Supplementary Information (SI) for Catalysis Science & Technology.

High-temperature calcination enhances the activity of MnO_x catalyst for soot oxidation

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Materials Preparation

In this work, MnO_x was synthesized via a hydrothermal method. $KMnO_4$ (10.84 g) was dissolved in deionized water (200 ml), which was then added to a solution containing $MnAC_2 \cdot 4H_2O$ (18.34 g), deionized water (40 mL) and glacial acetic acid (12.5 mL) with agitation. Then, the mixed solution was placed into a 500 mL Teflon-lined autoclave and maintained at 100 °C for 24 h. After that, the obtained black slurry was filtered, washed with deionized water and dried at 110 °C overnight. Finally, the sample was calcined in a furnace at 500 ^oC or 900 °C for 3 h, and the obtained catalysts were denoted as MnO_x-500 and MnO_x-900, respectively.

Materials Characterization

X-ray powder diffraction (XRD) patterns of the as-prepared catalysts were measured on a X'Pert PRO instrument using CuKα radiation (λ = 1.5406 Å) at 40 kV and 40 mA. The diffractograms were taken over the 2θ range from 10° to 90°.

Thermogravimetric analysis experiment was carried out on a high temperature thermogravimetric analyzer (TGA/DSC1 Stare, Mettler Toledo, Switzerland).

H_2-TPR was measured by a Micromeritics Auto Chem II 2920 automatic chemical adsorption analyzer. After pre-treatment under He at 300 ^oC for 1 h, 100 mg sample was heated from room temperature to 700 ^oC at a constant rate (10 ^oC/min) in a U-shaped quartz reactor under 10% H_2 /Ar mixture gas (30 mL/min). The hydrogen consumption was monitored with a TCD detector calibrated by the signal obtained with the introduction of known amounts of hydrogen.

Raman spectra were recorded on a laser Raman spectrometer (LabRAM Aramis,

HORIBA Jobin Yvon, France) and excitation was provided by an He-Ne laser (532 nm).

The X-band electron paramagnetic resonance (EPR) spectra were recorded using an A300 spectrometer at - 196 ^{o}C.

X-ray photo electron spectroscopy (XPS) spectra of the catalysts were measured on a scanning X-ray micro probe (Axis Ultra, Kratos Analytical Ltd.) using Al Kα radiation. All the binding energies were calibrated using the C 1s peak (BE = 284.6eV) as standard.

A Soot-TPR test was performed involving the thermal reduction of soot without gaseous oxygen in the same apparatus as that used for H_2-TPR. The mixture of 10 mg soot and 100 mg catalyst under loose contact mode was pre-treated in He at 120 ^{o}C for 1 h, and then heated up from 30 to 1050 ^{o}C in Ar atmosphere. The productions of CO_2 were detected on line by a mass spectrometers (MS) with a quadrupole-type detector.

The EXAFS of Mn-K edges were tested in transmission mode at room temperature in the 1W1B beamline of Beijing Synchrotron Radiation Facility (BSRF). Before measurements, all samples were ground and then mixed with flour powder. The data analysis was carried out by the Athena analysis package.

DFT calculation

DFT calculation was executed by Vienna Ab initio Simulation Package (VASP). Considering the strong correlation effect in transition metals, DFT+U was used to guarantee the reliability and precision of the calculation results. According to the XRD results and reported works[1, 2], the (110) of α-MnO_2, (001) of δ-MnO_2 and (111)

of Mn_2O_3 were chosen to model the surface of α-MnO_2, δ-MnO_2 and Mn_2O_3. The energy calculation and convergence criteria optimization of the structure were set to force tolerances of 1.0 x10^{-5} eV and 0.02 eV/Å, respectively. In addition, the vacuum thickness was set to be 15 Å. The formation energy of oxygen vacancy was calculated by the following expression.

$$E_{ov}=E_{slab\ ov}-E_{slab}+1/2E_{o2}$$

where Eslab ov is the amount of energy a system when it lacked one oxygen atom, Eslab is the energy of a normal body system, and E_{O2} is the energy possessed by the system to adsorb an O_2 molecule.

Catalytic activity measurement

Soot oxidation activity was evaluated via TPO, which was carried out in a fixed-bed tubular quartz microreactor under the following reaction conditions: 0.1% NO (when used), 5% H_2O (when used), and 10% O_2 balanced by N_2. The soot-catalyst mixture (100 mg of catalyst and 10 mg of soot) was prepared with loose contact. The outlet gases were monitored by an Antaris IGS gas analyzer (Thermo Fisher).

Soot conversion and CO_2 selectivity were determined as follows:

$$\text{Soot conversion} = \frac{A_i}{A_t} \times 100\% \quad (1)$$

T_{10}, T_{50}, and T_{90} are defined as the temperatures achieving 10%, 50%, and 90% of soot conversion, respectively.

$$CO_2\ \text{selectivity} = \frac{A_{iCO_2}}{A_{iCO_2} + A_{iCO}} \times 100\% \quad (2)$$

A_i is the total peak areas of CO_2 and CO at a given temperature, A_t is the total peak areas of CO_2 and CO, A_{iCO2} is the total peak areas of CO_2 at a given temperature, A_{iCO} is the total peak areas of CO at a given temperature.

The utilization efficiency of NO_2

The utilization efficiency of NO_2 for the as-prepared catalysts was calculated by the following equation[3]:

$$\text{Efficiency of } NO_2 = \frac{(CO_2 + CO)_{\text{in soot TPO}(^{NO}/_{O_2})} - (CO_2 + CO)_{\text{in soot TPO}(O_2)}}{(NO_2)_{\text{in NO TPO}} - (NO_2)_{\text{in soot TPO}(^{NO}/_{O_2})}} \quad \text{(S1)}$$

Table S1 Textural Properties of the MnO_x-500 and MnO_x-900 catalysts

Sample	BET(m^2/g)	Pore vol (mL/g)	Por diam (nm)
MnO_x-500	61.4	0.42	37.3
MnO_x-900	3.1	0.01	19.4

Table S2 Curve-fitting results of Mn-K EXAFS for different samples

Sample	shell	CN	R(Å)	R factor(%)
MnO_x-500	(Mn-O)	(4.22)	(1.89)	0.98
MnO_x-900	(Mn-O)	(3.37)	(1.89)	0.78

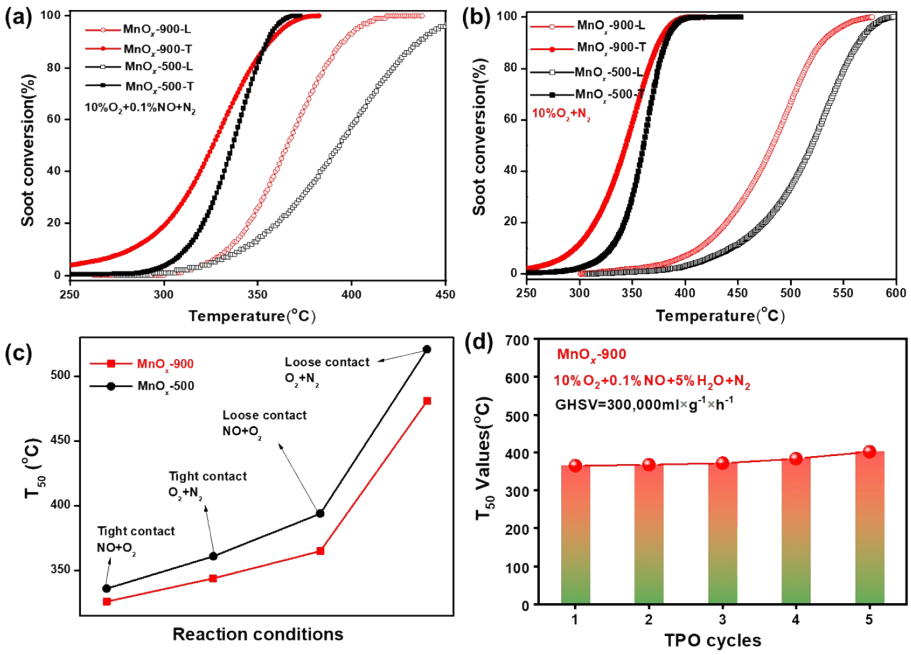

Figure S1 Soot conversion over the MnO_x-500 and MnO_x-900 catalysts **(a, b)**, the T_{50} values of the MnO_x-500 and MnO_x-900 catalysts in different reaction conditions **(c)**, and the stability of the MnO_x-900 catalyst in five soot-TPO cycles **(d)**. Reaction conditions: 5% H_2O (when used), 0.1% NO (when used), 10% O_2 balanced by N_2 under loose contact and heating rate = 2 °C/min.

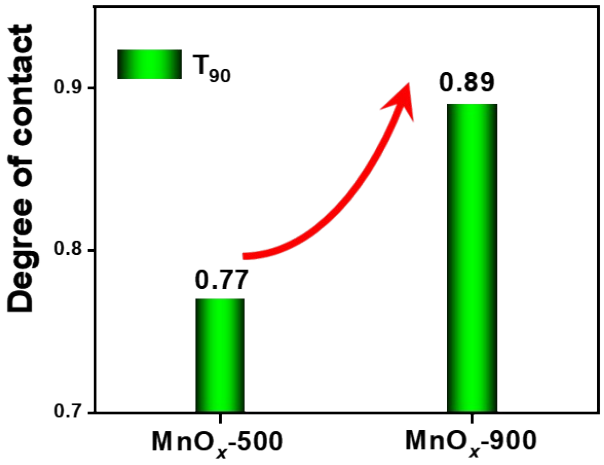

Figure S2. The contact efficiency of T_{90} for the as-prepared catalysts.

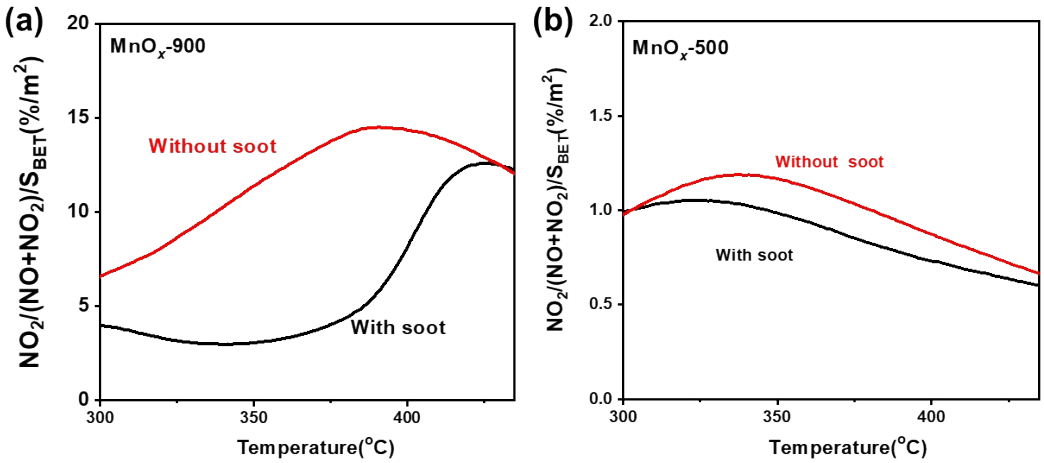

Figure S3. Specific activity of NO-to-NO_2 normalized by the specific surface area over the as-prepared catalysts in catalytic experiments performed with and without soot.

REFERENCES

1 D. Yu, Y. Ren, X. Yu, X. Fan, L. Wang, R. Wang, Z. Zhao, K. Cheng, Y. Chen, Z. Sojka, A. Kotarba, Y. Wei, and J. Liu, Facile synthesis of birnessite-type $K_2Mn_4O_8$ and cryptomelane-type $K_{2-x}Mn_8O_{16}$ catalysts and their excellent catalytic performance for soot combustion with high resistance to H_2O and SO_2. *Appl. Catal. B: Environ.* 2021, **285**, 119779.

2 G. Zhu, J. Zhu, W. Jiang, Z. Zhang, J. Wang, Y. Zhu, and Q. Zhang, Surface oxygen vacancy induced α-MnO_2 nanofiber for highly efficient ozone elimination. *Appl. Catal. B: Environ.* 2017, **209**, 729-737.

3 M. Zhao, J. Deng, J. Liu, Y. Li, J. Liu, Z. Duan, J. Xiong, Z. Zhao, Y. Wei, W. Song, and Y. Sun, Roles of surface-active oxygen species on 3DOM cobalt-based spinel catalysts $M_xCo_{3-x}O_4$ (M = Zn and Ni) for NO_x-assisted soot oxidation. *ACS Catal.* 2019, **9**, 7548-7567.