Electronic Supplementary Information

De-NO_x in alternative lean/rich atmospheres on $La_{1-x}Sr_xCoO_3$ 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 $La_{1-x}Sr_xCoO_3$ (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 $La(NO_3)_3 \cdot 6H_2O$, $Sr(NO_3)_2$ and $Co(NO_3)_2 \cdot 6H_2O$ (Tianjin Guangfu Technol. Development Co. Ltd.) were dissolved together in 300 mL diluted water. Then, a certain amount of citric acide (CA) and ethylenediaminetetraacetic 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 % $NH_3 \cdot H_2O$ 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 $La_{0.7}Sr_{0.3}CoO_3$ 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 NO_x 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 N_2 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 N_2 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 1*s* 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 A^{-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 H_2O and CO_2 trap containing CaO and NaOH materials. For the H_2-TPR test, 50 mg of the powdered catalyst was loaded into the quartz tube reactor, and was purged by 5% H_2/N_2 to get a stable TCD signal baseline, and then was heated from room temperature to 900 °C in 5% H_2/N_2 (20 mL min^{-1}) with a rate of 10 °C min^{-1}. For the O_2-TPD experiments, a pure O_2 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. NO_x trapping process

The NO_x trapping experiments were carried out with with a conventional fixed bed quartz reactor (i.d. = 8 mm) under atmospheric pressure at the desired NO_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_2 balanced with N_2 (400 mL min^{-1}) passed through the loaded sample. Here, the space velocity was around 80,000 h^{-1}. The on-line chemiluminescence NO_x analyzer (Model 42i-HL, Thermo Scientific) was occupied to determine the concentration of NO, NO_2 and NO_x. The calculation of the NO_x storage capacity (NSC) and NO conversion was defined as the following formula:

$$NSC = (NOx_{\text{inlet}} \times V \times t) / (N_0 \times m) \times storageratio \times 10^{-3}$$

$$= 28.07 \times t \times storageratio \ (\mu mol\ g^{-1}{}_{catalyst})$$

$$NO\ Conversion\ (\%) = (NO_{inlet} - NO_{outlet}) / NO_{inlet} \times 100\%$$

Here, *NO* and NO_x is the concentration of NO and NO_x in *ppm* unit, *V* is the flow rate of the introduced gas, i.e. 400 mL min^{-1}, N_0 is a constant, i.e. 22.4 mol L^{-1}, *m* is the weight of the used catalyst, i.e. 0.5 g, and *storageratio* is the percentage of the amount of the stored NO_x to that of the inlet NO_x. NO_{inlet} is the NO concentration before NO_x trapping, while NO_{outlet} is the NO concentration after NO_x trapping process reached a balance. It usually took 1 – 4 h depending on the catalysts' NO_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_3H_6 or 1000 ppm CO/ 6.7 % O_2 and He as balance) or rich mix reaction (500 ppm NO/ 1000 ppm C_3H_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 ºC. We used an IR online analyser (EMERSON NGA 2000) for CO, CO_2, N_2O and NO; an UV analyser (EMERSON NGA 2000) for NO_2; and a gas micro-chromatograph (VARIAN CP2003) for C_3H_6, N_2, and O_2.

The NO_x conversion for a complete representative cycle was calculated according to the following formula:

$$NO_x\ conversion(\%) = 100 \times (NO_{x,\,in} - NO_{x,\,out}) / NO_{x,\,in}$$

2. Results

2.1. XRD results of $LaCoO_3$ perovskite

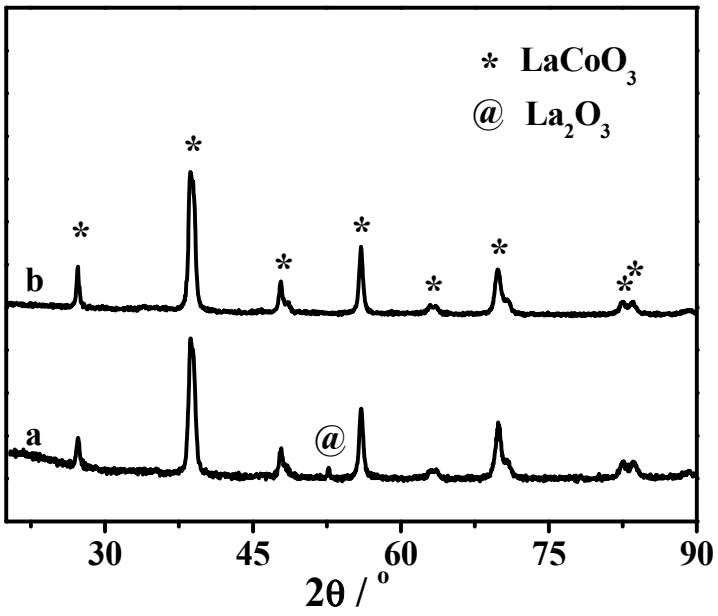

Figure 1S XRD patterns of $LaCoO_3$ perovskite: (a) Fresh, and (b) after NO_x storage at 300 °C.

2.2. BET surface area of the $La_{1-x}Sr_xCoO_3$ perovskite.

Table 1S BET surface area of the $La_{1-x}Sr_xCoO_3$ perovskite.

	$La_{0.9}Sr_{0.1}CoO_3$	$La_{0.8}Sr_{0.2}CoO_3$	$La_{0.7}Sr_{0.3}CoO_3$	$La_{0.6}Sr_{0.4}CoO_3$	$La_{0.7}Sr_{0.3}CoO_3$ [a]
BET Surface area ($m^2\ g^{-1}$)	12.6	8.4	19.1	11.6	17.8

[a] After experiencing a destruction/regeneration process.

2.3. O_2-TPD spectra

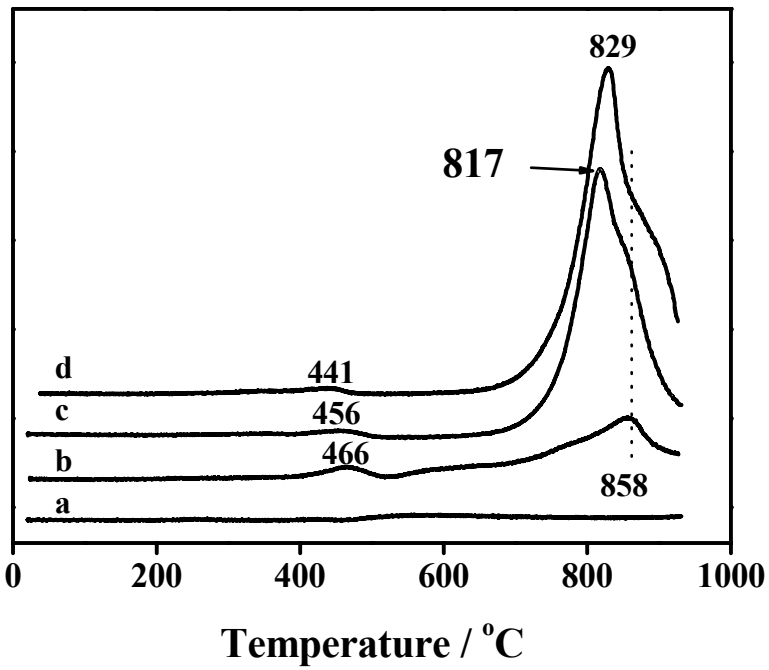

Figure 2S O_2-TPD profiles of the perovskite: (a) $LaCoO_3$, (b) $La_{0.8}Sr_{0.2}CoO_3$, (c) $La_{0.7}Sr_{0.3}CoO_3$, and (d) $La_{0.6}Sr_{0.4}CoO_3$.

2.4. H_2-TPR spectra

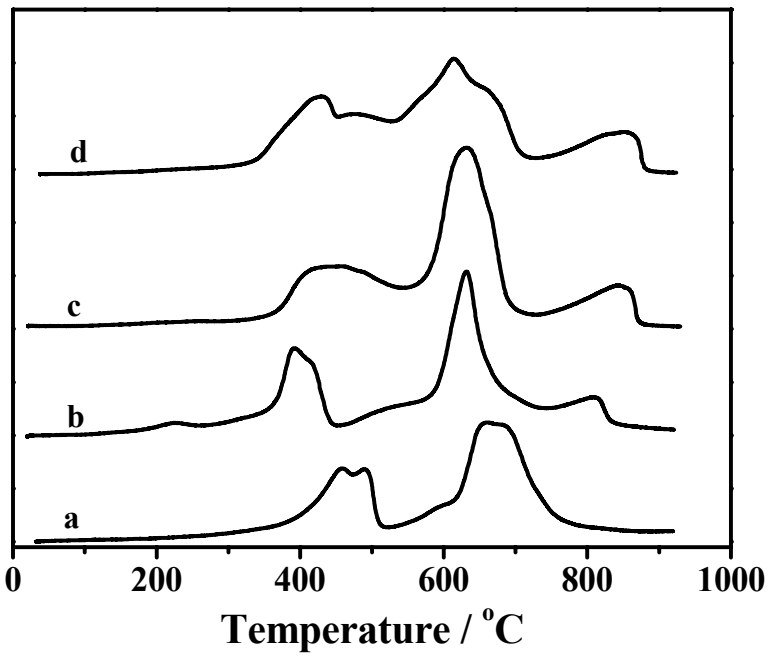

Figure 3S H_2-TPD profiles of the perovskite: (a) $LaCoO_3$, (b) $La_{0.8}Sr_{0.2}CoO_3$, (c) $La_{0.7}Sr_{0.3}CoO_3$, and (d) $La_{0.6}Sr_{0.4}CoO_3$.

2.5. NO_x storage tests

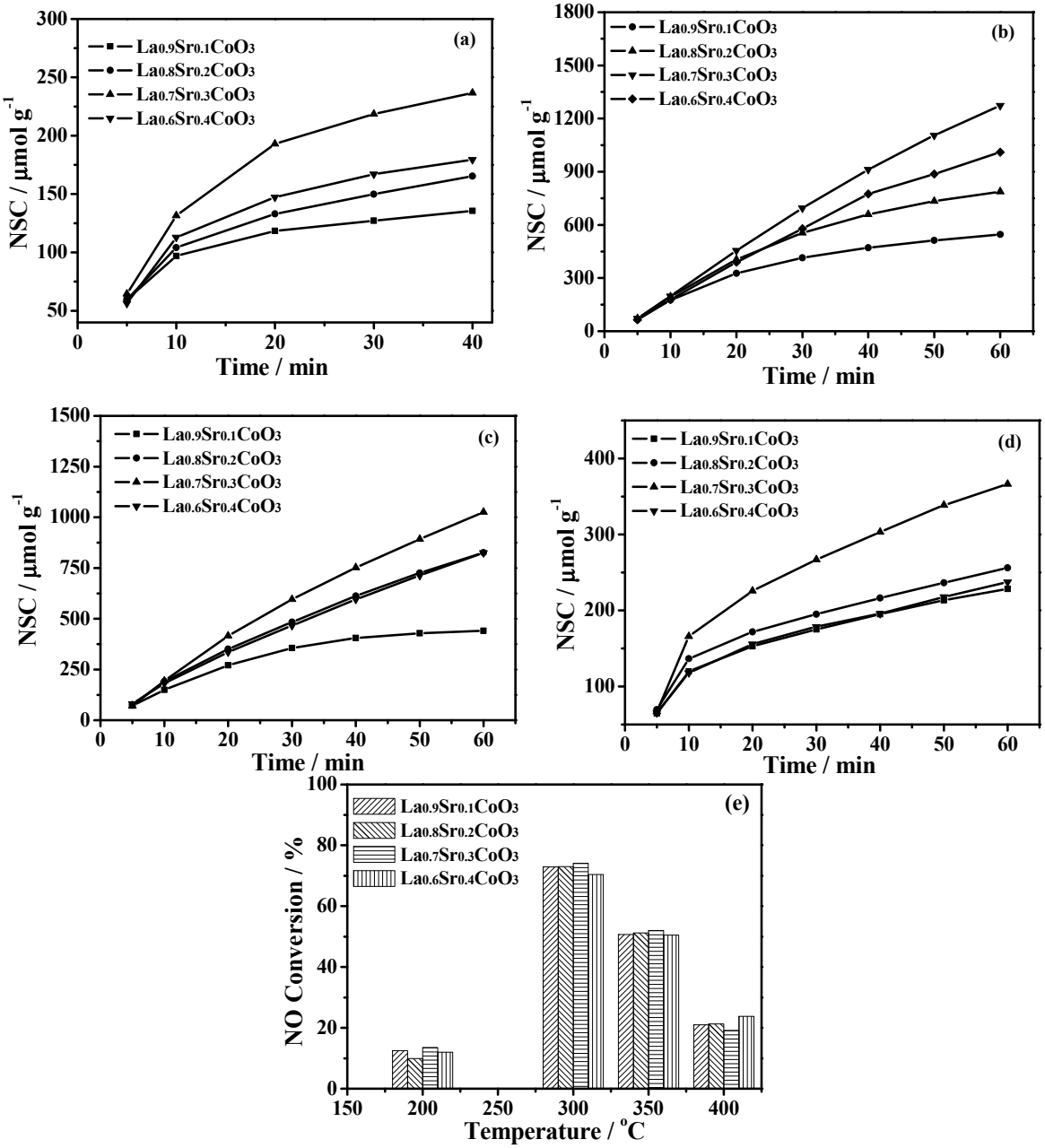

Figure 4S NSC of the $La_{1-x}Sr_xCoO_3$ at 200 (a), 300 (b), 350 (c), and 400 °C (d); and NO conversion (e).

2.6. $La_{0.7}Sr_{0.3}CoO_3$ perovskite regeneration test

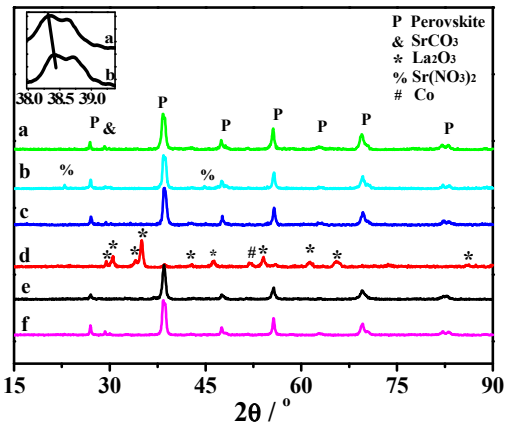

Figure 5S XRD patterns of the fresh $La_{0.7}Sr_{0.3}CoO_3$ sample (a); after NO_x storage at 250 °C (b); the sample (b) reduced in 5% H_2 at 300 °C for 10 min (c); the sample (a) reduced at in pure H_2 at 400 °C for 1 h (d); the sample (d) oxidized in air at 700 °C for 3 h (e); and the sample after experiencing the successive lean-rich cycles for 1 h (f).