Electronic Supplementary Information

De-NOx in alternative lean/rich atmospheres on La1-xSrxCoxO3 perovskites

Xin-Gang Li, * Hui Xian, Yan-Hua Dong, Willinton Yesid Hernández, Ming Meng*, Hong-Hu Zou, Ai-Jing Ma, Tian-Yong Zhang, Zheng Jiang, Noritatsu Tsubaki, Philippe Vernoux

1. Experimental Section

1.1 Catalyst preparation

The La1-xSrxCoxO3 (x=0, 0.1, 0.2, 0.3, 0.4, and 0.5) perovskite catalysts were prepared by a sol-gel method. Briefly, the required amount of La(NO3)3·6H2O, Sr(NO3)2 and Co(NO3)2·6H2O (Tianjin Guangfu Technol. Development Co. Ltd.) were dissolved together in 300 mL diluted water. Then, a certain amount of citric acide (CA) and ethylenediaminetetraacetie acid (EDTA) (Tianjin Guangfu Technol. Development Co. Ltd.) was added into the solution as mentioned above with a molar ratio of metal ion : CA : EDTA = 1 : 1 : 1.5. Meanwhile, the solution was ultrasonic-treated for 0.5 h to dissolve the solid chemicals. Thereafter, the pH value of the aqueous solution was adjusted to 4.0-5.0 with a 28 % NH3·H2O solution (Tianjin Guangfu Technol. Development Co. Ltd.), and the temperature of the aqueous solution was maintained at 80 °C. After vigorous stirring and evaporation, a transparent purple gel was formed, which was then dried at 120 °C overnight. The obtained xerogel precursor was firstly calcined from room temperature to 300 °C in air with a rate of 1 °C min⁻¹, stayed for 2 h to completely burn CA and EDTA, and was then calcined at 700 °C for 8 h with a rate of 5 °C min⁻¹. The whole calcination process was carried out in static air. Besides calcined at 700 °C, the La0.7Sr0.3CoO3 perovskite was also synthesized at different temperatures, i.e. 600, 800, 900, and 1000 °C, to investigate the influence of the perovskite calcination temperatures to their NO oxidation and NOx storage ability behaviors.

1.2. Catalyst characterizations

The XRD tests were conducted on an X’pert pro rotatory diffractometer, using Co Kα (λ = 0.17890 nm) as radiation source. The X-ray tube was operated at 40 kV and 40 mA.

The BET surface area was determined by N2 physisorption using an automatic gas adsorption system.
(NOVA 2000, Quantachrome Co.) at -196 °C. The sample was outgassed at 300 °C for 8 h prior to N₂ physisorption.

For the FT-IR experiment, a mixture of the sample and the vacuum-dried IR-grade KBr with a weight ratio of 1:100 was pressed into a disc, and then recorded with a Nexus FT-IR spectrometer apparatus (Thermo Nicolet Co.) equipped with a MCT detector using 64 scans and a resolution of 4 cm⁻¹ in the range from 400 to 4000 cm⁻¹.

The X-ray photoelectron spectroscopy (XPS) measurements were carried out on a PHI-1600 ESCA spectrometer with an accuracy of 0.2 eV. Mg-Kα (1253.6 eV) was used as radiation source, and the base pressure was 5×10⁻⁸ Pa. The recorded spectra were calibrated by the characteristic binding energy (BE) peak at 284.6 eV belonging to the contaminant carbon in 1s region.

XAFS signal of Co K-edge was collected using a transmission mode at 14W1 beamline of the Shanghai Synchrotron Radiation Facility (SSRF). The storage ring was operated at 3.5 GeV with a current of ~ 250 mA. A Si (111) double-crystal monochromator was used to reduce the harmonic content in the source beam. The radial structure functions (RSFs) was achieved by Fourier transforming of the $k^3$-weighted EXAFS data in the range of $k = 2.5–14$ Å⁻¹ using a Hanning function window.

The temperature programmed experiments were performed on a TPDRO 1100 SERIES instrument (Thermo-Finnigan Co.) with a thermal conductivity detector (TCD). Before the detection with the TCD, the introduced gas was purified by a H₂O and CO₂ trap containing CaO and NaOH materials. For the H₂-TPR test, 50 mg of the powdered catalyst was loaded into the quartz tube reactor, and was purged by 5% H₂/N₂ to get a stable TCD signal baseline, and then was heated from room temperature to 900 °C in 5% H₂/N₂ (20 mL min⁻¹) with a rate of 10 °C min⁻¹. For the O₂-TPD experiments, a pure O₂ flow was introduced into the reactor, where 0.2 g of the sample was loaded, for oxygen adsorption (50 mL min⁻¹). The sample was then heated to 300 °C, stayed for 30 min, and cooled down to room temperature. Thereafter, the sample was purged by a pure He flow until reaching a stable TCD baseline, and then heated from room temperature to 900 °C in pure He (20 mL min⁻¹) with a rate of 10 °C min⁻¹.

1.3. NOₓ trapping process
The NO\textsubscript{x} trapping experiments were carried out with a conventional fixed bed quartz reactor (i.d. = 8 mm) under atmospheric pressure at the desired NO\textsubscript{x} trapping temperature (200, 250, 300, 350, or 400 °C). 0.5 g of the catalyst was used. A gas mixture of 800 ppm NO and 5 % O\textsubscript{2} balanced with N\textsubscript{2} (400 mL min\textsuperscript{-1}) passed through the loaded sample. Here, the space velocity was around 80,000 h\textsuperscript{-1}. The on-line chemiluminescence NO\textsubscript{x} analyzer (Model 42i-HL, Thermo Scientific) was occupied to determine the concentration of NO, NO\textsubscript{2} and NO\textsubscript{x}. The calculation of the NO\textsubscript{x} storage capacity (NSC) and NO conversion was defined as the following formula:

\[
\text{NSC} = \frac{(\text{NO}_{\text{inlet}} \times V \times t)}{(N_0 \times m) \times \text{storageratio}} \times 10^{-3} = 28.07 \times t \times \text{storageratio} \left(\mu\text{mol g}^{-1}\text{catalyst}\right)
\]

\[
\text{NO Conversion} (\%) = \frac{(\text{NO}_{\text{inlet}} - \text{NO}_{\text{outlet}})}{\text{NO}_{\text{inlet}}} \times 100\%
\]

Here, NO and NO\textsubscript{x} is the concentration of NO and NO\textsubscript{x} in ppm unit, \(V\) is the flow rate of the introduced gas, i.e. 400 mL min\textsuperscript{-1}, \(N_0\) is a constant, i.e. 22.4 mol L\textsuperscript{-1}, \(m\) is the weight of the used catalyst, i.e. 0.5 g, and \text{storageratio} is the percentage of the amount of the stored NO\textsubscript{x} to that of the inlet NO\textsubscript{x}. \(\text{NO}_{\text{inlet}}\) is the NO concentration before NO\textsubscript{x} trapping, while \(\text{NO}_{\text{outlet}}\) is the NO concentration after NO\textsubscript{x} trapping process reached a balance. It usually took 1 – 4 h depending on the catalysts’ NO\textsubscript{x} storage ability.

The NSR cyclic measurements were conducted on 0.5 g of the catalysts without pre-treatment, using a fixed-bed quartz reactor. The reactor was connected to four-way valve, which provides a quick switching between the lean and rich atmospheres. Constant flows (10 L/h) of lean mix reaction (500 ppm NO/ 1000 ppm C\textsubscript{3}H\textsubscript{6} or 1000 ppm CO/ 6.7 % O\textsubscript{2} and He as balance) or rich mix reaction (500 ppm NO/ 1000 ppm C\textsubscript{3}H\textsubscript{6} or 1000 ppm CO and He as balance) were introduced alternately. The cycling experiments with a lean period of 3 min and a rich period of 1 min were performed at 300 °C. We used an IR online analyser (EMERSON NGA 2000) for CO, CO\textsubscript{2}, N\textsubscript{2}O and NO; an UV analyser (EMERSON NGA 2000) for NO\textsubscript{2}; and a gas micro-chromatograph (VARIAN CP2003) for C\textsubscript{3}H\textsubscript{6}, N\textsubscript{2}, and O\textsubscript{2}.

The NO\textsubscript{x} conversion for a complete representative cycle was calculated according to the following formula:

\[
\text{NO}_x \text{ conversion (\%)} = 100 \times (\text{NO}_x, \text{in} - \text{NO}_x, \text{out}) / \text{NO}_x, \text{in}
\]
2. Results

2.1. XRD results of LaCoO₃ perovskite

![XRD patterns of LaCoO₃ perovskite: (a) Fresh, and (b) after NOₓ storage at 300 °C.](image)

Figure 1S XRD patterns of LaCoO₃ perovskite: (a) Fresh, and (b) after NOₓ storage at 300 °C.

2.2. BET surface area of the La₁₋ₓSrₓCoO₃ perovskite.

Table 1S BET surface area of the La₁₋ₓSrₓCoO₃ perovskite.

<table>
<thead>
<tr>
<th></th>
<th>La₀.₉Sr₀.₁CoO₃</th>
<th>La₀.₈Sr₀.₂CoO₃</th>
<th>La₀.₇Sr₀.₃CoO₃</th>
<th>La₀.₆Sr₀.₄CoO₃</th>
<th>La₀.₇Sr₀.₃CoO₃ a</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET Surface area (m² g⁻¹)</td>
<td>12.6</td>
<td>8.4</td>
<td>19.1</td>
<td>11.6</td>
<td>17.8</td>
</tr>
</tbody>
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a After experiencing a destruction/regeneration process.
2.3. \( \text{O}_2\)-TPD spectra

Figure 2S \( \text{O}_2\)-TPD profiles of the perovskite: (a) \( \text{LaCoO}_3 \), (b) \( \text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3 \), (c) \( \text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3 \), and (d) \( \text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3 \).
2.4. $H_2$-TPR spectra

Figure 3S $H_2$-TPD profiles of the perovskite: (a) LaCoO$_3$, (b) La$_{0.8}$Sr$_{0.2}$CoO$_3$, (c) La$_{0.7}$Sr$_{0.3}$CoO$_3$, and (d) La$_{0.6}$Sr$_{0.4}$CoO$_3$. 
2.5. NO\textsubscript{x} storage tests

Figure 4S NSC of the La\textsubscript{1-x}Sr\textsubscript{x}CoO\textsubscript{3} at 200 °C (a), 300 °C (b), 350 °C (c), and 400 °C (d); and NO conversion (e).
2.6. La$_{0.7}$Sr$_{0.3}$CoO$_3$ perovskite regeneration test

![XRD patterns](image)

Figure 5S XRD patterns of the fresh La$_{0.7}$Sr$_{0.3}$CoO$_3$ sample (a); after NO$_x$ storage at 250 °C (b); the sample (b) reduced in 5% H$_2$ at 300 °C for 10 min (c); the sample (a) reduced at in pure H$_2$ at 400 °C for 1 h (d); the sample (d) oxidized in air at 700 °C for 3 h (e); and the sample after experiencing the successive lean-rich cycles for 1 h (f).