Supporting Information

Porous Mn-based Oxides for Complete Ethanol and Toluene Catalytic Oxidation: The Relationship between Structure and Performance

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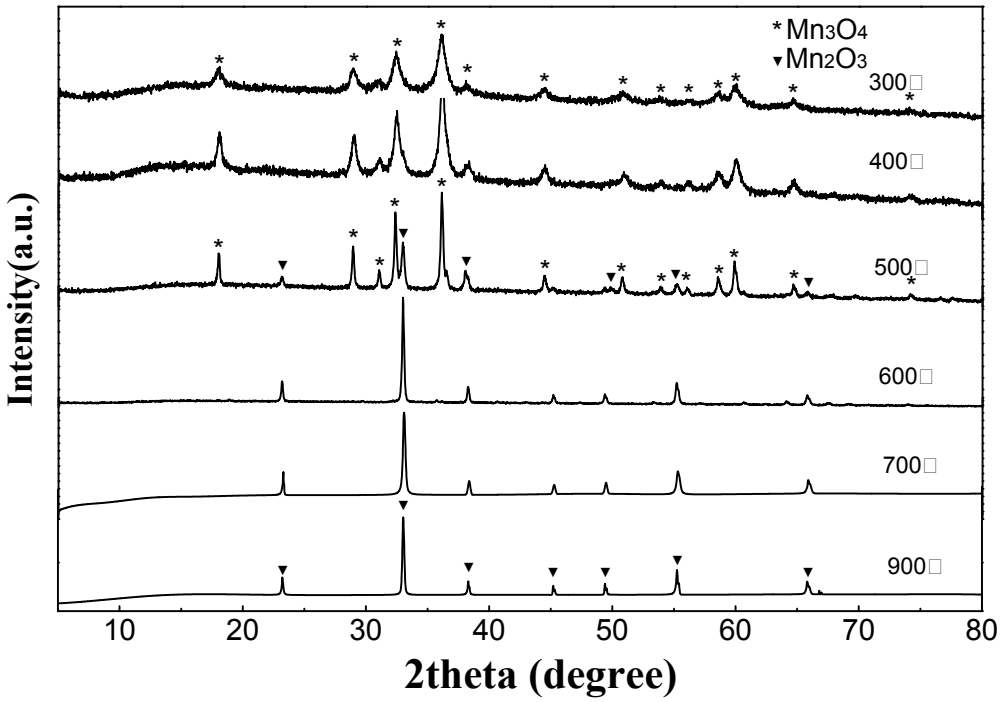

Fig. S1 XRD patterns of MnO_x prepared by organic solvent combustion at different calcination temperatures.

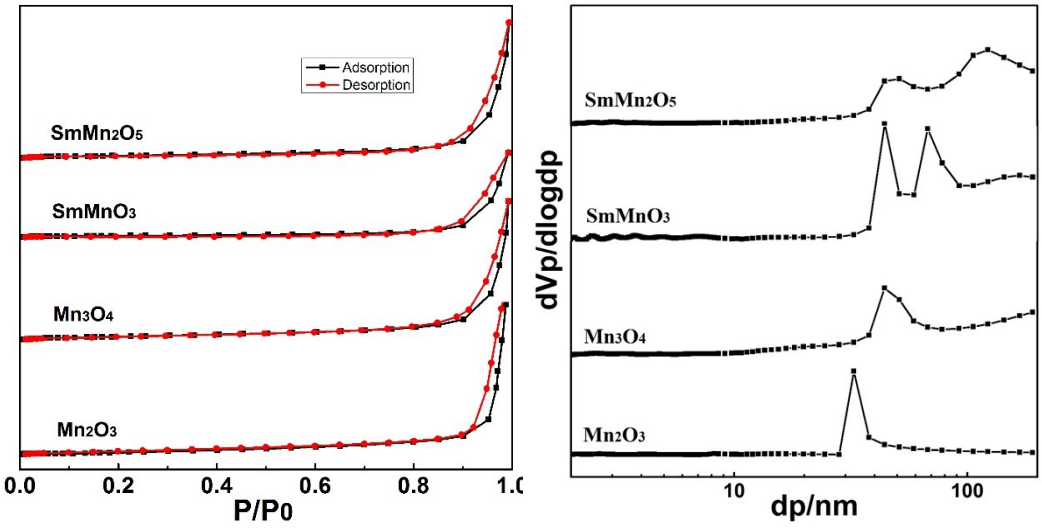

Fig. S2 N_2 adsorption-desorption isotherms at 77K and BJH pore size distribution of $SmMn_2O_5$, $SmMnO_3$, Mn_3O_4 and Mn_2O_3.

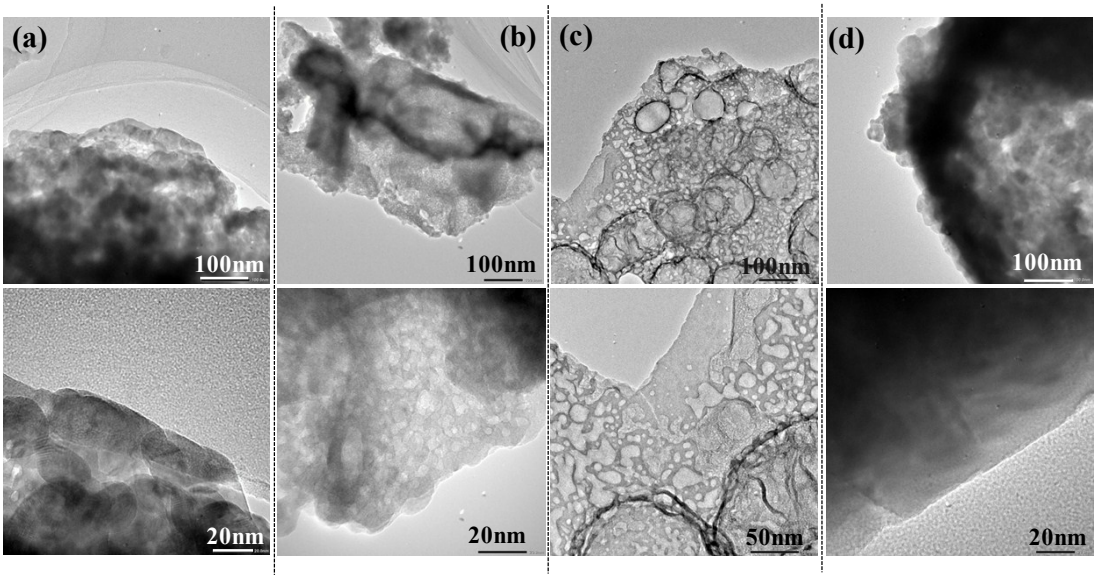

Fig. S3 TEM images of the (a) MnOx-400, (b) Sm-MnOx=0.3-400, (c) Sm-MnOx=0.3-600, (d) Cu-MnOx=0.3-400. 0.3 represents the molar ratio of (Sm or Cu)/Mn, 400 or 600 represents the calcination temperature.

Sm-MnOx=0.3 (Sm/Mn = 0.3) was prepared using same method at 400 ^{o}C and 600 ^{o}C. Compared with the MnO_x, abundant mesopore was formed in Sm-MnOx=0.3-400. With the calcination temperature increasing, obvious macropore was observed in Sm-MnO_x=0.3-600.

The precursors in organic solvent combustion are ethylene glycol, $Mn(Ac)_2$ and $Sm(NO_3)_3$, respectively. The decomposition temperatures of these precursors are 197.3, 118.2 and 291 ^{o}C, respectively. Therefore, ethylene glycol and $Mn(Ac)_2$ decomposed firstly during the combustion. After that, remaining $Sm(NO_3)_3$ would continue to decompose as the temperature increases, and mesopore was formed due to a large amount of gas released. The increase in calcination temperature accelerates the decomposition of $Sm(NO_3)_3$ and results in the formation of macropore. As a contrast, $Sm(NO_3)_3$ was replaced by $Cu(NO_3)_2$, whose decomposition temperature is only 170 ^{o}C. No mesoporous or macroporous formation was observed.

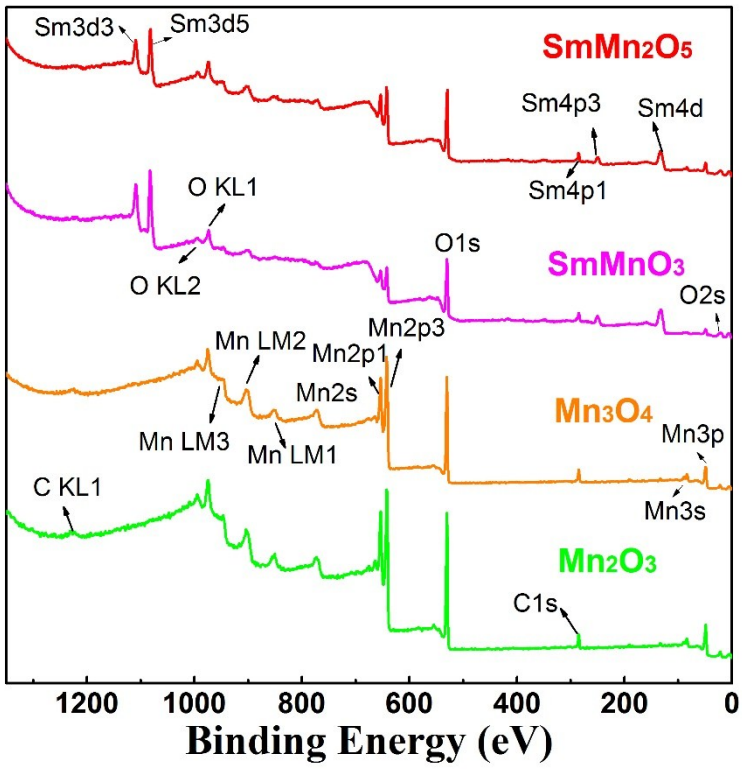

Fig. S4 Survey spectra in the XPS measurement for $SmMn_2O_5$, $SmMnO_3$, Mn_3O_4 and Mn_2O_3.

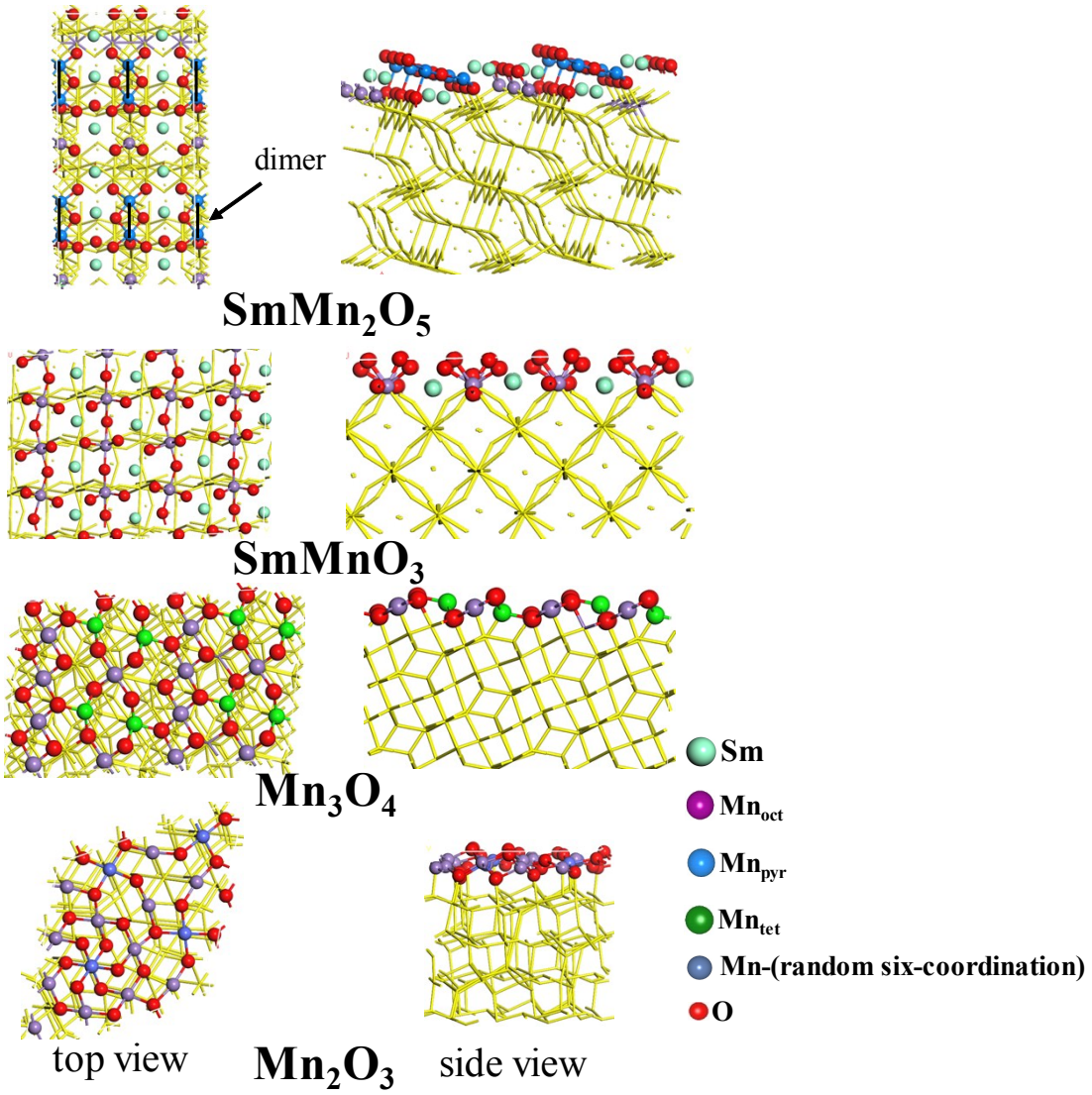

Fig. S5 The theoretical model on the surface of $SmMn_2O_5$, $SmMnO_3$, Mn_3O_4 and Mn_2O_3 from top and side view. Only the surface atoms are showed to be more easily distinguishable, in which light green, purple, blue, dark green, dark blue, and red atom represent Sm, Mn_{oct}, Mn_{pyr}, Mn_{tet}, a random six-coordinate Mn and O atom, respectively.

Table S1. Textural characterization of MnO_x by organic solvent combustion at different calcination temperatures.

Sample-temperature (°C)	Total Pore Volume (cc/g)	Avg. Pore Diameter (nm)	SSA(m^2/g)
MnO_x-300	0.17	21.5	31
MnO_x-400	0.11	27.1	17
MnO_x-600	0.15	33.8	18
MnO_x-700	0.02	14.7	6
MnO_x-900	0.01	8.6	4

Table S2. Reduction temperature and H_2 consumption of different Mn-based oxides.

Samples	Reduction temperature (°C)				H_2 consumption (μmol)				
	Peak1	Peak2	Peak3	Peak4	Peak1	Peak2	Peak3	Peak4	Total
$SmMn_2O_5$	200	408	499	-	38.5	122.1	57.7	-	218.3
$SmMnO_3$	234	354	453	673	16.0	18.5	31.8	77.1	143.4
Mn_3O_4	247	279	419	459	50.1	35.4	160.6	57.0	303.1
Mn_2O_3	230	371	466	-	20.1	171.5	190.0	-	381.6