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Author(s)	Jing, Yuan; Wang, Gang; Ting, Kah Wei et al.
Citation	Journal of catalysis, 400, 387-396 https://doi.org/10.1016/j.jcat.2021.06.016
Issue Date	2021-08-01
Doc URL	https://hdl.handle.net/2115/86492
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Type	journal article
File Information	Main text_PdMAL203.pdf



Roles of the Basic Metals La, Ba and Sr as Additives in Al₂O₃-supported Pd-based Three-Way Catalysts

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Abstract

Three-way catalytic converters are widely used to regulate emissions from gasoline-powered vehicles. Although significant effort over the past 40 years has resulted in the discovery of several metal additives that improve the thermal stability of three-way catalysts (TWCs), their effects on the actual catalytic process have not been studied systematically. The present work examined the roles of the typical basic metal additives La, Ba and Sr in Pd-based TWC systems, using various spectroscopic and kinetic studies. Metallic Pd⁰ species on Sr/Al₂O₃ and Ba/Al₂O₃ supports were found to be more electron-rich compared with those on pristine Al₂O₃, whereas those on La/Al₂O₃ were more electron-deficient. Consequently, Pd/La/Al₂O₃ showed a lessened CO poisoning effect during NO reduction reactions. Evaluations were performed using powdered catalysts as well as monolithic honeycomb catalysts under conditions simulating actual use. Pd/La/Al₂O₃ was observed to promote the catalytic reduction of NO most efficiently, while Pd/Ba/Al₂O₃ exhibited the highest activity for the oxidations of CO and C₃H₆. The present data suggest that the optimal metal additive for a Pd-based TWC will be determined by the specific application. The selection of such metals should take into account not only the stability but also the promotional effect during the exhaust purification process.

Keywords

Three-way catalysts, basic metals, *in situ/operando* spectroscopy, XAS

1. Introduction

Three-way catalysts (TWCs) provide an efficient means of reducing the pollutant emissions from gasoline-powered vehicles, by simultaneously removing compounds such as NO_x, CO and hydrocarbons (HCs) [1–3]. These catalysts are typically made of platinum group metals (PGMs), including Pt, Pd and Rh [4,5], because these elements exhibit superior catalytic performance and durability in comparison to nonprecious metals such as Cu, Ni and Fe [6–9]. As the regulatory requirements to reduce automotive emissions become increasingly strict, the development of effective support materials to improve the catalytic performance of PGMs is of great importance [10–13].

Al₂O₃ is widely used as a support material in TWCs because it has the advantages of possessing suitable mechanical strength, relatively good thermal stability and a high surface area [14,15]. Alkaline and alkaline earth metals as well as lanthanides are frequently combined with Al₂O₃ as structural stabilizers to suppress the transformation of Al₂O₃ from the γ to α phase [16–21]. Certain basic metals, such as La and Ba, are also known to stabilize Pd species during thermal treatment, resulting in improved dispersion of the Pd [22–25]. However, to date, only limited studies have been conducted to investigate the promotional effect of these basic metal additives on the catalytic performances of TWCs [26–30]. As an example, Muraki and coworkers reported that the addition of

La promoted the NO_x chemisorption, leading to the selective reduction of NO_x rather than O₂, and also inhibited the HCs adsorption on Pd, resulting in more efficient reduction of NO_x [31–34]. In addition, Sekiba et al confirmed that the introduction of La₂O₃ and BaO into a Pd/CeO₂/Al₂O₃ catalyst enhanced the catalytic performance of this material during NO conversion under reducing conditions [35]. Kobayashi and co-workers have also reported that the abilities of Pd-based catalysts to catalytically remove NO_x were improved following the addition of basic elements, including La, Ba and Sr [36]. Prior reports such as these have suggested that the electron densities of Pd species are increased by the addition of these elements. Our own group recently reported work assessing the promotional effect of La in La-loaded Al₂O₃-supported Pd (Pd/La/Al₂O₃) catalysts serving as TWCs [37,38]. These prior studies demonstrated that metallic Pd⁰ species in Pd/La/Al₂O₃ are more electron-deficient than those in Pd/Al₂O₃, which in turn suppresses the poisoning effect of CO and increases the catalytic activity for the removal of NO. Moreover, we reexamined the effective loading amount of La, which has conventionally been in the range of 3–5 wt%, with the aim of optimizing the specific surface area of the La/Al₂O₃ supports, and found that substantially increasing the La loading to 15 wt% provided a more effective TWC that was more reactive with NO, and suppressed the poisoning effect of CO. Although such work greatly contributed to the body of knowledge concerning TWCs, our present understanding of the roles of practically-used basic metal additives such as La, Ba or Sr in reactions over Pd-based catalysts remains insufficient. It would therefore be highly beneficial to systematically investigate the functions of such additives in TWCs especially under working conditions so as to develop efficient support materials that maximize the catalytic activity of Pd, which is the most commonly used active metal in modern commercial TWCs [39–41].

The present study performed a systematic investigation of the promotional effect of the basic metals La, Ba and Sr on the TWC process. A series of Pd/M/Al₂O₃ catalysts (M = La, Ba or Sr) was synthesized and these materials were investigated using various (*in situ/operando*) spectroscopic methods together with kinetics analyses. The results showed that metallic Pd⁰ species loaded on Ba/Al₂O₃ and Sr/Al₂O₃ were more electron-rich than those on Al₂O₃, while the Pd⁰ species on La/Al₂O₃ were more electron-deficient. The present data also indicated that Pd/La/Al₂O₃ promoted the catalytic reduction of NO most efficiently and that Pd/Ba/Al₂O₃ showed higher catalytic activity for the oxidations of C₃H₆ and CO.

2. Methods

2.1 Materials and Preparation of Catalysts

Chemicals were obtained from commercial suppliers and used as received. $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (purity >99.0%), $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ (purity >97.0%), and $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ (purity >95.0%) were obtained from Kanto Chemical Co. A nitric acid aqueous solution containing $\text{Pd}(\text{NH}_3)_2(\text{NO}_2)_2$ (Pd content = 50.4 g L^{-1} , Nitric acid content = 66.9 g L^{-1}) was supplied by Kojima Chemicals. $\gamma\text{-Al}_2\text{O}_3$ (purity >97.5%) was obtained from Sasol. He (purity >99.995%), H_2 (purity >99.99%), O_2 (purity >99.5%), N_2 (purity >99.99%), Ar (purity >99.99%), NO (purity >99.5%), CO (purity >99.95%), CO_2 (purity >99.99%), C_3H_6 (purity >99.95%) gases were obtained from Air Water Inc. and were used for catalyst preparations, catalytic reactions using powdered catalysts, and *in situ/operando* experiments. For catalysts aging under hydrothermal redox conditions and catalytic reactions using honeycomb catalysts, purities of gases used are as follows; >99.9999% for H_2 , >99.5% for O_2 , >99.0% for NO, >99.9% for CO, >99.5% for CO_2 , and 99.9999% for C_3H_6 .

The introduction of basic metal (La, Ba, or Sr) to $\gamma\text{-Al}_2\text{O}_3$ was carried out as described in previous studies [37,38]. The basic-metal-loaded Al_2O_3 was dried at 120°C for 2 h, followed by calcination in air at 600°C for 2 h and were noted as $\text{M}/\text{Al}_2\text{O}_3$ (M = La, Ba, or Sr). Supported Pd (3wt % Pd) catalysts were prepared by an impregnation method as follows. 5 g of $\text{M}/\text{Al}_2\text{O}_3$ (or Al_2O_3) and 100 mL of aqueous solution containing 1.45 mmol (0.338 g) of $\text{Pd}(\text{NH}_3)_2(\text{NO}_2)_2$ were added to a glass vessel. The mixture was then stirred for 15 min (200rpm) at room temperature. After stirring, the mixture was evaporated to dryness at 50°C under reduced pressure, dried at 90°C for 12 h, and calcined in air at 300, 500 or 600°C for 3h. Afterward, the calcined samples were pretreated under a flow of pure H_2 (20 mL min^{-1}) at 500°C for 0.5 h in a Pyrex tube. The samples pretreated under the flow of pure H_2 (20 mL min^{-1}) were used for the characterization experiments unless otherwise stated. Before each catalytic activity test and *in situ/operando* experiments, the samples were reduced again under flowing 10% H_2 /He (100 mL min^{-1}) at 400°C for 0.5 h.

The slurry, which was composed of an inorganic binder, the calcined catalyst powders, and water, was coated onto a cordierite honeycomb ($25.4 \text{ mm}\phi \times 50 \text{ mm}$, 400 cells/in²; NGK Insulators, Ltd.) to prepare the monolithic honeycomb catalysts. The thus prepared monolithic honeycomb catalysts were dried in air at 120°C for 1h, followed by calcination at 600°C for 2 h.

Monolithic honeycomb catalysts were aged at 1000°C for 4 h under hydrothermal redox conditions. The gas compositions for rich (3% H_2 , 3% CO, 10% H_2O , and N_2 balance), lean (3% O_2 , 10% H_2O , and N_2 balance), and stoichiometric (10% H_2O and N_2 balance) conditions were applied with intervals of 180 s for rich, 10 s for stoichiometric, 180 s for lean, and 10 s for stoichiometric atmospheres with flow rate = 3 L min^{-1} (space velocity (SV) = $7,200 \text{ h}^{-1}$).

2.2 Catalyst Characterization

X-ray diffraction (XRD) patterns were measured using Cu-K α radiation using Miniflex (Rigaku). N₂ adsorption measurements were conducted using AUTOSORB 6AG (Yuasa Ionics). High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were collected using JEM-ARM200F (JEOL). CO adsorption experiments were performed at -20 °C using BELCAT (MicrotracBEL). It should be noted that the samples were pretreated under the flow of pure H₂ (20 mL min⁻¹) at 500 °C before these characterizations.

X-ray photoelectron spectroscopy (XPS) was performed on ESCA-3400HSE (Shimadzu), equipped with a modified UHV chamber using Mg K α radiation. Binding energies were calibrated using the Al 2s peak of Al₂O₃ (119.5 eV). The reduced samples were measured using an Ar-filled glove box to avoid exposure of the samples to air.

2.3 (*Operando/in situ*) IR

Operando IR measurements were carried out at 150 °C using FT/IR-4200 (JASCO) with a Mercury-Cadmium-Telluride (MCT) detector. Samples (40 mg) were pressed to make pellets (ϕ = 20 mm), which were placed in the quartz IR cell having CaF₂ windows. The samples were heated under flowing 10% H₂/He (100 mL min⁻¹) at 400 °C for 0.5 h prior to the measurements. After cooling to 150 °C under flowing He, 0.5% NO/He was introduced for 10 min. After being purged by He for 10 min, 0.5% CO/He was introduced into the system for 10 min. The composition of the eluent was analyzed by a high-sampling-rate TCD GC (490 Micro GC; Agilent) and IR gas cell (JASCO FT/IR-4100). A reference spectrum, recorded at 150 °C under a flow of pure He, was subtracted from each spectrum.

The *in situ* IR measurements for CO adsorption was carried out at 40 °C by using the same apparatus described above. Prior to the adsorption experiments, the samples were exposed to 10% H₂/He (100 mL min⁻¹) for 30 min at 400 °C, followed by cooling to 40 °C under the flow of He. *In situ* IR spectra were collected after the introduction of 0.5% CO/He, followed by purge in the flow of He for 10 min.

2.4 (*Operando*) XAS

X-ray absorption spectroscopy (XAS) were performed in transmittance mode at the BL14B2 beamline of SPring-8 with a Si(311) double crystal monochromator. For measurements at the La, Ba and Sr K-edges, samples were sealed in polyethylene cells in air, and the spectra were measured at room temperature. For *operando* Pd K-edge XAS measurements, the high-sampling-rate TCD GC was employed for the analysis of N₂, N₂O, and CO. 150 mg of the samples in pellet form (ϕ : 10 mm) were added into a quartz cell with Kapton film windows. The catalyst was pretreated under a flow of 10% H₂/He (100 mL min⁻¹) at 400 °C for 0.5 h, followed by cooling to 150 °C. Subsequently, 0.5% NO/He, 0.5% CO/He, and 0.5%NO+0.5%CO/He (1000 mL min⁻¹) were introduced. The SV employed was ~ 30, 000 h⁻¹. The analysis was performed using Athena software ver. 0.9.25 included in the Demeter package [42]. The Fourier transformation of the k^3 -weighted extended X-ray absorption fine structure

(EXAFS) was carried out over a k range of 3–12 Å⁻¹.

2.5 Catalytic Reactions

For the catalytic NO–CO reaction using the powdered catalysts, 15 mg of the catalyst was placed in a reactor using quartz wool in the catalyst bed. After the reduction of the catalyst under 10% H₂/He flow (100 mL min⁻¹) at 400°C for 0.5 h, the catalyst was cooled to 100 °C and the catalytic NO–CO reaction was started by supplying a gas mixture (0.5% CO, 0.5% NO, and He) at 100 mL·min⁻¹ (W/F corresponds to 1.5×10⁻⁴ g·min·cm⁻³). Products were analyzed by GC (Shimadzu GC-8A with a SHINCARBON ST column). The yields were calculated based on the following equation.



For the catalytic NO–C₃H₆ reaction using the powdered catalysts, a mixed gas containing 0.45% NO and 0.05% C₃H₆ (He balance) was fed to 15mg catalysts at 100 mL min⁻¹ (W/F corresponds to 1.5×10⁻⁴ g·min·cm⁻³) after the reduction under the flow of 10% H₂/He at 400°C for 0.5 h and cooling to 200 °C. The yield was calculated based on the following equation.



For catalytic reactions on the honeycomb catalysts using MEXA-series (Horiba Ltd.), the catalysts were placed in a tubular-type reactor, and their catalytic performance was investigated by supplying a gas mixture containing NO, CO, C₃H₆, O₂, H₂, CO₂, H₂O, and N₂ balance at SV = 100,000 h⁻¹. Conversions of NO, CO, and C₃H₆, were monitored using a gas analyzer (ABB, AO-2020). Before each catalytic activity test, the honeycomb catalyst was pre-treated under a flow of the reaction gas (1 Hz perturbation between $\lambda = 0.95$ and $\lambda = 1.05$) at 400 °C for 0.5 h, followed by cooling to 100 °C under N₂. The λ values were calculated according to the following equation (see **Tables 1** for detailed gas compositions).

$$\lambda = \frac{\text{O}_2 + 0.5\text{CO} + 0.5\text{H}_2\text{O} + \text{CO}_2 + 0.5\text{NO}}{0.5\text{H}_2 + \text{CO} + 1.5\text{C}_3\text{H}_6 + 0.5\text{H}_2\text{O} + \text{CO}_2} \quad (3)$$

Table 1. Composition of the simulated exhaust gas mixtures for TWC light-off tests.

λ	NO / %	CO / %	C ₃ H ₆ / ppm	O ₂ / %	H ₂ / %	CO ₂ / %	H ₂ O / %	N ₂ / %
0.95	0.1	2.4	420	0.6	0.8	15	10	balance
1.00	0.1	0.6	420	0.6	0.2	15	10	balance
1.05	0.1	0.6	420	1.65	0.2	15	10	balance

3. Results and Discussion

3.1 Catalysts Characterization

The conditions used to prepare the Pd/M/Al₂O₃ and Pd/Al₂O₃ catalysts as well as the physicochemical properties of these materials are summarized in **Table 2**. We have employed higher Pd loading of 3 wt% in the present research than that used in the previous study (1 wt%) for ease of various measurements. Note that the 3 wt% Pd loading is within the range for the real-world applications. The loading amount of M was adjusted to be the same in the mol% (6.4, 10 and 10 wt% for Sr, Ba and La, respectively). The average Pd particle size in each catalyst was adjusted to approximately 6 nm by controlling the calcination temperature. Pd/Al₂O₃ was found to have a higher Brunauer–Emmett–Teller (BET) surface area compared with the Pd/M/Al₂O₃ series of samples in the as-prepared state (fresh). The XRD patterns provided in **Figure S1** demonstrate that each catalyst generated broad diffraction peaks attributable to γ -Al₂O₃. Peaks related to BaCO₃ and SrCO₃ were also present in the XRD patterns obtained from the Pd/Ba/Al₂O₃ and Pd/Sr/Al₂O₃ catalysts, respectively, confirming the presence of these carbonate species. These results are consistent with previous reports [37,38].

Characterization of the M/Al₂O₃ specimens using HAADF-STEM demonstrated that La, Ba and Sr were thoroughly dispersed on the atomic level over the γ -Al₂O₃ support (**Figure 1**). The data acquired from characterizations of the samples and of reference compounds using XAS at the La, Ba and Sr K edges are presented in **Figure S2**. Curve-fitting analyses of the EXAFS results are summarized in **Table S1**, and show that the spectrum of each Pd/M/Al₂O₃ specimen contained only a single M–O contribution. The results of M (M = La, Ba or Sr) K-edge XAS combined with the HAADF-STEM images indicated that La, Ba and Sr loaded on the γ -Al₂O₃ were highly dispersed and have a spatial uniformity of dopants dispersion, in agreement with reports based on earlier studies of similar materials [37,38,43–45].

Table 2. Preparation conditions and physicochemical characteristics of Pd/Al₂O₃ and Pd/M/Al₂O₃.

Catalyst ^a	Loading amount of M	$T_{\text{Calcination}}$ / °C	$T_{\text{H}_2 \text{ reduction}}$ / °C	S_{BET} / m ² g ⁻¹	CO adsorbed ^b / $\mu\text{mol g}^{-1}$	Particle size of Pd ^c / nm
Pd/Al ₂ O ₃	-	600	500	155	52.6	6.0
Pd/Sr/Al ₂ O ₃	6.4 wt%	500	500	146	51.9	6.1
Pd/Ba/Al ₂ O ₃	10 wt%	300	500	139	47.8	6.5
Pd/La/Al ₂ O ₃	10 wt%	500	500	134	55.1	5.7

^a Pd loading amount = 3 wt%. ^b Measured at at -20 °C. ^c Estimated from the CO adsorption experiments.

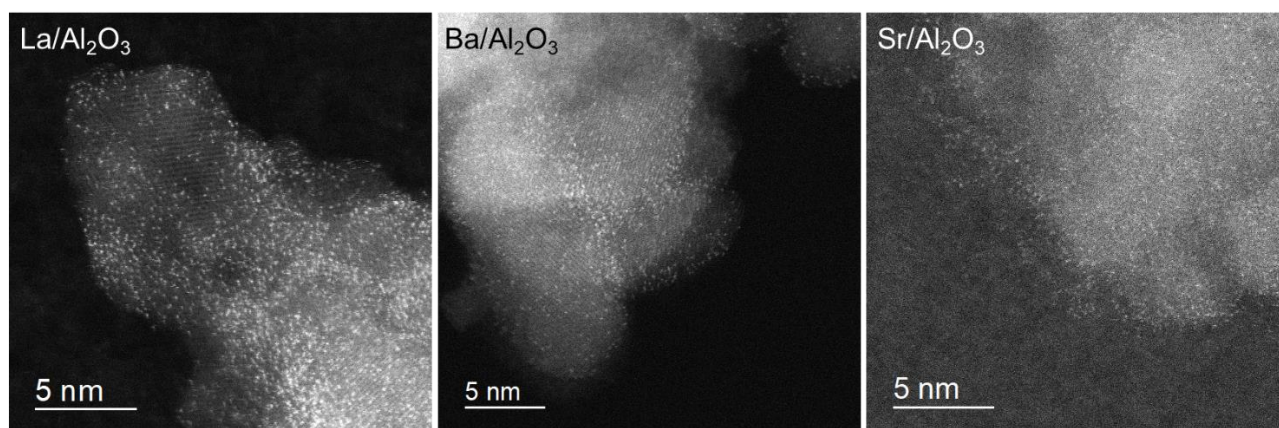


Figure 1. HAADF-STEM images of the M/Al₂O₃ (M = La, Ba or Sr) supports.

The electronic structures of the Pd nanoparticles in the Pd/Al₂O₃ and Pd/M/Al₂O₃ catalysts were assessed using IR spectroscopy in conjunction with CO adsorption as well as XPS. **Figure 2A** presents the *in situ* IR spectra acquired from the Pd catalysts following CO adsorption. In these spectra, the peak at approximately 2080 cm⁻¹ is attributed to CO molecules bound to the on-top sites of metallic surfaces [46]. The centers of the peaks generated by the Pd/Ba/Al₂O₃ and Pd/Sr/Al₂O₃ appeared at lower wavenumbers (2078 and 2080 cm⁻¹, respectively) compared with the peak produced by the Pd/Al₂O₃ (2082 cm⁻¹), whereas the peak in the Pd/La/Al₂O₃ spectrum was located at a higher wavenumber (2084 cm⁻¹). It is well known that the adsorption strength of CO on transition metals is mostly determined by the contribution from π back-donation of transition metals to the CO 2 π^* antibonding orbital, which is the lowest unoccupied molecular orbital (LUMO) [47,48]. The stronger the back-donation is, the weaker the C $\equiv$ O bonds become, resulting in more activation of adsorbed CO molecules [49]. That is, in the present case, $\nu_{\text{C=O}}$ is weaker (red-shifted) when CO is adsorbed on negatively charged Pd due to the enhanced back-donation character of Pd to CO 2 π^* antibonding orbitals. Therefore, the metallic Pd⁰ species supported on Sr/Al₂O₃ and Ba/Al₂O₃ were determined to be more electron-rich compared to those on pristine Al₂O₃, whereas those on La/Al₂O₃ were more electron-deficient.

Figure 2B provides Pd 3d XPS spectra obtained from the Pd/Al₂O₃ and Pd/M/Al₂O₃ specimens immediately after H₂ reduction, avoiding any subsequent exposure to air by using a glove box connected to the XPS sample chamber. These spectra include signals from both the 3d_{5/2} and 3d_{3/2} Pd core levels, and the 3d_{5/2} signal in the binding energy range of 335-336 eV can be assigned to metallic Pd [50–52]. Notably, the 3d_{5/2} signals generated by the Pd/Sr/Al₂O₃ (335.2 eV) and Pd/Ba/Al₂O₃ (335.3 eV) appeared at lower energies, while that produced by the Pd/La/Al₂O₃ (335.7 eV) was located at a higher energy compared with the result for the Pd/Al₂O₃ (335.5 eV). These data indicate that the Pd⁰ species loaded on the Ba/Al₂O₃ and Sr/Al₂O₃ were more electron-rich but those on the La/Al₂O₃ were electron-poor relative to the Pd/Al₂O₃. Thus, the XPS spectra were consistent

with the results of the *in situ* IR analyses following CO adsorption.

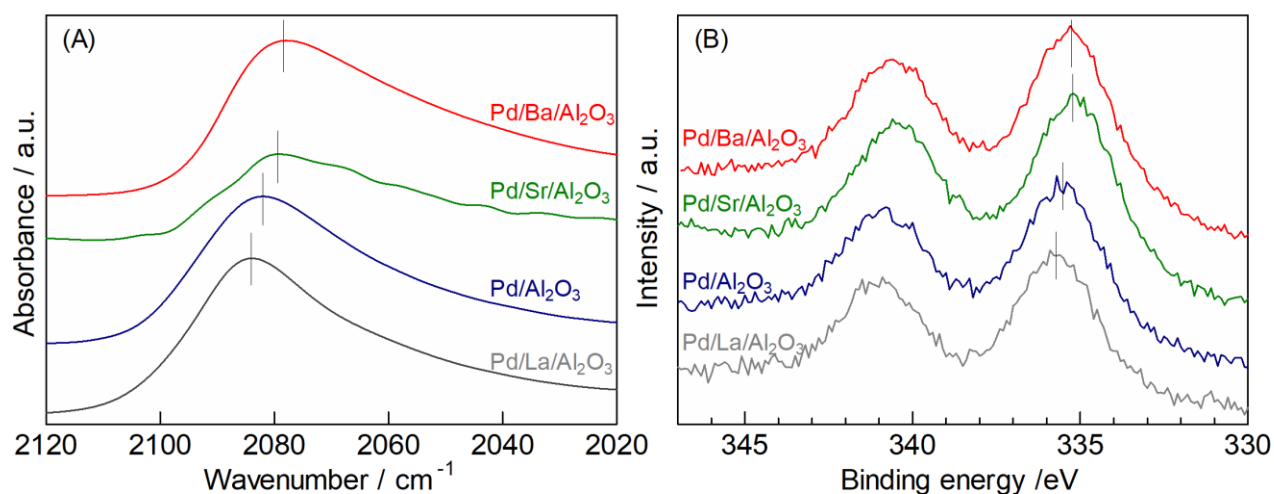


Figure 2. (A) *In situ* IR spectra of CO adsorbed on the Pd/Al₂O₃ and Pd/M/Al₂O₃ (M = La, Ba or Sr) catalysts. These spectra were collected under a flow of He following a 30 min exposure to CO. (B) Pd 3d XPS spectra for the Pd/Al₂O₃ and Pd/M/Al₂O₃ (M = La, Ba or Sr) catalysts. Spectra were obtained from the samples immediately after H₂ reduction without any exposure to air using a glove box connected to the XPS chamber.

3.2 Promotional Effect of the Basic Metal Additives on the NO Reduction Activity

Figure 3(A) summarizes the catalytic conversions of NO during the NO–CO reaction, which is a primary DeNO_x reaction [53–56], over the Pd/Al₂O₃ and Pd/M/Al₂O₃ catalysts in powder form under steady state conditions. The complete reaction results are provided in **Figure S3** in the Supporting Information. The introduction of La, Ba or Sr evidently enhanced the catalytic conversions of both NO and CO, especially at low temperatures (below 250 °C). It should be noted that N₂O and CO₂ were the main products in this low temperature region, and mass balance was 100% for all the temperature regime. Also, we have performed Weisz-Prater analysis [57] and confirmed that our activity tests were performed in the kinetic regimes. The catalytic activities of these materials, in terms of the conversions of both NO and CO, were found to decrease in the order of Pd/La/Al₂O₃ > Pd/Ba/Al₂O₃ > Pd/Sr/Al₂O₃ > Pd/Al₂O₃. In addition, the NO–C₃H₆ reaction, which is another important primary DeNO_x reaction [58,59], were also carried out to study the effect of basic metal additives on the NO reduction activity (**Figure S4**). Pd/Ba/Al₂O₃ showed the highest NO conversion at 300 °C, followed by Pd/La/Al₂O₃ and Pd/Sr/Al₂O₃. The results indicate that the introductions of La, Ba or Sr are also effective for the NO–C₃H₆ reaction.

To further investigate the role of these metals in the NO–CO reaction, the effects of the CO concentration on the reaction rates over Pd/Al₂O₃ and the Pd/M/Al₂O₃ specimens were examined, with the results presented in **Figure 3(B)**. It should be noted that turnover frequency (TOF) based on reaction rates and amount of CO adsorbed (**Table 2**) were determined from the reaction data for NO conversions up to 30%. The apparent reaction orders based on these log-log plots with respect to CO were determined to be -0.50, -1.07, -1.00 and -0.94 over the Pd/La/Al₂O₃, Pd/Ba/Al₂O₃, Pd/Sr/Al₂O₃ and Pd/Al₂O₃, respectively. The negative values indicate that CO inhibited the NO–CO reaction over the catalysts used in the present study, in association with the strong adsorption of CO molecules on the surfaces of the supported Pd nanoparticles [60,61]. The apparent reaction order associated with the Pd/La/Al₂O₃ was more positive than that over the other catalysts, suggesting that the poisoning effect of CO was weakened following the introduction of La [37]. In contrast, the apparent reaction orders obtained for the Pd/Ba/Al₂O₃ and Pd/Sr/Al₂O₃ were more negative than that for the pristine Pd/Al₂O₃. The most probable explanation for these results is that electron-deficient Pd⁰ species on the La/Al₂O₃ weakened the adsorption of CO molecules on the Pd surface, thus suppressing the poisoning effect of CO, whereas electron-rich Pd⁰ species on the Ba/Al₂O₃ and Sr/Al₂O₃ enhanced this adsorption, thus promoting the poisoning effect. It should also be noted that the reduction in the CO poisoning effect obtained following La addition in the present study was less than that observed in previous work using Pd/La/Al₂O₃ with La and Pd loadings of 15 and 1 wt%, respectively. This discrepancy can presumably be ascribed to the larger Pd particle size resulting from the higher Pd loading of 3 wt% in the present research, which reduced the support effects to change the electronic properties of the supported Pd species.

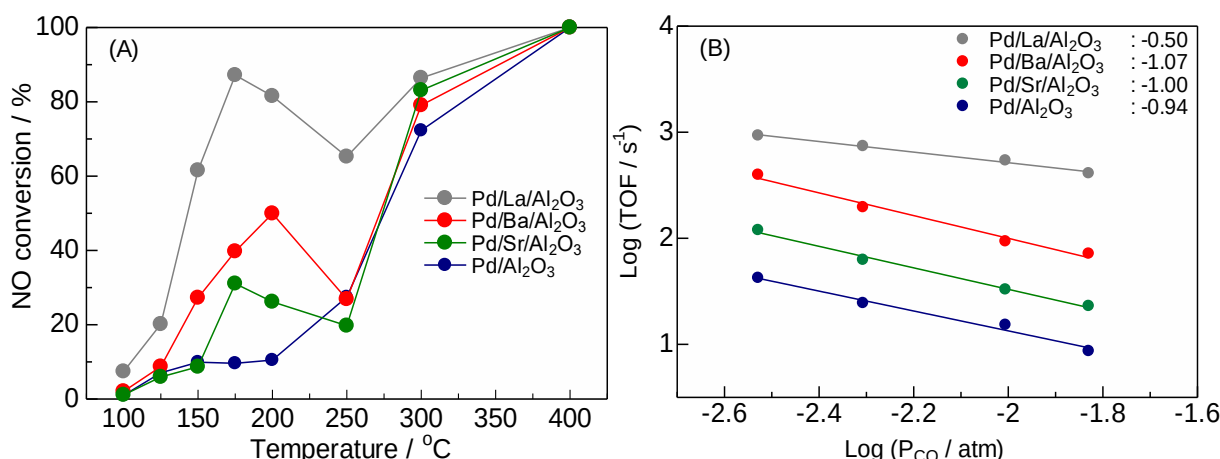


Figure 3. (A) Catalytic conversion of NO during the NO–CO reaction over the Pd/Al₂O₃ and Pd/M/Al₂O₃ (M = La, Ba or Sr) catalysts as fresh powders. Feed composition: 0.5% NO, 0.5% CO with He as the balance. (B) The log of the TOF as a function of the log of the CO concentration during the NO–CO reaction for each material. Conditions: 0.5% NO, 0.3–1.5% CO with He as the balance at 200 °C.

The effects of these metal additives on the chemical states of Pd during the NO–CO reaction were further investigated by performing *operando* Pd K-edge XAS analyses [62,63] under 0.5% NO/He, 0.5% CO/He or 0.5%NO+0.5%CO/He flows at 200 °C. Prior to analysis, each sample was pre-reduced at 500 °C under a flow of 10% H₂/He, and then reduced again in the XAS cell under 10% H₂/He at 400 °C just prior to the experiment. The *operando* Pd K-edge X-ray absorption near-edge structure (XANES) data and the FT of the *k*³-weighted EXAFS spectra acquired under a 0.5% NO/He flow are shown in **Figures 4 and S5**. Note that the Pd/La/Al₂O₃ spectra are included in the main text as representative data. In each case, the absorption edge positions gradually shifted to higher energies following exposure to NO, while the intensity of the FT peak corresponding to Pd–Pd bonds (at approximately 2.5 Å) decreased. These results demonstrate that the Pd in these materials was oxidized by the NO. It was also found that no Pd–O contribution was seen in the FT of the *k*³-weighted EXAFS spectra of Pd/Al₂O₃, which is in accordance with our previous study [37]. This lack of evidence for Pd–O bonds is attributed to the formation of oxidized and highly dispersed Pd species, which do not generate PdO species with well-defined Pd–O bonds. Similar phenomena have been reported for related materials [64–67]. In contrast, a Pd–O contribution was observed in the Pd/M/Al₂O₃ spectra, especially those of the Pd/La/Al₂O₃ and Pd/Ba/Al₂O₃. This finding reflects the strong anchoring effects of La and Ba, which would be expected to limit the deactivation of Pd species under the harsh TWC reaction conditions [24,25].

During these oxidation trials, N₂O was formed as the gas phase product and was monitored using a gas chromatograph with a thermal conductivity detector operating at a high sampling rate (**Figure 4C**). The Pd⁰ fraction (Pd⁰/(Pd⁰+Pd^{II})) obtained from linear combination fitting of the XANES data indicated that the Pd species were oxidized by the NO introduced into the system (**Figure 4D**). Thirty

minutes after the introduction of NO, the Pd⁰ fraction was determined to be 0.71 in the case of the Pd/La/Al₂O₃, which exhibited the highest level of oxidation among the four catalysts that were tested. After a He purge to remove residual gaseous NO, CO was introduced such that the partly oxidized Pd species were reduced with the simultaneous formation of N₂O and a small amount of CO₂. The results demonstrated that surface-adsorbed NO_x species that had been generated upon exposure to NO and retained during the He purge served as the source of N₂O. The incorporation of the basic metal additives evidently promoted the oxidation of Pd with decreasing effect in the order of La > Ba > Sr. It is also worth noting that the formation of CO₂ was observed along with the reduction of partially oxidized species. Based on these results, it is apparent that the NO–CO reaction over supported Pd catalysts comprises a redox cycle involving Pd species with NO as an oxidant and CO as a reductant.

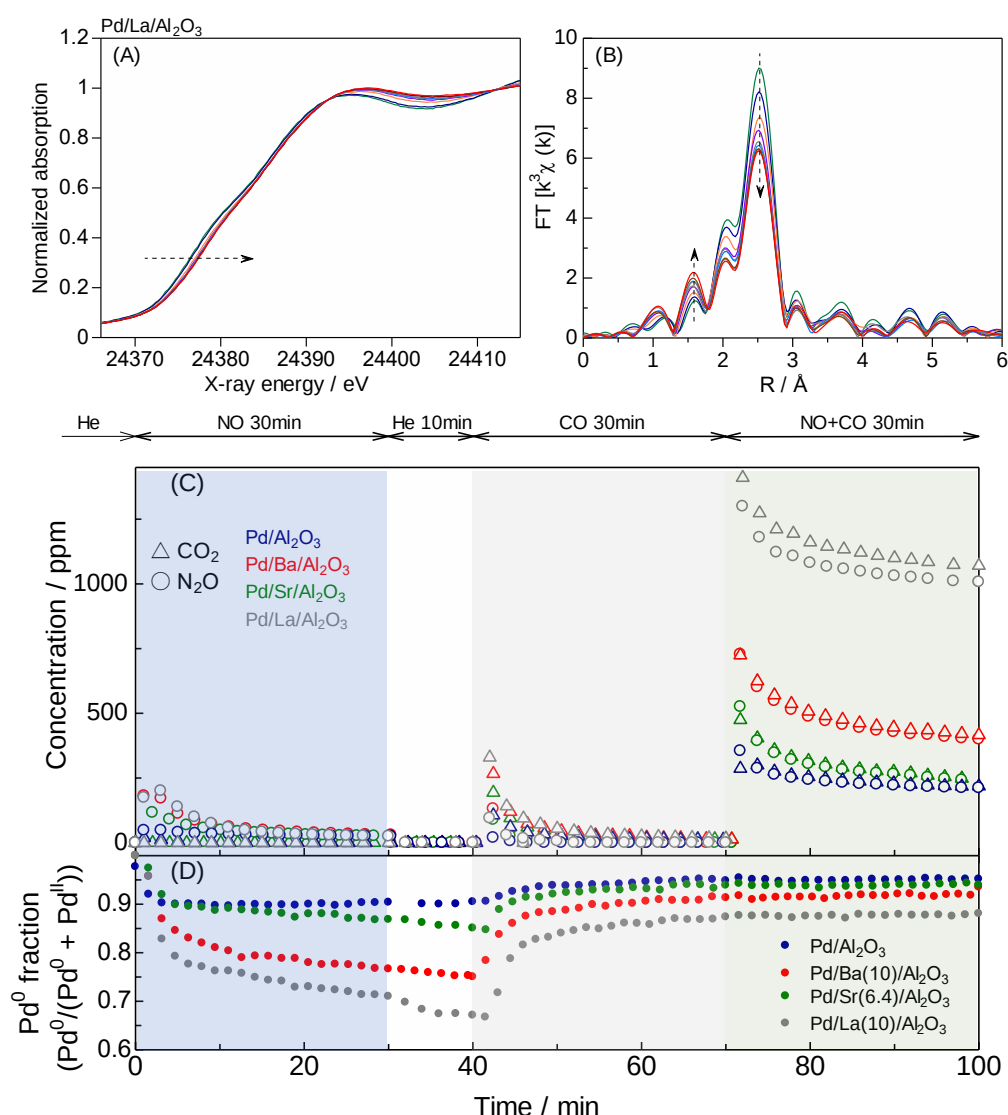


Figure 4. Results of the *operando* Pd K-edge XAS analyses. Pd K-edge (A) XANES spectra and (B) k^3 -weighted EXAFS FTs for Pd/La/Al₂O₃, acquired under flowing 0.5% NO/He (1000 mL min⁻¹) at 150 °C after the pretreatment. Changes in (C) the product concentrations in the gas phase and (D) the fraction of Pd⁰ under NO, CO and NO+CO flows at 150 °C.

Operando IR data were acquired to assess the roles of La, Ba and Sr in the formation of surface adsorbed species as well as the reactivities of these metals during the NO reduction. The results are provided in **Figure 5**. These spectra were collected under a flow of He after the introduction of 0.5% NO/He for 30 min followed by a flow of 0.5% CO/He. Subsequent to exposure to NO, various NO_x species were produced on the surfaces of the catalysts, as reflected in the peaks that appeared in the 1100–1700 cm⁻¹ region [68–70]. Specifically, the peaks at 1191 and 1232 cm⁻¹ are attributed to surface nitrite species [38,71,72]. The intensities of these peaks in the spectra of each Pd/M/Al₂O₃ specimen were higher than that generated by the Pd/Al₂O₃, indicating that the introduction of La, Ba or Sr promoted the formation of surface nitrite species more efficiently. The absorption bands in the 1250–1650 cm⁻¹ region are due to the presence of nitrate species with different adsorption modes [38,73–75]. The band at around 1660 cm⁻¹ is assigned to Pd-adsorbed NO species [38,76,77]. Considering that the *operando* XAS data demonstrated that N₂O was formed when solely NO was introduced, it is believed that the disproportionation reaction of NO occurred to produce both gaseous N₂O and surface nitrite species on the Pd/M/Al₂O₃. It is also important to note that the peaks obtained from the Pd/M/Al₂O₃ samples were essentially absent in the spectra generated by the M/Al₂O₃ without Pd (shown in seagreen), indicating the importance of combining Pd and M/Al₂O₃ as supports.

During the subsequent exposures of the Pd/Al₂O₃ and Pd/M/Al₂O₃ series to a flow of 0.5% CO/He, two strong peaks appeared at approximately 1560 and 1360 cm⁻¹ that are attributed to carbonate adsorbed on the catalyst surfaces [78]. After the introduction of CO, the intensities of the peaks related to nitrite species on the Pd/M/Al₂O₃ samples decreased. As demonstrated in **Figure 5B**, the intensities of these peaks in the Pd/La/Al₂O₃ spectra declined more rapidly than in the Pd/Ba/Al₂O₃ and Pd/Sr/Al₂O₃ spectra, indicating that nitrites on the Pd/La/Al₂O₃ were more reactive with CO. Simultaneous with the decline in surface nitrite species, higher concentrations of N₂O and CO₂ were formed on the Pd/La/Al₂O₃ than on the Pd/Ba/Al₂O₃ and Pd/Sr/Al₂O₃, as shown in **Figure 5C**. This trend is in agreement with the results obtained during the catalytic NO–CO reaction trials described above. These data confirm that the efficient formation of nitrites and the reactivity of these species with CO played important roles in promoting the NO–CO reaction.

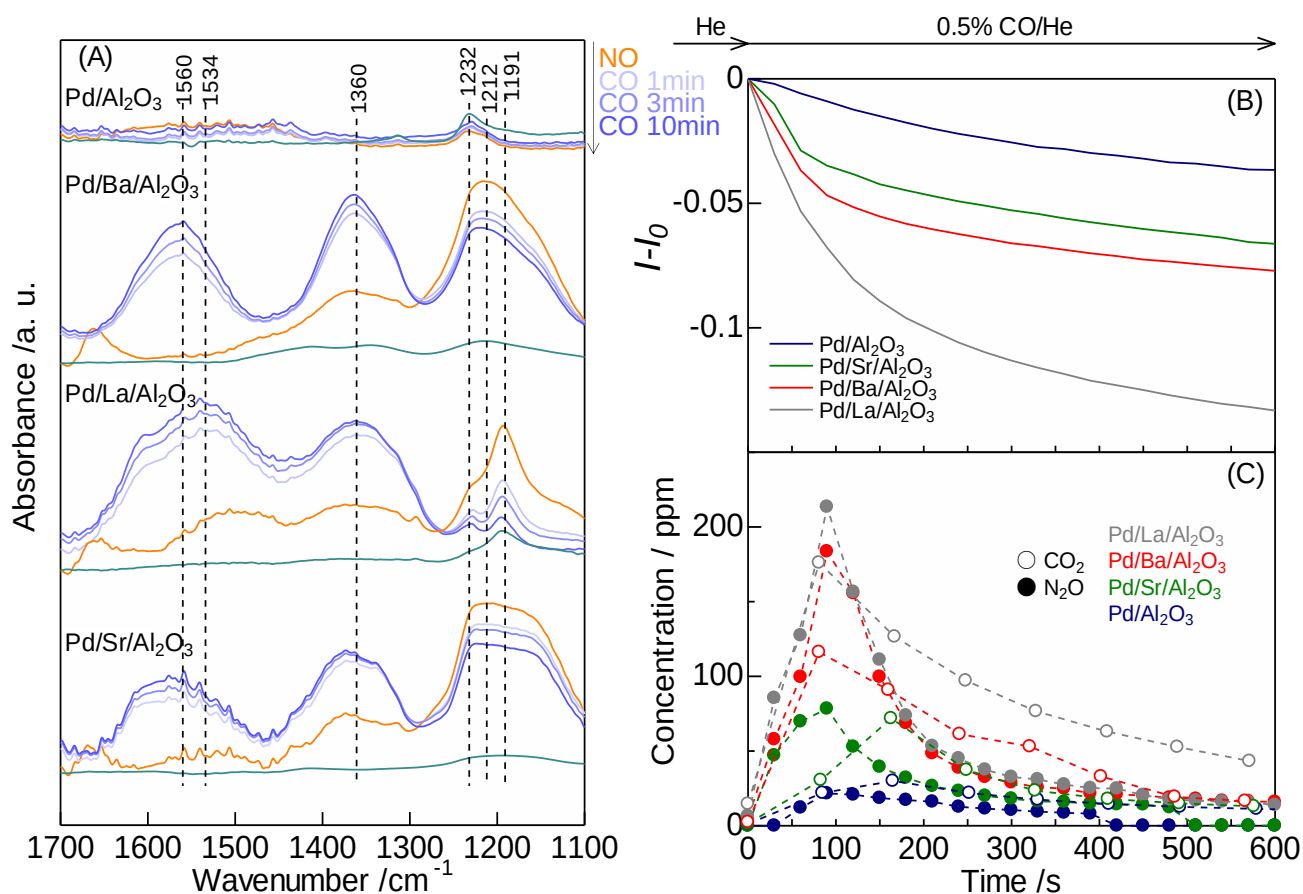


Figure 5. (A) *Operando* IR spectra showing the evolution of surface species adsorbed on the Pd/Al₂O₃ and Pd/M/Al₂O₃ (M = La, Ba or Sr) as well as the supports without Pd at 150 °C. The orange (Pd/Al₂O₃ and Pd/M/Al₂O₃) and seagreen (Al₂O₃ and M/Al₂O₃) spectra were collected under a flow of He after exposure to NO for 10 min. Subsequently, 0.5% CO/He was introduced into the cell in trials with the Pd/Al₂O₃ and Pd/M/Al₂O₃ and spectra were continuously acquired with simultaneous analysis of the gas phase products. Variations in (B) the intensities of peaks related to surface nitrite species and (C) the concentrations of N₂O and CO₂ in the effluent gas upon the introduction of 0.5% CO/He.

3.3 Catalytic activity test using honeycomb catalysts under TWC condition.

The results of TWC light-off tests over the honeycomb catalysts are shown in **Figure 6**. The fresh monolithic Pd/M/Al₂O₃ exhibited higher NO conversion than the Pd/Al₂O₃, suggesting that the basic metal additives enhanced the ability of these honeycomb materials to remove NO from automotive emissions under TWC conditions. In addition, the La-loaded catalyst exhibited a higher degree of NO conversion in comparison with the others, in agreement with the NO–CO reaction data and corresponding *operando* XAS and IR results. In contrast, throughout the C₃H₆ and CO oxidation trials, the Ba-loaded sample showed higher CO and C₃H₆ conversions relative to the materials incorporating Sr and La. Ba is known to provide exceptional performance when added to Pd/Al₂O₃ catalysts intended for the oxidation of HCs such as methane, especially in the presence of water vapor [23,79,80]. This promotional effect has been attributed to electron donation from the Ba to the Pd on the support, in agreement with the findings of the present study.

The stability of these honeycomb catalysts was investigated using aged catalysts that were exposed to hydrothermal redox conditions. Information concerning stability is vitally important with regard to real-world applications of these catalysts because they will be exposed to harsh conditions in association with dynamic changes in temperature and ambient atmosphere during use [81–83]. It is also important to note that the hydrothermal aging of such materials, as an aspect of TWC research, must be conducted under varying lean/stoichiometric/rich conditions to simulate the actual operating conditions [84,85]. Although the conversions of NO, CO and C₃H₆ over each of the catalysts decreased after the aging treatment, the aged Pd/M/Al₂O₃ catalysts still exhibited higher catalytic performance than the aged Pd/Al₂O₃. The data also indicated that La was the most effective additive in terms of NO conversion, while Sr and Ba promoted the oxidations of C₃H₆ and CO to the greatest extent. Again, the high oxidation activities observed following the addition of these electron-donating basic metals are in good agreement with previous studies in which the oxidations of HCs were examined using Pd/Al₂O₃ catalysts modified with these elements [79,80].

The aged catalysts were characterized by XRD and N₂ adsorption techniques as shown in **Figure 7**. Note that the powder catalysts were subjected to the hydrothermal aging treatment for these measurements. Sharp peaks related to metallic Pd were observed in each of the XRD patterns, indicating that the Pd nanoparticles had aggregated into large particles that were detectable by XRD during aging. Peaks attributed to BaAl₂O₄ and SrAl₂O₄ were also observed in the XRD patterns obtained from the aged Pd/Ba/Al₂O₃ and Pd/Sr/Al₂O₃, respectively, whereas the XRD pattern generated by the aged Pd/La/Al₂O₃ showed no peaks assignable to LaAlO₃. In addition, α -Al₂O₃ peaks appeared in the pattern of the aged Pd/Al₂O₃, suggesting a phase transformation from γ -Al₂O₃ to α -Al₂O₃. Conversely, the aged Pd/M/Al₂O₃ materials were comprised mainly of γ -Al₂O₃, with no evidence of α -Al₂O₃ being formed. The Sr, Ba, and La K-edge EXAFS FTs for the aged materials are shown in **Figure S6**. Results of the curve fitting analysis of EXAFS summarized in **Table S2** show that the aged

Pd/Sr/Al₂O₃ and Pd/Ba/Al₂O₃ catalysts only contained M–O contribution, and the aged Pd/La/Al₂O₃ catalyst comprises both La–O and slight La–(O)–Al contribution. The S_{BET} values for both the fresh and aged catalysts are given in **Figure 7B**. These data show that the Pd/M/Al₂O₃ specimens retained high surface areas during the aging. Therefore, the addition of basic metals appears to have enhanced the thermal stability of the Al₂O₃ in these materials. These results are in agreement with previous reports of research focused on improving the thermal stability of Al₂O₃ by using basic metal additives as modifiers [18].

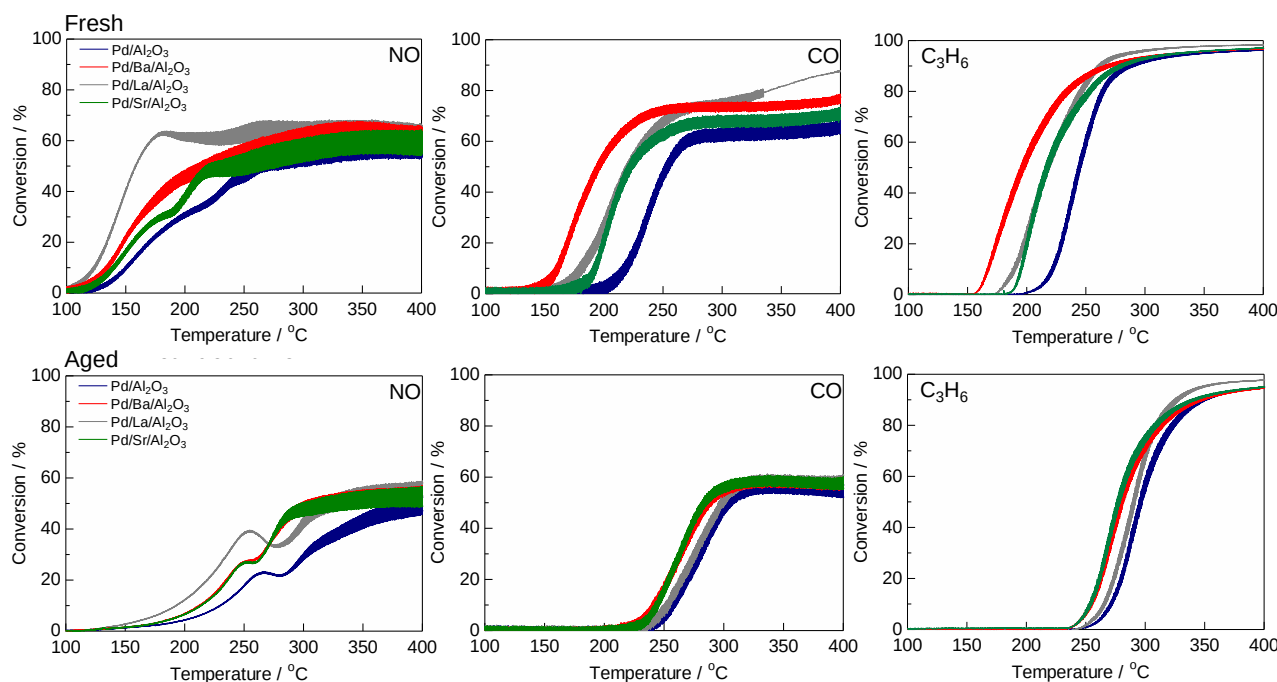


Figure 6. The conversions of NO, CO and C₃H₆ during TWC light-off tests over fresh and aged Pd/Al₂O₃-and Pd/M/Al₂O₃-coated honeycomb catalysts under gases perturbed at 1 Hz between $\lambda = 0.95$ and $\lambda = 1.05$. Heating rate: 25 °C/min; Gases: NO (0.1%), CO (2.4-0.6%), C₃H₆ (420 ppm), O₂ (0.6-1.65%), H₂ (0.8%), CO₂ (15%), H₂O (10%), N₂ balance; SV = 100,000 h⁻¹.

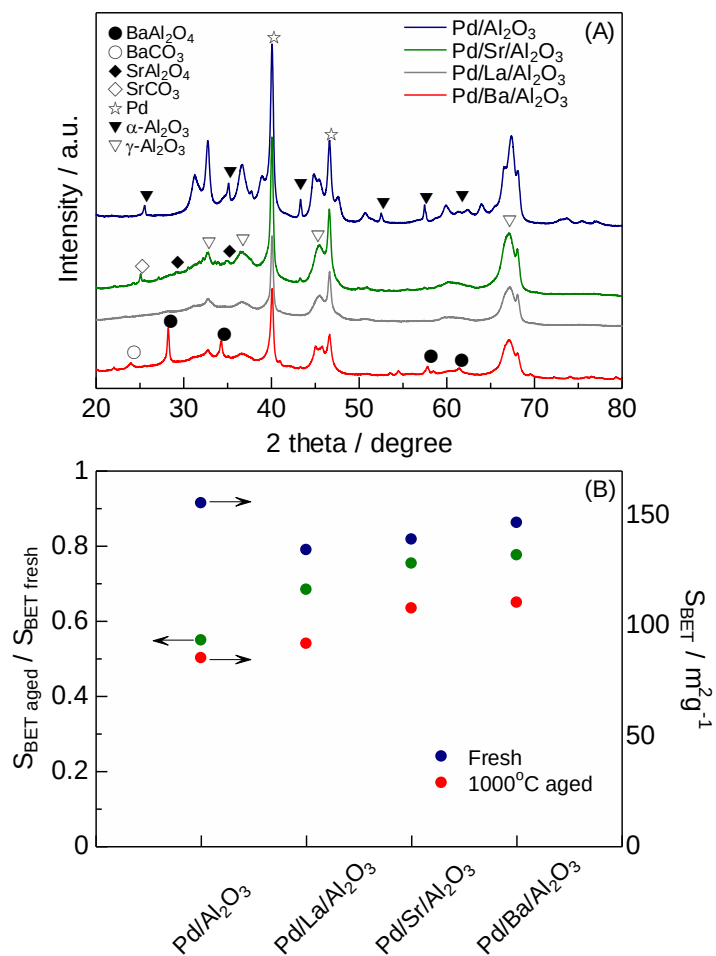


Figure 7. (A) XRD patterns obtained from aged Pd/Al₂O₃ and Pd/M/Al₂O₃ (M = La, Ba or Sr). (B) S_{BET} values of fresh (S_{BET} fresh) and aged (S_{BET} aged) Pd/Al₂O₃ and Pd/M/Al₂O₃ (M = La, Ba or Sr) and the ratios of S_{BET} aged to S_{BET} fresh.

Conclusions

In this study, we examined the role of basic metal additives in Pd/M/Al₂O₃ (M = La, Ba or Sr) during the three-way catalytic process, using spectroscopic and kinetic measurements. Those catalysts loaded with the basic metals (the Pd/M/Al₂O₃ series) exhibited enhanced catalytic activity during the conversions of NO and CO. In addition, metallic Pd nanoparticles supported on La/Al₂O₃ were found to have a decreased electron density, such that the CO poisoning effect was suppressed. Conversely, Pd supported on Sr/Al₂O₃ and Ba/Al₂O₃ showed increased electron density. The presence of the atomically dispersed basic metals promoted the efficient formation of surface nitrite species, such that the DeNO_x activity of the powdered catalysts was improved. Honeycomb-type monolithic catalysts were also prepared and their performance was examined under simulated TWC conditions. The results showed that the Pd/M/Al₂O₃ catalysts were superior in terms of promoting the reactions of NO, CO and C₃H₆ compared with the Pd/Al₂O₃ catalyst. Pd/La/Al₂O₃ was found to enhance NO reduction to a greater extent than the catalysts investigated in this work, while Pd/Ba/Al₂O₃ demonstrated superior catalytic performance during the oxidation of CO and C₃H₆.

ACKNOWLEDGEMENTS

This study was supported by KAKENHI (20H02775, 20H02518, 20KK0111, and 20F20345), “Integrated Research Consortium on Chemical Sciences (IRCCS)”, “Elements Strategy Initiative to Form Core Research Center” (JPMXP0112101003), and the JST-CREST project JPMJCR17J3. G.W. acknowledges a JSPS postdoctoral fellowship (No. P20345). The authors thank the technical division of Institute for Catalysis for manufacturing experimental equipment. XAS measurements were conducted at the BL-14B2 beamline of SPring-8 (2019B1686 and 2020A1695).

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Graphical Abstract

