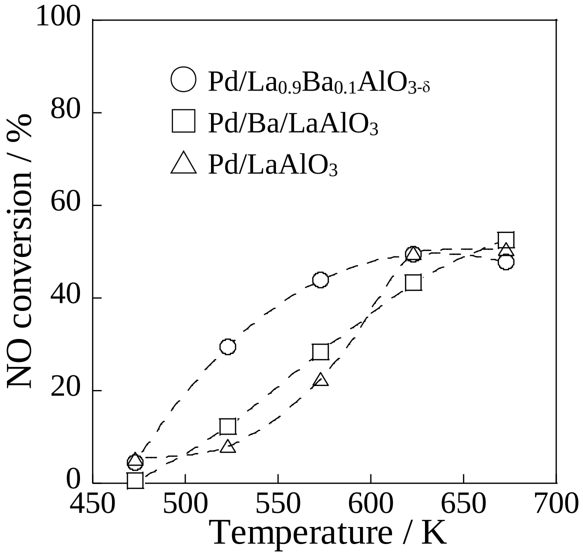

Figure 3. NO conversion of Pd/$La_{0.9}Ba_{0.1}AlO_{3-\delta}$, Pd/Ba/$LaAlO_3$ and Pd/$LaAlO_3$.