

# Effect of basic metal additives on $\text{NO}_x$ reduction property of Pd-based three-way catalyst

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## Abstract

The three-way catalytic (TWC) performance, especially CO and  $\text{NO}_x$  conversion, of a Pd-only catalyst was improved by the addition of basic elements, and the activity increased as the electronegativity of the additive cations decreased ( $\text{Ba} > \text{Sr} > \text{La}$ ), indicating that the basicity or electron-donating ability of the additives played a significant role in the improvement of the TWC performance. Thermal decomposition temperature of PdO in promoted catalysts became higher with decreasing the ionic electronegativity of the promoters. XPS analysis proved that the electron density around Pd(II) in the Ba-promoted catalyst was higher than that of Pd-only catalyst. The improvement of the TWC performance by the addition of basic promoters is discussed in terms of the stabilization of PdO, which may suppress the sintering, as well as of electron enrichment, which endows palladium with the Rh-like catalytic behavior. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Pd-based three-way catalyst; Basic metal additive; Thermal stability; Electron donation

## 1. Introduction

The first catalytic converter installed in automobiles was an oxidation catalyst for carbon monoxide (CO) and hydrocarbons (HC) [1]. Then, the catalyst was evolved to three-way conversion catalyst (TWC) that could reduce  $\text{NO}_x$  simultaneously with a new engine management and Rh usage. It is well known that Rh has superior  $\text{NO}_x$  reduction activity to other active ingredients such as Pt and Pd [2–4].

Recent emission regulations have been mainly focusing on the reduction of HC emission due to reducing a photochemical smog [5–6]. Recently, Pd has been widely used in TWC for its effectiveness in HC oxidation [7–8], but its weakness in  $\text{NO}_x$  reduction activity requires the combination of Pd with Rh in

order to obtain robust TWCs. Rh has been known for its superior  $\text{NO}_x$  reduction activity, while its scarcity and high cost have been requiring minimum usage.

In this study, the addition of basic promoters was examined to improve the  $\text{NO}_x$  conversion and thermal stability of a Pd-based TWC, and the origin of the observed promotion effect was investigated.

## 2. Experimental

### 2.1. Engine dynamometer test

For the examination of the promoter's effect on the TWC performance, basic elements (Sr, Ba and La) were added to a commercial Pd/ $\text{Al}_2\text{O}_3$ -based TWC catalyst (N.E. ChemCat Corp.). The catalysts were washcoated on a ceramic honeycomb (62 cell/ $\text{cm}^2$ ) so as for the Pd loading to be 2.0 g-Pd (L-substrate) $^{-1}$ .

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Loadings of additives were  $15 \text{ g (L-substrate)}^{-1}$  as a metal oxide.

An engine dynamometer evaluation was conducted with an eight-chamber reactor on the engine dynamometer. The reactor consisted of eight independent chambers and allows a simultaneous sample aging. The exhaust gas from the engine was led to the reactor and divided to each chamber. The test sample volume was  $35.6^{\text{ph}} \times 127.0^{\text{L}} \text{ mm}$  ( $125 \text{ cm}^3$ ). In the engine bench test, the catalyst was aged for 50 h on the engine dynamometer at the catalyst inlet temperature of  $850^{\circ}\text{C}$ . These catalysts were subjected to a sweep test evaluation. This evaluation was performed on a 2.0-liter engine with an external electric controller, which allows control of air/fuel ratio (A/F) and perturbation (amplitude and frequency). The evaluations were conducted by scanning A/F from rich (A/F = 14.9) to lean (A/F = 14.2) at a perturbation of  $\pm 1.0$ , 1.0 Hz at a catalyst inlet temperature of  $400^{\circ}\text{C}$ , space velocity of  $68,000 \text{ h}^{-1}$  [9]. The A/F condition was changed stepwise every 0.1 in A/F and was kept for 1 min, and conversion efficiency was calculated every 6 s.

The catalysts used in the engine dynamometer test were ground to a powder, and provided to XRD analysis (MAC Science MXP3/MXP21 VAHF<sup>22</sup>).

## 2.2. Characterization and laboratory test

Samples for instrumental analysis were prepared by impregnating an alumina support with aqueous Pd nitrate, followed by the air-calcination at  $500^{\circ}\text{C}$  for 30 min in an electric oven ( $\text{Pd}/\text{Al}_2\text{O}_3$ ). An aqueous solution of a metal (M) acetate was impregnated to the  $\text{Pd}/\text{Al}_2\text{O}_3$  powder and calcined again under the same condition ( $\text{Pd-M}/\text{Al}_2\text{O}_3$ ). The loadings of both Pd and a promoter were 5 wt.%.

Thermal decomposition temperature of PdO on alumina with and without promoters was measured by TG analysis (Rigaku Thermo Plus TG-8120) with the following conditions: sample weight, 100 mg; air flow rate,  $50 \text{ cm}^3 \text{ min}^{-1}$ ; temperature range, r.t.  $1000^{\circ}\text{C}$ ; ramping rate,  $20^{\circ}\text{C min}^{-1}$ . The electronic state of Pd was analyzed by XPS (VG Scientific, ESCALAB220i-XL) with monochromated Al K $\alpha$  radiation. Binding energies (BE) were calibrated with reference to the C1s<sub>1/2</sub> peak of contaminant aliphatic carbon at 285.0 eV.

The catalytic activity for the water-gas-shift reaction was conducted in a fixed-bed flow reactor at  $450^{\circ}\text{C}$  and  $60,000 \text{ h}^{-1}$  by feeding a mixture of CO (0.6%), H<sub>2</sub>O (10%) and N<sub>2</sub> (balance). Catalysts used were home-made  $\text{Pd}/\text{Al}_2\text{O}_3$ ,  $\text{Pd-Ba}/\text{Al}_2\text{O}_3$  and  $\text{Rh}/\text{Al}_2\text{O}_3$  washcoated on the ceramic honeycomb ( $25 \text{ cm}^3$ ), in which loadings of precious metals and Ba were the same as in those used in the engine dynamometer test.

## 3. Results and discussion

### 3.1. Effect of additives on TWC performance

The effect of additives on catalytic performance was examined by the engine dynamometer evaluation after catalysts had been aged at  $850^{\circ}\text{C}$  for 50 h. Fig. 1 compares the sweep test profiles of the reference Pd-only catalyst and the Ba-promoted catalyst. Over the wide Air/Fuel ratio investigated, the Ba-promoted catalyst exhibited higher conversions of HC, CO and NO, namely higher TWC performance, than the reference catalyst. TWC performances around a stoichiometric air/fuel ratio (A/F = 14.5–14.7) of catalysts with and without promoters are summarized in Fig. 2. The TWC performance, especially CO and NO<sub>x</sub> conversion, was significantly improved by the addition of not only Ba but also Sr and La, and alkaline earth elements, Sr and Ba, were more effective than La. In Fig. 3, conversions of HC, CO and NO are plotted against the electronegativity of a metal ion ( $\chi_i$ ), which is calculated from the equation of  $\chi_i = (1 + 2z)\chi_0$  [10]. Here,  $\chi_0$  and  $z$  are Pauling's electronegativity

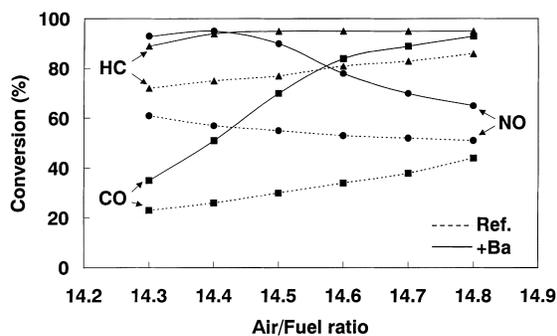


Fig. 1. Three-way catalytic performance of reference Pd-only and Pd-Ba catalysts.

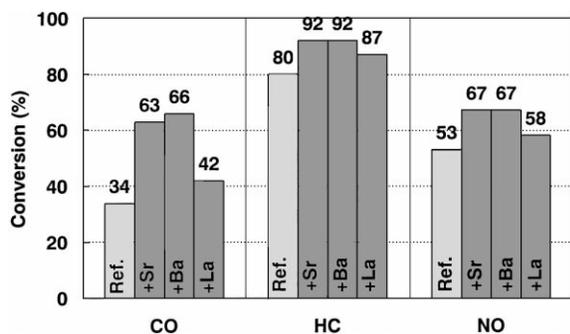


Fig. 2. Effect of the promoters (Sr, Ba and La) on three-way catalytic performance of Pd-based catalyst around the stoichiometric air/fuel ratio.

of the element and the ionic charge, respectively. Conversion of each species tends to increase with decreasing the  $\chi_i$  value, suggesting that the basicity or electron-donating property of the additives contributes the promotion of the TWC performance.

In the present dynamometer test, the catalysts were experienced the aging pretreatment before the TWC performance evaluation. Accordingly, it should be necessary to discuss the promoter's effect in terms not only of the intrinsic catalytic property but also of the stability of Pd species.

### 3.2. Thermal stability of Pd species

The reference and Ba-promoted catalysts before and after the aging pretreatment at 850°C were subjected to XRD analysis. In the fresh catalysts, no XRD peak

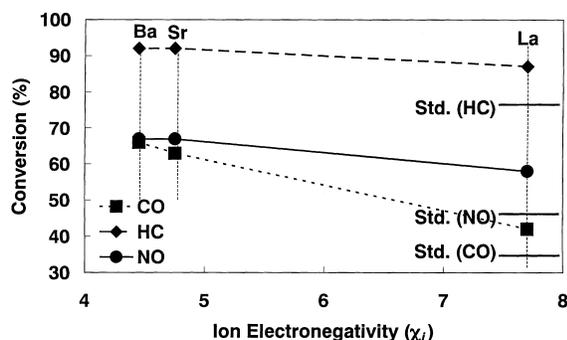


Fig. 3. Conversion of CO, HC and NO as a function of electronegativity of promoter cations. Std.(X); conversion of X over the reference Pd-only catalyst.

originated from Pd species (Pd or PdO) was observed, indicating that Pd species are highly dispersed in both the reference and Ba-promoted catalysts. Both the fresh catalysts carrying highly dispersed Pd species showed comparable TWC performance with almost complete conversion of CO, HC and NO<sub>x</sub>. In the aged catalysts, on the other hand, crystalline PdO was detected and crystalline sizes estimated by Scherrer's equation were 127 and 101 Å in the reference and Ba-promoted catalysts, respectively. The smaller crystalline size of PdO in the Ba-promoted catalyst implies that sintering of Pd species is suppressed by the Ba addition. It is well known that PdO decomposes into Pd and gaseous oxygen around 850°C in an ambient air, so that the thermal decomposition of PdO might occur during the aging pretreatment at 850°C. Since the sintering progresses more readily in the metallic state (Pd<sup>(0)</sup>) than in the oxide state (Pd<sup>(II)</sup>O) [11], the suppression of the sintering may have relation to the increased stability of PdO. In order to investigate this point, decomposition temperatures of PdO in a series of promoted catalysts were measured by TG. Fig. 4 shows TG profiles of Pd/Al<sub>2</sub>O<sub>3</sub> and Pd–Ba/Al<sub>2</sub>O<sub>3</sub> as representative examples. The decomposition temperature of PdO in Pd/Al<sub>2</sub>O<sub>3</sub> was 850°C, which is characteristic to PdO free from any stabilization effect. On the other hand, the PdO decomposition temperature in Pd–Ba/Al<sub>2</sub>O<sub>3</sub> increased to 928°C, confirming the stabilization of PdO by the addition of Ba. Such a stabilization effect was more or less observed for all the additives investigated. It was found that the

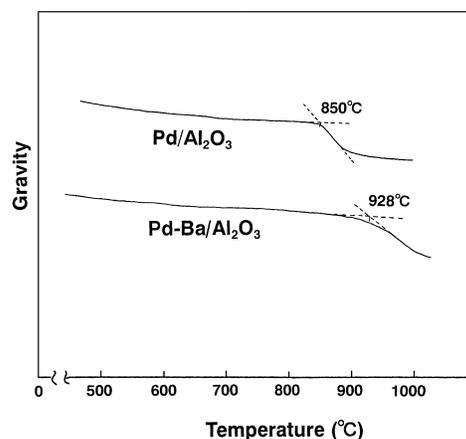


Fig. 4. TG profiles in air of Pd/Al<sub>2</sub>O<sub>3</sub> and Pd–Ba/Al<sub>2</sub>O<sub>3</sub>.

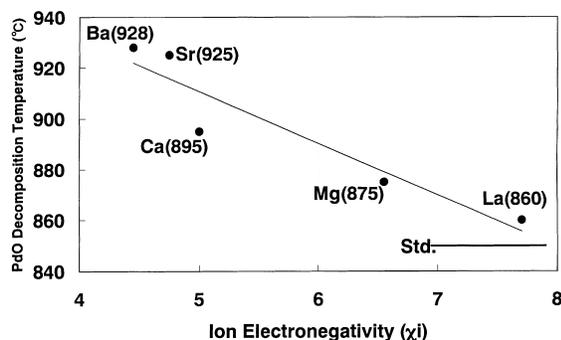


Fig. 5. Relation between decomposition temperature of PdO in Pd–M/Al<sub>2</sub>O<sub>3</sub> and ionic electronegativity of the additive (M).

stabilization of PdO was well correlated with the electronegativity of promoter ions. As shown in Fig. 5, the decomposition temperature of PdO becomes higher when more basic promoter is added. It is reasonably expected that the population of metallic Pd during the aging treatment becomes lower as the thermal stability of PdO increases. Accordingly, the improved stability of PdO by the addition of basic additives results in the suppression of the sintering of Pd species, which proceeds more readily in the metallic state than in the oxide state, as stated above. The agreement of the order of the TWC performance (Figs. 2 and 3) and the PdO decomposition temperature (Fig. 5), Pd–Ba > Pd–Sr > Pd–La > Pd, indicates that the stabilization of PdO should be one of origins of the promotion effect.

The increased stability of palladium oxide is observed on a variety of metal oxide supports, and it is ascribed, for example, to the formation of surface or near-surface oxide complex [12] or to the result of the strong PdO-support interaction [13]. In this sense, the strong PdO-additive interaction in the present promoted catalysts causes the stability enhancement of PdO, and the relation shown in Fig. 5 may suggest that the stabilization effect is related to the electron-donating property of additives. This will be discussed later.

### 3.3. Electronic state of Pd species

Another possible origin of the promotion effect, which is caused by the addition of basic elements, is change of electronic state of Pd species. Fig. 6 shows

Pd 3d XPS spectra of Pd/Al<sub>2</sub>O<sub>3</sub> and Pd–Ba/Al<sub>2</sub>O<sub>3</sub>. The BE value of Pd 3d<sub>5/2</sub> in Pd/Al<sub>2</sub>O<sub>3</sub> was 336.3 eV corresponding to PdO state. In Pd–Ba/Al<sub>2</sub>O<sub>3</sub>, on the other hand, the peak shifted to lower BE side, but the BE value of 335.8 eV is in between those of PdO and metallic Pd (around 335.3 eV). It was reported that the core-level BE of Pd significantly depended on the particle size of PdO and that the BE value of Pd 3d<sub>5/2</sub> increased with decreasing the particle size of PdO supported on Al<sub>2</sub>O<sub>3</sub> or NiO–Al<sub>2</sub>O<sub>3</sub> [13]. As stated above, the particle size of PdO in Ba-promoted catalyst is smaller than that in the Pd-only catalyst. Therefore, the BE shift towards the lower value by the addition of Ba cannot be explained by the particle-size-induced effect. The most plausible explanation to the BE shift is that electron density around Pd<sup>(II)</sup> in Pd–Ba/Al<sub>2</sub>O<sub>3</sub> increases as a result of the electron donation from the added Ba species.

Electron configuration of Pd<sup>(II)</sup> is Kr[4d<sup>8</sup>]. When an electron is donated to Pd<sup>(II)</sup>, the electron density in Pd 5s orbital would increase because the energy level of 5s is lower than that of 4d. Accordingly, the Pd<sup>(II)</sup> species in Pd–Ba/Al<sub>2</sub>O<sub>3</sub>, the electron density of which is higher than the usual Pd<sup>(II)</sup> (Kr[4d<sup>8</sup>]), is expected to have the configuration close to that of Rh metal, Kr[4d<sup>8</sup>5s<sup>1</sup>].

As stated above, the addition of basic additives results in the significant improvement in CO and NO<sub>x</sub> conversion activity. Basically, Pd has the weakness in its NO<sub>x</sub> reduction activity while Rh is the effective in the NO<sub>x</sub> reduction. Consequently, changes in the catalytic activity and the electron density may imply that the electron-rich Pd species in the promoted catalysts might show the catalytic property similar to Rh. In order to confirm the speculation, the catalytic activity for the water–gas shift reaction was examined. Because NO<sub>x</sub> reduction by hydrogen was a major path of NO<sub>x</sub> reduction in TWC system, and superior steam reforming activity of Rh leads to the significant contribution of Rh to the NO<sub>x</sub> reduction [14,15]. As shown in Fig. 7, Rh/Al<sub>2</sub>O<sub>3</sub> showed the highest activity, followed by Pd–Ba/Al<sub>2</sub>O<sub>3</sub> and Pd/Al<sub>2</sub>O<sub>3</sub>. The higher activity of Pd–Ba/Al<sub>2</sub>O<sub>3</sub> than Pd/Al<sub>2</sub>O<sub>3</sub> indicates, though indirectly, that the Pd species in Pd–Ba/Al<sub>2</sub>O<sub>3</sub> shows Rh-like catalytic behavior as a consequence of the electron donation from Ba.

It has turned out that the addition of basic additives, especially Ba, brings about the enhancement of

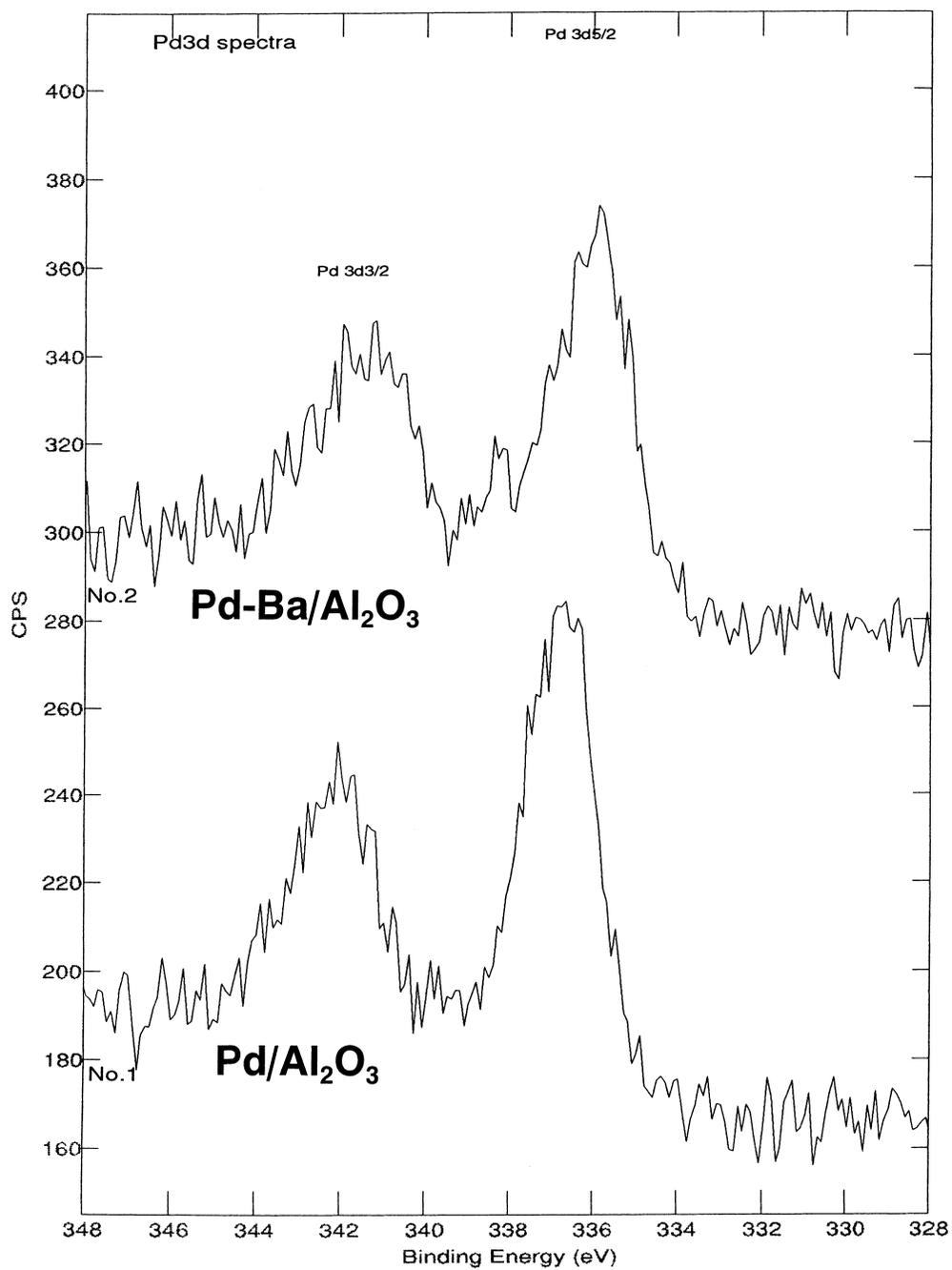


Fig. 6. Pd 3d XPS spectra of Pd/Al<sub>2</sub>O<sub>3</sub> and Pd-Ba/Al<sub>2</sub>O<sub>3</sub>.

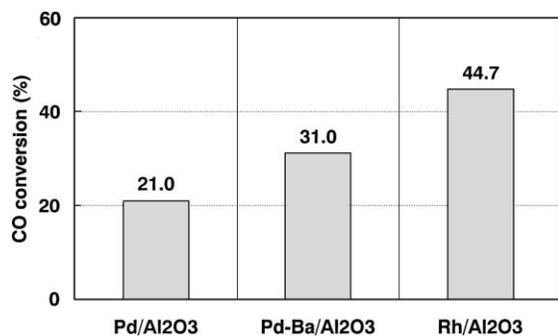


Fig. 7. Comparison of catalytic activity for water-gas shift reaction at 450°C among Pd/Al<sub>2</sub>O<sub>3</sub>, Pd-Ba/Al<sub>2</sub>O<sub>3</sub> and Rh/Al<sub>2</sub>O<sub>3</sub>.

the stability of PdO against the thermal decomposition and the increase in the electron density around Pd<sup>(II)</sup>. In order to appear such a promotion effect, the additives and Pd species should exist in close proximity each other and interact intimately. The increased electron density around Pd<sup>(II)</sup> can be reasonably explained by the electron-donating property of the basic additives. As for the increased stability of PdO, on the other hand, more investigation and consideration should be necessary, but the following might be a possible explanation based on the electronic interaction. In the event of the thermal decomposition of PdO, Pd<sup>(II)</sup>O → Pd<sup>0</sup> + (1/2)O<sub>2</sub>, two electrons have to come back to Pd, but it becomes more difficult as the electron density around Pd<sup>(II)</sup> increases.

#### 4. Conclusions

To improve the TWC activity of Pd-based catalyst, the effect of basic promoters was examined and the results obtained can be summarized as follows.

1. The TWC performance, especially CO and NO<sub>x</sub> conversion, was boosted up by the basic elements, and the performance tended to increase as the electronegativity of the additive ions decreased.
2. Thermal decomposition temperature of PdO became higher with decreasing the ionic electronegativity of the promoters. The increased stability of the oxide form may contribute the suppression

of the sintering which proceeds more readily in the metallic state.

3. The increase in the electron density around Pd<sup>(II)</sup> by the addition of Ba was evidenced by XPS analysis. The electron-rich Pd<sup>(II)</sup>, which may have electron configuration similar to Rh, showed the Rh-like catalytic properties in water-gas shift reaction and in TWC reaction, especially in NO<sub>x</sub> conversion.
4. The addition of Ba caused an increase in the electron density around Pd<sup>(II)</sup>, which may have electron configuration similar to Rh. The electron-rich Pd<sup>(II)</sup> showed the Rh-like catalytic property in the water-gas shift reaction, which may intimately relate to the enhancement of the TWC performance, especially of the NO<sub>x</sub> conversion.

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