Supplementary Information

Identifying Descriptor of Governing NO Oxidation on Mullite Sm(Y, Tb, Gd, Lu)Mn_2O_5 for Diesel Exhaust Cleaning

Hao-Bo Li[1], Wei-Hua Wang[1], Xinyu Qian[1],Yahui Cheng[1], Xinjian Xie[2], Jieyu Liu[1], Shuhui Sun[3], Jigang Zhou[4], Yongfeng Hu[4], Jianping Xu[5], Lan Li[5], Yan Zhang[6], Xiwen Du[6], Kuanghong Gao[7], Zhiqing Li[7], Cui Zhang[8], Shudong Wang[9], Haijun Chen[9], Yidong Zhao[10], Feng Lu[1,†], Weichao Wang[1,†], Hui Liu[1]

[1]*Nankai University, College of Electronic Information and Optical Engineering, Tianjin, China, 300071*

[2]*School of Materials Science and Engineering, Hebei University of Technology, Tianjin, China, 300130*

[3]*Institut National de la Recherche Scientifique, Québec, Canada J3X 1S2*

[4]*Canadian Light Source, Saskatoon, Canada, S7N 2V3*

[5]*Tianjin University of Technology, College of Science, Tianjin, China, 300384*

[6]*Tianjin University, School of Materials Science and Engineering, Tianjin, China, 300072*

[7]*Tianjin University, Department of Physics, Tianjin, China, 300072*

[8]*Nankai University, College of Chemistry, Tianjin, China, 300071.*

[9]*Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, China, 116023.*

[10]*Beijing Synchrotron Radiation Facility, Chinese Academy of Sciences, Beijing, China, 100049.*

†To whom correspondence should be addressed.

Email: lufeng@nankai.edu.cn; weichaowang@nankai.edu.cn

Index **Page**

Supplementary methods

Hydrothermal synthesis of Sm(Tb, Y)Mn_2O_5. All the Sm(Y, Tb)Mn_2O_5 nanoparticles were synthesized by hydrothermal method. Rare-earth nitrate, $Mn(CH_3CO_2)_2 \cdot 4H_2O$ and $KMnO_4$ (all 99.98%, Aladdin) were dissolved in 25 ml deionized water in a molar ratio of 5:7:3 and stirred for 30 minutes. Then the NaOH (99.98%, Aladdin) solution of 5 M was added slowly and the mixture was stirred for another 10 minutes. The precursor was transferred to a 100 ml stainless steel Teflon-lined autoclave which was then filled to 60% of its capacity. The hydrothermal treatment was processed under 200 ^oC for 12 hours. After the autoclave was cooled down to the room temperature, the product was filtered and washed by deionized water and 1% HNO_3 for 3~5 times. The precipitant was dried at 80 ℃ for 4 hours. To determine the phase purity, all the samples were characterized by X-ray diffraction (Rigaku Corporation, D/max-2500). The morphology of the nanoparticles was obtained from transmission electron microscope (TEM) by TECNAI F30.

X-ray diffraction spectra. The X-ray diffraction (XRD) spectra is plotted in Figure S1 and the pure mullite crystalline are in orthorhombic phases with space group of *Pbam*.

BET surface area measurement. The BET surface areas of samples were determined from N_2 adsorption-desorption experiments，which was carried out at -196 ℃ on

Microporous instrument Tristar 3000. The samples were outgassed for 10 hours at 300 °C to remove any moisture or adsorbed contaminants that may have been present on their surface. The specific surface area (SBET) was calculated using the Brunauer-Emmett-Teller (BET) method, which was presented in Tristar 3000 apparatus.

Catalytic characterization. All the samples are in powder form and the catalytic measurement was carried out using a flow through powder reactor system equipped with a Fourier Transform Infrared (FT-IR) spectrometer (Nicolet 6700) with a gas sampling cell at atmospheric pressure. The samples weight was 0.6 g and the total flow rate was 200 sccm, which consists of 450 ppmv NO and 10% O_2/He. The NO conversion was obtained by calculating the molar ratio between the produced NO_2 to the entered NO.

DFT calculations of bulk mullite oxides. The Sm(Y, Tb)Mn_2O_5 system belongs to orthorhombic space group *Pbam* containing two different types of Mn-O ligand field of octahedral and square pyramid as shown in Figure S2. In fact neutron and x-ray diffraction studies claim that the actual symmetry group is $Pb2_1m$, which results in complicated magnetic structures and macroscopic electric polarization along the *b* direction[1-3]. In order to fit the magnetic period, the calculated structure of Sm(Y, Tb)Mn_2O_5 contains a $2\times1\times1$ unit cell which is in line with other collinear calculations on mullite[4-6]. Along the *b* direction, the spin ordering of the Mn ions in Sm(Y,

Tb)Mn_2O_5 could be schematically represented as a chain of $Mn^{\uparrow}_{pyr} - O_{bulk} - Mn^{\uparrow}_{oct} - O_{bulk} - Mn^{\downarrow}_{pyr}$ as shown in Figure S2. The $Mn^{\uparrow}_{pyr} - O_{bulk} - Mn^{\uparrow}_{oct}$ part of the chain plays key role in governing the O* releasing difficulty. The spin-splitting *d*-band alignment is verified by investigating the partial charge distribution within the certain range of the projected density of states of Mn ions. As the *d*-orbitals expand, the *d*-orbitals overlap with each other, thus the regions contributed by certain *d*-orbitals are labeled in Figure S3 to identify the *d*-orbitals sequence.

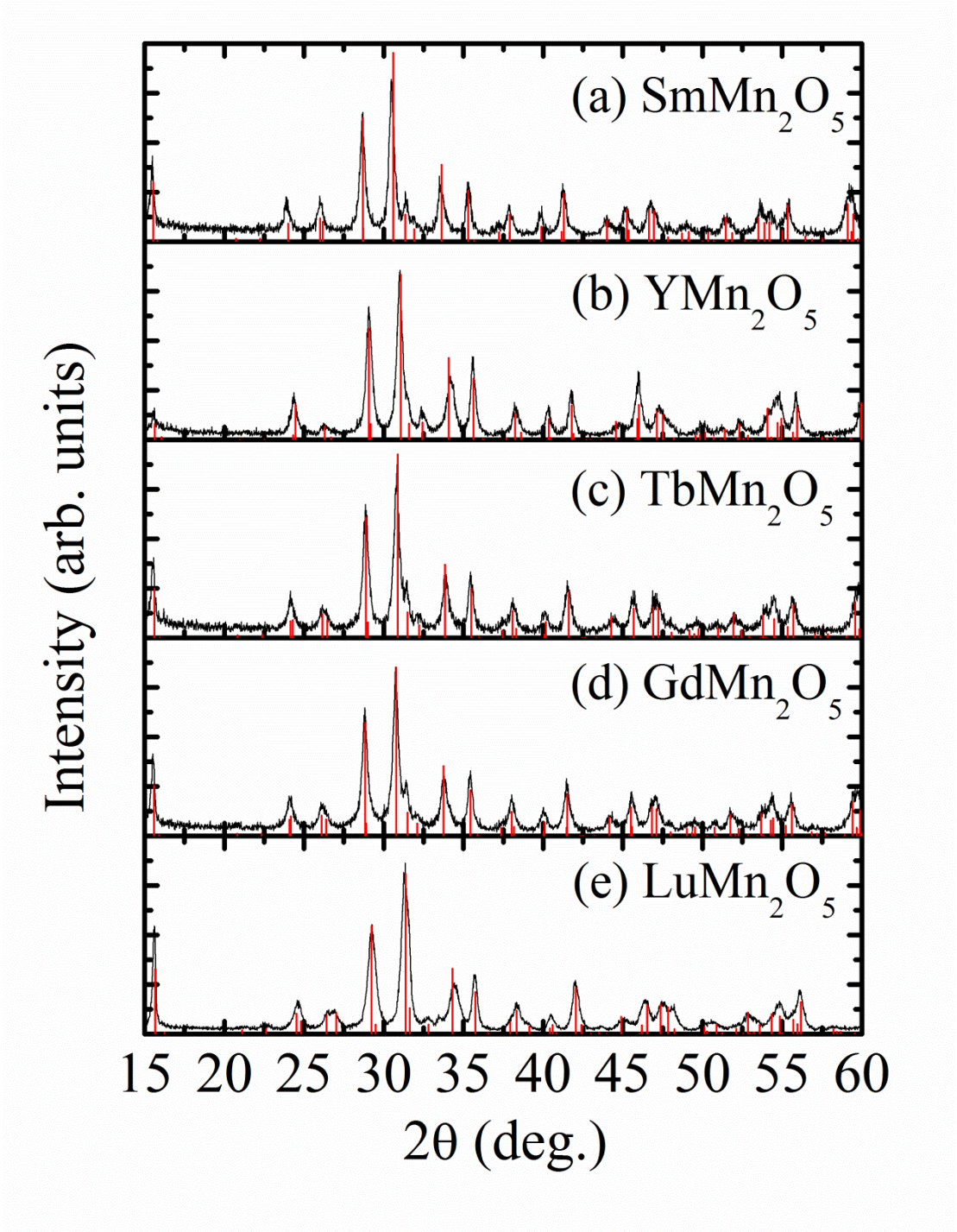

Figure S1. The XRD spectra of AMn_2O_5 (A=Sm, Y, Tb, Gd, Lu). The red line are the standard peaks.

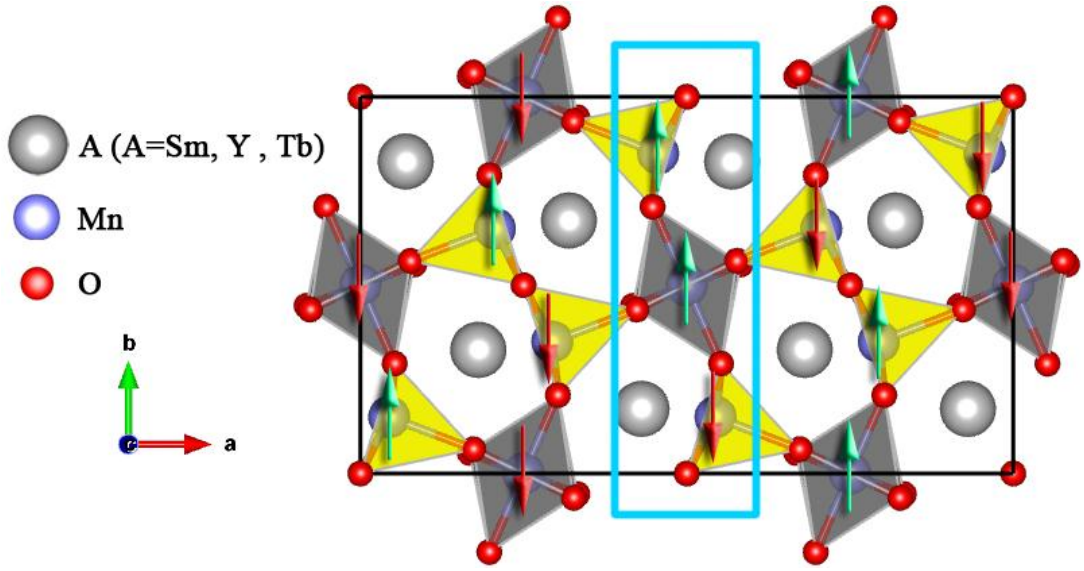

Figure S2. (Color online) The 2×1×1 unit cell of Sm(Y, Tb)Mn_2O_5. The two types of ligand field: octahedral and square pyramid are labeled by grey and yellow area, respectively. The arrows represent the spin configuration in collinear approximation in calculations. The blue square denotes the $Mn^{\uparrow}_{pyr} - O_{bulk} - Mn^{\uparrow}_{oct} - O_{bulk} - Mn^{\downarrow}_{pyr}$ chain.

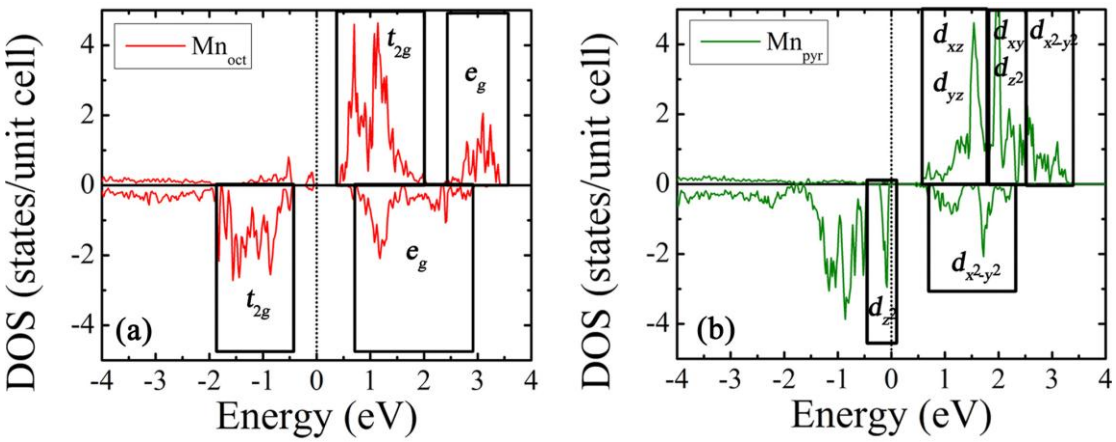

Figure S3. (Color online) Spin-polarized projected density of states (PDOS). (a), PDOS of Mn_{oct}-3*d*. **(b),** PDOS of Mn_{pyr}-3*d*. Regions contributed by different orbitals are labeled.

Table S1: The BET surface area of different samples.

Sample	**BET surface area (m^2/g)**
$SmMn_2O_5$	54.3
YMn_2O_5	55.6
$TbMn_2O_5$	52.1
$LuMn_2O_5$	54.4
$GdMn_2O_5$	68.0

Reference

[1] I. Kagomiya, S. Mastumoto, K. Kohn, Y. Fukuda, T. Shoubu, H. Kimura, Y. Noda, and N. Ikeda, Ferroelectrics **286,** 167 (2003).

[2] L. C. Chapon, G. R. Blake, M. J. Gutmann, S. Park, N. Hur, P. G. Radaelli, S-W. Cheong, Phys. Rev. Lett. **93,** 177402. (2004).

[3] J. A. Alonso, M. T. Casais, M. J. Martínez-Lopey, J. L. Martínez, and M. T. Fernández-Díaz, J. Phys.: Condens. Matter **9,** 8515 (1997).

[4] C. Wang, G.-C. Guo and L. He, Phys. Rev. Lett. **99,** 177202 (2007).

[5] G. Giovannetti and J. Brink, Phys. Rev. Lett. **100,** 227603 (2008).

[6] T. -R. Chang, H.-T. Jeng, C.-Y. Ren and C.-S. Hsue, Phys. Rev. B **84,** 024421. (2011).