

Improved low-temperature activity of La-Sr-Co-O nano-composite for CO oxidation by phase cooperation

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Table of contents

Experimental section

Figure S1. XRD patterns for the series of La-B-O samples (B = Fe, Co, Ni, Cu)

Figure S2. TEM images for (A) Co_3O_4 , (B) La-Co-O prepared without template PMMA, (C) La-Co-O prepared with template PMMA

Figure S3. (A) La 3d, (B) Sr 3d, (C) Co 2p and (D) O 1s spectra for $\text{La}_{1-x}\text{-Sr}_x\text{-Co-O}$ surveyed from the XPS measurements

Figure S4. N_2 physisorption isotherms of the $\text{La}_{0.7}\text{-Sr}_{0.3}\text{-Co-O}$ and the porous LaCoO_3 prepared using PMMA as template

Figure S5. (A) O_2 -TPD and (B) H_2 -TPR profiles of Co_3O_4 , $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$ and $\text{La}_{0.7}\text{-Sr}_{0.3}\text{-Co-O}$

Figure S6. CO oxidation activity obtained from the La-Co-O sample prepared with and without template PMMA

Figure S7. Long-term stability of Co_3O_4 for CO oxidation within 36 h conducted at 145 °C

Figure S8. Characteristic results from XRD, N_2 physisorption isotherms and XPS for the used $\text{La}_{0.7}\text{-Sr}_{0.3}\text{-Co-O}$

Table S1. Comparison in the activity (T_{ign} , T_{50} and T_{100}) of $\text{La}_{0.7}\text{-Sr}_{0.3}\text{-Co-O}$ with that of LaCoO_3 reported in literature

Experimental

Catalyst's Preparation.

The samples were prepared by a sol-gel method using ethylene glycol and formic acid as complexing agents. Briefly, 5 mmol of $\text{La}(\text{NO}_3)_3$ and/or $\text{Sr}(\text{NO}_3)_2$, and 5 mmol of $\text{Co}(\text{NO}_3)_3$, $\text{Fe}(\text{NO}_3)_3$, $\text{Ni}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2$ or $\text{Zn}(\text{NO}_3)_2$ were first dissolved in a mixed solution containing 3 mL ethylene glycol and 2 mL formic acid and stirred for 6 h. The resulting solution was then aged at 95 °C overnight, yielding a gel-like product, which was calcined in a static air oven at 600 °C for 5 h (heating rate 1 °C min^{-1}). Such obtained samples showed a multi-phase structure and thus were denoted as $\text{La}_{1-x}\text{Sr}_x\text{B-O}$ (B = Fe, Co, Ni, Cu, $0 \leq x \leq 0.7$). For comparison, a perovskite $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$ was prepared by calcination at 800 °C, and a metal oxide Co_3O_4 was prepared without the addition of La or Sr, with otherwise identical conditions.

Catalyst's Characterizations

X-Ray diffraction (XRD) patterns were collected using a Bruker D8 Advance X-ray diffractometer with Cu $\text{K}\alpha$ ($\lambda = 1.5406 \text{ \AA}$) irradiation; Transmission electron microscopy (TEM) images were obtained on a Tecnai G² 20 S-Twin apparatus with high-resolution transmission electron microscope (200 kV). The sample was dispersed in ethanol by ultrasonic method before being deposited on the copper mesh. N_2 physisorption isotherms were measured on a TriStar II 3020 measurement at liquid nitrogen temperature (-196 °C) and the surface areas were calculated using the Brunauer–Emmett–Teller (BET) method. Before measurement the sample was treated in vacuum at 200 °C for 5 h. X-ray photoelectron spectroscopy (XPS) spectra were recorded on a Thermo Electron Corporation VG Multilab 2000 apparatus using a monochromatic Al $\text{K}\alpha$ X-ray source (300 W) and analyzer pass energy of 25 eV. Binding energies were obtained by referencing to the C 1s binding energy of carbon taken at 284.6 eV.

Temperature-programmed reduction by H_2 (H_2 -TPR) was performed on a

FINESORB-3010 apparatus (Fantai technology company, China) equipped with TCD detector. The sample (0.10 g) was first treated in Ar atmosphere at 500 °C for 1 h and then cooled to room temperature. Thereafter 10 vol.% H₂/Ar mixture with flow rate of 25 cm³ min⁻¹ was switched on. After a stabilized baseline is reached, the sample was heated from RT to 800 °C at a rate of 10 °C min⁻¹ to record the profile.

Temperature-programmed desorption of O₂ (O₂-TPD) was carried out on the same apparatus. The sample (0.10 g) was first treated in O₂ atmosphere at 500 °C for 1 h and then cooled to room temperature. Thereafter Helium with flow rate of 25 cm³ min⁻¹ was switched on. After a stabilized baseline is reached, the sample was heated from RT to 800 °C at a rate of 10 °C min⁻¹ to record the profile.

Catalytic tests

Catalytic tests were measured using a continuous flow fixed-bed quartz microreactor (*i.d.* = 8 mm) equipped with a temperature programmed controller at atmospheric pressure. 0.1 g catalyst was loaded into the microreactor without dilution. The reactant 0.5% CO + 7.5% O₂ in Ar was passed at a flow rate of 50 mL min⁻¹, corresponding to space velocity (SV) of ca. 30,000 mL g⁻¹ h⁻¹. The effluent gases were analyzed by an on-line GC (Agilent 7890) equipped with a thermal conductivity detector and two packed columns (Porapak Q and 5A molecular sieve columns). CO oxidation activity was evaluated in terms of CO conversion: % Conversion = $\{[CO]_{in} - [CO]_{out}\} / [CO]_{in} * 100$, where $[CO]_{in}$ and $[CO]_{out}$ represent the inlet and outlet concentration of CO, respectively.

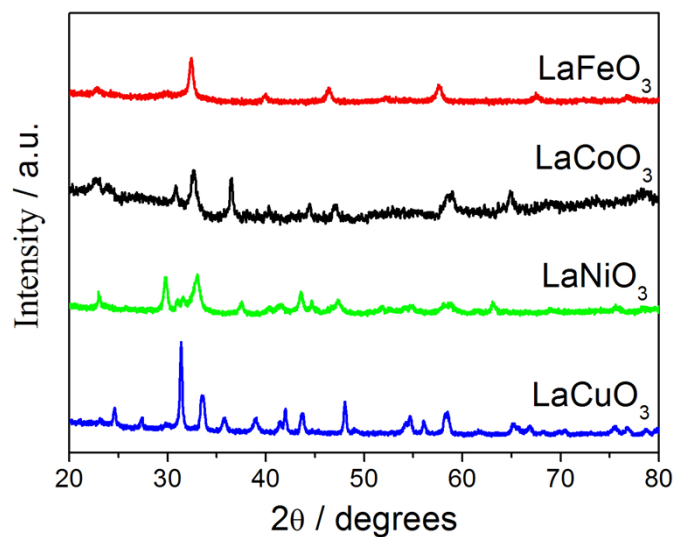


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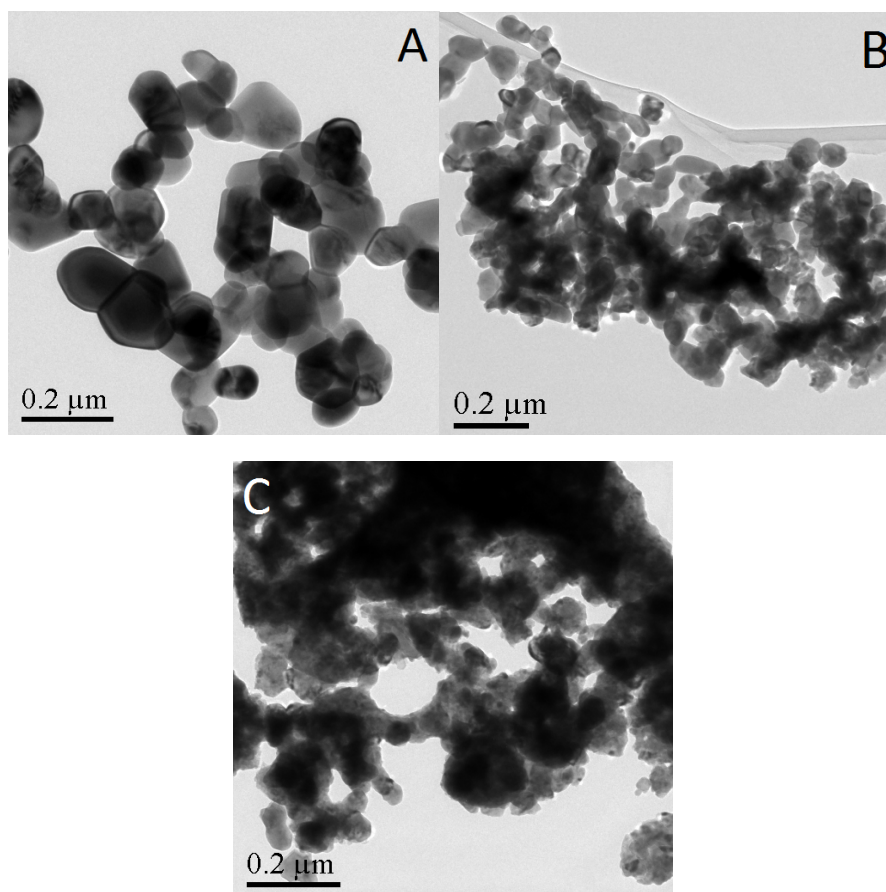


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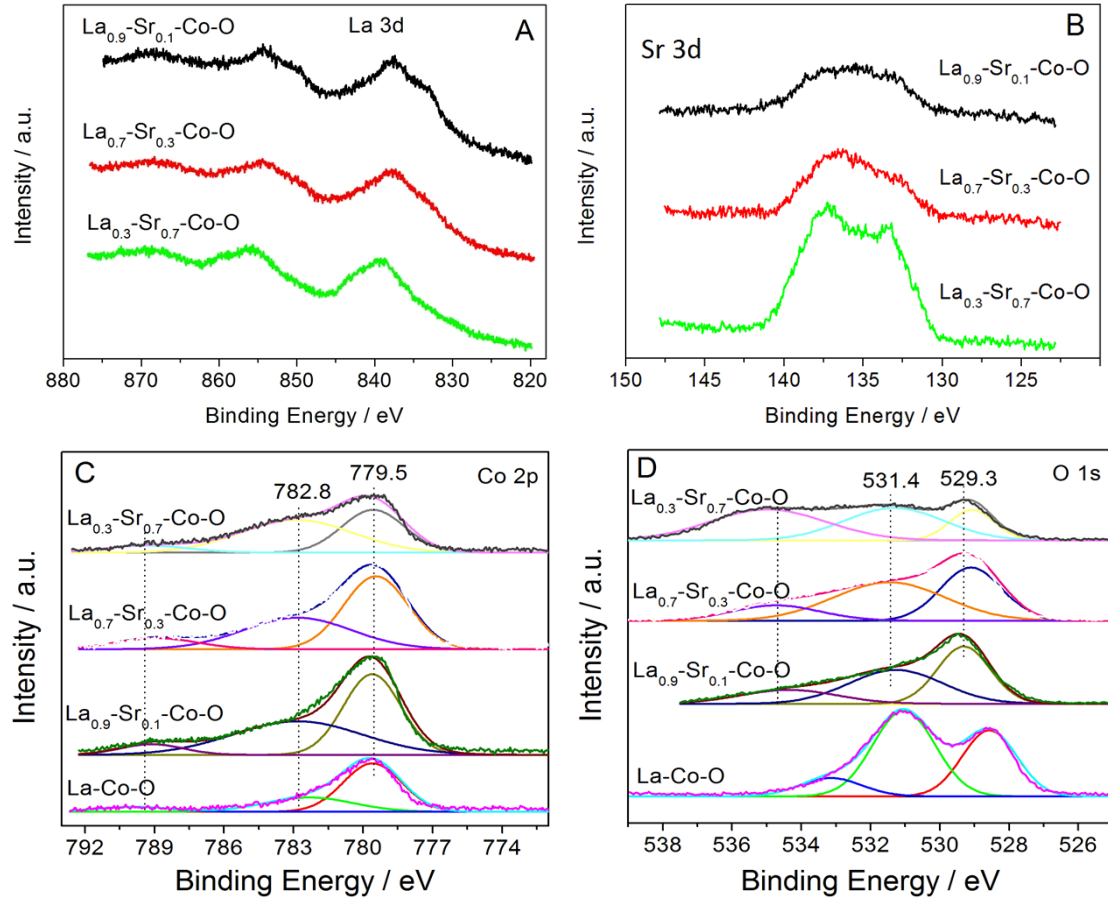


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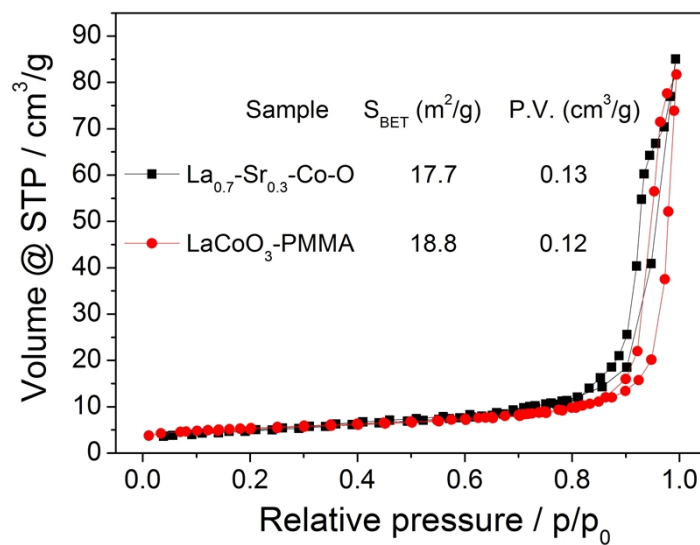


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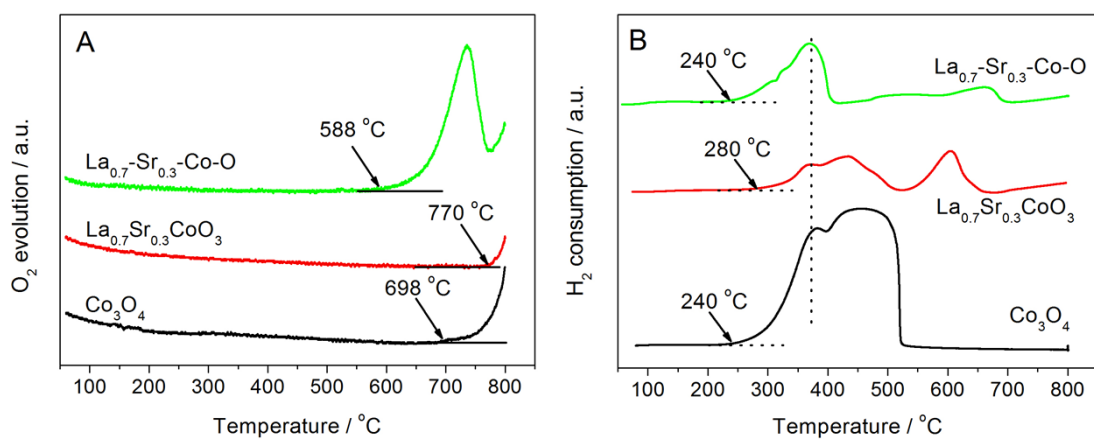


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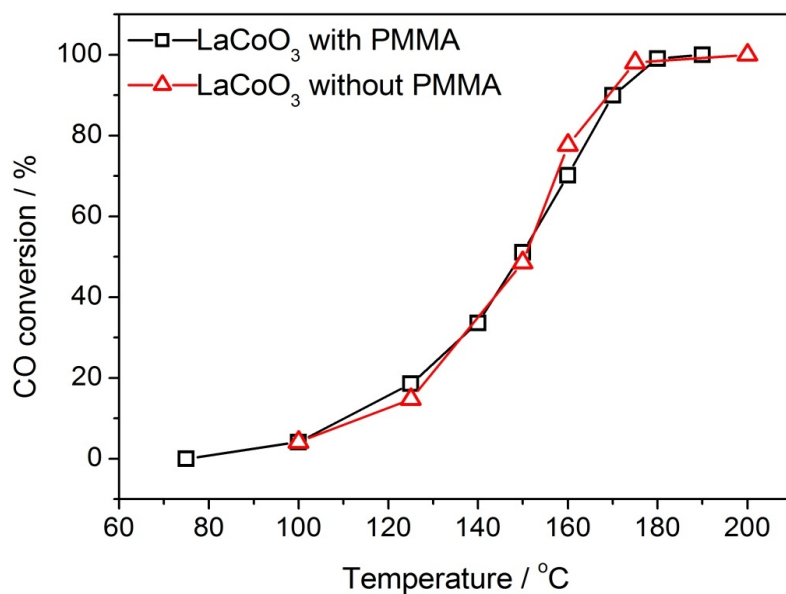


Figure S6. CO oxidation activity obtained from the LaCoO_3 sample prepared with and without template PMMA

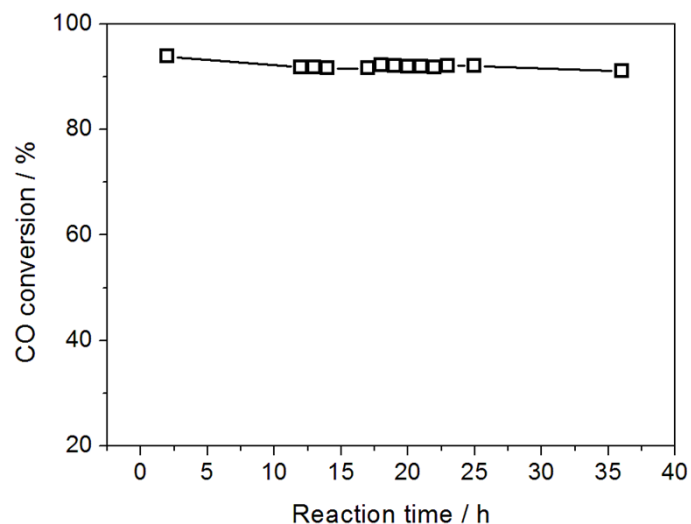


Figure S7. Long-term stability of Co_3O_4 for CO oxidation within 36 h measured at 145°C

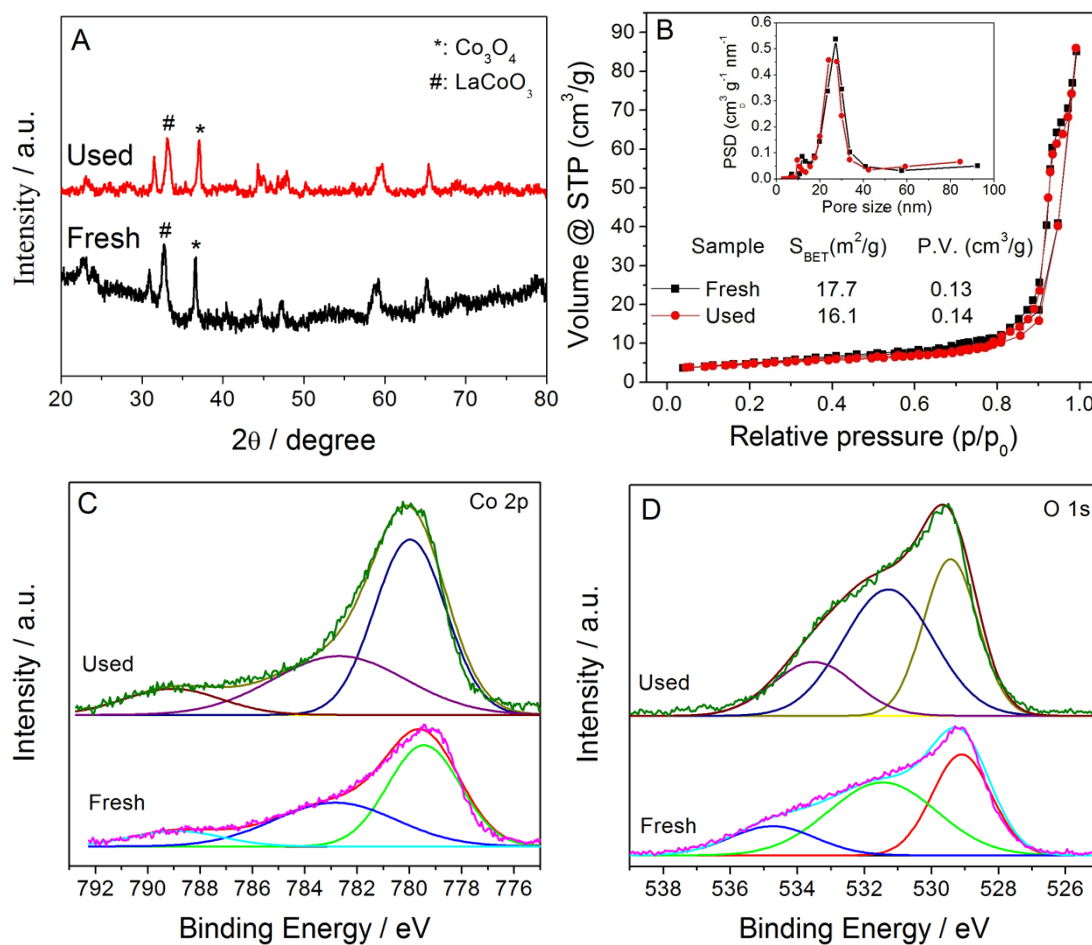


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Table S1. Comparison in the activity (T_{ign} , T_{50} and T_{100}) of $\text{La}_{0.7}\text{-Sr}_{0.3}\text{-Co-O}$ with that of LaCoO_3 reported in literature

Catalyst	T_{ign}^a	T_{50}^b	T_{100}^c	Reaction conditions	Refs.
$\text{La}_{0.7}\text{-Sr}_{0.3}\text{-Co-O}$	75	130	174	0.5% CO, 7.5% O ₂ , WHSV = 30000 mL/(g h)	This work
La-Co-O	100	150	200	0.5% CO, 7.5% O ₂ , WHSV = 30000 mL/(g h)	This work
LaCoO_3 (porous)	60	145	175	0.5% CO, 7.5% O ₂ , WHSV = 30000 mL/(g h)	1
LaCoO_3 (Nano-sized)	100	161	200	1% CO, 20% O ₂ , WHSV = 10000 mL/(g h)	2
LaCoO_3 (spherical)	70	131	170	1% CO, 20% O ₂ , WHSV = 10000 mL/(g h)	2
LaCoO_3 (3DOM)	50	162	190	1% CO, 20% O ₂ , WHSV = 10000 mL/(g h)	3
LaCoO_3	120	182	215	1% CO, 20% O ₂ , WHSV = 10000 mL/(g h)	3
LaCoO_3 (porous)	110	170	207	1% CO, 21% O ₂ , WHSV = 3000 mL/(g h)	4
LaCoO_3	140	187	237	1% CO, 21% O ₂ , WHSV = 3000 mL/(g h)	4
$\text{La}_{0.9}\text{K}_{0.1}\text{CoO}_3$	160	245	335	Not applicable from the literature	5
LaCoO_3	130	205	246	0.5% CO, 10% O ₂ , SV = 96,000 h ⁻¹	6
LaCoO_3	160	238	270	2% CO, 20% O ₂ , SV = 6000 h ⁻¹	7
LaCoO_3	115	172	210	0.5% CO, 10% O ₂ , SV = 30,000 h ⁻¹	8
LaCoO_3	260	280	400	2% CO, 1% O ₂ , WHSV = 30000 mL/(g h)	9

a Ignition temperature for CO oxidation; b Temperature for 50% CO conversion; c Temperature for 100% CO conversion

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