Supporting Information

Facile synthesis of spinel $Cu_{1.5}Mn_{1.5}O_4$ microspheres with high activity for the catalytic combustion of diesel soot

H. Zhao,[ab] X. X. Zhou,[a] L. Y. Pan,[ab] M. Wang,[ab] H. R. Chen,*[ac] and J. L. Shi[ac]

[a.] *State Key Laboratory of High Performance Ceramics and Superfine Microstructures, Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Dingxi Road, Shanghai 200050, China.*

[b.] *University of Chinese Academy of Sciences, Beijing, 100049, P. R. China.*

[c.] *Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), Jiangsu, China.*

* Corresponding Author: Hangrong Chen (*Email address*: hrchen@mail.sic.ac.cn)

Experimental

To investigate the effect of residual Na on catalytic activity, three additional reference catalysts with different Na content have been prepared for further comparison: Cu1Mn1-NR (Non-Rinsed) was obtained through the same procedure with Cu1Mn1, except that no rinse was applied; Na/Cu1Mn1 sample was prepared by impregnating certain amounts of $NaNO_3$ onto Cu1Mn1 (result in 10 wt % Na); and Cu1Mn1-NH_3 was obtained by the following procedure: Ammonia water containing 60 mmol of $NH_3 \cdot H_2O$ was quickly adding into 55 mL of solution containing 3.75 mmol of $Cu(NO_3)_2 \cdot 3H_2O$ and 3.75 mmol of $Mn(NO_3)_2$, which was kept under stirring at 95 ^oC. After 30 min of reaction, the mixture was cooled to room temperature, then the precursor was centrifuged and dried at 100 ^oC overnight. Next, the as-prepared samples were grinded and then calcined under static air at 500 ^oC for 2 h with a heating rate of 1 ^oC/min.

Table S1 Characteristic temperatures (T_i, T_m and T_f) and selectivity to CO_2 for catalytic soot combustion over different Cu*x*Mn*y* mixed oxides and references CuO and MnO_δ under loose contact mode. [Reaction condition: 350 ppm NO + 10% O_2 in balance N_2 with a total flow of 200 mL/min, the space velocity is 120 000 $mL\cdot g^{-1}\cdot h^{-1}$, the mass of soot-catalyst-silica is 10-100-1000 mg]

Sample	T_i (°C)	T_m (°C)	T_f (°C)	S_{CO2} (%)
Pure soot	424	560	606	58.6
CuO	319	352	392	93.6
Cu2Mn1	311	358	399	92.4
Cu1Mn1	299	330	360	91.9
Cu1Mn2	331	386	435	94.9
MnO_δ	276	344	441	94.4

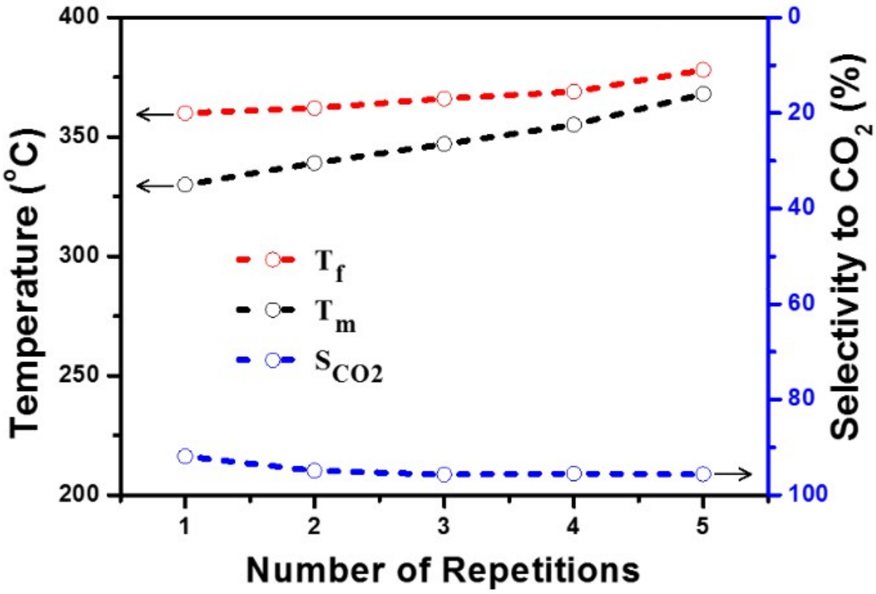

Fig. S1 Characteristic temperatures (T_f and T_m) and selectivity to CO_2 (S_{CO2}) for cyclic soot combustion tests over CuMnO(K) and CuMnO. (Reaction conditions: 350 ppm NO and 10% O_2 in N_2 with a total flow of 200 mL/min, mass of soot-catalyst-silica is 10-100-1000 mg)

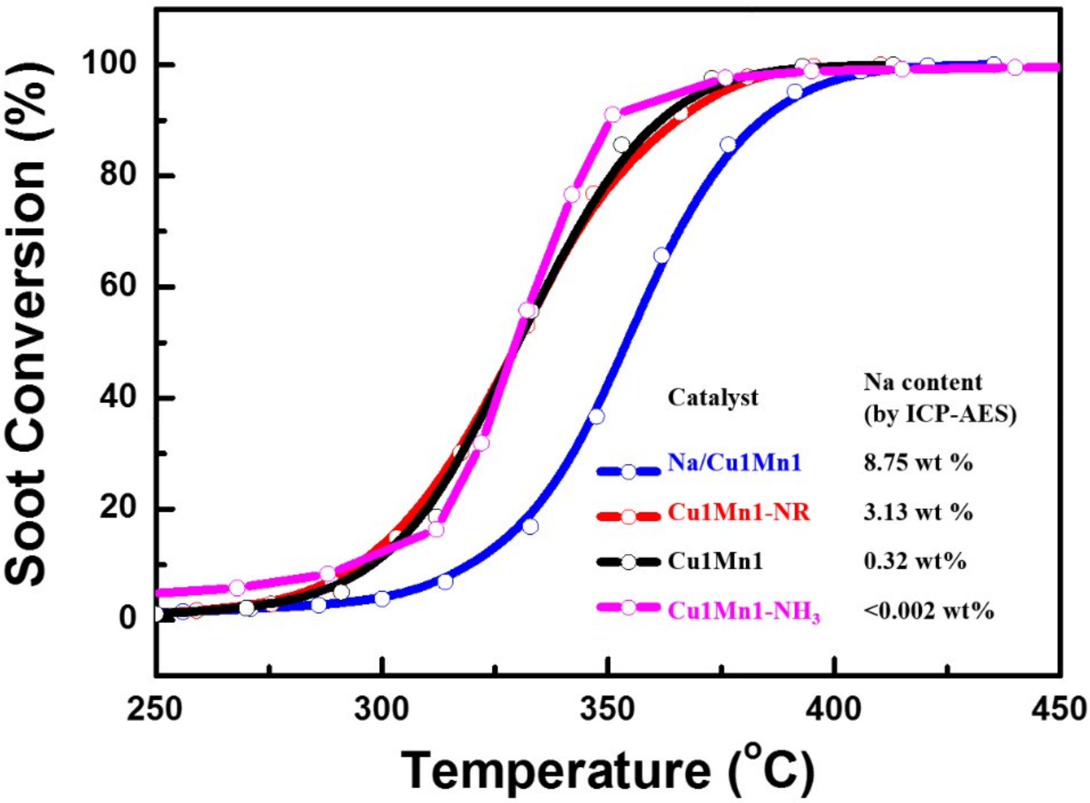

Fig. S2 Catalytic soot combustion over four different catalysts as indicated with different Na contents. (Preparation procedures for these samples are shown in the Experimental section in SI.) (Reaction conditions: 350 ppm NO and 10% O_2 in N_2 with a total flow of 200 mL/min, mass of soot-catalyst-silica is 10-100-1000 mg)

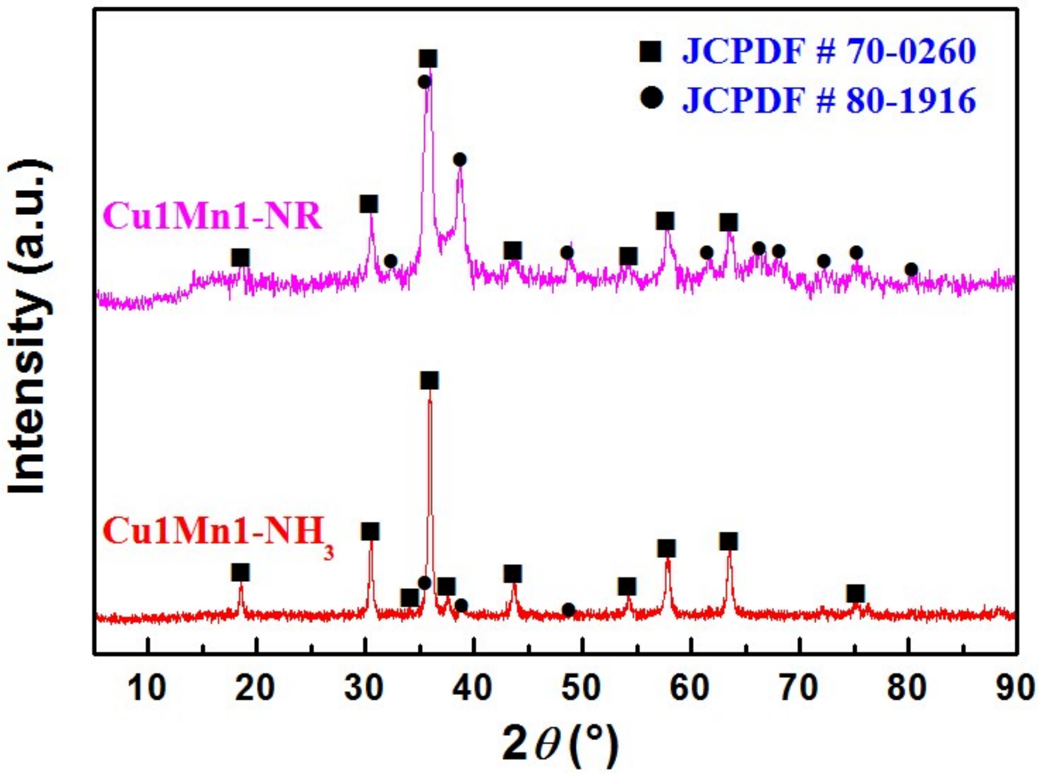

Fig. S3 XRD patterns of Cu1Mn1-NR and Cu1Mn1-NH_3. (■: $Cu_{1.5}Mn_{1.5}O_4$, ●: CuO)

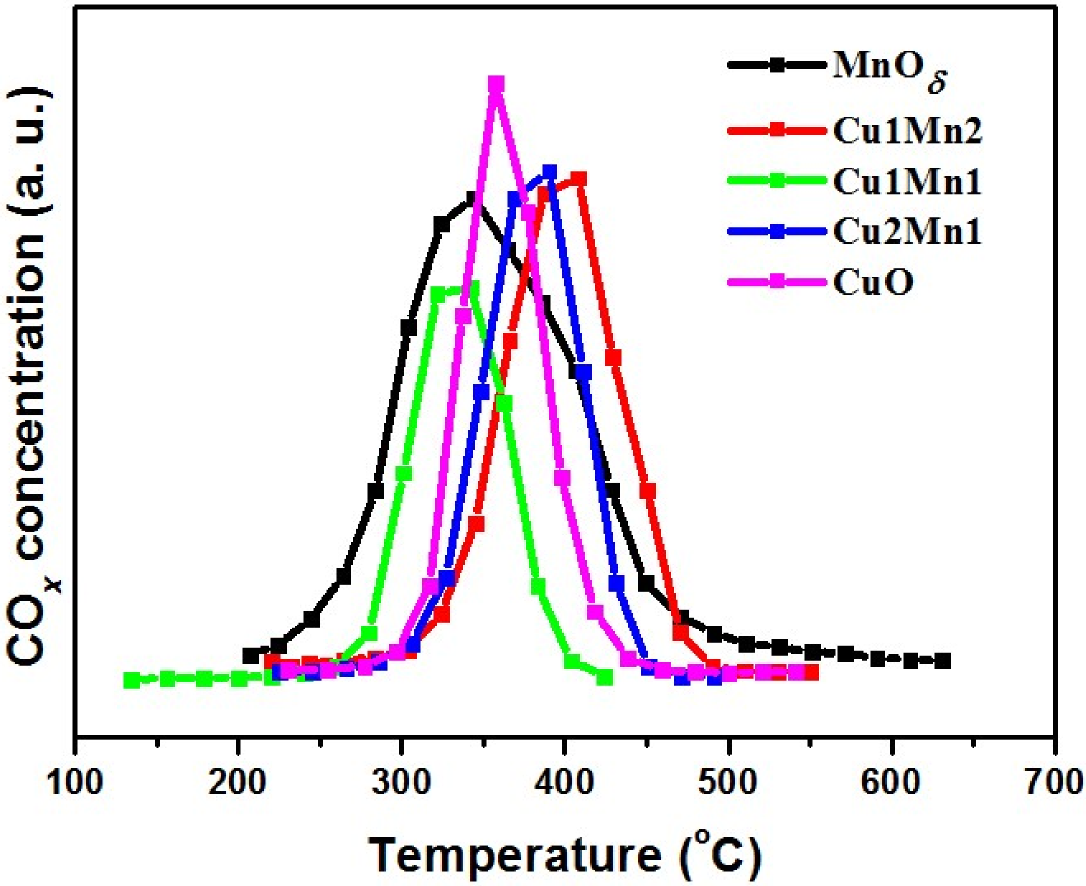

Fig. S4 Soot combustion performance with different catalysts under loose contact mode. (Reaction conditions: 350 ppm NO and 10% O_2 in N_2 with a total flow of 200 mL/min, mass of soot-catalyst-silica is 10-100-1000 mg)

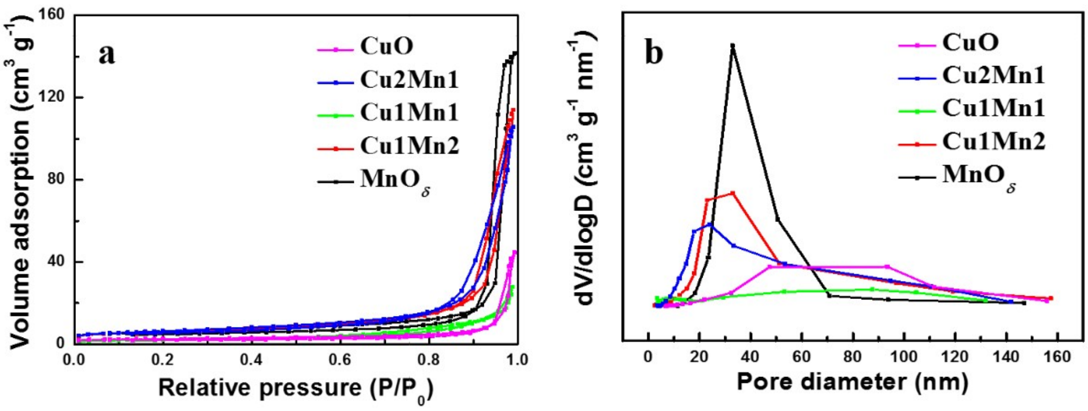

Fig. S5 (a) N_2 adsorption/desorption isotherms and (b) the corresponding pore size distributions of the different Cu*x*Mn*y* mixed oxides and references CuO and MnO$_\delta$.

Table S2 The specific surface areas, pore volumes and average pore diameters of different Cu*x*Mn*y* mixed oxides and references CuO and MnO_δ.

Catalyst	S_{BET} ($m^2 \cdot g^{-1}$) [a]	V_{BJH} ($cm^3 \cdot g^{-1}$) [b]	D_p (nm) [a]
CuO	9	0.07	10-156
Cu2Mn1	22	0.16	10-143
Cu1Mn1	8	0.04	10-132
Cu1Mn2	22	0.18	28
MnO_δ	21	0.22	33

[a]Determined by BET method.
[b]Determined by BJH method.

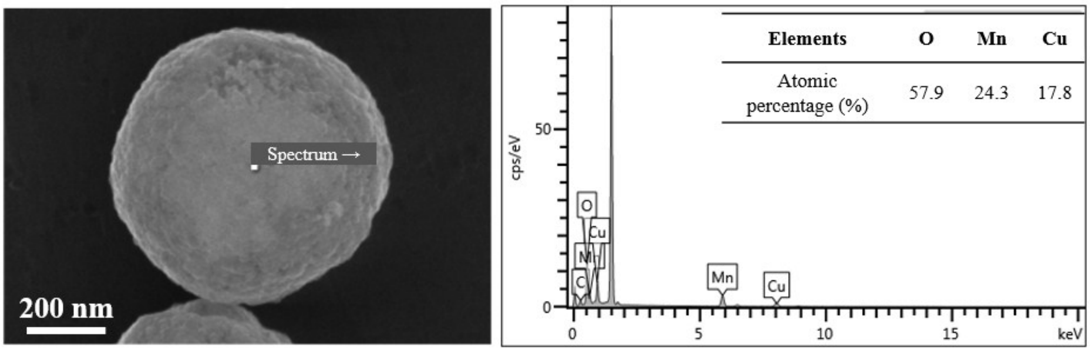

Fig. S6 The typical SEM image and corresponding EDS spectrum of Cu1Mn2.

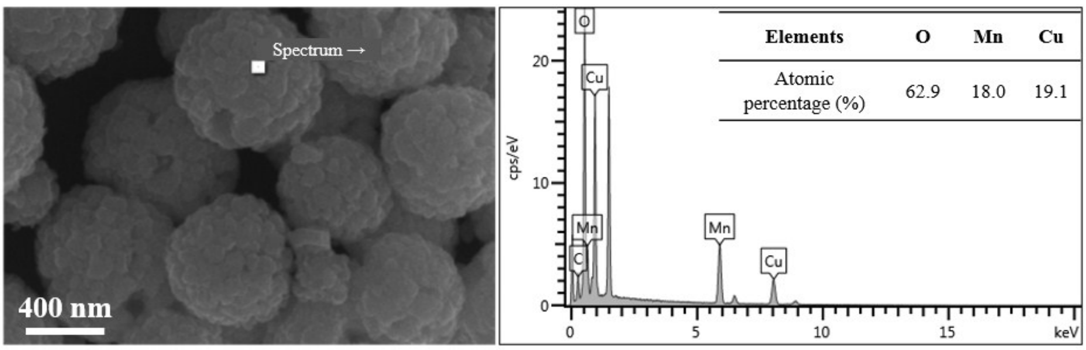

Fig. S7 The typical SEM image and corresponding EDS spectrum of Cu1Mn1.

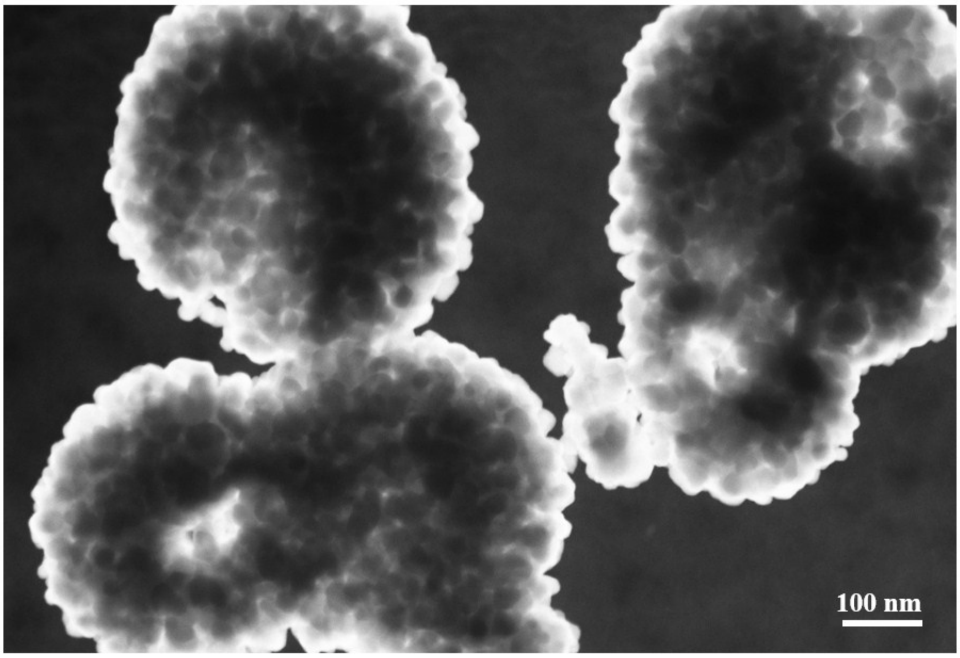

Fig. S8 The typical STEM image of Cu1Mn1.

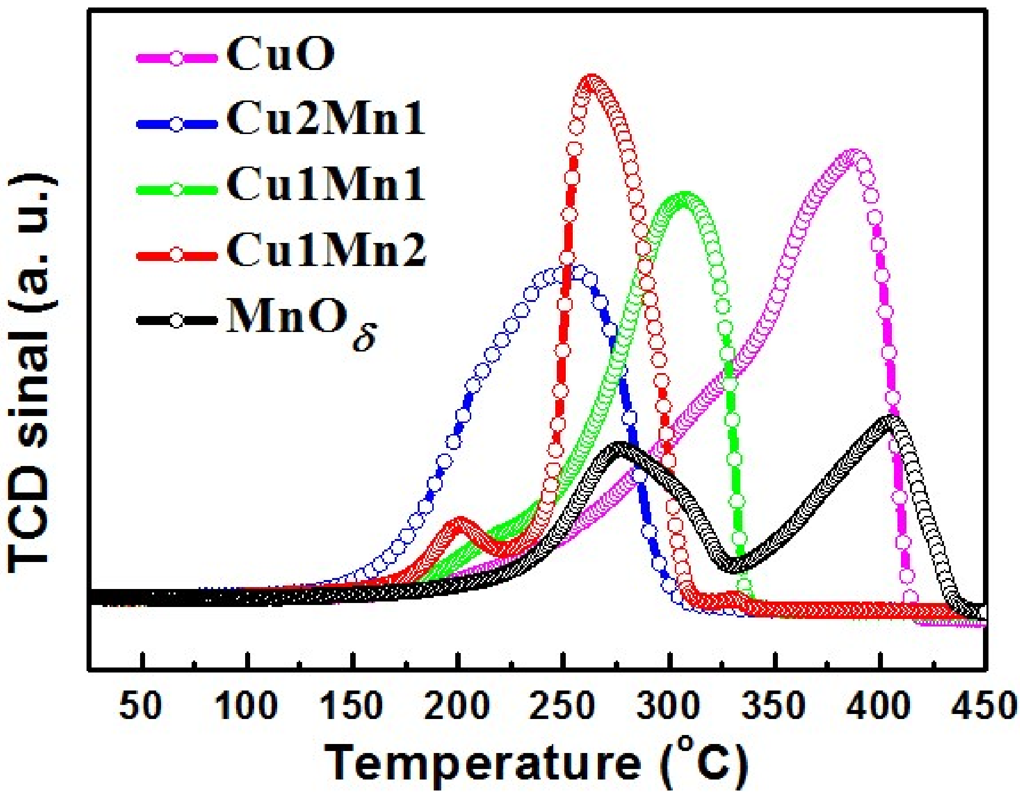

Fig. S9 H_2-TPR curves of different catalysts as indicated.

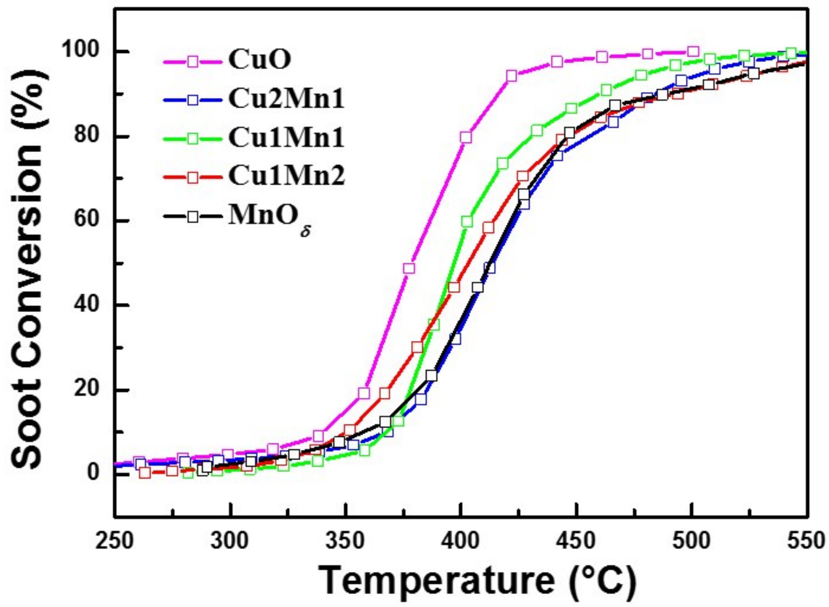

Fig. S10 Catalytic soot oxidation in O_2/N_2 under loose contact mode over different CuxMny mixed oxides and references CuO and MnO_{δ}. (Reaction condition: 10% O_2 in balance N_2 with a total flow of 200 mL/min, the space velocity is 120 000 $mL\cdot g^{-1}\cdot h^{-1}$, the mass of soot-catalyst-silica is 10-100-1000 mg)

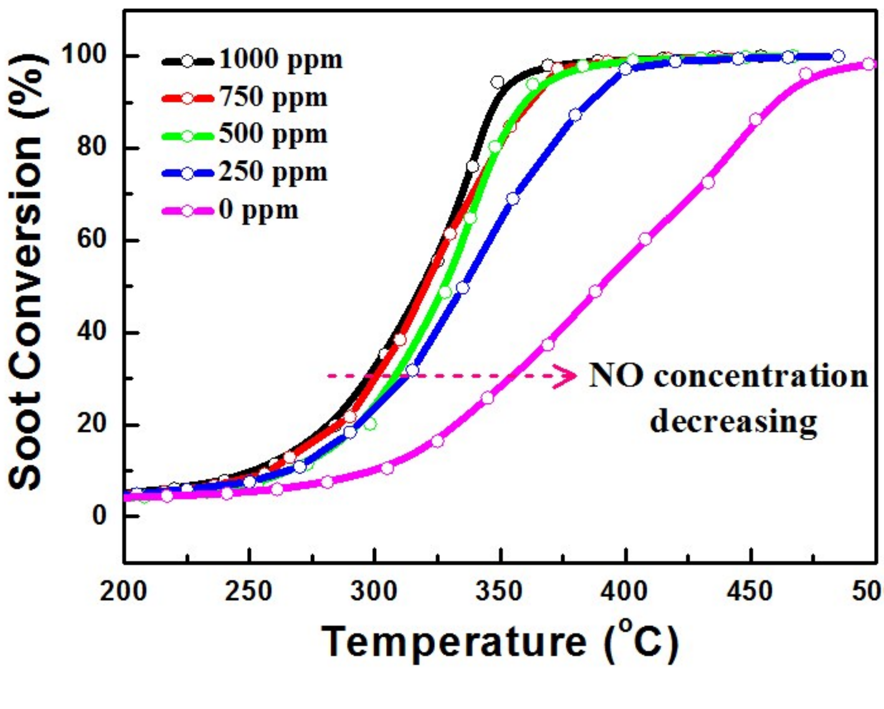

Fig. S11 The effect of NO_x concentration on catalytic soot combustion activity. (Reaction condition: 10% O_2 in balance N_2 with a total flow of 200 mL/min, NO concentrations are set as indicated above, the space velocity is 120 000 $mL\cdot g^{-1}\cdot h^{-1}$, the mass of soot-catalyst-silica is 10-100-1000 mg)

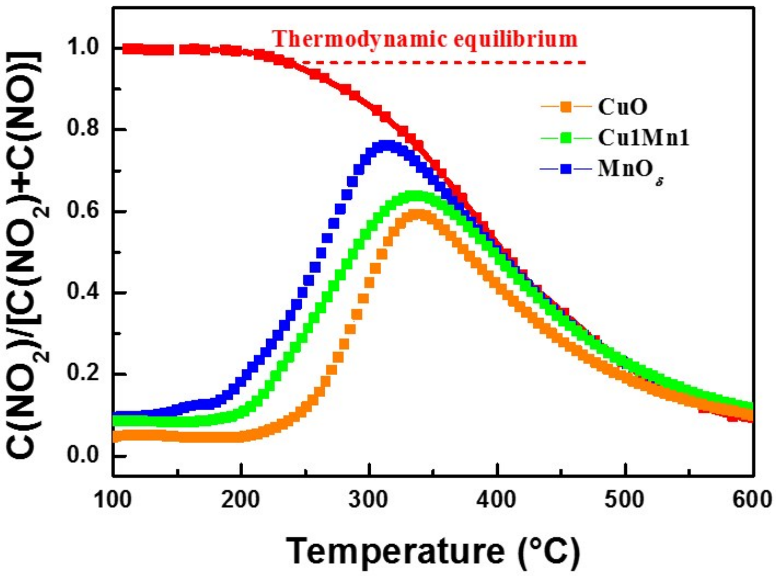

Fig. S12 Catalytic NO oxidation over CuO, Cu1Mn1 and MnO_δ. Thermodynamic equilibrium profile is also shown for reference. [Reaction condition: 350 ppm NO + 10% O_2in balance N_2 with a total flow of 200 mL/min, the space velocity is 120 000 $mL\cdot g^{-1}\cdot h^{-1}$]

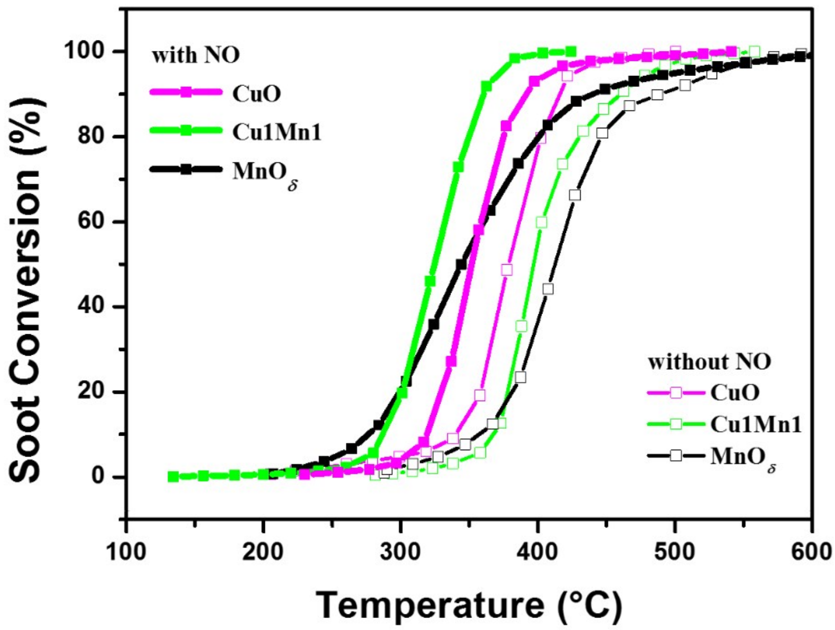

Fig. S13 Catalytic soot combustion over CuO, Cu1Mn1 and MnO_δ with or without NO. [Reaction conditions: (350 ppm NO +) 10% O_2in balance N_2 with a total flow of 200 mL/min, the space velocity is 120 000 $mL\cdot g^{-1}\cdot h^{-1}$, mass of soot-catalyst-silica is 10-100-1000 mg]