

Supporting information for:

Highly efficient NO_x purification in alternative lean/rich atmospheres over non-platinic mesoporous perovskite-based catalyst K/LaCoO₃

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1. Experimental section

1.1 Catalyst preparation

The hard template SBA-15 was prepared using a reported method in the literature (Dongyuan Zhao, Jianglin Feng, Qisheng Huo, et al., *Science*, 1998, vol.548, 279). Nanocasting process: the precursor was prepared by dissolving the equimolar amount of lanthanum nitrate and cobalt nitrate in the aqueous solution of citric acid according to the molar ratio of citric acid to total metal ions (La + Co) was 1 : 1. Then 1.0 g of the hard template was added to this solution; this mixture was subsequently stirred for several hours at 80 °C until it became viscous. After dried at 120 °C for 24 h, the precursor was calcined at 350 °C for 2h (5 K/min) to remove the citric acid and decompose the nitrate species; then it was continuously calcined at 700 °C for 5 h (5 K/min) in flow air (30 mL/min). The silica framework was etched by using a 2M NaOH aqueous solution at 120 °C for three times. After centrifugation, washing with water and ethanol, the LaCoO₃ precursor was dried at 120 °C overnight to obtain black mesoporous LaCoO₃ (denoted as M-LaCoO₃) powder. For comparison, the perovskite LaCoO₃ was also prepared by a sol-gel method at the same calcination condition. The M-LaCoO₃ supported K₂CO₃ catalyst (denoted as K/M-LaCoO₃) with a K₂CO₃ loading of 5 wt. % was prepared by incipient wetness impregnation.

1.2 Catalyst characterization

Specific surface area (S_{BET}) was measured at -196 °C on Quantachrome QuadraSorb SI instrument using nitrogen adsorption. S_{BET} was determined from the linear part of the BET curve. Before measurements, the samples were outgassed at

300°C in vacuum for 6 h. The pore size distributions were derived from the desorption branches of the isotherms by using the Barrett Joyner Halanda (BJH) method. The total pore volume was estimated at a relative pressure of 0.975.

The scanning electron microscopy (SEM) images were observed on an FEI Quanta 200F SEM. The internal morphology and grain characteristics were observed by transmission electron microscopy (TEM), using a JEO1 JEM 2100 electron microscope equipped with a field emission source at an accelerating voltage of 200 kV.

XRD patterns were recorded on a D8 diffractometer (Bruker Company) using Cu K α as radiation source ($\lambda=0.15418$ nm). The operating voltage and current are 40 kV and 40 mA, respectively. Data in the range of 10–90° for 2θ were collected with a step size of 0.02° per second.

Fourier transform infrared spectroscopy (FT-IR) experiments were measured on a Nicolet Nexus FT-IR spectrometer (Thermal Nicolet Co.) equipped with a MCT detector. The spectra were collected in the range of 400 to 4000 cm^{-1} at a resolution of 4 cm^{-1} based on 16 scans.

Temperature-programmed reduction (TPR) measurements were conducted on a TPDRO 1100 apparatus supplied by Thermo-Finnigan company. Before detection by the thermal conductivity detector (TCD), the gas was purified by a trap containing CaO + NaOH materials in order to remove the H₂O and CO₂. For the TPR measurement, 50 mg of the sample was loaded into quartz tube reactor; after the sample was purged with 5 vol. % H₂/N₂ to remove gaseous oxygen and to make the

TCD signal baseline stable; then it was heated from room temperature to 900 °C at a rate of 10 °C/min. A mixture gas of 5 vol. % H₂/N₂ was used as reductant at a flow rate of 30 mL/min.

The X-ray photoelectron spectroscopy (XPS) measurements were carried out on a PHI-1600 ESCA spectrometer. Mg-K α (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 of C1s at 284.6 eV.

X-ray absorption fine structure (XAFS) of Co K-edge of the samples was determined at 14W1 beamline of Shanghai Synchrotron Radiation Facility (SSRF) using a transition mode. 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) were achieved by Fourier transforming of the k^3 -weighted EXAFS data in the range of $k=2.5-14 \text{ \AA}^{-1}$ using a Hanning function window. The standard perovskite LaCoO₃(S) used for EXAFS fitting was prepared in the same sol-gel method as the sample LaCoO₃, but it was calcined at 800 °C for 6 h.

1.3 NO_x storage capacity (NSC) and cyclic NO_x storage/reduction (NSR) measurements

The catalytic oxidation of nitrogen monoxide was carried out in a fixed-bed quartz microcatalytic flow reactor (I.d.= 8 mm) at atmospheric pressure. The temperature of the reactor was monitored by a thermocouple. The catalyst powder (ca. 500 mg) was pelleted, crushed and sieved to 40-60 mesh before loading into the

reactor. The feed gas consisting of NO (400 ppm), O₂ (5%), and N₂ (balance) has a total flow rate of 400 mL/min, corresponding to a gas hourly space velocity (GHSV) of ~80000 h⁻¹. NO, NO₂ and NO_x concentrations were monitored online by a Chemiluminescence NO–NO₂–NO_x Analyzer (42i-HL, Thermal Scientific). By integrating the NO_x concentration curve after reaching the steady state, the molar amount of NO_x from the reactor outlet can be obtained. Based on the flow rate of NO_x at the reactor inlet, the total amount of NO_x passed through catalyst bed can be calculated. So, the stored NO_x namely NSC could be acquired by deducting the molar amount of NO_x at the reactor outlet from the total molar amount of NO_x passed through catalyst bed.

At steady state the reactor outlet concentration of NO_x (NO+NO₂) is almost the same as that of inlet. However, the outlet concentrations of NO and NO₂ are different from those of inlet, which is caused by the oxidation of NO to NO₂ catalyzed by the catalysts. So, the NO conversion of this moment is always used to evaluate the oxidation capability of the catalysts. The NO conversion was calculated as follows.

$$NO \text{ conversion } \% = \frac{NO(inlet) - NO(outlet)}{NO(inlet)} \times 100\%$$

Here, *NO (inlet)* and *NO (outlet)* represent the NO concentration in the inlet and the outlet of the reactor at the steady state, respectively.

The cyclic NSR measurements were conducted in the same fixed-bed quartz reactor using 0.5 g catalyst each time. The reactor was connected to four-way valve, which provides a quick switching between lean and rich atmospheres. Lean atmosphere (400 ppm NO and 5 % O₂ balanced by N₂) and rich atmosphere (1000

ppm C₃H₆ balanced by helium) were introduced alternatively to the catalyst bed at a constant flow rate (150 mL/min) and 350 °C. The cyclic NSR experiments use a lean period of 3 min and a rich period of 1 min, respectively. NO and NO₂ concentrations were measured online by a Chemiluminescence NO–NO₂–NO_x Analyzer (42i-HL, Thermo Scientific), and the N₂O concentration was monitored by an online N₂O Analyzer (Model: SICK-MAIHAK 710).

The NO_x reduction percentage during a complete lean/rich cycle was calculated according to the following formula:

$$\text{NO}_x \text{ reduction (\%)} = [1 - (\text{NO}_x\text{-out} / \text{NO}_x\text{-in})] \times 100\%$$

Here, NO_x-in and NO_x-out represent the total NO_x amount passed through the catalyst bed and flowing out from the reactor outlet, respectively.

2. Supplementary figures

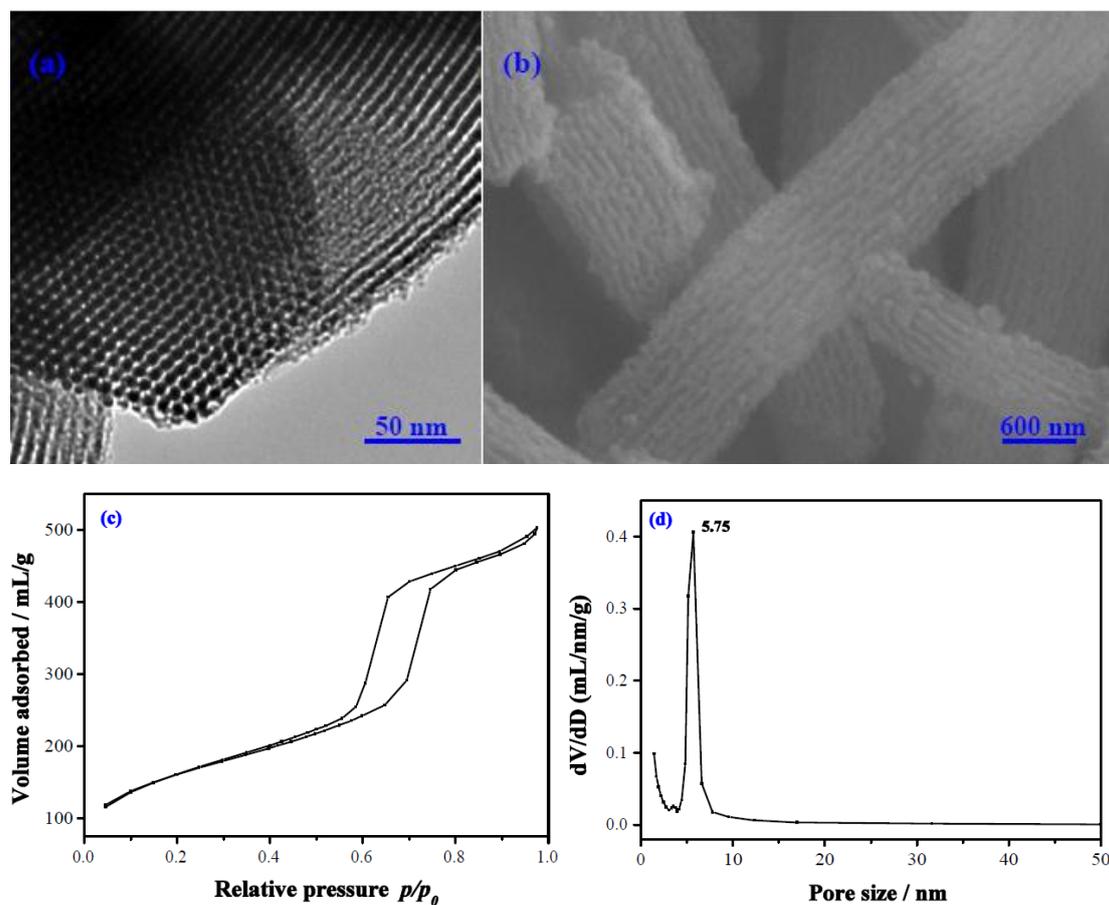


Fig.S1 The morphology images (a, b), N₂-sorption/desorption isotherms (c) and pore size distribution of the as-prepared SBA-15.

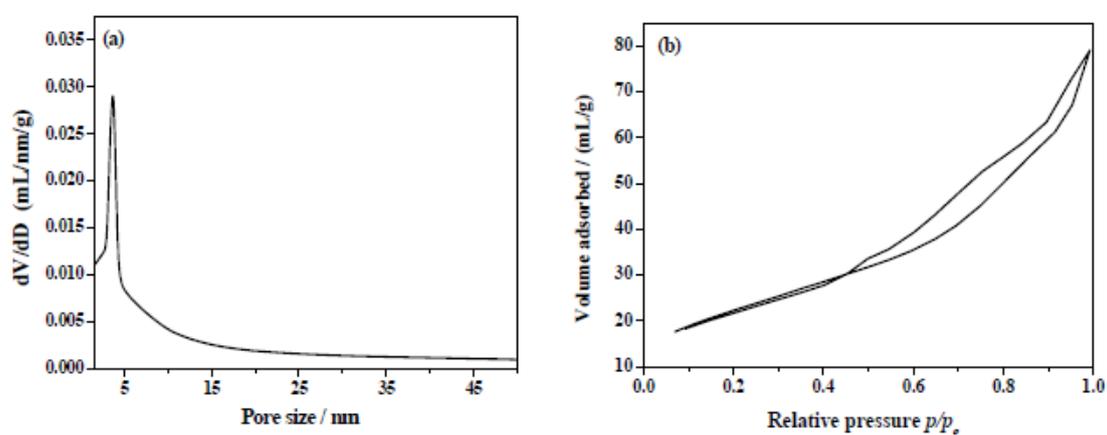


Fig.S2 Pore size distribution and N₂-sorption/desorption isotherms of M-LaCoO₃

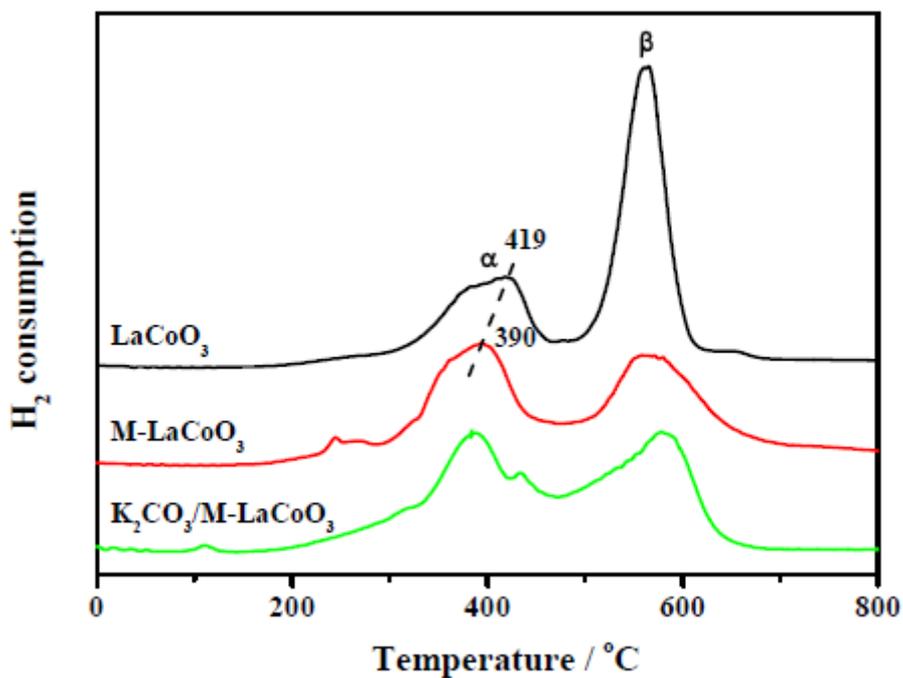


Fig.S3 H₂-TPR profiles of different catalysts

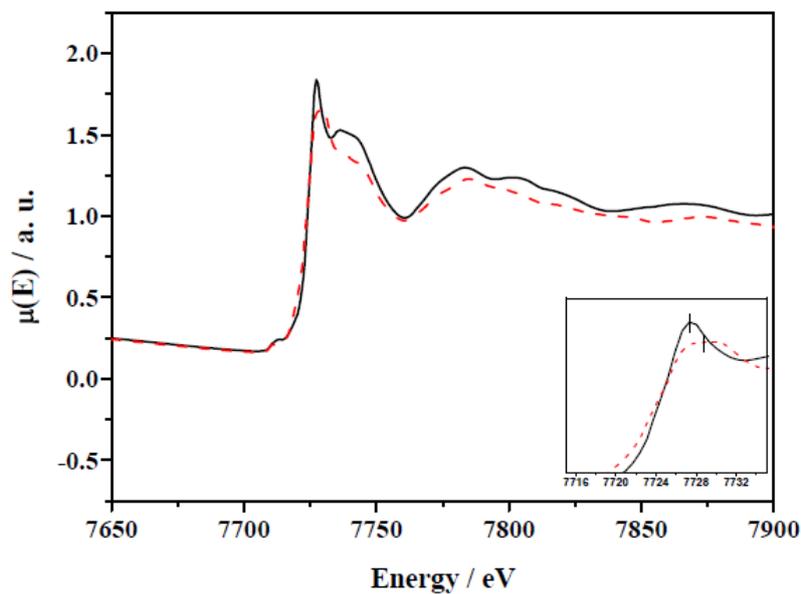


Fig.S4 Co K-edge XANES spectra of the catalysts LaCoO₃ (black solid line) and M-LaCoO₃ (red dash line)

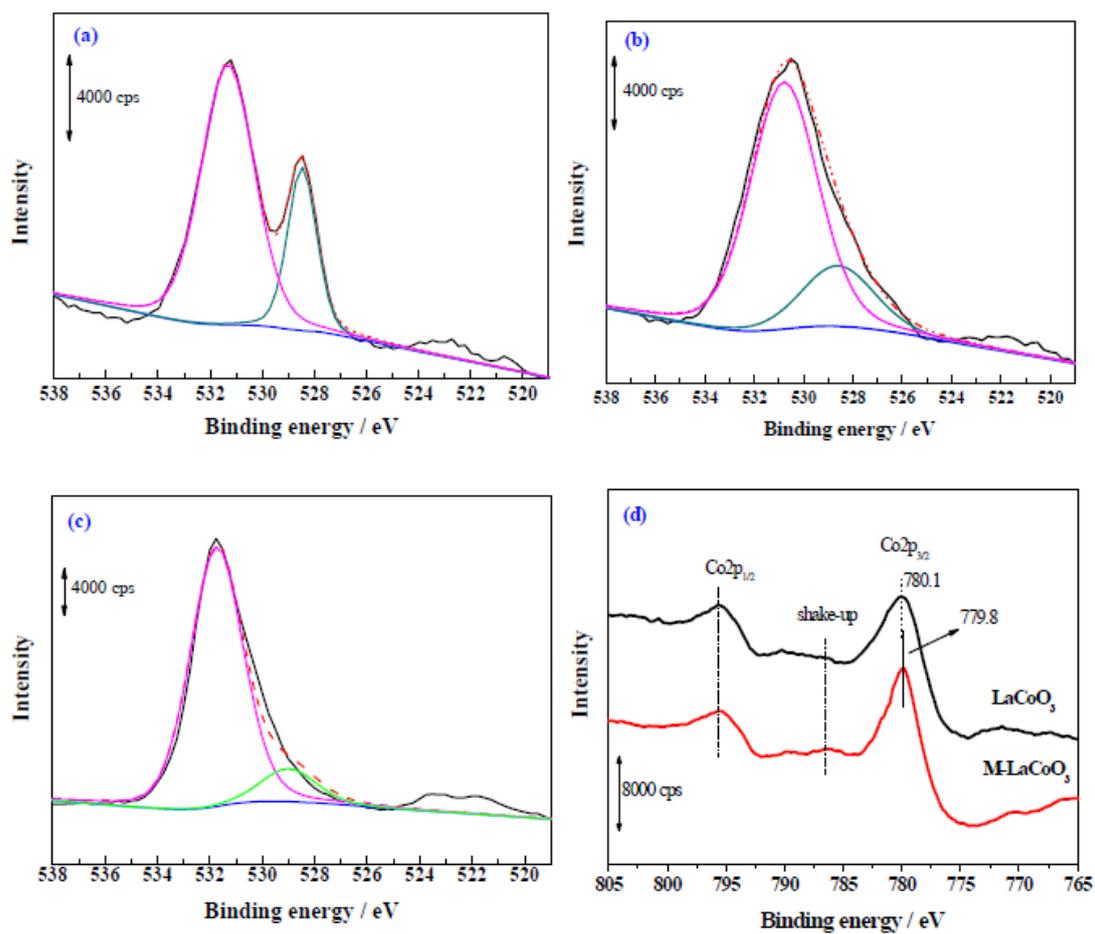


Fig.S5 O1s binding energy spectra of LaCoO₃ (a), M-LaCoO₃ (b), K/M-LaCoO₃ (c); and Co2p binding energy spectra for LaCoO₃ and M-LaCoO₃ (d).

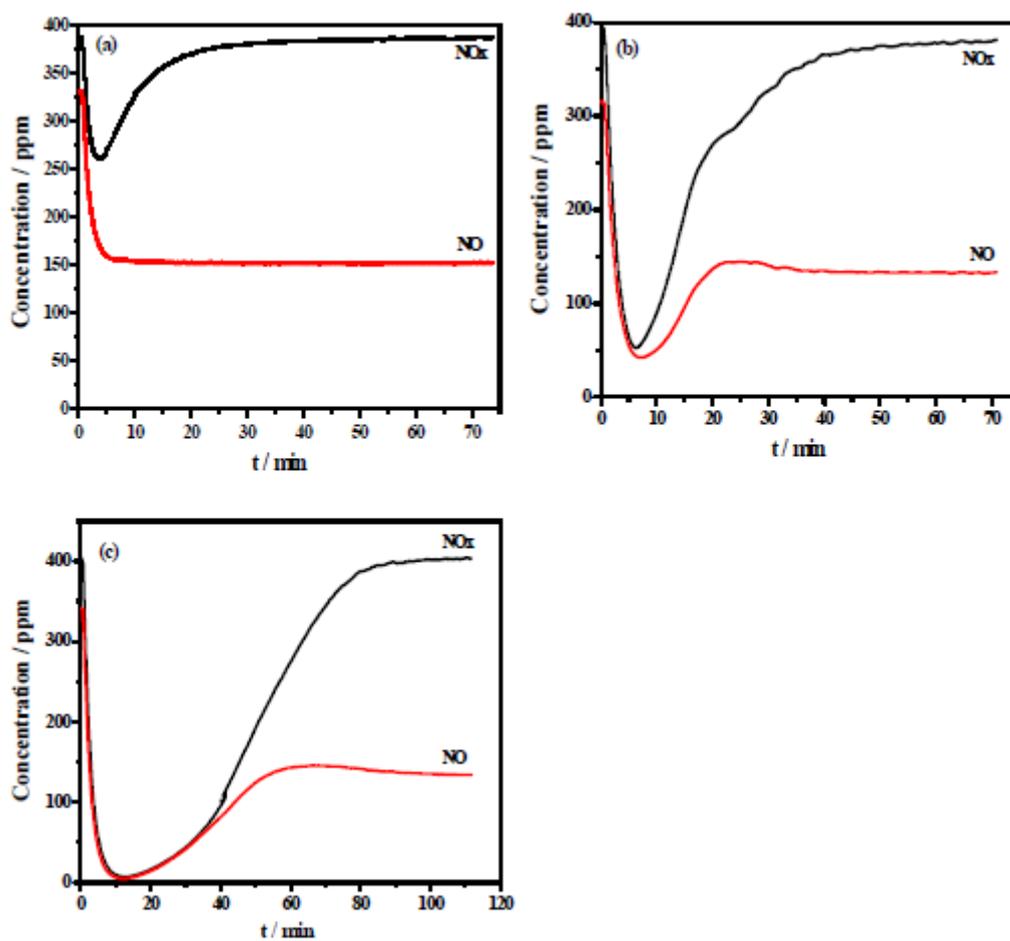


Fig.S6 NO_x storage curves of different catalysts recorded at 350 °C
(a) LaCoO₃, (b) M-LaCoO₃, (c) K/M-LaCoO₃

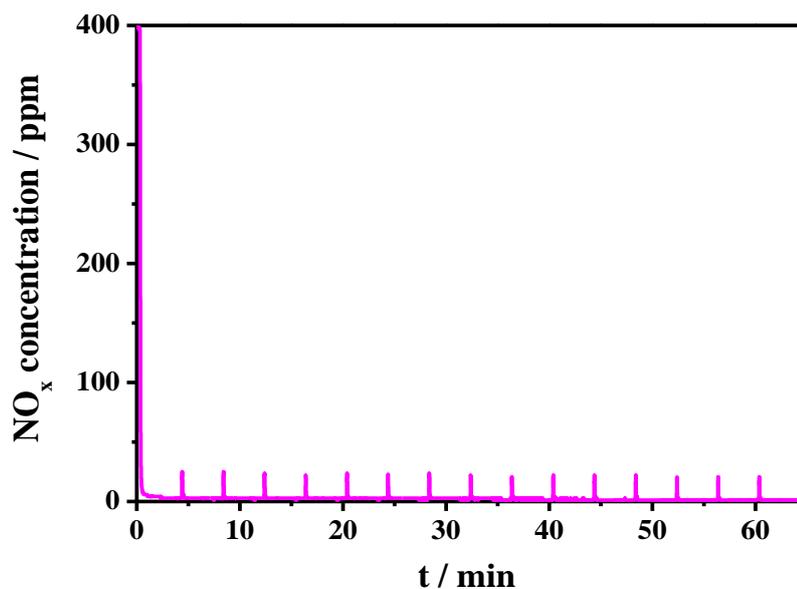


Fig.S7 NO_x storage-reduction in alternative lean-rich atmospheres on as-prepared noble metal Pt-containing NSR catalysts Pt-K/CeO₂ at 350 °C. Lean atmosphere: 400 ppm NO + 1000 ppm C₃H₆ + 5% O₂ + balance N₂; rich atmosphere: 1000 ppm C₃H₆ + balance N₂. After 3 min of lean period the feed was switched to rich atmosphere for 1 min.

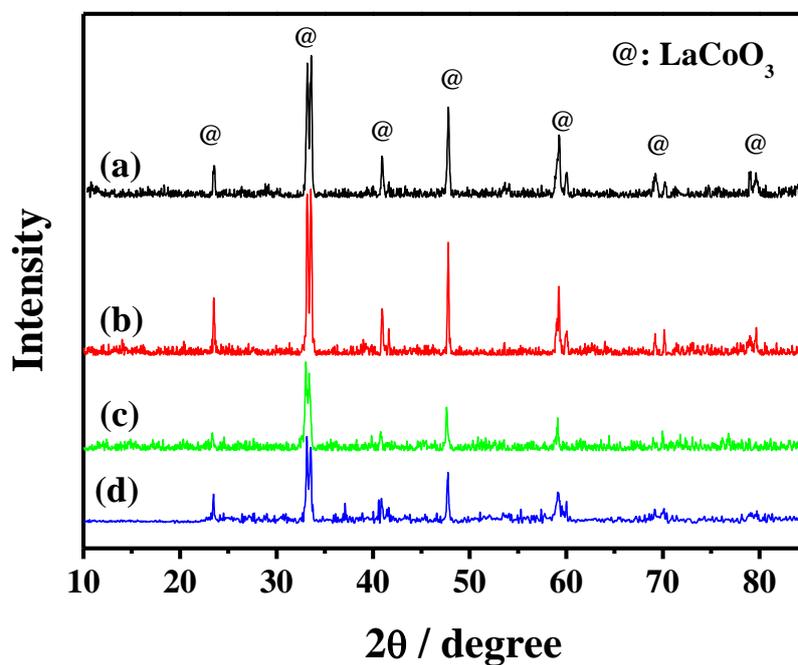


Fig.S8 XRD patterns of the catalysts after NO_x storage and reduction tests
(a) LaCoO₃, (b) K/LaCoO₃, (c) M-LaCoO₃, (d) K/M-LaCoO₃

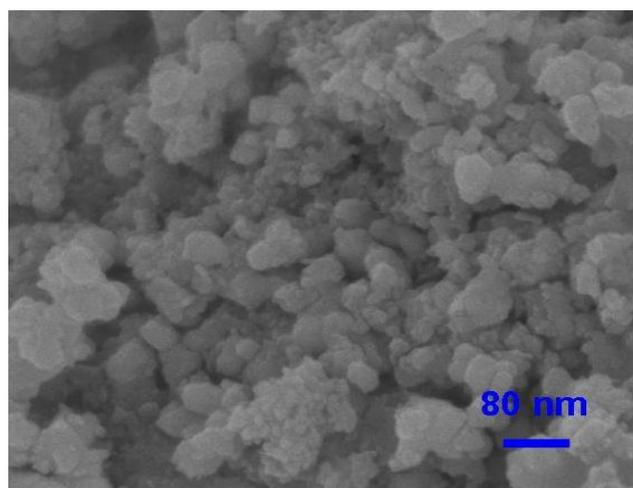


Fig. S9 The SEM image of K/M-LaCoO₃ after NSR measurement

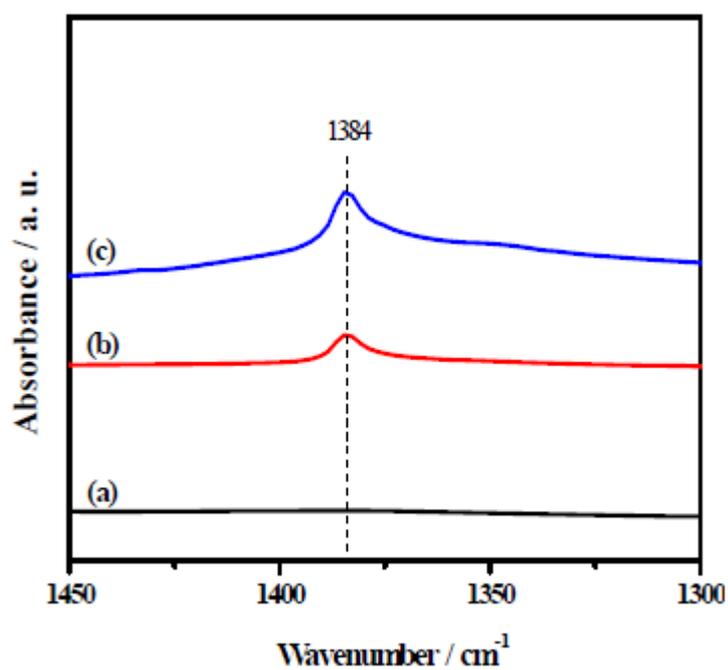


Fig.S10 FT-IR spectra of the catalysts after NO_x storage experiments
(a) LaCoO₃, (b) M-LaCoO₃, (c) K/M-LaCoO₃

Supplementary tables

Tab. 1 Specific surface area (SSA), average pore diameter (APD) and pore volume of the samples derived for N₂ adsorption/desorption, and the crystallite size (d_{XRD}) of LaCoO₃ perovskite in different samples

Samples	SSA (m ² /g)	APD (nm)	PV (mL/g)	d _{XRD} ^a (nm)
SBA-15	644	5.7	0.785	/
LaCoO ₃	10	1.9	0.036	19.5
M-LaCoO ₃	75	3.8	0.139	15.0
K/M-LaCoO ₃ (fresh)	68	3.6	0.134	18.8
K/M-LaCoO ₃ after NSR tests	65	3.6	0.133	19.0

^aThe crystallite sizes were calculated using Scherrer equation based upon the crystal plane (110).

Tab. 2 Besting-fitting values of the structural parameters for the first coordination shell (Co-O) isolated from EXAFS data

Samples	Shell	N	R (nm)	Δσ ² (nm ²)
LaCoO ₃ (S)*	Co-O	6.0	0.193	
LaCoO ₃	Co-O	5.3	0.193	1.58E-08
M-LaCoO ₃	Co-O	4.6	0.193	2.60E-08
K/M-LaCoO ₃	Co-O	4.7	0.193	2.38E-08

*The parameters of the standard LaCoO₃(S) were taken from the reference: *Journal of Solid State Chemistry*, 2004, vol.177, 1000.

Tab. 3 Binding energies (B.E.) and deconvoluted areas of O1s peaks for different oxygen species on the samples

Samples	O_{lat}		O_{ads}	
	B. E.(eV)	Area	B. E.(eV)	Area
LaCoO ₃	528.6	0.254	531.1	0.746
M-LaCoO ₃	528.6	0.208	530.8	0.792
K/M-LaCoO ₃	528.9	0.116	531.7	0.884

Tab. 4 NO to NO₂ conversion and NO_x storage capacity (NSC) after reaching a steady state during NO_x storage at lean condition *

Samples	NO to NO ₂ conversion (%)	NSC (μmol/g)
LaCoO ₃	50.2	93
M-LaCoO ₃	57.9	252
K/M-LaCoO ₃	54.5	981

* Lean condition: 400 ppm NO + 5% O₂ + balance N₂.