

# Pd-Doped Perovskite: An Effective Catalyst for Removal of NO<sub>x</sub> from Lean-Burn Exhausts with High Sulfur Resistance

Xingang Li,<sup>†,‡,§</sup> Cheng Chen,<sup>†,‡</sup> Cheng Liu,<sup>†,‡,§</sup> Hui Xian,<sup>\*,†,⊥</sup> Li Guo,<sup>†,‡,§</sup> Jiaolong Lv,<sup>†,‡,§</sup> Zheng Jiang,<sup>||</sup> and Philippe Vernoux<sup>||</sup>

<sup>†</sup>School of Chemical Engineering & Technology, Tianjin University, Tianjin, 300072, China

<sup>‡</sup>Tianjin Key Laboratory of Applied Catalysis Science & Technology, Tianjin, 300072, China

<sup>§</sup>The Co-Innovation Center of Chemistry and Chemical Engineering of Tianjin, Tianjin, 300072, China

<sup>⊥</sup>Pei-Yang Distillation Engineering Limited Company, Tianjin, 300072, China

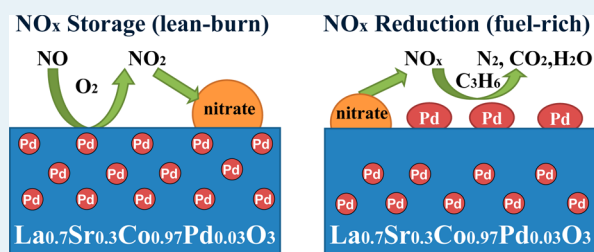
<sup>||</sup>Shanghai Synchrotron Radiation Facility, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai, 201800, China

<sup>||</sup>Institute of Researches on Catalysis and Environment in Lyon, Université Lyon 1, F-69626 Villeurbanne, France

## Supporting Information

**ABSTRACT:** Herein, we report the Pd-doped perovskite La<sub>0.7</sub>Sr<sub>0.3</sub>CoO<sub>3</sub> as an effective lean NO<sub>x</sub> trap (LNT) catalyst. This smart perovskite displays excellent NO<sub>x</sub> reduction activities for lean-burn exhausts (NO<sub>x</sub> conversion >90%, N<sub>2</sub> selectivity >90%) over a wide operating temperature range (275–400 °C), as well as an extremely high sulfur tolerance. Our results evidenced Pd dissolving into or segregating out of perovskite in lean-burn and fuel-rich atmospheres. The segregated metallic Pd from perovskite in fuel-rich atmospheres is crucial for obtaining these promising achievements. These findings provide a new possibility for the application of the Pd-based LNT catalysts.

**KEYWORDS:** Pd-doped, perovskite, lean-burn, NO<sub>x</sub> reduction, sulfur resistance



Reducing CO<sub>2</sub> emissions is one of the great challenges in the world. Lean-burn engines are attractive because of their high fuel economy efficiency;<sup>1</sup> however, nitrogen oxides (NO<sub>x</sub>, including NO and NO<sub>2</sub>) emitted from lean-burn engines are hardly reduced in excessive oxygen using a traditional three-way catalyst (TWC). A lean NO<sub>x</sub> trap (LNT)<sup>2</sup> is one of the most promising methodologies<sup>2–4</sup> for removing NO<sub>x</sub> from lean-burn exhausts. The LNT catalysts, generally containing Pt (e.g., Pt/BaO/Al<sub>2</sub>O<sub>3</sub>), can oxidize and store NO<sub>x</sub> in a long-term oxygen-rich atmosphere; thereafter, the stored NO<sub>x</sub> is released and removed by hydrocarbons and CO within a short-term fuel-rich pulse.<sup>2</sup> Here, no additional reductant storage tank is required, such as urea tanks used for NO<sub>x</sub> selective catalytic reduction (SCR) by ammonia. This greatly reduces the volume of the exhaust aftertreatment system, especially for diesel cars. Unfortunately, the Pt-based LNT catalysts are expensive and readily poisoned by sulfur dioxide (SO<sub>2</sub>).<sup>5</sup>

Perovskite-type catalysts with an ABO<sub>3</sub> formula have excellent redox properties, high temperature stabilities, and low costs.<sup>6</sup> They are potential catalysts to remove NO<sub>x</sub> in SCR and TWC systems, but the poor sulfur resistance limits their industrial applications.<sup>7</sup> Nowadays, in LNT-type catalytic aftertreatment systems, the perovskites act mainly as NO oxidation components<sup>8</sup> or NO<sub>x</sub> adsorbents with the alkaline-earth metal element at the A sites.<sup>9</sup> Recently, we found that the

La<sub>0.7</sub>Sr<sub>0.3</sub>CoO<sub>3</sub> perovskite could reduce NO<sub>x</sub> by hydrocarbon (C<sub>3</sub>H<sub>6</sub>) in alternative lean-burn/fuel-rich (denoted as lean/rich) atmospheres with 100% selectivity to N<sub>2</sub>.<sup>10</sup> La<sub>0.7</sub>Sr<sub>0.3</sub>CoO<sub>3</sub> exhibits a sufficient activity for NO<sub>x</sub> oxidation and storage in lean-burn atmospheres; however, it displays a relatively poorer NO<sub>x</sub> reduction efficiency in fuel-rich atmospheres compared with the Pt-based commercial LNT catalysts.<sup>10</sup>

The Pd-doped perovskite catalysts showed good stability in gasoline engine aftertreatment systems: in oxidizing atmospheres, Pd dissolved into perovskite as cations, whereas in reducing atmospheres, the metallic Pd nanoparticles were segregated out of the perovskite.<sup>11</sup> Regarding the NO<sub>x</sub> reduction, these perovskites are mainly used for TWC systems to avoid thermal aggregation under the transient air/fuel ratio oscillation conditions of gasoline engines.<sup>11</sup> Considering the drawbacks of the perovskite La<sub>0.7</sub>Sr<sub>0.3</sub>CoO<sub>3</sub> as an LNT catalyst, Pd doping becomes a possible solution because of the reversible states of Pd in periodically lean/rich atmospheres. Herein, we report the excellent performances of the perovskite Pd-doped La<sub>0.7</sub>Sr<sub>0.3</sub>CoO<sub>3</sub> as an LNT catalyst in a wide range of operating

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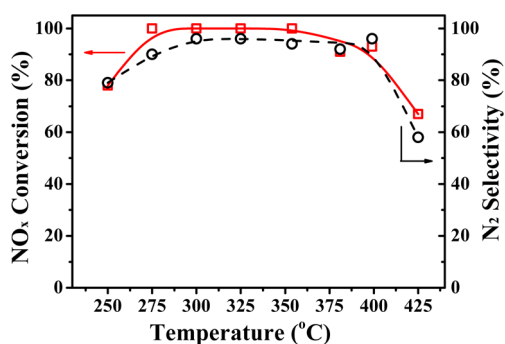


temperatures: 250–400 °C. This smart perovskite can effectively work for the NO<sub>x</sub> reduction by hydrocarbon through alternative lean/rich operations with the advantage of its extremely high sulfur tolerance.

We synthesized the La<sub>0.7</sub>Sr<sub>0.3</sub>Co<sub>0.97</sub>Pd<sub>0.03</sub>O<sub>3</sub> perovskite (denoted as Pd0.03) by a facile sol–gel method. For comparison, the La<sub>0.7</sub>Sr<sub>0.3</sub>CoO<sub>3</sub> perovskite was also synthesized under the same conditions and denoted as LSC. The X-ray diffraction (XRD) results show that the La<sub>0.7</sub>Sr<sub>0.3</sub>CoO<sub>3</sub>-based perovskite structures (JPCDS No. 48-0137) were well constructed for both samples (Supporting Information Figure S1). Meanwhile, the presence of the SrCO<sub>3</sub> phase (JPCDS No. 71-2394) was also clearly identified on the LSC sample. After comparing the LSC and Pd0.03 samples with the diffraction peak (Supporting Information Figure S1) and the IR band (Supporting Information Figure S2) belonging to carbonate and the amount of CO<sub>2</sub> desorbed during the thermal treatment (Supporting Information Figure S3), we can conclude that more carbonate existed on the LSC sample. These findings strongly suggest that the incorporation of Pd in perovskite inhibits the formation of SrCO<sub>3</sub> (Supporting Information Figures S1–S3).

NO<sub>x</sub> storage and cyclic lean/rich tests were performed at 280 °C. Both perovskites displayed excellent NO oxidation ability, ~85% of NO → NO<sub>2</sub> conversion (Supporting Information Table S1). Nevertheless, the Pd-doped perovskite, Pd0.03, presented the much higher NO<sub>x</sub> removal efficiency (97.6% of NO<sub>x</sub> conversion) through cyclic lean/rich operations as compared with the LSC (61.1% of NO<sub>x</sub> conversion) (Supporting Information Figure S4). These findings indicate that Pd doping in perovskite may have little effect on the oxidation of NO in a lean-burn atmosphere, but is critical to the reduction of NO<sub>x</sub> in a fuel-rich atmosphere.

Figure 1 shows the catalytic performances of the Pd0.03 sample as a function of the operating temperatures. Between

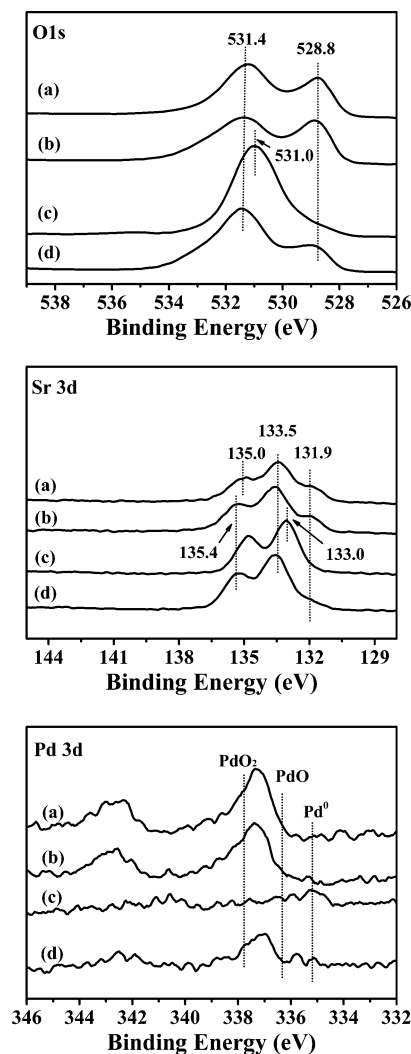


**Figure 1.** NO<sub>x</sub> conversion and N<sub>2</sub> selectivity of the Pd0.03 sample in the lean/rich cyclings as a function of the operating temperatures with a space velocity of 32 000 h<sup>−1</sup>.

275 and 400 °C, both the NO<sub>x</sub> conversion and the N<sub>2</sub> selectivity were no less than 90%, demonstrating an extraordinarily high NO<sub>x</sub> removal efficiency in a wide operating temperature window. Herein, a small amount of N<sub>2</sub>O was produced as the byproduct. The slight drop of the N<sub>2</sub> selectivity after the addition of Pd to the LSC perovskite might be due to direct dissociation of NO to N<sub>2</sub>O on the metallic Pd in fuel-rich atmospheres. For comparison, the catalytic activities of the Pt/BaO/Al<sub>2</sub>O<sub>3</sub> sample were also presented in Supporting Information Figure S5. Clearly, the Pd0.03 sample had an

excellent NO<sub>x</sub> removal efficiency similar to the Pt/BaO/Al<sub>2</sub>O<sub>3</sub> sample.

We used X-ray photoelectron spectroscopy (XPS) to determine the chemical state of the surface elements of the perovskites. Figure 2 presents the XPS spectra of the Pd0.03



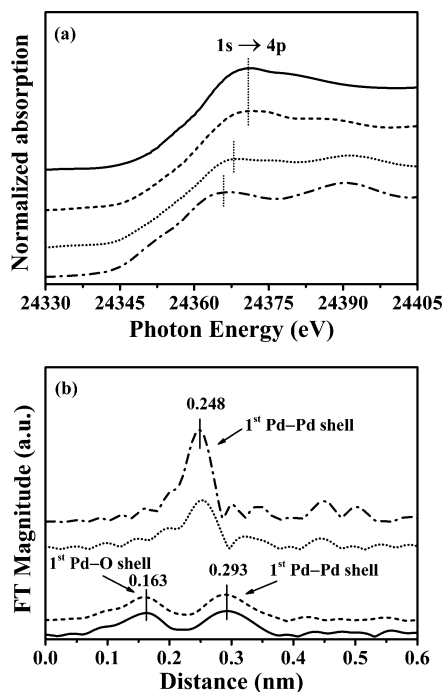
**Figure 2.** XPS spectra of the Pd0.03 sample: (a) the fresh sample, (b) the sample experienced the lean/rich cyclings at 325 °C for 1 h, (c) the fresh sample reduced by 5% H<sub>2</sub> at 325 °C for 0.5 h, and (d) sample c operated in the lean/rich cyclings at 325 °C for 1 h.

sample pretreated under different conditions. The XPS spectra recorded after the sample was treated upon the lean/rich cyclings at 325 °C for 1 h are similar to those of the fresh sample. Nevertheless, after reduction in 5% H<sub>2</sub> at 325 °C, the oxygen in perovskite cells (528.8 eV) and the chemisorbed oxygen species (531.4 eV)<sup>12,13</sup> vanished, and a new peak (531.0 eV) appeared, which might be assigned to the overlap of the surface oxygen species and the lattice oxygen in metal oxides and, probably, SrCO<sub>3</sub>, as well.

Simultaneously, the peak belonging to strontium in perovskite cells (131.9 eV)<sup>12</sup> disappeared. Thereafter, this pre-reduced sample was operated in the lean/rich cyclings at 325 °C for 1 h. The XPS spectra (Figure 2d) show that the superficial perovskite structure was partially reconstructed through this operation according to the appearance of the O 1s peak at 528.8 eV as well as the Sr 3d peak at 131.9 eV. All of these

experiments suggest that the perovskite structure is stable upon the periodically alternative lean/rich operations. Furthermore, the cyclic lean/rich operations were beneficial to the reconstruction of the perovskite cells destroyed by the severe reduction. These findings are in good agreement with our XRD results (Supporting Information Figure S6). Moreover, we also investigated the XPS spectra in the Pd3d region. For the fresh sample, only one BE peak located between PdO and PdO<sub>2</sub> was observed.<sup>14</sup> As we expected, the lean/rich cyclings had little effect on the chemical states of Pd. After the reduction in H<sub>2</sub>, the Pd species on the perovskite surface was reduced to Pd<sup>0</sup>. Thereafter, the metallic Pd could be reoxidized to the initial state in the fresh perovskite sample upon the lean/rich cyclings.

At this point, we decided to use the X-ray absorption fine structures to further highlight the chemical states of Pd in perovskite during the lean-burn and fuel-rich periods. Figure 3



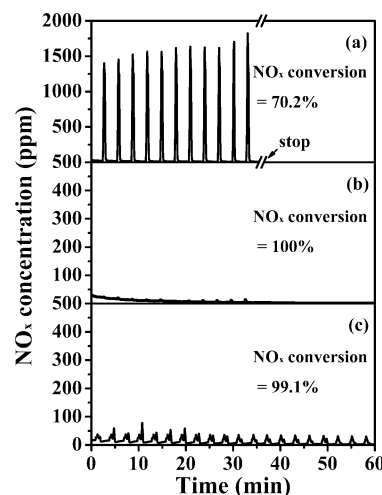
**Figure 3.** XANES (a) and RSFs (b) of the fresh Pd0.03 sample (solid line); the Pd0.03 sample treated upon 500 ppm NO/6.7% O<sub>2</sub> at 325 °C for 1 h (dashed line); the Pd0.03 sample treated upon 500 ppm NO/0.1% C<sub>3</sub>H<sub>6</sub> at 325 °C for 1 h (dotted line); and standard Pd foil (dashed-dotted line).

displays the X-ray absorption near edge structures (XANES) and radial structure functions (RSFs) of the Pd K-edge of the Pd0.03 sample. For the sample pretreated upon the NO/O<sub>2</sub> flow at 325 °C for 1 h, the position of the adsorption edge, as well as the intensity of whiteline (1s → 4p transition), in the XANES spectra had little difference compared with the fresh one (Figure 3a). Moreover, their first coordination shells of Pd–O and Pd–Pd in perovskite were located at the same position as shown in the RSF profiles (Figure 3b). This suggests that incorporating Pd into the perovskite did not result in a significant change in the lean-burn atmosphere. However, for the sample pretreated upon NO/C<sub>3</sub>H<sub>6</sub> at 325 °C for 1 h, the adsorption edge shifted by 3.5 eV toward lower photon energy compared with the fresh one. This evidence a lowered valence of Pd. Meanwhile, the intensity of whiteline weakened and broadened, and the shape was quite similar to that of the

Pd foil (Figure 3a); moreover, only the coordination peak at 0.248 nm corresponding to the first Pd–Pd shell in the metallic Pd was observed (Figure 3b). These findings indicate that the dissolved Pd cations in perovskite could be reduced to Pd<sup>0</sup> by C<sub>3</sub>H<sub>6</sub> in the fuel-rich atmosphere.

We can conclude that the Pd cations in perovskite may have little effect on NO oxidation in lean-burn atmospheres, since the La<sub>0.7</sub>Sr<sub>0.3</sub>CoO<sub>3</sub> (LSC) perovskite alone presented activity similar to that of the Pd0.03 sample (Supporting Information Table S1). On the other hand, with the prolonged fuel-rich atmospheric treatment, the Pd cations in perovskite could be eventually reduced to the metallic state (Figure 3). Accordingly, in cyclic lean/rich operations, the Pd cations located nearby at the surface or subsurface of perovskite would be reduced to Pd<sup>0</sup> during the short-term fuel-rich periods. These segregated metallic Pd play an essential role to reduce NO<sub>x</sub> with hydrocarbon,<sup>11</sup> especially in the presence of lanthanum.<sup>15</sup>

On the basis of these promising results, we decided to investigate the sulfur resistance of the Pd0.03 sample, as shown in Figure 4. For the presulfated sample, the NO<sub>x</sub> conversion at



**Figure 4.** Lean (500 ppm NO/6.7% O<sub>2</sub>, 2 min)/rich (500 ppm NO/0.1% C<sub>3</sub>H<sub>6</sub>, 1 min) cyclings of the differently pretreated Pd0.03 samples at 325 °C: (a) after presulfation in 300 ppm SO<sub>2</sub>/6.7% O<sub>2</sub> at 325 °C for 1 h, (b) after reduction of the presulfated sample a in 5% H<sub>2</sub> at 325 °C for 0.5 h, and (c) after directly adding 100 ppm SO<sub>2</sub> to the feeding gas.

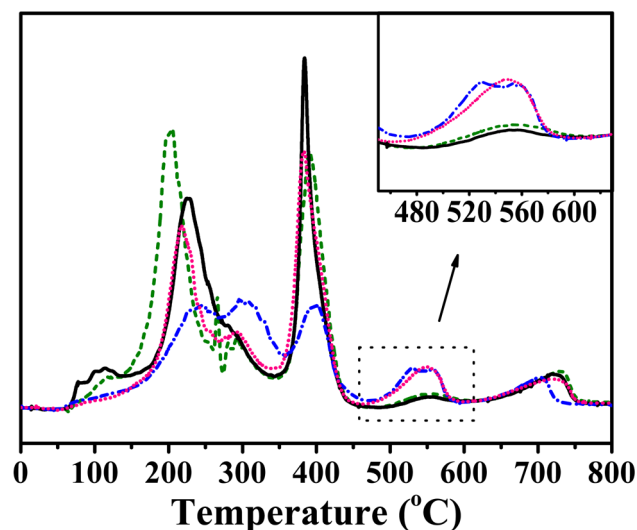
325 °C dropped from 100 to 70.2%, but could be fully restored after reduction in H<sub>2</sub> (Figures 1 and 4). Interestingly, the direct addition of SO<sub>2</sub> to the reactant gas had little influence on the NO<sub>x</sub> elimination activity (99.1% of NO<sub>x</sub> conversion). Meanwhile, little difference was observed for the N<sub>2</sub> selectivity (Supporting Information Table S2). In contrast, we found that the LSC sample was readily poisoned by sulfur, since the NO<sub>x</sub> conversion dropped from 69.5 to 30.5% after SO<sub>2</sub> was directly added to the feeding gas (Supporting Information Figure S7). We also evaluated the catalytic activity of the presulfated Pt/BaO/Al<sub>2</sub>O<sub>3</sub> sample (Supporting Information Table S3). The Pt/BaO/Al<sub>2</sub>O<sub>3</sub> sample was readily poisoned by sulfur (NO<sub>x</sub> conversion dropping from 99.2 to 54.9%, N<sub>2</sub> selectivity dropping from 96.1 to 85.3%) and could not recover its initially catalytic activity by reducing in H<sub>2</sub> at mild temperatures, such as 325 °C. Apparently, the Pd-doped perovskite provides a new possibility for overcoming the problems caused by sulfur poisoning for the LNT systems.

Herein, the XPS, FT-IR, and  $H_2$  temperature-programmed reduction ( $H_2$ -TPR) techniques were implemented to elucidate the processes of the sulfur poisoning and the regeneration of the catalytic activity of the Pd-doped perovskite. The XPS results of the Pd0.03 sample (Table 1) show that after the

**Table 1. The Surface Elemental Analysis of the Pd0.03 Sample after Different Sulfur Treatments Determined by XPS**

	composition (atom %)					
	O	Sr	Co	La	Pd	S
fresh sample	77.9	3.6	9.7	8.7	0.2	0
presulfated sample	66.4	4.8	13.5	13.2	0.2	1.8
after reduction of the presulfated sample in $H_2$	68.7	5.2	9.5	15.1	0.1	1.4
sample after cyclic lean/rich tests in the presence of $SO_2$	68.3	4.9	12.9	13.6	0.2	0

pretreatment in  $SO_2/O_2$  at 325 °C, sulfur was deposited on the sample. Surprisingly, the reduction in  $H_2$  could fully regenerate the deactivated sample by removing only a small amount of sulfur from the perovskite. Furthermore, no sulfur was detected on the sample for the cyclic lean/rich operations in the presence of  $SO_2$ . The FT-IR results (Supporting Information Figure S8) for the presulfated Pd0.03 samples show that sulfates were formed on the presulfated samples, and reduction in  $H_2$  at 325 °C could not remove them. Moreover, no obvious IR band belonging to the sulfate species was observed for the sample after the lean/rich cycling tests in the presence of 100 ppm  $SO_2$ . These findings coincide with the XPS results listed in Table 1. Figure 5 displays the  $H_2$ -TPR profiles of the Pd0.03 sample with the different pretreatments. For the fresh sample, the broad and weak peak located at 450–600 °C was attributed to the decomposition of the residual carbonates (Supporting Information Figure S3). For the presulfated samples, the intensity of the peak over this range was strengthened as a



**Figure 5.**  $H_2$ -TPR profiles of the Pd0.03 sample: the fresh sample (black solid line), the sample that experienced direct addition of 100 ppm  $SO_2$  to the alternative lean/rich feeding gases at 325 °C for 1 h (green dashed line), the sample presulfated in 300 ppm  $SO_2/6.7\%$   $O_2$  at 325 °C for 1 h (pink dotted line), and the presulfated sample reduced by 5%  $H_2$  at 325 °C for 0.5 h (blue dashed-dotted line).

result of the reduction of the formed sulfate.<sup>9</sup> In contrast, sulfur was hardly deposited on the sample by directly adding  $SO_2$  to the feeding gas, since little change was observed from the  $H_2$ -TPR profiles in the temperature range of 450–600 °C compared with the fresh one. This finding is in good agreement with the XPS (Table 1) and FT-IR (Supporting Information Figure S8) results. Interestingly, the reduction in  $H_2$  at 325 °C could not thoroughly remove these sulfates from the presulfated sample, and most of them remained; however, the catalytic activity of the presulfated sample could be fully restored (Figure 4b).

In oxygen-rich atmospheres, the oxidized state of Pd in perovskite can easily oxidize  $SO_2$  to  $SO_3$  forming sulfates.<sup>16</sup> The adsorbed  $SO_3$  or  $SO_4^{2-}$  on Pd might spill over onto the adjacent perovskite, which was then seriously poisoned by forming the bulk sulfates after the long-term  $SO_2/O_2$  pretreatment (1 h). In the following cyclic lean/rich operations, the Pd sulfate could be easily reduced to  $Pd^0$  during the short-term fuel-rich periods, but its adjacent bulk sulfates were hardly reduced. Using  $C_3H_6$  to reduce  $NO_x$  over the supported Pd catalysts would result in the formation of the isocyanate species on the catalyst surface, which was one of the important intermediates in the  $NO_x$  reduction process.<sup>17</sup> Herein, the deposition of the bulk sulfates surrounding Pd would inhibit the formation of these intermediates, leading to a serious decrease in the  $NO_x$  removal efficiency.

As indicated in Figure 5, it is generally insufficient to reduce bulk sulfates in  $H_2$  below 450 °C. After reduction of the presulfated sample in  $H_2$  at 325 °C, only the Pd sulfates could be readily reduced to the metallic state. However, the dissociated H atoms on  $Pd^0$  might spill over onto the adjacent sites to reduce the formed bulk sulfates. This induced the dramatic recovery of the  $NO_x$  removal efficiency, although much of the unreduced sulfates far from  $Pd^0$  still remained on the Pd0.03 sample (Figure 5 and Table 1). These findings strongly suggest that the metallic  $Pd^0$  sites combined with their adjacent perovskite are critical for the reduction of  $NO_x$  under the fuel-rich conditions.

As for the direct introduction of 100 ppm  $SO_2$  into the cyclic lean/rich feeding gases,  $SO_2$  was preferentially adsorbed on Pd to form the Pd sulfates during the lean-burn period. A part of them would probably migrate further to the adjacent perovskite, forming the superficial sulfates and regenerating the Pd sites. This inhibited the deposition of sulfates on the perovskite far from the Pd sites due to the limited lean-burn period (2 min), as compared with the presulfation treatment (1 h). After switching to the fuel-rich atmosphere, these Pd sulfates were easily and rapidly reduced to regenerate the  $Pd^0$  sites; meanwhile, their neighboring superficial sulfates might be efficiently reduced as a result of the spillover of the dissociated H atoms from the adjacent  $Pd^0$  sites to the perovskite. This assumption could well explain the high catalytic activity for the reduction of  $NO_x$  even in the presence of  $SO_2$ .

In summary, we have demonstrated the Pd-doped  $La_{0.7}Sr_{0.3}CoO_3$  perovskite ( $La_{0.7}Sr_{0.3}Co_{0.97}Pd_{0.03}O_3$ ) to be an effective LNT catalyst operating in periodically alternative lean/rich atmospheres. This smart perovskite displayed the extraordinarily high  $NO_x$  reduction activities for diesel exhausts ( $NO_x$  conversion > 90%,  $N_2$  selectivity > 90%) over a wide operating temperature window (275–400 °C). Surprisingly, little difference in the catalytic activity for the reduction of  $NO_x$  was observed after the direct addition of 100 ppm  $SO_2$  to the cyclic lean/rich feeding gases, demonstrating its extremely high



sulfur tolerance. Our findings show that the segregated metallic Pd from perovskite in fuel-rich atmospheres plays a significant role in obtaining these promising achievements. This provides a new possibility for the application of the Pd based LNT catalyst and for solving the problems caused by simultaneous sulfur poisoning and noble metal aggregation at high temperatures.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

Additional information as noted in text. This information is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*E-mail: [hui\\_xiantju@126.com](mailto:hui_xiantju@126.com).

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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## ■ REFERENCES

- (1) Parks, J. E., II *Science* **2010**, 327, 1584.
- (2) (a) Takahashi, N.; Shinjoh, H.; Iijima, T.; Suzuki, T.; Yamazaki, K.; Yokota, K.; Suzuki, H.; Miyoshi, N.; Matsumoto, S.; Tanizawa, T.; Tanaka, T. *Catal. Today* **1996**, 27, 63. (b) Epling, W.; Campbell, L.; Yezerets, A.; Currier, N.; Parks, J. *Catal. Rev.* **2004**, 46, 163. (c) Ren, Y.; Harold, M. P. *ACS Catal.* **2011**, 1, 969. (d) Roy, S.; Baiker, A. *Chem. Rev.* **2009**, 109, 4054. (e) Granger, P.; Parvulescu, V. I. *Chem. Rev.* **2011**, 111, 3155.
- (3) Wang, X.; Ma, X.; Zhao, S.; Wang, B.; Song, C. *Energy Environ. Sci.* **2009**, 2, 878.
- (4) (a) Mou, X.; Zhang, B.; Li, Y.; Yao, L.; Wei, X.; Su, D.; Shen, W. *Angew. Chem., Int. Ed.* **2012**, 51, 2989. (b) Deka, U.; Lezcano-Gonzalez, I.; Weckhuysen, B. M.; Beale, A. M. *ACS Catal.* **2013**, 3, 413.
- (5) Dawody, J.; Skoglundh, M.; Olsson, L.; Fridell, E. *J. Catal.* **2005**, 234, 206.
- (6) Tejuca, L.; Fierro, J.; Tascón, J. *Chem. Rev.* **1989**, 36, 237.
- (7) Pena, M.; Fierro, J. *Chem. Rev.* **2001**, 101, 1981.
- (8) (a) Kim, C. H.; Qi, G. S.; Dahlberg, K.; Li, W. *Science* **2010**, 327, 1624. (b) He, X.; Meng, M.; He, J.; Zou, Z.; Li, X.; Li, Z.; Jiang, Z. *Catal. Commun.* **2010**, 12, 165.
- (9) (a) Xian, H.; Li, F.; Li, X.; Zhang, X.; Meng, M.; Zhang, T.; Tsubaki, N. *Fuel Proc. Technol.* **2011**, 92, 1718. (b) Xian, H.; Zhang, X.; Li, X.; Li, L.; Zou, H.; Meng, M.; Li, Q.; Tan, Y.; Tsubaki, N. *J. Phys. Chem. C* **2010**, 114, 11844. (c) Xian, H.; Zhang, X.; Li, X.; Zou, H.; Meng, M.; Zou, Z.; Guo, L.; Tsubaki, N. *Catal. Today* **2010**, 158, 215. (d) Ding, Q.; Xian, H.; Tan, Y.; Tsubaki, N.; Li, X. *Catal. Sci. Technol.* **2013**, DOI: 10.1039/C3CY00105A.
- (10) Li, X.; Dong, Y.; Xian, H.; Hernández, W.; Meng, M.; Zou, H.; Ma, A.; Zhang, T.; Jiang, Z.; Tsubaki, N.; Vernoux, P. *Energy Environ. Sci.* **2011**, 4, 3351.
- (11) Nishihata, Y.; Akao, T.; Tanaka, H.; Uenishi, M.; Kimura, M.; Okamoto, T.; Hamada, N. *Nature* **2002**, 418, 164.
- (12) Kuhn, J.; Ozkan, U. *J. Catal.* **2008**, 253, 200.
- (13) Tan, R.; Zhu, Y. *Appl. Catal., B* **2005**, 58, 61.
- (14) Uenishi, M.; Taniguchi, M.; Tanaka, H.; Kimura, M.; Nishihata, Y.; Mizuki, J.; Kobayashi, T. *Appl. Catal., B* **2005**, 57, 267.
- (15) Muraki, H.; Shinjoh, H.; Fujitani, Y. *Appl. Catal.* **1986**, 22, 325.
- (16) Ordóñez, S.; Hurtado, P.; Sastre, H.; Diez, F. V. *Appl. Catal., A* **2004**, 259, 41.
- (17) Abdulhamid, H.; Dawody, J.; Fridell, E.; Skoglundh, M. *J. Catal.* **2006**, 244, 169.