Supporting information for

Identification of Active Oxygen Species for Soot Combustion on LaMnO$_3$ Perovskite

Xiao Wang, Yexin Zhang, Qian Li, Zhongpeng Wang, and Zhaoliang Zhang *

School of Chemistry and Chemical Engineering, Shandong Provincial Key Laboratory of Fluorine Chemistry and Chemical Materials, University of Jinan, 106 Jiwei Road, Jinan 250022, China;

Supporting information includes:

- Experimental section.

- Table S1.

- Figures S1 to S5.

- The calculation of the active oxygen amount.

- References.

1. Experimental section

LaMnO$_3$ was prepared by a citric acid method. The desired amounts of La(NO$_3$)$_3$·6H$_2$O and 50% Mn(NO$_3$)$_2$ solution were dissolved in distilled water with citric acid monohydrate. Citric acid was added in a factor of 1.5 to the metal ions. The solution was stirred for 1 h at room temperature and then heated to 80 °C under continuous stirring. The resulting viscous gel was introduced into a muffle furnace preheated to 350 °C. The fast combustion process yields a fine and voluminous solid powder, which is further calcined at 700 °C for 5 h in flowing air.

X-ray powder diffraction (XRD) patterns were recorded on a Rigaku D/max-2500/PC diffractometer employing Cu Kα radiation (λ=1.5418 Å) operating at 50 kV and 200 mA.

The oxidation states of Mn were determined by titration[1, 2].

Transmission electron microscopy (TEM) equipped with energy dispersive spectroscopy (EDS) was conducted on a JEOL JEM–2010 at an accelerating voltage of 200 kV.

The Brunauer–Emmett–Teller (BET) surface area and pore structure were measured by N$_2$ adsorption/desorption using a Micromeritics ASAP 2020M instrument. Before N$_2$ physisorption, the sample was outgassed at 300 °C for 5 h.

Raman spectra were measured using a Raman spectroscope (HR800) with a CCD camera. The 632.8 nm line of a He–Ne laser was used to simulate the Raman spectra. The measurements were carried out with a microscope by using a ×50 objective lens (focus diameter larger than 1 micron) and the data are recorded in a backscattering geometry. Use of the cell allowed control of the sample temperature in static atmosphere.

Soot–TPR in the absence of gas phase oxygen was done in a fixed-bed flow reactor. A 50 mg sample of the soot/catalyst mixture (1:9, weight ratio) under tight contact was pretreated

in He (100 ml/min) at 200 ℃ for 1 h, and then heated at 5 ℃/min from room temperature to 850 ℃.

For O_2–TPD experiments, the samples were pretreated *in situ* at 700 °C for 1 h in a flow of O_2 and cooled to room temperature in the presence of O_2. TPD was conducted at 10 °C/min up to 900 °C in a 30 mL/min flow of He. A quadruple mass spectrometer (MS, OmniStar 200, Balzers) was used to monitor the O_2 concentration at a *m/z* of 32.

The details for the TPO reactions, isothermal reactions and isothermal anaerobic titrations at 280 °C can be found in our previous papers[3, 4]. Printex–U from Degussa was used as the model soot. As a measure of activity, the ignition temperature T_{10} from the TPO pattern is defined as the temperature at which 10% of the soot is converted[3]. The selectivity to CO_2 formation is defined as the percentage CO_2 outlet concentration divided by the sum of the CO_2 and CO outlet concentrations. The reaction rates for soot combustion at 280 °C were obtained by isothermal reactions. The active oxygen (O*) amounts (mol/g) was obtained by isothermal anaerobic titrations, in which soot is regarded as the probe molecule. Thus the turnover frequency (TOF) value can be calculated.
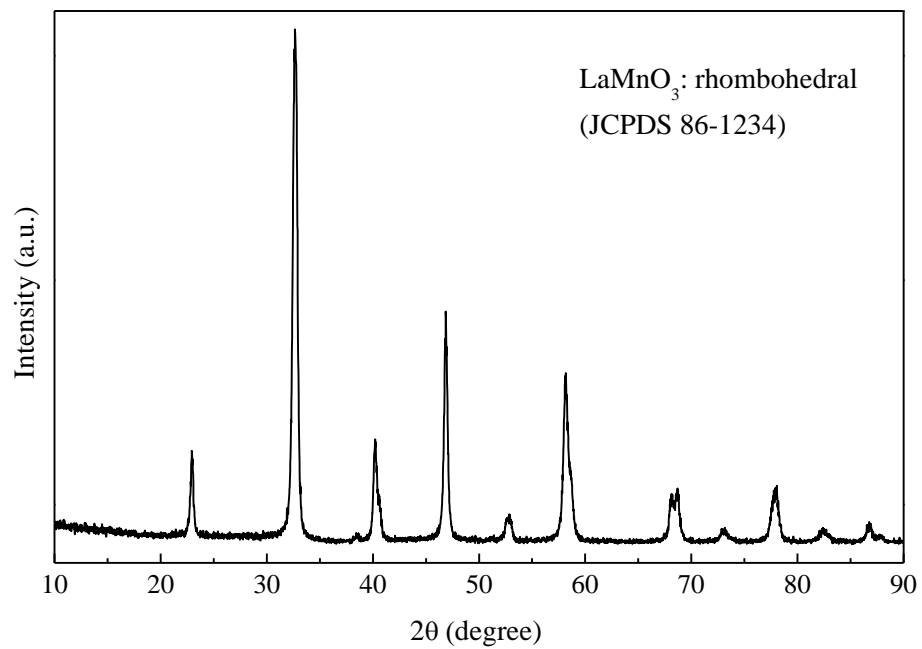
2. Fig. S1

LaMnO$_3$: rhombohedral
(JCPDS 86-1234)

Intensity (a.u.)

2θ (degree)

Fig. S1 XRD pattern of LaMnO$_3$ after calcination at 700 °C for 5 h.

.

3. Table S1

Table S1 Structure and textural properties of LaMnO$_3$

Sample	Unit cell parameter (Å)		Crystallite size	Mn^{3+}/Mn^{4+}	δ	BET surface area
	$a=b$	c	(nm)			(m^2/g)
LaMnO$_{3+\delta}$	5.5060±0.0023	13.3331±0.0053	21.4	67.5/32.5	0.16	13.2

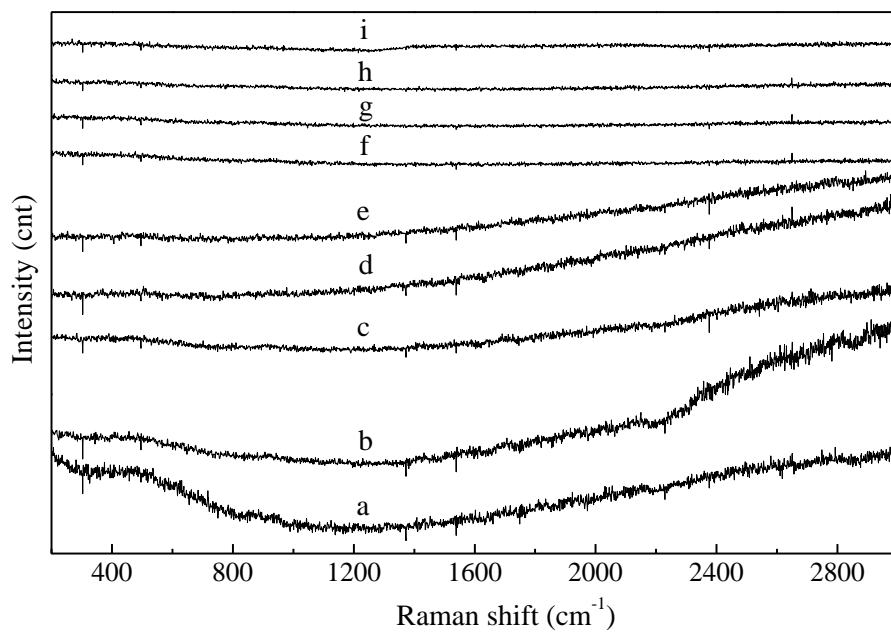**4. Fig. S2**
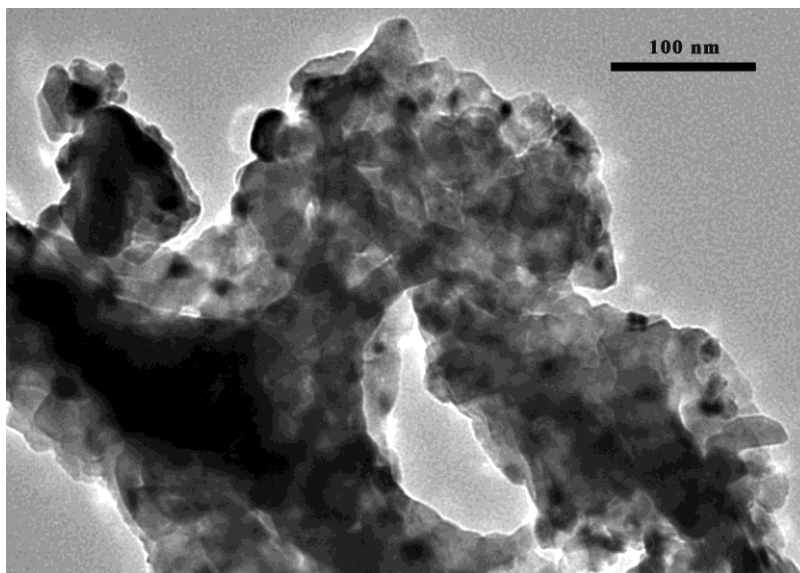
Fig. S2 TEM image of LaMnO₃

5. Fig. S3

Fig. S3 In situ Raman spectra of LaMnO$_3$ in static air. (a) room temperature, (b) 150 °C, (c) 200 °C, (d) 250 °C, (e) 300°C, (f) 350 °C, (g) 400 °C, (h) 450 °C for 1 min, (i) 450 °C for 10 min.

6. The calculation of the active oxygen amount

A stable and low conversion of soot (< 10%) was achieved in a kinetic regime for the isothermal soot combustion with O_2 at 280 °C on $LaMnO_3$ (Figure S4). The reaction rate can be obtained from the slope of the line, which is 8.3×10^{-8} mol s^{-1} g^{-1}. Then, O_2 is instantaneously removed from the reactant stream and is replaced with a flow of He. The transient decay in concentrations from the steady state was monitored using a quadruple mass spectrometer (MS, OmniStar 200, Balzers) with a m/z of 44 for CO_2 (Figure S5). The number of active oxygen sites available to soot under these reaction conditions can be quantified by integrating the diminishing rate of CO_2 formation over time.

Amount of active oxygen (mol/g): $$\frac{2FAP_0 \times 10^{-6}}{RTm}$$

Where A is the shaded area (s) in Figure S5, F is the volumetric flow rate (L/s), m is the mass of the catalyst (g), P_0 is the atmospheric pressure (Pa), R is the gas constant and T is room temperature (K). Based on the above formula, the amount of active oxygen is 3.7×10^{-5} mol g^{-1}.
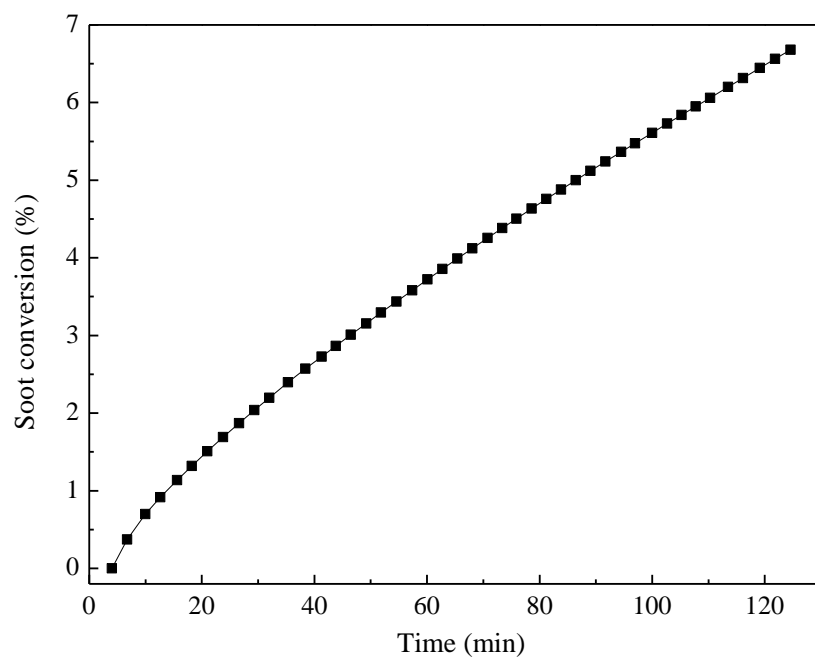
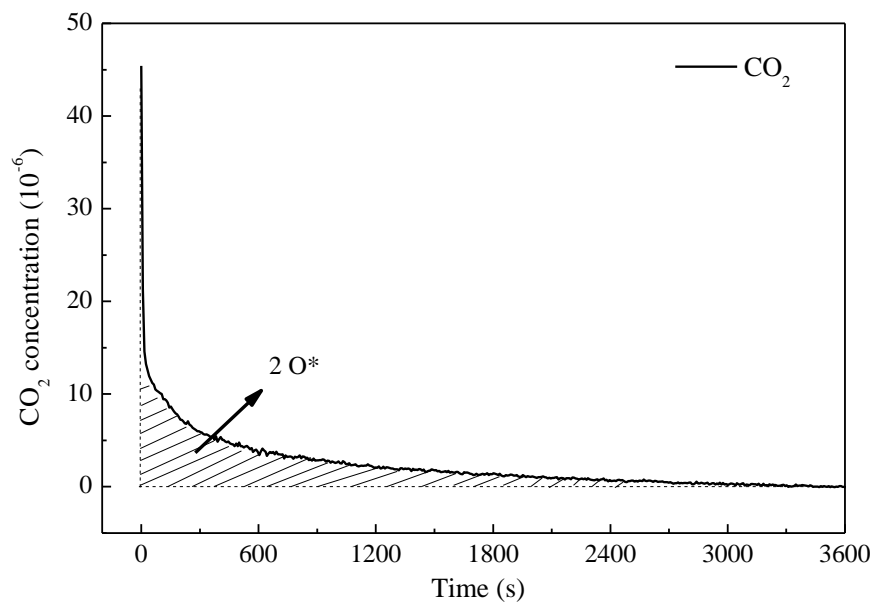Fig. S4 Soot conversion at 280 °C as a function of time on LaMnO$_3$

Fig. S5 CO$_2$ concentrations at 280 °C as a function of time over LaMnO$_3$ after O$_2$ is removed

from the reactant feed.

References:

1. Deng, J.; Zhang, L.; Dai, H.; He, H.; Au, C. *Industrial & Engineering Chemistry Research* 2008, *47*, 8175.

2. Niu, J.; Deng, J.; Liu, W.; Zhang, L.; Wang, G.; Dai, H.; He, H.; Zi, X. *Catalysis Today* 2007, *126*, 420.

3. Zhang, Z.; Han, D.; Wei, S.; Zhang, Y. *Journal of Catalysis* 2010, *276*, 16.

4. Li, X.; Wei, S.; Zhang, Z.; Zhang, Y.; Wang, Z.; Su, Q.; Gao, X. *Catalysis Today* 2011, *175*, 112.