Supporting information

NO Oxidation Catalysis on Copper Doped Hexagonal Phase $LaCoO_3$: A Combined Experimental and Theoretical Study

Chen Zhou,[‡a] Xiao Liu,[‡b,c] Chunzheng Wu,[a] Yanwei Wen,[c] Yejian Xue,[a] Rong Chen,[b] Zhaoliang Zhang,[d] Bin Shan,[*,c] Hongfeng Yin,[*,a] andWei Guo Wang[a]

[a]Division of Fuel Cell & Energy Technology, Ningbo Institute of Material Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, Zhejiang, People's Republic of China

[b]State Key Laboratory of Digital Manufacturing Equipment and Technology and School of Mechanical Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, Hubei, People's Republic of China

[c]State Key Laboratory of Material Processing and Die and Mould Technology and School of Materials Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, Hubei, People's Republic of China

[d]College of Chemistry and Chemical Engineering, University of Jinan, Jinan 250022, Shandong People's Republic of China

1 Experimental methods

Appropriate amounts of $La(NO_3)_3 \cdot 6H_2O$, $Sr(NO_3)_2$, $Co(NO_3)_2 \cdot 6H_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$ were dissolved in deionized water followed by vigorous stirring for 1 hours. Subsequently, CA and EDTA were added with the molar ratio of EDTA: CA: total metal ions (TM) = 1:2:1. The mixture was kept in a water bath at 90 ºC with constant stirring. Water was slowly evaporated until the solution became a viscous gel and began evolving NO/NO_2 gas. Subsequently the gel was dried in the oven at 120 ºC for 3 hours and then heated up to 150 ºC and kept at 150 ºC overnight. The resulting solid was grounded and heat-treated in two steps: the first calcination step was performed at 550 ºC for 2 hours in air to eliminate organic constituents and the second at 700 ºC for 5 hours to form the perovskite oxide.

The reference sample 2% Pt/Al_2O_3 was prepared by the wet-impregnation method. A certain amount of γ-Al_2O_3 was immersed in $Pt(NO_3)_2$ solution at known concentration. The mixture was stirred at room temperature until the powders were well moistened and the solution was fully absorbed. The precursor was heated at 100 ^oC for 6 hours and then was calcined at 500 ^oC for 2 hours.

2 Results

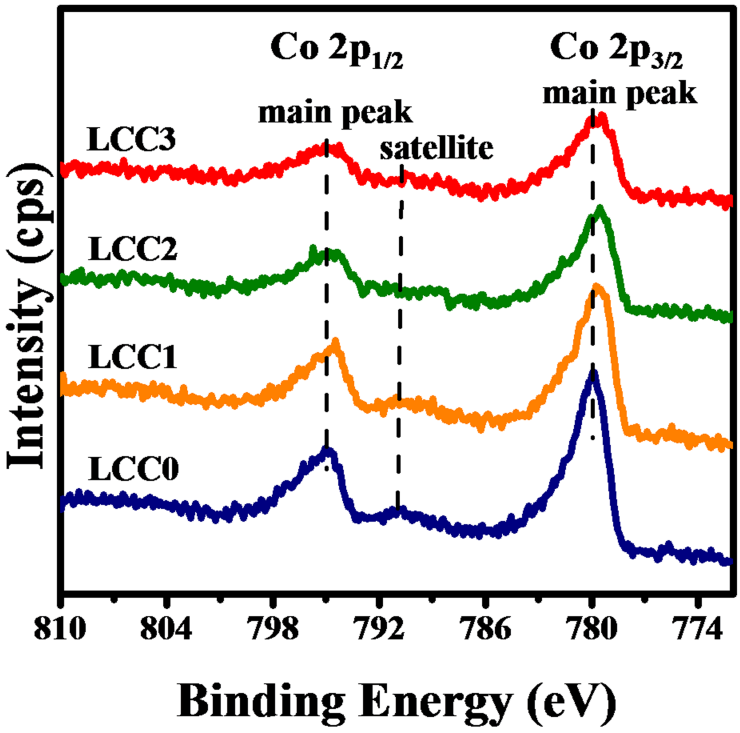

Figure S1 (color online) XPS spectra of Co 2p as a function of composition.

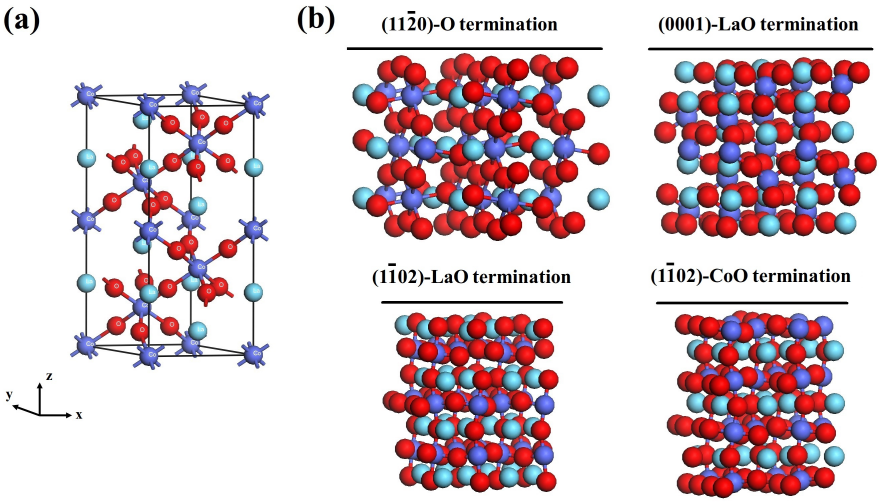

Figure S2 (color online) Schematic unit cell (a) and four stable terminations (b) of hexagonal $LaCoO_3$.

Table S1. $LaCoO_3$'s structural parameters of our calculation and experiment in reference.

Structural parameters			
Parameters	Calculation	Experiment [1]	Percentage Error (%)
a=b (Å)	5.426	5.426	0.00
c (Å)	12.950	12.991	0.32
c/a	2.387	2.394	0.29
La-O (Å)	2.384	2.428	1.81
La-O (Å)	3.042	2.999	1.43
La-O (Å)	2.687	2.688	0.03
Co-O (Å)	1.930	1.925	0.25
∠O-Co-O	91.79	91.48	0.34
∠Co-O-Co	160.38	162.93	1.57

Compared with the experimental structural properties of $LaCoO_3$, our calculating results were in good agreement with the experiments, which indicated our computational method was an accurate and reliable approach to investigate the catalytic performance of $LaCoO_3$.

Table S2. The ground state energy of $LaCoO_3$ (La, Co) bulk and all slabs. N_{La}, N_{Co} and N_O are the number of atoms corresponding to La, Co and O elements in slabs.

Surface-terminations	E_{slab} (eV)	N_{La}	N_{Co}	N_O
(0001)-Co	-769.484	20	24	60
(0001)-LaO	-867.455	24	20	72
$(10\bar{1}0)$-LaCoO	-491.701	14	14	38
$(10\bar{1}0)$-O	-391.576	10	10	34
$(11\bar{2}0)$-LaCoO	-798.886	24	24	60
$(11\bar{2}0)$-O	-734.861	18	18	66
$(1\bar{1}02)$-CoO	-1049.685	24	32	88
$(1\bar{1}02)$-LaO	-1039.826	32	24	80

E_{LaCoO3} = -37.99 eV	E_{La} = -19.69 eV	E_{Co} = -14.19 eV	E_{O2} = -9.86 eV

In Table S2, E_{LaCoO_3} was the total energy of bulk per formula unit $LaCoO_3$. E_{La}

was the total energy of perfect La crystal which was hexagonal structure with four atoms in the unit cell. As the same, E_{Co} was the total energy of cubic Co crystal with two atoms and E_{O_2} was the energy of O_2 molecule. In the article, $\mu^0_{La} = E_{La}/4$, $\mu^0_{Co} = E_{Co}/2$, $\mu^0_{O} = E_{O2}/2$.

Reference

1. P. G. Radaelli and S. W. Cheong, *Phys. Rev. B*, 2002, **66**, 094408.