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A high-efficiency γ-MnO_2-like catalyst on toluene combustion

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Supplementary Information

Experimental section

Synthesis of monodisperse PMMA microspheres

Monodisperse PMMA microspheres were synthesized as the following procedures. Firstly, 0.40 g (3.00 mmol) potassium peroxydisulfate ($K_2S_2O_8$) was dissolved in 1500 mL deionized water under stirring at 400 rpm. Then the resulting solution was heated at 70 ºC, and degassed with flowing N_2 in a three-necked flask. After the temperature of the solution was kept at 70 ºC, 115 mL of methyl methacrylate was added into the flask, and the resulting suspension was stirred at 70 ºC for 60 min until turned to be white. After centrifuged for 75 min, the supernatant was taken out and the precipitate was washed three times with deionized water to remove the left $K_2S_2O_8$, and then the deionized water was evaporated in a water bath at 80 ºC. The resulting wet solid was first dried at room temperature (RT) for 48 h and then ground well.

Synthesis of LMO sample

13 g $La(NO_3)_3\cdot 6H_2O$ and 6.97 mL $Mn(NO_3)_2$ (50 wt% aqueous solution) were dissolved in 14 mL deionized water at room temperature under stirring until a transparent solution was obtained. Then about 2.00 g PMMA microsphere was added to the above mixed solution and impregnated till the PMMA microspheres were thoroughly wetted. Then the excessive liquid was filtered and the solid was dried at RT for 24 h. The resulting solid was calcined to acquire the final 3DOM materials. The calcination procedure was as following: Firstly, the precursor was heated under N_2 flow at a rate of 1°C/min up to 300 ºC and maintained at this temperature for 3 h, and then cooled down to RT in the same atmosphere. After that the flow was changed to air. The solid was heated at a rate of 1ºC/min up to 300 ºC and stayed for 1 h, and

then still at a rate of 1ºC/min up to 750 ºC and kept for 4 h. Finally, the product was the LMO sample.

Preparation of γ-MnO_2-SR sample (selective removal method)

Selective dissolution method was adopted here by immersing the LMO powder in diluted HNO_3 solution. When no obvious bubbles could be observed, it was considered to be the end of the reaction. Then the solid was filtered and washed by abundant of deionized water. At last, the sample was dried at 60 ºC over night. This product was denoted as γ-MnO_2-SR.

Preparation of other MnO_2 samples (α, β, δ-MnO_2)

α, β, δ-MnO_2 samples were prepared via the methods reported in the early literature. Synthesis of α-MnO_2 was using a solid state approach: 19 mmol of $Mn(Ac)_2·4H_2O$ and 6 mmol of $KMnO_4$ (the molar ratio of Mn^{2+} /Mn^{7+} was 3 : 2) were mixed in an agate mortar and fully ground. Then the resulting mixed powder was sealed in a glass via and heated at 120 °C for 4 h. After cooling to room temperature, the sample was washed and then dried at 80 °C overnight. β-MnO_2 was prepared by a typical hydrothermal method. 20 mmol of $MnSO_4$ was added into a 13mL solution containing 20 mmol of $NaMnO_4$ (the molar ratio of Mn^{2+} /Mn^{7+} was 1:1). The mixture was transferred to a Teflon-lined autoclave. The autoclave was sealed and kept at 240°C for 4 days. After the hydrothermal reaction, the product was washed and dried at 80 °C overnight. When it comes to the preparation of δ-MnO_2, 10 mmol of $KMnO_4$ was firstly dissolved in 65 mL of distilled water. Then the solution was added to a Teflon-lined autoclave. The reaction was took place at 220°C for 2 days. At last, the product was washed and dried at 80°C overnight.

Catalyst activity test

The catalytic activities for the toluene combustion were measured by a continuous flow fixed-bed quartz microreactor (i.d. = 9.0 mm) using 0.05 g sample (40–60 mesh) diluted with 0.25 g quartz sands (40–60 mesh). The gaseous toluene was produced by a nitrogen-blowing method, passing N_2 flow through a bottle containing pure toluene chilled in an ice-water isothermal bath. The gas mixture contained 2000 ppm toluene, 20% O_2 and N_2 (balance gas). The total flow rate was

100 mL/min, giving a GHSV of 120,000 mL/(g h). The concentrations of toluene were monitored on line by a gas chromatograph (Agilent 7890A) equipped with a flame ionization detector (FID, using the column of Porapack-Q/molecular sieve 5A, 2 m in length) and a thermal conductivity detector (TCD, using the column of RT-QPlot divinylbenzene PLOT, 30 m in length).

Characterization

XRD

The crystal structure was determined by X-ray diffraction (XRD) measurements (Rigaku, D/MAX 2500 V/PC) from 10° to 70° operated at 40 kV and 200 mA using Cu Kα radiation.

SEM/EDS

The morphologies information of the samples were given by scanning electron microscopy (SEM) (Philips XL30 microscope) operating at an accelerating voltage of 30 kV. In order to confirm the chemical compositions of the samples, the energy-dispersive spectroscopy (EDS DX-4 analysis system) were adopted to obtain the EDS results. A thin Pt deposit layer was used for improving the conductivity of the samples.

BET

The porosity information of the samples was acquired by N_2 adsorption at -196 ºC using a Quantachrome Autosorb-1MP adsorption instrument. The samples were first degassed at 300 ºC for 4 h. The surface areas and pore size distributions were measured by the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods.

H_2-TPR

Temperature programmed reduction (TPR) of H_2 studies were performed on a chemisorption analyzer (Micromeritics, Autochem II 2920) under 5 % H_2/Ar gas flow (50 mL/min) at a rate of 10 °C/min up to 1000 °C. The reduction peak was calibrated against that of complete reduction of a known standard of powdered CuO (Aldrich, 99.995%).

O_2-TPD

Temperature programmed desorption (TPD) of O_2 was performed using an adsorption analyzer (Micromeritics ChemiSorb 2720). The sample was pre-treated at 300 ºC in He for 1 h. During the whole test, the gas flow was set to 50 mL/min all the time. After being cooled to room temperature, the sample first exposed on a 5% O_2 gas flow for 1 h, and then allowed to undergo isothermal desorption under He for 30 min. The TPD test was performed in He at a rate of 10 °C/min up to 1000 °C.

XPS

In order to determine the La 3d, Mn 2p, and O 1s binding energies (BEs) of surface lanthanum, manganese, and oxygen species, the X-ray photoelectron spectroscopic (XPS) was used with Mg Kα (hν = 1253.6 eV) X-ray source. The C 1s signal (BE = 284.6 eV) of contaminant carbon was employed to calibrate the BE values of La 3d, Mn 2p, and O 1s.

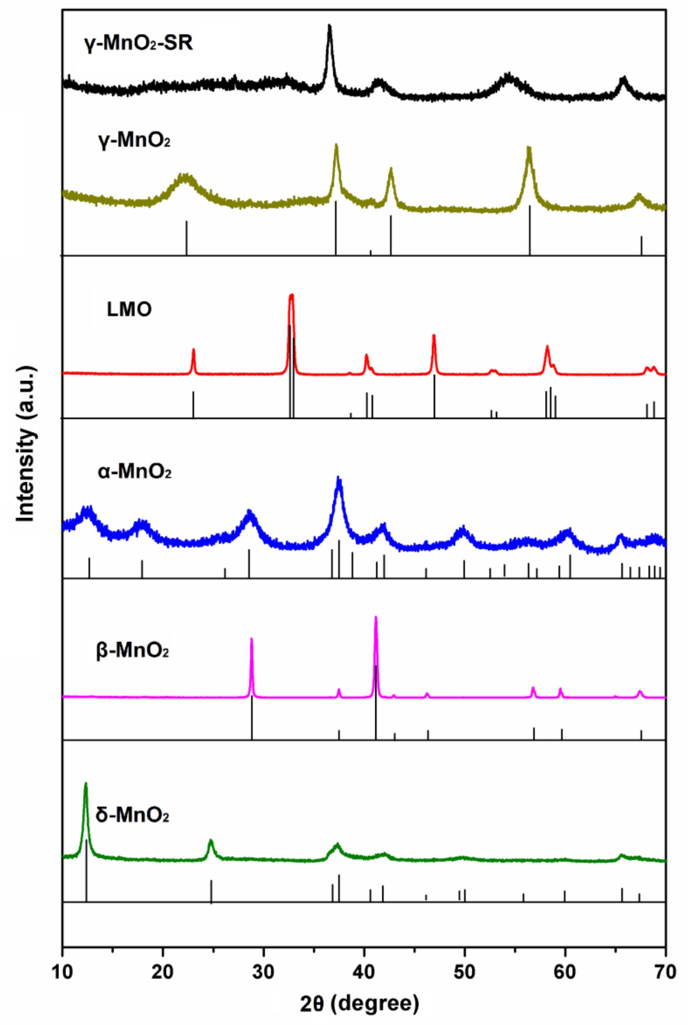

Fig. S1 XRD patterns of the manganite samples.

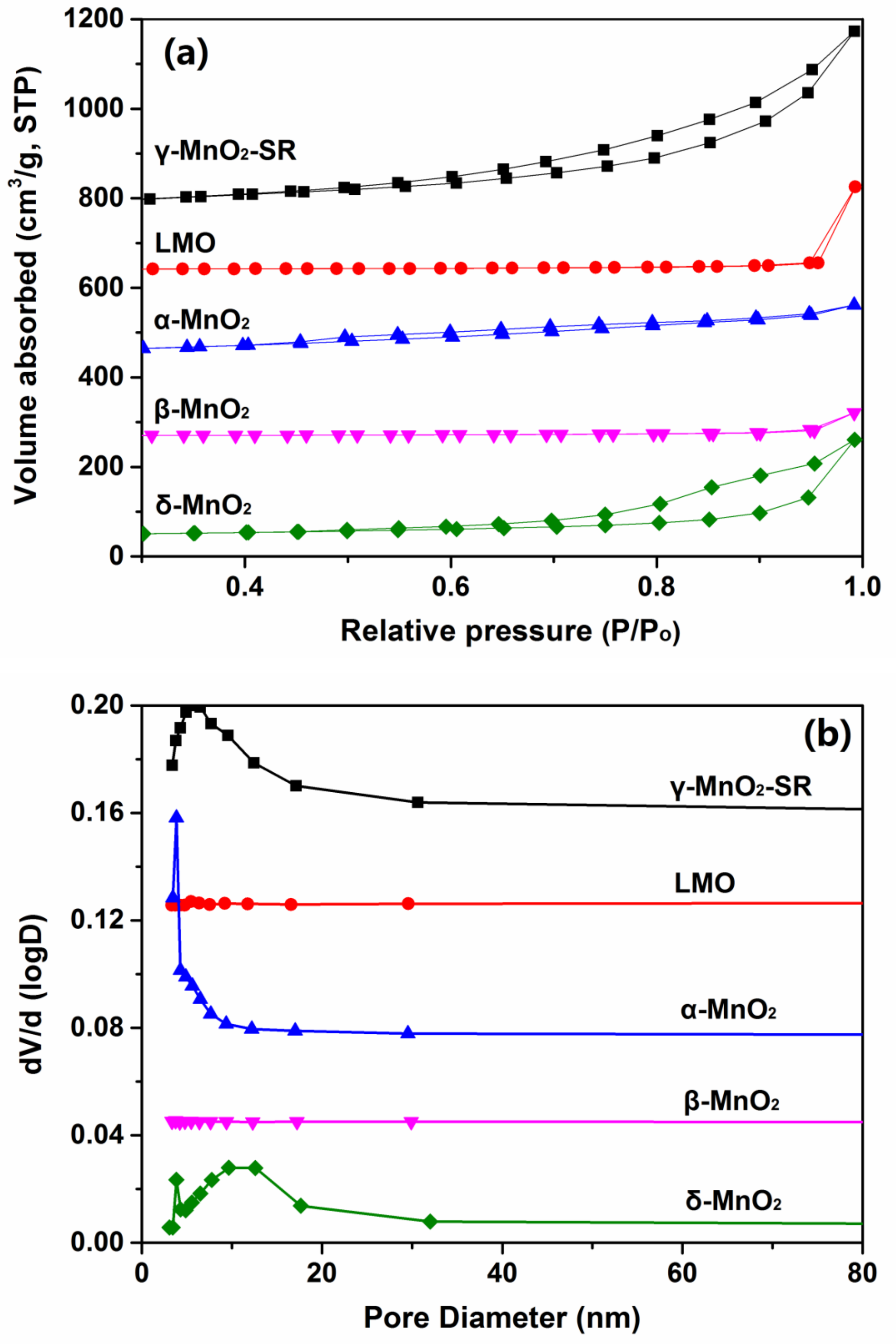

Fig. S2 (a) N_2 adsorption–desorption isotherms and (b) pore-size distributions of the five samples.

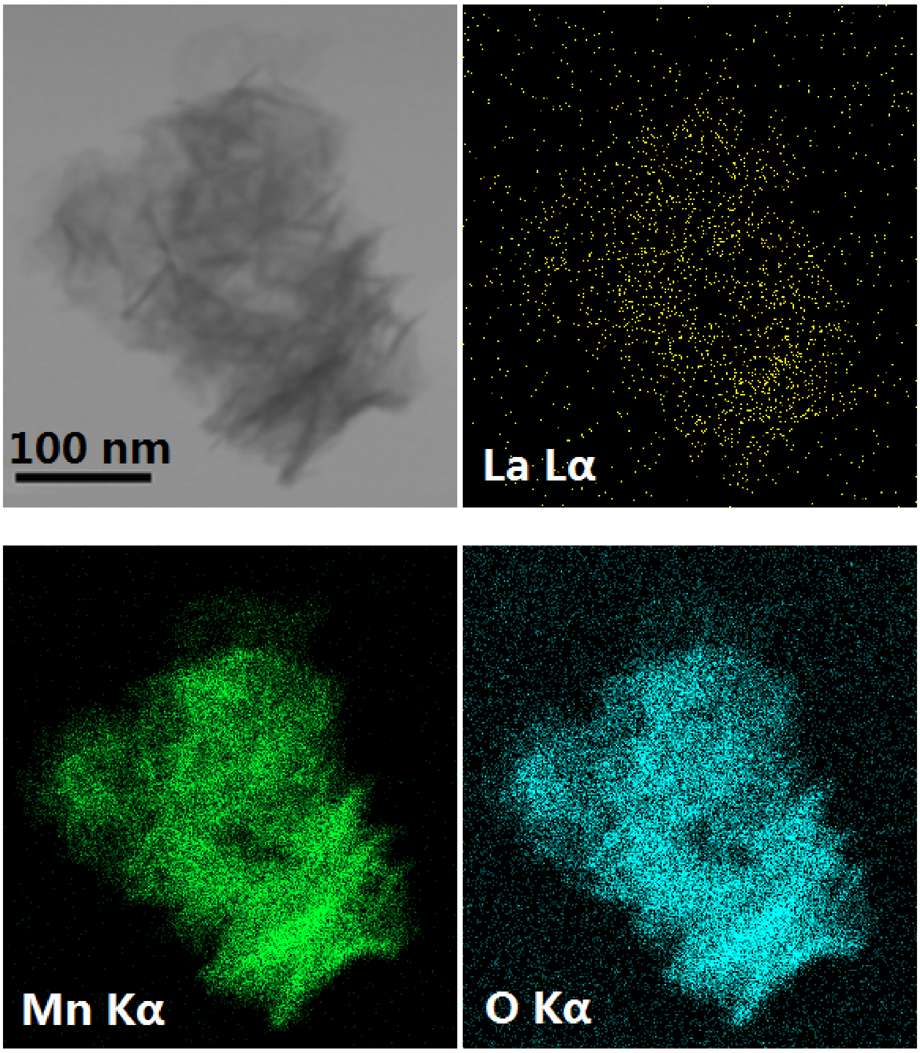

Fig. S3 TEM-EDS elemental mapping of γ-MnO_2-SR by TEM.

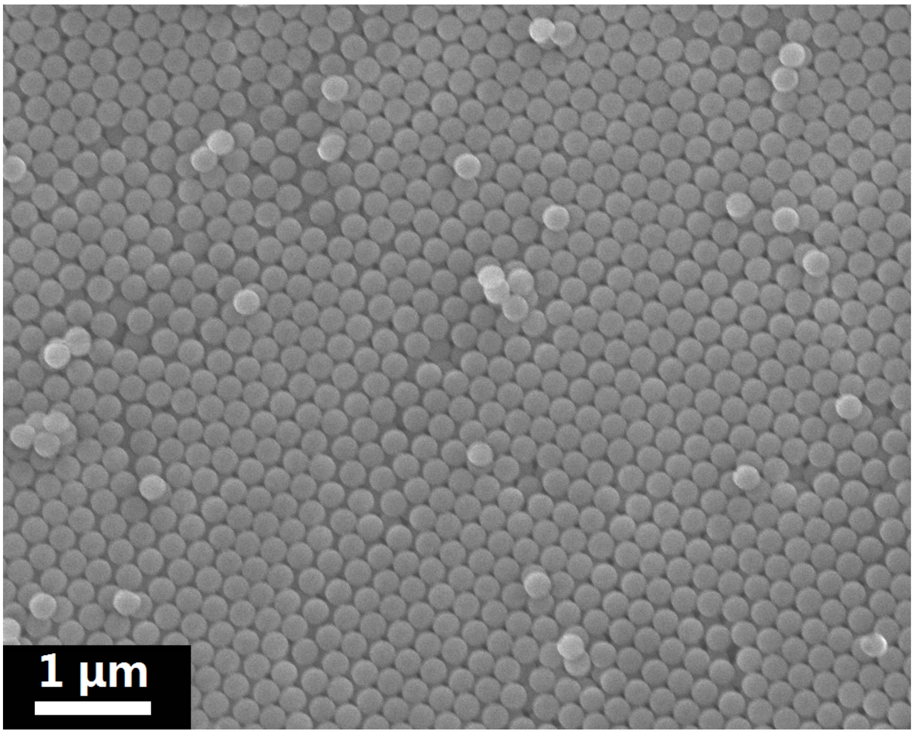

Fig. S4 SEM image of the PMMA template.

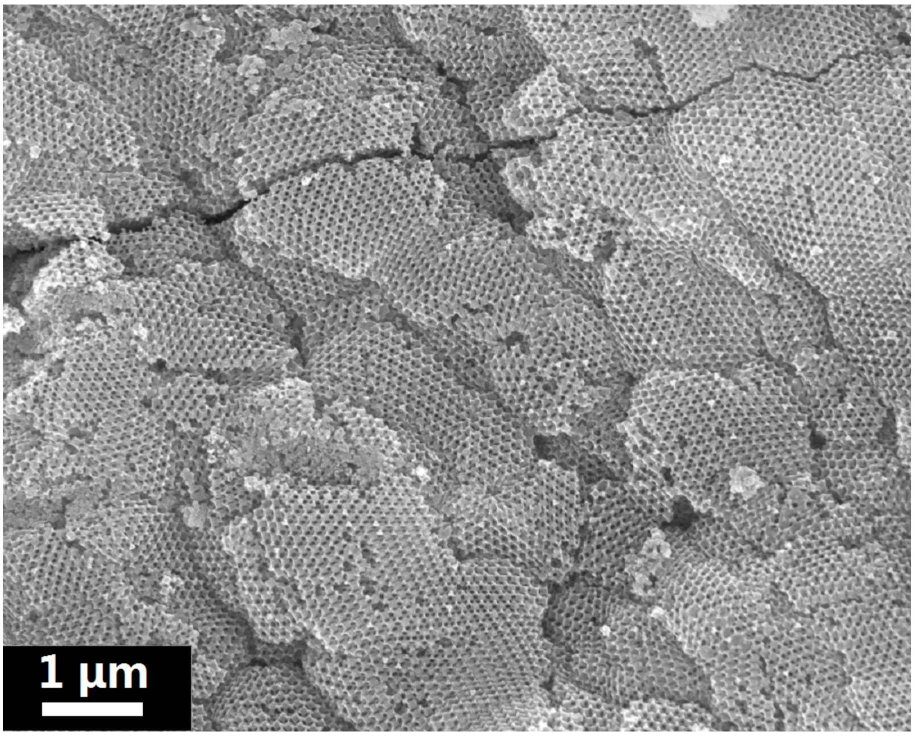

Fig. S5 SEM image of LMO sample.

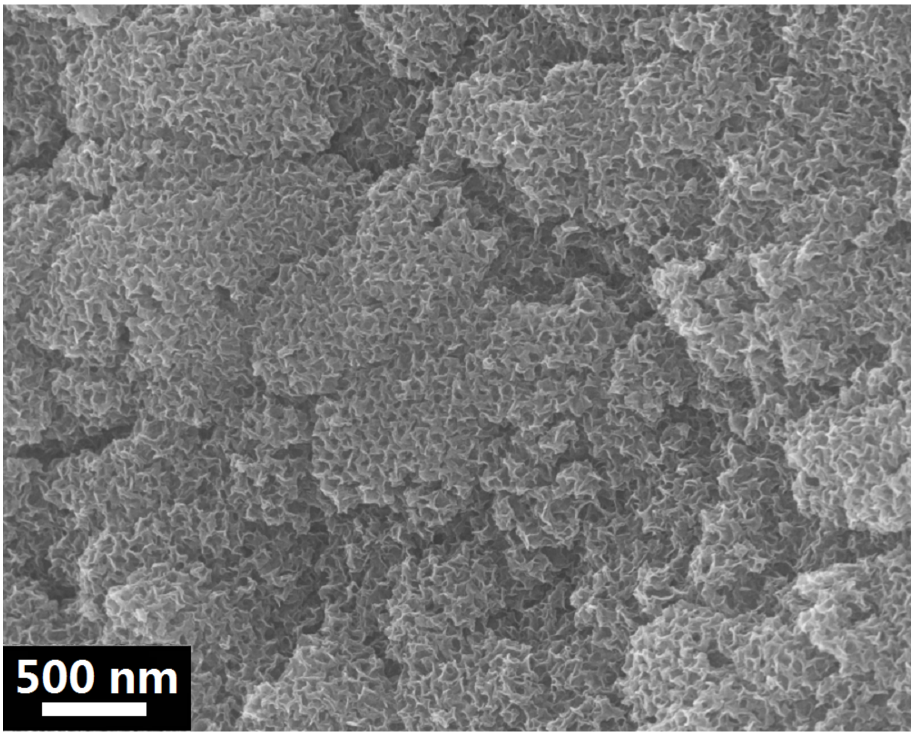

Fig. S6 SEM image of γ-MnO_2-SR sample.

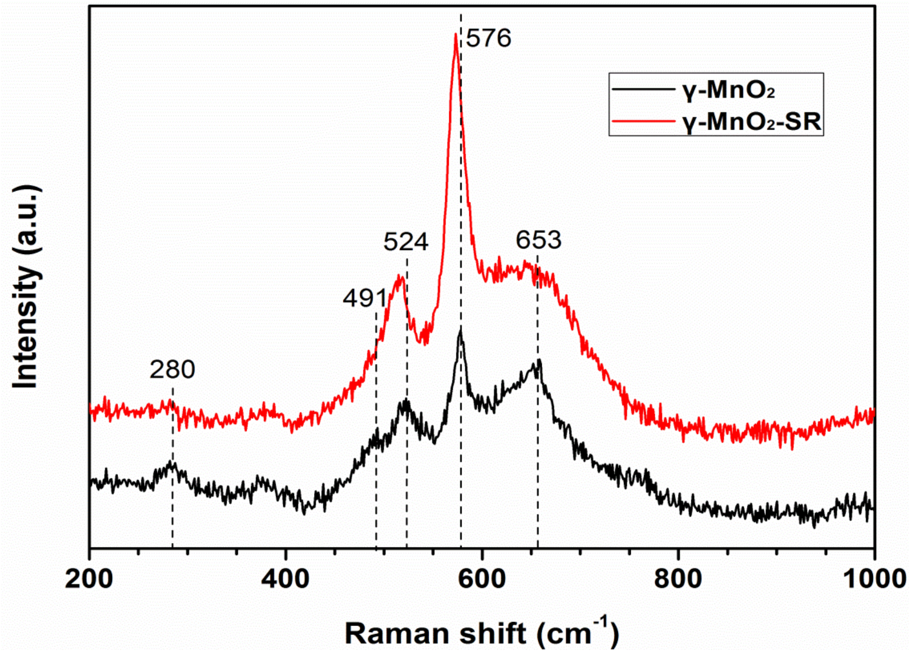

Fig. S7 Raman scattering spectra of γ-MnO_2 and γ-MnO_2-SR samples.

γ-MnO_2 sample was prepared by traditional method, which was mentioned in our previous work.[18] As shown in Fig. S7, the Raman spectrum of the γ-MnO_2 displays five main bands at 280, 491, 524, 576 and 653 cm^{-1}, which are fairly consistent with previous studies.[S1, S2] The peak located at 576 cm^{-1} is attributed to the asymmetric stretching vibration of the Mn-O bonds. For γ-MnO_2-SR sample, this peak moved towards lower Raman shifts. This phenomenon might be one of the evidences that the Mn-O bonds in γ-MnO_2-SR are weakened and longer.

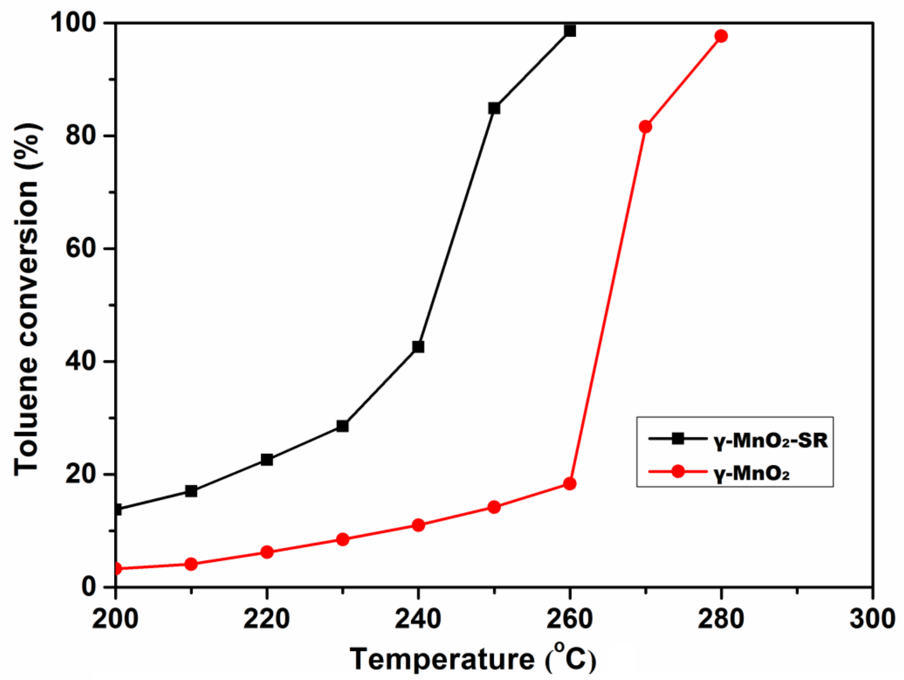

Fig. S8(a) Toluene conversion of γ-MnO_2 and γ-MnO_2-SR samples.

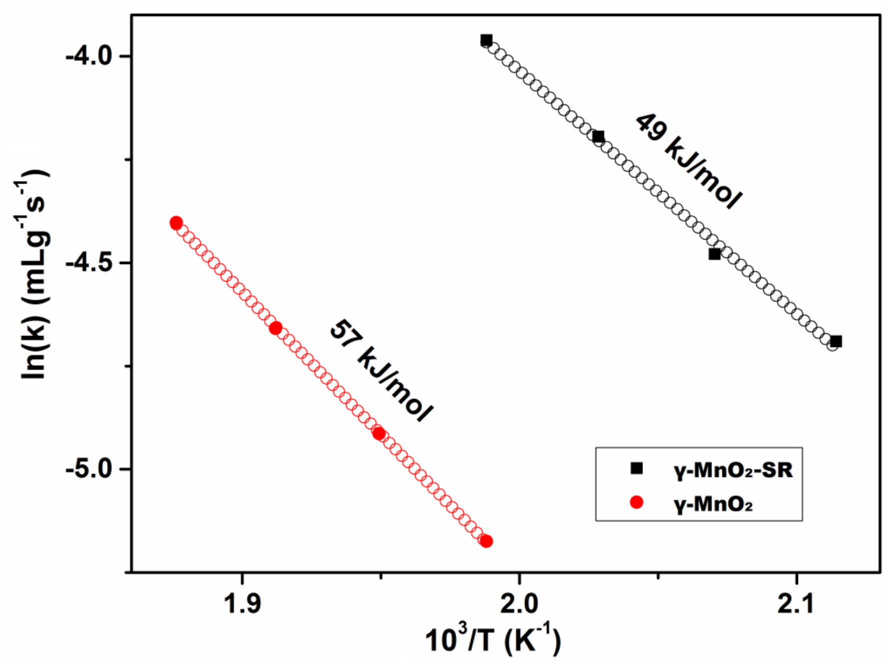

Fig. S8(b) Arrhenius plots of γ-MnO_2 and γ-MnO_2-SR samples.

From the activity profiles of toluene oxidation (Fig. S8(a)) over the γ-MnO_2-SR and on γ-MnO_2 samples, it can be found that the γ-MnO_2-SR possessed better catalytic activity. Meanwhile, activation energy was calculated to eliminate the effect of the surface area (Fig. S8(b)). The sample with lower activation energy can completely oxidize toluene more easily. It can be found that the γ-MnO_2-SR possessed the lower activation energy on toluene oxidation. Thus it is suggested that the porous structure will be benefit to the reaction of toluene oxidation.

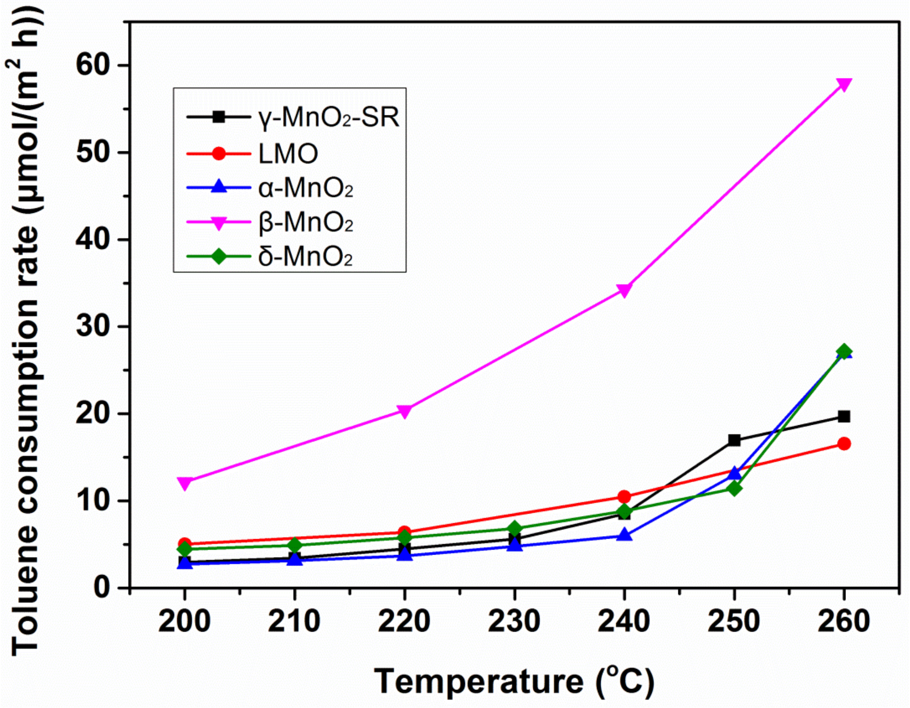

Fig. S9 Toluene consumption rate normalized per surface area as a function of reaction temperature over the five catalysts at GHSV = 120,000 mL/(g h).

Specific reaction rates of the samples have been calculated in Fig. S9. Toluene consumption rate for β-MnO_2 sample, which possess the lowest surface area, was the highest among the five catalysts. For other samples, toluene consumption rates were nearly the same (about 20 μmol/(m^2 h) at 260 °C). These results were similar to the previous literature.[S3] It is indicated that surface area is not the only influence factor of the catalytic activity. In this manuscript, "three-dimensional macroporous and mesoporous morphology and the γ-MnO_2-like structure were responsible for the excellent catalytic performance, in which the former favor the accessibility of toluene molecules to the catalyst and the latter improved the O_{latt} mobility of the material".

References

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