Supporting information

Giant Effect of Oxygen Vacancy Defects on the Catalytic Oxidation of OMS-2 Nanorods

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Experimental

Synthesis. OMS-2 nanorod samples were prepared by a facile method of hydrothermal redox reaction between $Mn(NO_3)_2$ and $KMnO_4$ at different temperature. The detailed procedure is as follows. 3.5790 g of $Mn(NO_3)_2$ (50 wt%) was dissolved in 40 mL of distilled water in a beaker. 3.1608 g of $KMnO_4$ was rapidly added into the $Mn(NO_3)_2$ aqueous solution under magnetic vigorous stirring until it was dissolved. Then, the mixture solution was transferred to a 100 mL Teflon bottle, and sealed tightly in a stainless-steel autoclave. The autoclave was placed in an electrical oven, heated to 70, 90, and 180 ^oC, and kept at the temperature for 24 h. After the autoclave was cooled to room temperature, the resulting precipitate was washed with distilled water, and dried under an infrared lamp. The obtained samples were denoted as OMS-70, OMS-90, and OMS-180, respectively.

Characterization. X-ray diffraction (XRD) patterns were observed on a Rigaku Dmax X-ray diffractometer using Cu Kα radiation. Scanning electron microscopy (SEM) images were obtained by using a Hitachi S-4800 scanning electron microscope. Transmission electron microscopy (TEM) images were obtained by using a JEM-100CX electron microscope. The BET surface area of the OMS-2 samples was measured on AUTOSORB-1 using N_2 adsorption at –196 ^oC. Raman spectra were recorded on a Renishaw inVia Raman microscope using an excitation of 514.5 nm laser light. The OMS-2 samples were analyzed by a VG Multilab 2000 X-ray photoelectron spectrometer (XPS) using Mg Kα radiation. The XPS spectra of the OMS-2 samples were calibrated by referencing the binding energy to adventitious carbon (C 1s 284.6 eV) and were deconvoluted using a special software program.

CO temperature-programmed reduction (CO-TPR) and O_2 temperature-programmed oxidation (O_2-TPO) were conducted on a TP-5080 multifunctional adsorption apparatus equipped with a TCD detector. 0.0100 g of the OMS-2 sample was located in a quartz reactor. A NaOH particle trap was placed in the front of the detector to adsorb the water and CO_2 produced. Before the TPR analysis, the OMS-2 samples were pre-treated in 5 vol% O_2/He at 200 ^oC for 1 h, and then cooled to room temperature. TPR was performed by heating the pre-treated OMS-2 sample at 10 ^oC min^{-1} to 700 ^oC in the flow of 5 vol% CO/He at 40 mL min^{-1}. Before the TPO analysis, the OMS samples were reduced in 5 vol% CO/He at 220 ^oC for 1 h, and then cooled to room temperature. TPO was performed by heating the pre-reduced OMS-2 sample at 10 ^oC min^{-1} to 700 ^oC in a flow of 5 vol% O_2/He mixture at 24 mL min^{-1}.

Catalytic Activity. The catalytic activity measurements for the catalytic oxidation of benzene, toluene, and xylene were carried out at atmospheric pressure in a continuous flow fixed-bed quartz tubular reactor on a WFS-2015 online gas-phase reaction apparatus. 0.0500 g of the catalyst was loaded in the middle of the quartz reactor (with an inner diameter of 16 mm and a length of 600 mm) supported by glass wool. A thermocouple placed inside the reactor, which contacted to the catalyst bed, monitored the reaction temperature. The reactor was placed in a temperature-controlled tubular electrical oven. Gaseous reactant such as benzene, toluene, and xylene was generated by causing air to flow into a vapor saturator, which was kept at 6 ^oC in a temperature-controllable water bath. The air stream saturated with the reactant was diluted with another flow of air to yield a final reactant concentration of 2000 mg m^{-3}. The total flow rate was 40 mL min^{-1} (SV = 48,000 mL $g^{-1}{}_{-catalyst}$ h^{-1}). The reactor was connected to a GC9560 gas chromatograph (GC) equipped with a flame ionization detector (FID), a methane converter, a Porapak R column, and PEG20M column through an automatically sampling ten-way valve (VALCO) with an air actuator. The effluent reaction products contained only CO_2 and H_2O, and no other byproducts were detected. The conversion was calculated based on the reactant consumption. The unreacted reactant in the effluent from the reactor was collected by a cooling tank placed in a salt-ice bath.

DFT calculation method. Density functional theory (DFT) calculations were used to study OMS-2 (KMn_8O_{16}). The calculations were performed using the Vienna Ab-initio Simulation Package (VASP).[1-3] The valence electronic states are expanded in a set of periodic plane waves and the interaction between core electrons and the valence electrons is implemented through the projector augmented wave (PAW) approach. The Perdew-Burke-Ernzerhof (PBE) GGA exchange-correlation functional is applied in the calculations.[4-6] In relaxation, summations over the Brillouin zone (BZ) are performed with a 2 × 2 × 2 Monkhorst-Pack k-point mesh. The smooth part of the wave functions is expanded in plane waves with a kinetic energy cutoff of 400 eV and the convergence criteria for the electronic and ionic relaxation are 10^{-4} eV and 0.02 eV $Å^{-1}$, respectively. Our calculated lattice parameters of bulk KMn_8O_{16} are a = 9.755 Å and c = 2.96 Å, close to Cockayne' report.[7] To ensure the convergence of the calculations, we repeated all the calculations with a larger super cell size of 100 atoms (1 × 1 × 4) (Figure S4). The lowest-energy position of K atoms is at eight oxygen near neighbors.[7]

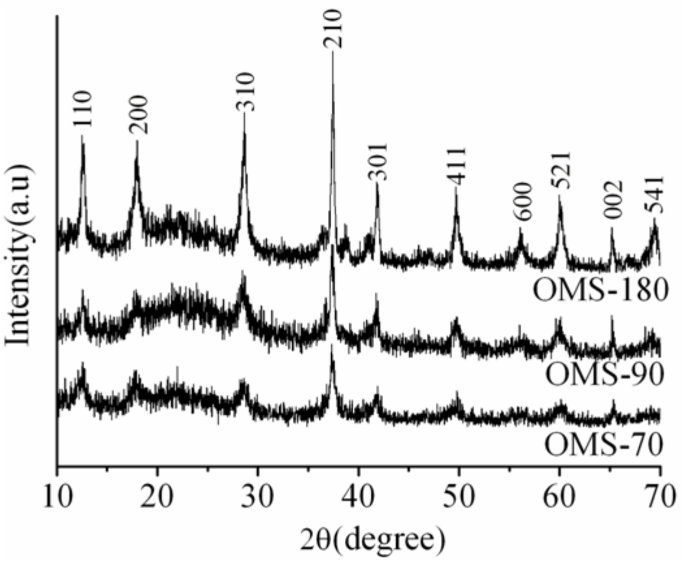

Figure S1. XRD patterns of the OMS-2 nanorod samples.

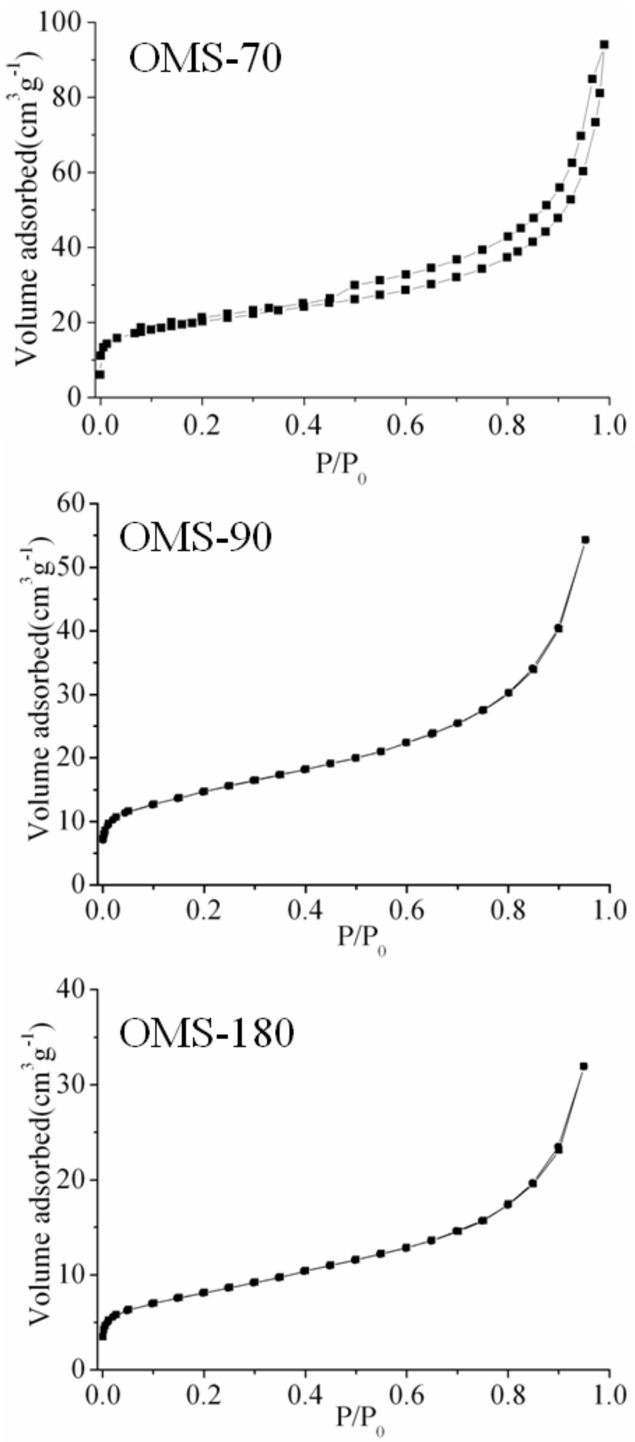

Figure S2. The N_2 adsorption-desorption isotherm of the OMS-2 nanorod samples: The volumes and surface area of micropores are obtained using the Dubinin-Radushkevich equation:[Ref 24]

$$V/V_0 = \exp(-1/(E_0\beta)^2\,(RT\ln(P_0/P))^2)$$

here V is the volume adsorbed, V_0 the micropore volume, E_0 the characteristic energy dependent on the pore structure, and β the affinity coefficient which is characteristic of the adsorber. The artifact hysteresis loop for OMS-70 (the pore size at around 4 nm) is due to the tensile strength effect.[8]

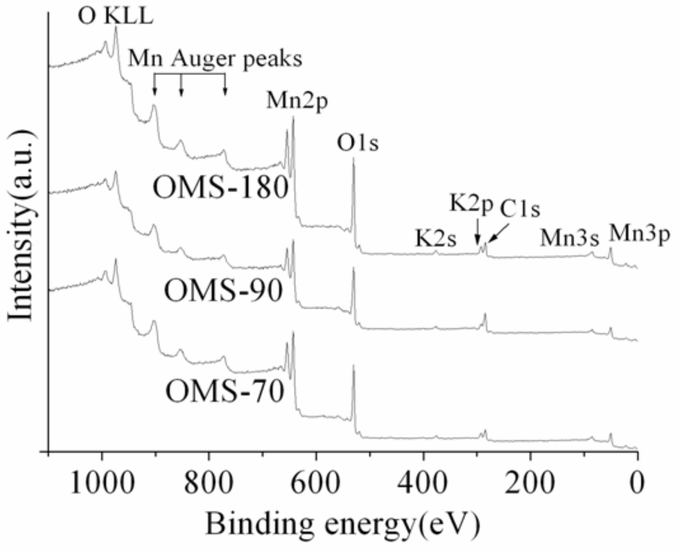

Figure S3. XPS full spectra of the OMS-2 nanorod samples (the weak C1s peak is due to the contamination of the samples).

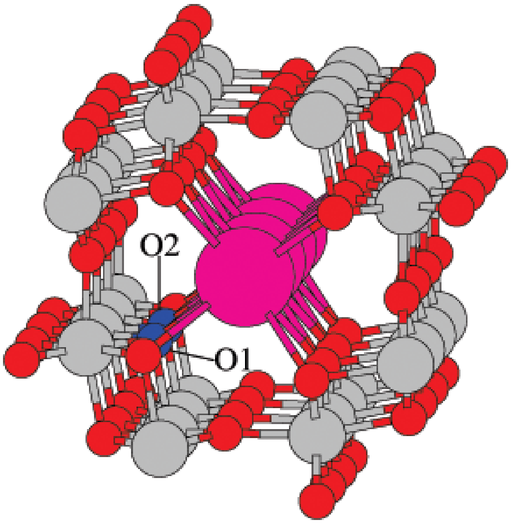

Figure S4. The calculated super cell of KMn_8O_{16}: purple (K), grey (Mn), red (O) and blue (oxygen to be removed)**.**

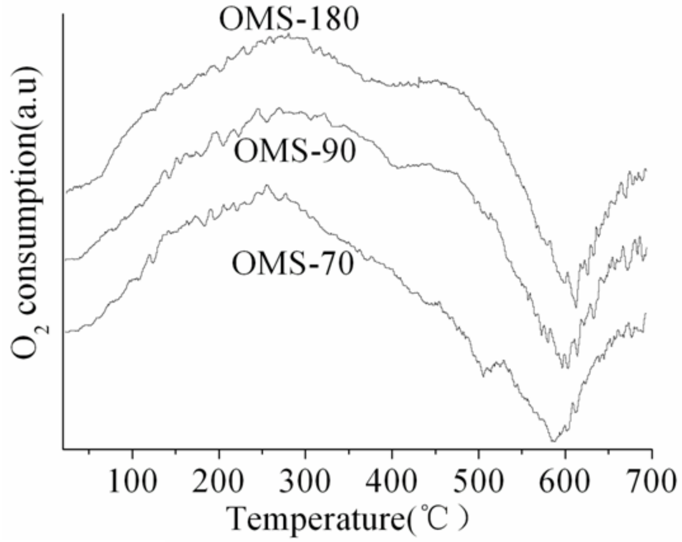

Figure S5. O_2-TPO profiles (C) of the OMS-2 nanorod samples pre-reduced at 220 °C for 1 h in the flow of 5 vol% CO/He: For the pre-reduced OMS-180 sample, the maximum O_2 consumption occurs around 269 and 450 °C. According to the assignment of the CO-TPR peaks as discussed above, the lower and higher temperature peaks are assigned to two-step re-oxidation for the OMS-2 nanorod samples pre-reduced by CO: Mn_3O_4 to KMn_8O_{16} and MnO to Mn_3O_4, respectively. The negative peak around ~600 °C is attributed to the evolution of lattice oxygen of the OMS-2 nanorod samples and the transformation of cryptomelane to Mn_2O_3.[9] The pre-reduced OMS-90 sample exhibits O_2-TPO profiles similar to the pre-reduced OMS-180 sample. Compared to the two samples, the lower temperature peak of the pre-reduced OMS-70 sample shifts to lower temperature (255 °C). The maximum re-oxidation peak temperature of the OMS-180, OMS-90, and OMS-70 samples pre-reduced by CO is lower than the corresponding maximum reduction peak temperature of OMS-180, OMS-90, and OMS-70 by CO (Figure 3B, Figure S5).

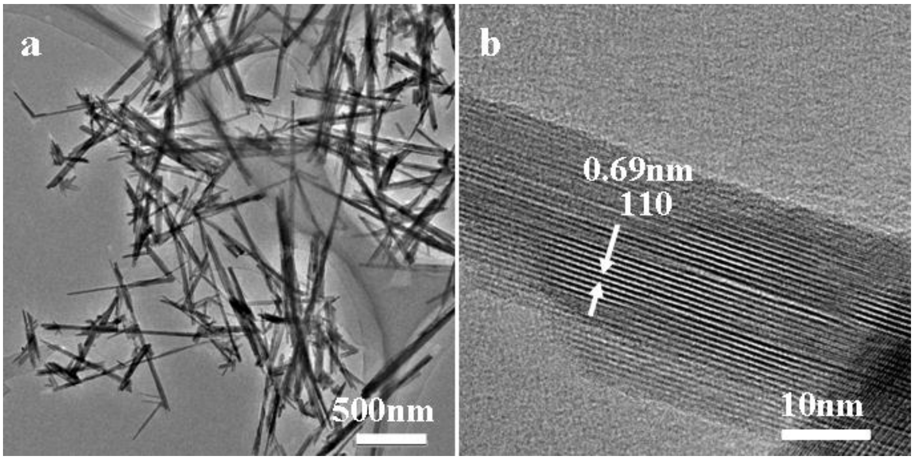

Figure S6. TEM and HTEM images of the used OMS-70 sample after the 96 h catalytic reaction.

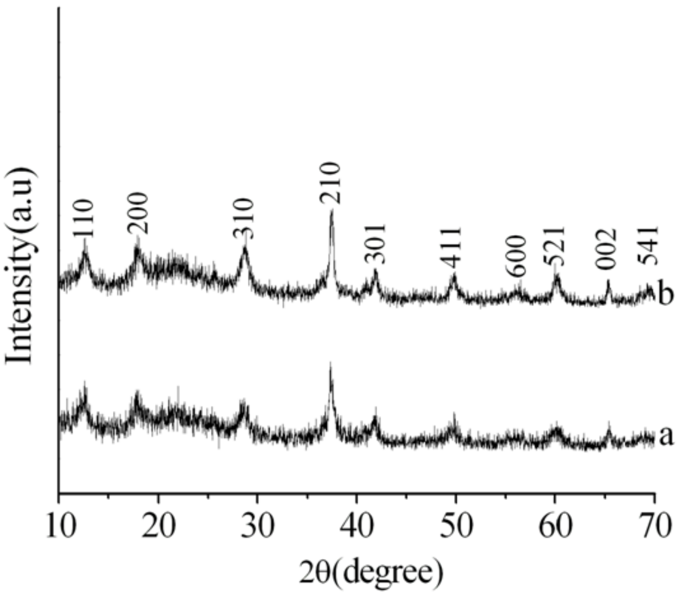

Figure S7. XRD pattern of the fresh OMS-70 sample (a) and the used OMS-70 sample after the 96 h catalytic reaction (b).

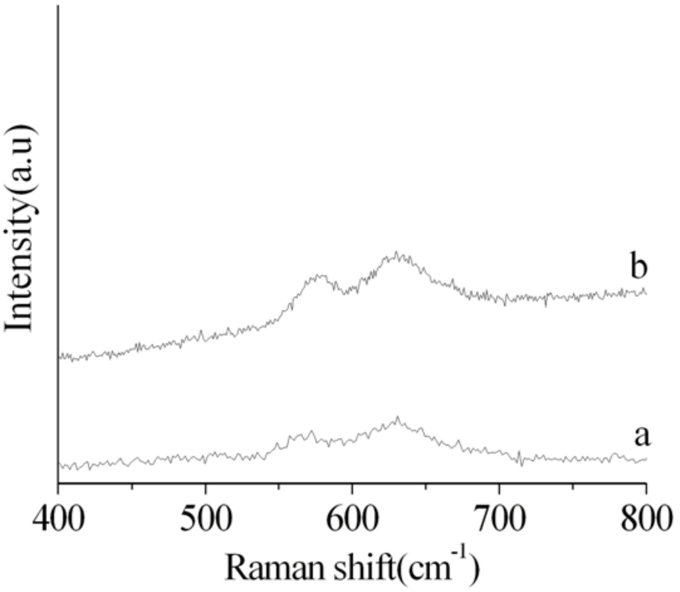

Figure S8. Raman spectra of the fresh OMS-70 sample (a) and the used OMS-70 sample after the 96 h catalytic reaction (b).

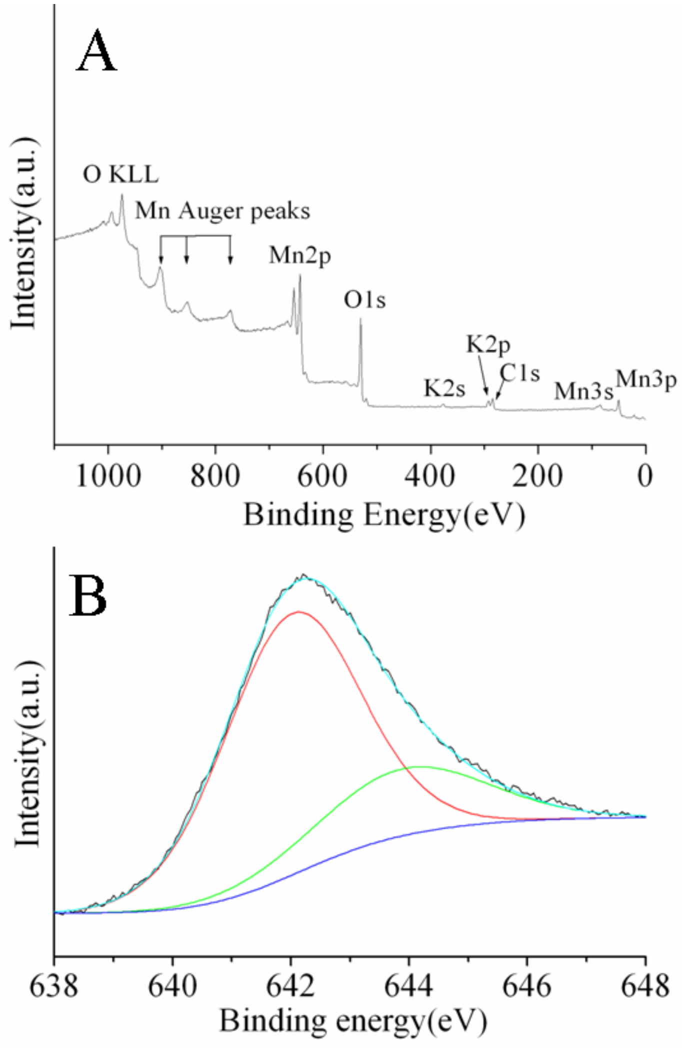

Figure S9. XPS full spectra (A) and Mn2p$_{3/2}$ spectra (B) of the used OMS-70 sample after the 96 h catalytic reaction: The relative atomic ratio of Mn^{3+}/Mn^{4+} in the used OMS-70 sample is 3.1.

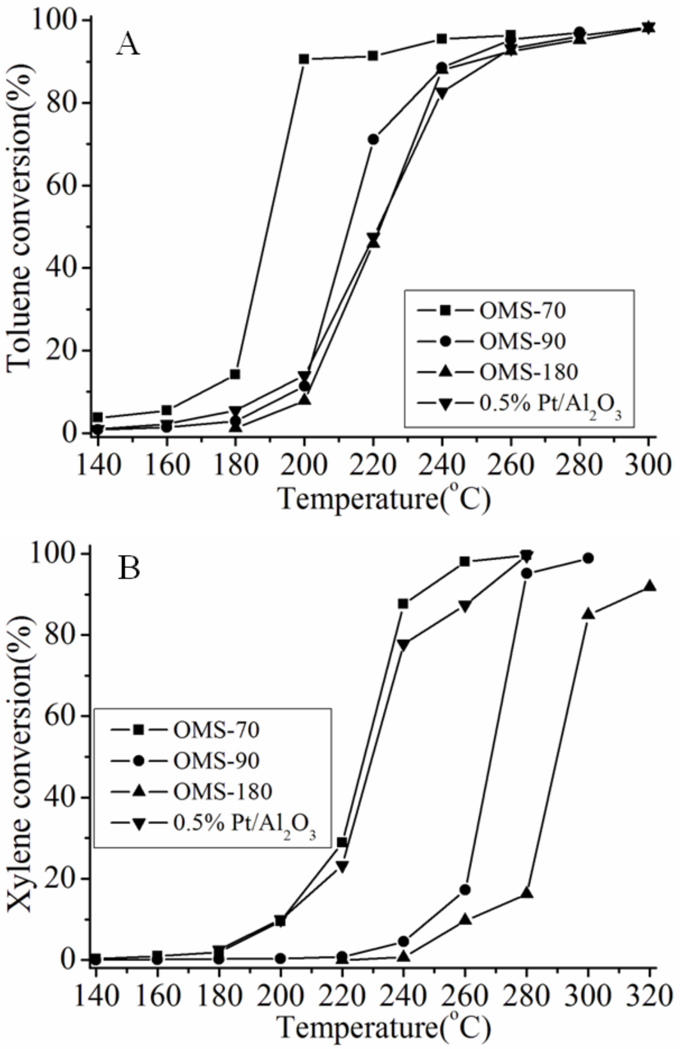

Figure S10. Toluene (A) and xylene (B) conversion versus reaction temperature over the catalysts under the condition of toluene or xylene concentration = 2000 mg m^{-3} and SV = 48000 mL g$^{-1}{}_{\text{-catalayst}}$ h^{-1}.

Table S1. T_{50} and T_{90} of toluene oxidation over the catalysts

Catalyst	Catalytic activity (℃)	
	T_{50}	T_{90}
OMS-70	189	200
OMS-90	213	244
OMS-180	222	254
0.5%Pt/Al_2O_3	221	248

Table S2. T_{50} and T_{90} of xylene oxidation over the catalysts

Catalyst	Catalytic activity (℃)	
	T_{50}	T_{90}
OMS-70	227	244
OMS-90	268	279
OMS-180	290	315
0.5%Pt/Al_2O_3	230	264

References

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