

## Supporting Information

### Original exploration of transition metal single-atom catalysts for NO reduction

Hongjian Zhu <sup>a</sup>, Rui Wang <sup>a\*</sup>

<sup>a</sup> School of Environmental Science and Engineering, Shandong University, Qingdao  
266237, China

\* Corresponding author.

E-mail: wangrui@sdu.edu.cn (R. Wang).

## **Table of Contents**

- 1. Experimental procedures**
- 2. Characterization methods**
- 3. NO Reduction tests**
- 4. Figures**
- 5. Tables**
- 6. References**

## 1. Experimental procedures

### *Preparation of catalysts*

The M-SAC catalysts were prepared with the modified method according to the previous literature [1]. Typically, for the synthesis of Mn-SAC, a certain amount of Mn acetate tetrahydrate and 1,10-phenanthroline with a molar ratio of 3 were dissolved in ethanol under magnetic stirring. Then, suitable graphite carbon was added into the solution to obtain the M-SAC with desired metal content, and the resulting solution was then heated at 60 °C for 4 h under continuous stirring. The resulting solid was then heated at 80 °C in air for 12 h to evaporate ethanol. The black solid was ground and then heated to 600°C in a tube furnace at 10 °C min<sup>-1</sup> under an different atmosphere (Ar and H<sub>2</sub>) for 2 h. For comparison, the Mn-SAC (containing 5 wt.% Mn) catalysts supported on various carbon materials (graphite carbon, Ketjenblack EC-300J, coconut charcoal and Printex-U soot) were prepared by a similar procedure and referred to Mn-G, Mn-K, Mn-C and Mn-U, respectively. The Fe-SAC and Co-SAC samples were prepared using a similar procedure to that described above for Mn-SAC. In the synthesis of Ni-SAC and Cu-SAC, dimethyl sulfoxide was used instead of ethanol as the solvent. Due to dimethyl sulfoxide with the higher boiling point, the solvent was evaporated at 190 °C for 12 h.

K doped catalysts were prepared by a typical wet impregnation method. 1 g of Mn-SAC catalyst was mixed in 20 mL of deionized water under ultrasound, then a corresponding amount of KNO<sub>3</sub> were added to above solution, stirred for 6 h, then dried in air at 80 °C for 12 h. The K doped samples were calcined at 500 °C for 4 h in Ar flow with different K content (4 wt%, 8 wt%, 12 wt% and 16 wt%). The HPW doped samples prepared with the similar method calcined at 400 °C for 4 h in Ar flow with different HPW content (25 wt%, 50 wt% and 100 wt%).

## 2. Characterization methods

Transmission electron microscope (TEM) were obtained on an JEOL 2010F operating at 200 kV. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was performed with an aberration-corrected JEM-ARM 200F microscope. Details of characterizing the solid phase with X-ray absorption fine

structure (XAFS) analyses. Mn K-edge analysis was performed with Si(111) crystal monochromators at the BL11B beamlines at the Shanghai Synchrotron Radiation Facility (SSRF) (Shanghai, China). Before the analysis at the beamline, samples were pressed into thin sheets with 1 cm in diameter and sealed using Kapton tape film. The XAFS spectra were recorded at room temperature using a 4-channel Silicon Drift Detector (SDD) Bruker 5040. Mn K-edge extended X-ray absorption fine structure (EXAFS) spectra were recorded in transmission mode. Negligible changes in the line-shape and peak position of Mn K-edge XANES spectra were observed between two scans taken for a specific sample. The XAFS spectra of these standard samples (Mn-foil and MnO) were recorded in transmission mode. The spectra were processed and analyzed by the software codes Athena and Artemis. The X-ray diffraction (XRD) patterns were obtained by a BRUKER-AXS D8 Advance X-ray Diffractometer with Cu K $\alpha$  radiation ( $\lambda = 0.15418$  nm) operated at 40 kV and 30 mA. The Fourier Transform infrared (FTIR) spectra were recorded with a Nicolet 5700 IR equipment. The X-ray photoelectron spectroscopy (XPS) analysis of the catalysts was carried out on a scanning X-ray microprobe (Thermo ESCALAB 250XI). Electron paramagnetic resonance (EPR) spectrometer (Bruker A300, Germany) was employed to probe the valence state of the catalysts. The surface areas and pore characterization of the catalysts were determined from N<sub>2</sub> adsorption-desorption isotherms performed via a Micromeritics ASAP 2020 surface area analyzer at  $-196$  °C. The thermal gravimetric analysis (TGA) were conducted on SDT Q600 Simultaneous DSC/TGA Analyzer (TA Instruments, Inc.) under air atmosphere with a heating rate of  $10$  °C min<sup>-1</sup>. The loading amount of metal in the catalysts was measured on an Agilent 720ES inductively coupled plasma optical emission spectroscopy (ICP-OES). The Raman spectra were obtained on an DXRxi Raman spectrophotometer (Thermo Fisher Scientific, America) using monochromatic radiation emitted by a laser ( $\lambda = 532$  nm). H<sub>2</sub> temperature programmed reduction (H<sub>2</sub>-TPR) were conducted on SP-6800 gas chromatograph (China, Lunan Ruihong). Diffuse reflectance infrared Fourier transform (DRIFT) spectra were recorded on a Thermo Nicolet 6700 spectrometer equipped with a liquid N<sub>2</sub>-cooled MCT detector by accumulating 32 scans with a

resolution of 4 cm<sup>-1</sup>.

### 3. NO Reduction tests

The catalytic activity of the samples was tested in a fixed-bed quartz tube reactor (inner diameter = 8 mm). In the test, the pretreated catalyst (40-80 mesh) was placed in a mixed gas containing 500 ppm NO, 2.5% O<sub>2</sub>, 5% H<sub>2</sub>O, and balance N<sub>2</sub> was introduced into the reactor at a gas hourly space velocity of 30000 h<sup>-1</sup>. The concentrations of NO<sub>x</sub> (NO and NO<sub>2</sub>) were measured by TH-990S NO and NO<sub>2</sub> analyzers (Wuhan Tianhong), and N<sub>2</sub>O was measured on a gas analyzer (Antaris™ IGS). The catalytic performances were calculated as follows:

$$\text{NO}_x \text{ conversion (\%)} = \left(1 - \frac{[\text{NO}_x]_{out}}{[\text{NO}_x]_{in}}\right) \times 100\% \quad (1)$$

$$\text{N}_2 \text{ selectivity (\%)} = \left(1 - \frac{2[\text{N}_2\text{O}]_{out}}{[\text{NO}_x]_{in} - [\text{NO}_x]_{out}}\right) \times 100\% \quad (2)$$

where  $[\text{NO}_x]_{in}$  and  $[\text{NO}_x]_{out}$  is the concentration of inlet and outlet at a steady-state.

## 4. Figures

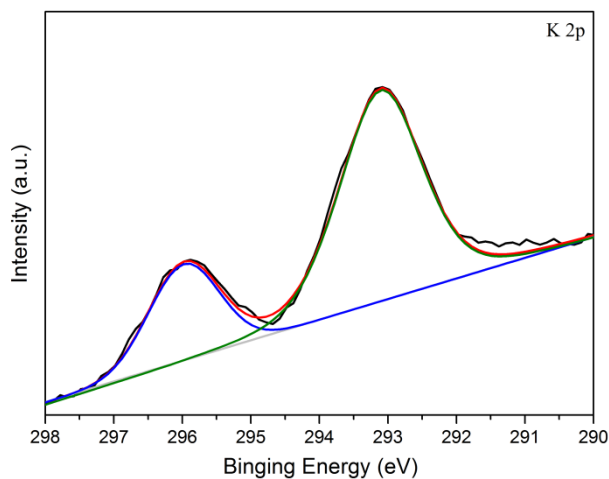


Fig. S1 K 2p XPS spectra of 4% K doped Mn-SAC.

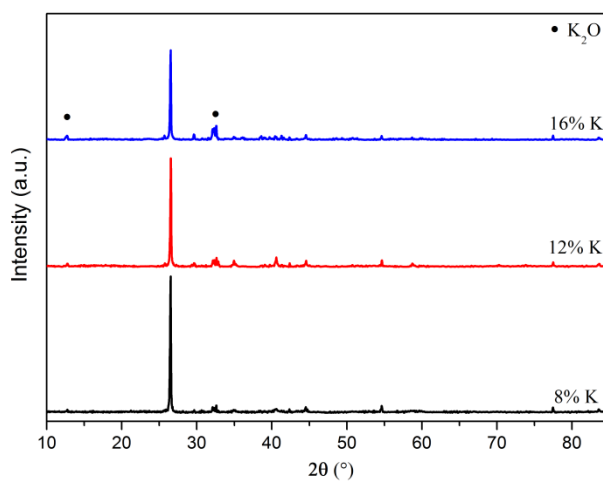


Fig. S2 XRD patterns of different mass ratio of K doped Mn-SAC catalysts.

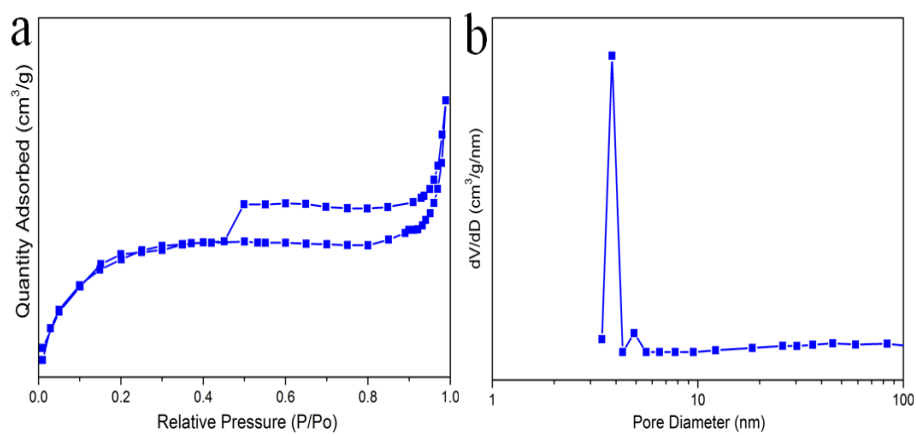


Fig. S3 N<sub>2</sub> adsorption-desorption isotherms and pore distributions of Mn-SAC.

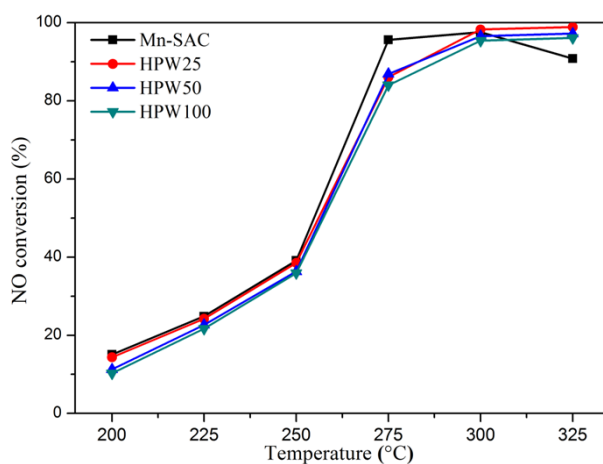


Fig. S4 NO<sub>x</sub> Conversion of different HPW doped Mn-SAC catalysts.

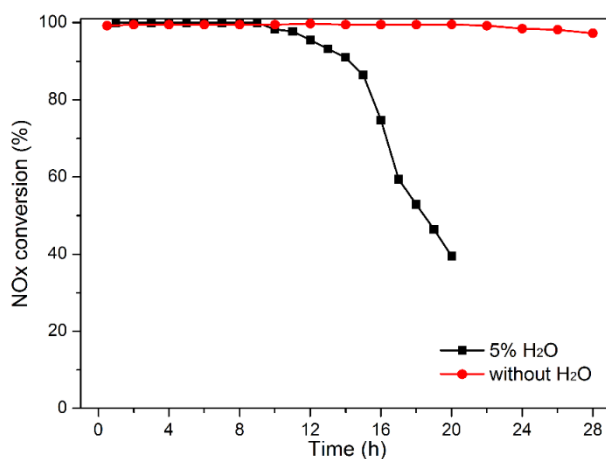


Fig. S5 Catalytic activity of 4%K/Mn-SAC under steady-state conditions at 275 °C.

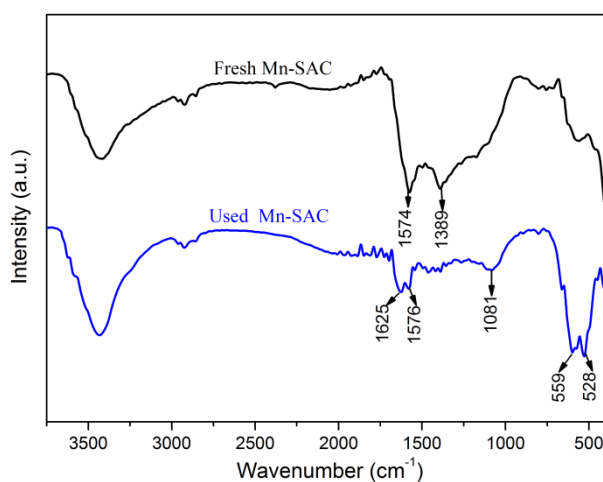


Fig. S6 FTIR spectra of Mn-SAC sample before and after NO reduction reaction.

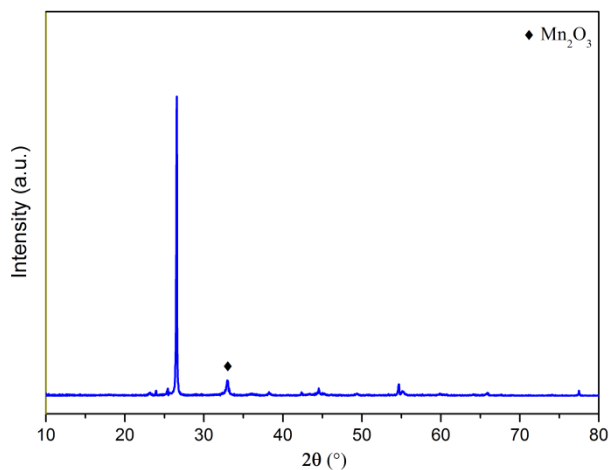


Fig. S7 XRD pattern of Mn-SAC sample after NO reduction reaction.

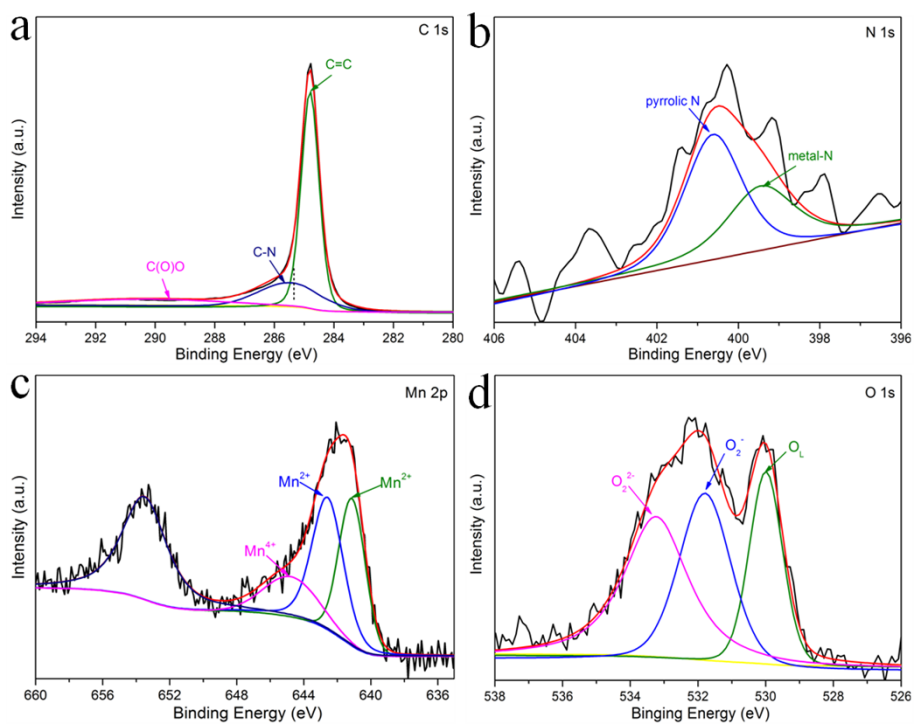


Fig. S8 High-resolution XPS spectra of (a) C 1s, (b) N 1s, (c) Mn 2p, and (d) O 1s for the Mn-SAC after NO reduction reaction.



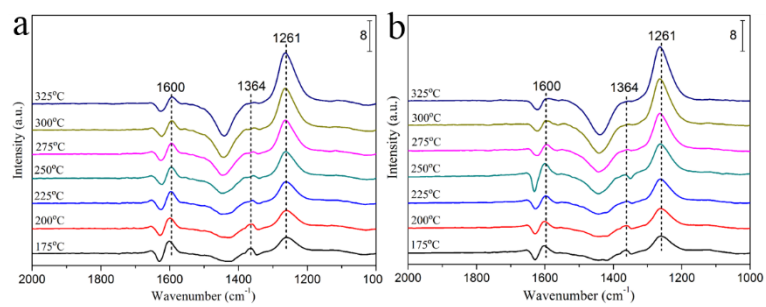


Fig. S9 DRIFT spectra of NO<sub>x</sub> reaction during the heating process under N<sub>2</sub> flow on (a) Mn-SAC and (b) 4%K/Mn-SAC catalyst.

## 5. Tables

Table S1. The surface atomic concentrations of the fresh, used Mn-SAC, and 4% K doped Mn-SAC.

Sample	atomic concentration (%)						
	Mn	O	N	C	P	W	K
Fresh	0.69	5.57	3.78	89.96	-	-	-
Used	0.52	2.24	0.52	96.72	-	-	-
4% K	1.14	7.87	4.1	85.41	-	-	1.48

Table S2. Summary of TOF values of reported different catalysts for NO<sub>x</sub> conversion.

Catalysts	NO <sub>x</sub> concentration (ppm)	GHSV (10 <sup>3</sup> h <sup>-1</sup> )	Temperature (°C)	NO <sub>x</sub> conversion (%)	TOF (h <sup>-1</sup> )
4%K/Mn-SAC (This work)	1000	30	275	98	1.8
Sm-MnO <sub>x</sub> [2]	500	48	32	33	0.85
Mn8/SEP-S [3]	600	30	200	-	1.1
MnO <sub>x</sub> -ZSM5 [4]	500	30	290	-	1.0
Mn <sub>0.5</sub> Co <sub>0.5</sub> O <sub>8</sub> /TiSiWO [5]	1000	20	100	90	2.0
MnFe <sub>0.6</sub> Co <sub>0.4</sub> O <sub>x</sub> [6]	500	60	180	90	2.1
MnO <sub>x</sub> -CeO <sub>2</sub> [7]	500	60	100	95	2.2
Mn-Cu <sub>1</sub> /Ti-C [8]	500	30	250	90	1.1
MnCe@CNTs-R [9]	500	10	100	-	1.0
MnO <sub>2</sub> nanosphere [10]	500	420	140	-	0.15

## 6. References

- [1] H. Yang, L. Shang, Q. Zhang, R. Shi, T. Zhang, A universal ligand mediated method for large scale synthesis of transition metal single atom catalysts, *Nat. Commun.* 10 (2019) 1-9.
- [2] D. Meng, W. Zhan, Y. Guo, Y. Guo, L. Wang, G. Lu, A highly effective catalyst of Sm-MnO<sub>x</sub> for the NH<sub>3</sub>-SCR of NO<sub>x</sub> at low temperature: Promotional role of Sm and its catalytic performance, *ACS Catal.* 5 (2015) 5973-5983.
- [3] X. Zhang, Q. Wu, Q. Diao, J. Wang, K. Xiao, B. Yang, X. Wu, Performance study for NH<sub>3</sub>-SCR at low temperature based on different methods of Mn<sub>x</sub>/SEP catalyst, *Chem. Eng. J.* 370 (2019) 364-371.
- [4] T. Qiao, Z. Liu, C. Liu, W. Meng, H. Sun, Y. Lu, MnO<sub>x</sub> location on MnO<sub>x</sub>-ZSM-5 to influence the catalytic activity for selective catalytic reduction of NO<sub>x</sub> by NH<sub>3</sub>, *Appl. Catal. A Gen.* 617 (2021) 118128.
- [5] L. Wang, Y. Ren, X. Yu, D. Yu, C. Peng, Q. Zhou, J. Hou, C. Zhong, C. Yin, X. Fan, Z. Zhao, K. Cheng, Y. Chen, Z. Sojka, A. Kotarba, Y. Wei, J. Liu, Facile preparation, catalytic performance and reaction mechanism of Mn<sub>x</sub>Co<sub>1-x</sub>O<sub>δ</sub>/3DOM-mTi<sub>0.7</sub>Si<sub>0.2</sub>W<sub>0.1</sub>O<sub>y</sub> catalysts for the simultaneous removal of soot and NO<sub>x</sub>, *Catal. Sci. Technol.* 12 (2022) 1950-1967.
- [6] Y. Li, S. Yang, H. Peng, W. Liu, Y. Mi, Z. Wang, C. Tang, D. Wu, T. An, Insight into the activity and SO<sub>2</sub> tolerance of hierarchically ordered MnFe<sub>1-δ</sub>Co<sub>δ</sub>O<sub>x</sub> ternary oxides for low-temperature selective catalytic reduction of NO<sub>x</sub> with NH<sub>3</sub>, *J. Catal.* 395 (2021) 195-209.
- [7] S. Xiong, J. Chen, N. Huang, T. Yan, J. Li, The poisoning mechanism of gaseous HCl on low-temperature SCR catalysts: MnO/CeO<sub>2</sub> as an example, *Appl. Catal. B: Environ.* 267 (2020) 118668.
- [8] S. Raja, M.S. Alphin, L. Sivachandiran, P. Singh, D. Damma, P.G. Smirniotis, TiO<sub>2</sub>-carbon nanotubes composite supported MnO<sub>x</sub>-CuO catalyst for low-temperature NH<sub>3</sub>-SCR of NO: Investigation of SO<sub>2</sub> and H<sub>2</sub>O tolerance, *Fuel* 307 (2022) 121886.
- [9] D. Zhang, L. Zhang, L. Shi, C. Fang, H. Li, R. Gao, L. Huang, J. Zhang, In situ supported MnO<sub>x</sub>-CeO<sub>x</sub> on carbon nanotubes for the low-temperature selective

catalytic reduction of NO with NH<sub>3</sub>, *Nanoscale* 5 (2013) 1127-1136.

[10] Y. Li, Y. Li, Y. Wan, S. Zhan, Q. Guan, Y. Tian, Structure–performance relationships of MnO<sub>2</sub> nanocatalyst for the low-temperature SCR removal of NO<sub>x</sub> under ammonia, *RSC Adv.* 6 (2016) 54926.