

Supplementary Information

Synthesis of a novel highly dispersed manganese oxide on porous calcium silicate for catalytic oxidation of toluene

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1. Experimental

1.1 Catalyst preparation

All of the chemicals applied to experiments were of analytical grade and were without further purification or modification. Manganese acetate ($\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, 99%), manganese nitrate (50 wt% $\text{Mn}(\text{NO}_3)_2$ solution) and manganese chloride ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, 99%) were purchased from Aladdin.

Synthesis of PCS: Industrial solid waste micro-silica powder and NaOH solution to generate a sodium silicate solution. $\text{Ca}(\text{OH})_2$ was added at a molar ratio of silicon and calcium of 1:1. The resulting solid powder was washed several times with ultrapure water, then put in an oven and dried at 105°C for 12h to get the PCS, and then the PCS was calcined in a tube furnace under flowing air from room temperature to 500°C at a heating rate of 5°C per minute and held for 3 h, that was used as the a support for the catalyst.

The PCS-supported manganese oxides catalysts were prepared by an impregnation method. $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, 50 wt% $\text{Mn}(\text{NO}_3)_2$ solution, and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ were used as precursors. Manganese oxide loading of the catalysts was nominally 15 wt%. The Mn precursor and PCS support were dissolved in ultrapure water. The Mn precursor solution was then added dropwise into the PCS aqueous solution under magnetic stirring with continuous stirring for 12 h at ambient temperature. The precipitates were then separated by filtration and washed several times with ultrapure water. The resulting solid products were then dried in an oven at 105°C for 10 h and calcined in a tube furnace under flowing air from room temperature to 500°C at a heating rate of 5°C per minute and held for 3 h. The resulting catalysts were denoted as $\text{MnO}_x\text{-Ac/PCS}$ ($\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ was the precursor), $\text{MnO}_x\text{-N/PCS}$ (50 wt% $\text{Mn}(\text{NO}_3)_2$ solution was the precursor), and $\text{MnO}_x\text{-Cl/PCS}$ ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ was the

precursor).

1.2 Catalyst characterization

The actual manganese contents of the catalysts were determined by an inductively coupled optical emission spectrometer (ICP-OES) on an Agilent 730 instrument. The N_2 adsorption-desorption isotherms were performed on Autosorb-6iSA surface aperture adsorption instrument (Quantachrome Corporation, USA) at liquid nitrogen temperature (-196°C). The specific surface area was calculated by the Brunauer Emmett Teller (BET) method and the pore structure parameters were calculated by the Barrett-Joyner-Halenda (BJH) method. All samples were degassed under vacuum at 300°C for 4 h to remove physically adsorbed impurities before the measurements. The powder X-ray diffraction (XRD) patterns of the catalysts were collected with a Bruker AXS D8 Advance X-ray diffractometer operating at 45 kv and 200 mA with a radiation source of $\text{Cu K}\alpha$ in range of $10\text{--}80^\circ$ with a resolution of 0.02° step size and a scan rate of $10^\circ/\text{min}$. The morphology of the catalysts was examined by scanning electron microscopy (SEM) images recorded on a HITACHI SU8020 apparatus at an accelerating voltage of 3.0 KV. The samples were coated with Au before measurement. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) observations used a FEI Tecnai G2 F30 microscope equipped with an energy dispersive X-ray (EDS) spectroscope with an acceleration voltage of 300 KV. Before testing, a suspension of the samples in ethanol was placed on a holey-carbon grid and then dried in air. X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB 250Xi from Thermo Fisher with monochromatic $\text{Al K}\alpha$ radiation. The binding energy values were calibrated using a C1s peak (284.8 eV). Electron paramagnetic resonance (EPR) profile spectra of catalysts were obtained by Bruker A300-10 spectrometer at room temperature. H_2 temperature-programmed reduction

(H₂-TPR) experiments were performed with an Autochem II 2920 analyzer (Micromeritics) equipped with a thermal conductivity detector (TCD). The catalyst was heated in 30 ml/min of 10 vol.% H₂ flow diluted with Ar between 40°C and 600°C with a heating rate of 10°C/min, before the TPR test, the catalysts were then pretreated in 30 ml/min of Ar at 300°C for 30 min to remove the adsorbed carbonates and hydrates.

1.3 Catalytic activity evaluation

Toluene catalytic oxidation tests used a continuous fixed-bed reactor at atmospheric pressure and a reaction temperature of 150–400°C. The catalytic reactor consisted of a quartz tube (8 mm in internal diameter and 350 mm in length). A K-type thermocouple was positioned in the catalyst bed to obtain accurate measurements of the catalyst temperature. The 0.2 g of catalyst (40-60 mesh) was mixed with 0.2 g of quartz to minimize the effect of possible hot spots, and both ends of the catalyst bed were fixed with quartz wool. Gaseous toluene was produced by N₂-bubbling in liquid toluene, and the sample was kept in a water bath at 20°C. The total flow rate of the reactant mixture was 100 ml/min, which consisted of 1000 ppm toluene, 21% O₂, and N₂ for the balance.

The toluene concentration of the inlet and exit gas stream was determined by on-line gas chromatography (GC-2014C, Shimadzu) equipped with a FID detector and the concentration of CO₂ in the exit was detected by an infrared gas analyzer (NK-500A, Xi'an Nuoke Instrument Co., Ltd.). The toluene concentration ($X_{C_7H_8}$) and CO₂ yield (Y_{CO_2}) was calculated according to the following equations:

$$X_{C_7H_8} = \frac{[C_7H_8]_{in} - [C_7H_8]_{out}}{[C_7H_8]_{in}} \times 100\%$$

$$Y_{\text{CO}_2} = \frac{[\text{CO}_2]_{\text{out}}}{7[\text{C}_7\text{H}_8]_{\text{in}}} \times 100\%$$

Here, $[\text{C}_7\text{H}_8]_{\text{in}}$ and $[\text{C}_7\text{H}_8]_{\text{out}}$ refer to the inlet and exit concentration of toluene and

$[\text{CO}_2]_{\text{out}}$ was the exit concentration of CO_2 .

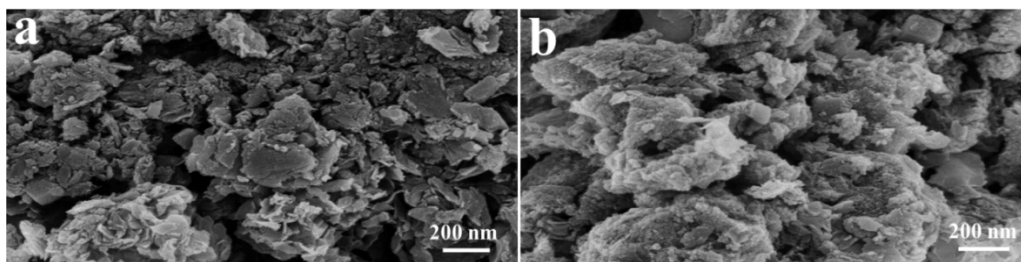


Fig.S1. SEM images of MnO_x-N/PCS catalyst (a) and MnO_x-Cl/PCS catalyst (b)

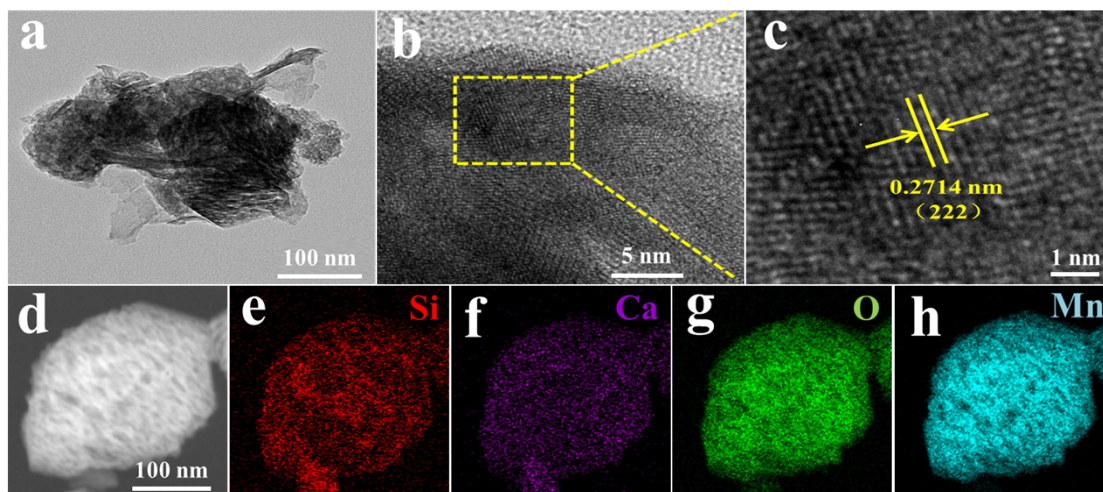


Fig.S2. TEM and corresponding to HRTEM images of $\text{MnO}_x\text{-N/PCS}$ catalyst (a, b, c), Elemental mappings images of $\text{MnO}_x\text{-N/PCS}$ catalyst (d, e, f, g, h)

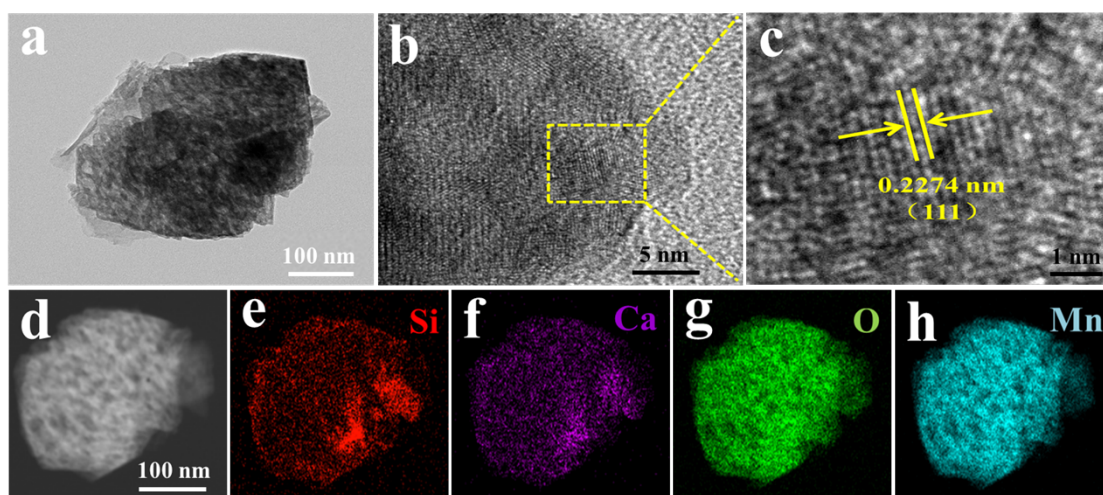


Fig.S3. TEM and corresponding to HRTEM images of MnO_x-Cl/PCS catalyst (a, b, c), Elemental mappings images of MnO_x-Cl/PCS catalyst (d, e, f, g, h)

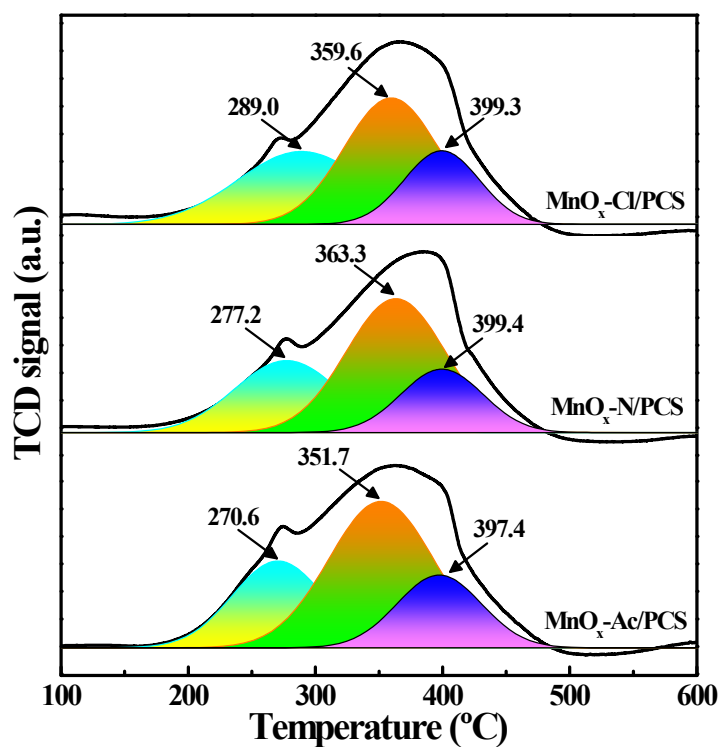


Fig.S4. H₂-TPR curves of the as-prepared catalysts.

Table S1. The hydrogen consumption of the Mn³⁺ and Mn⁴⁺ in as-prepared catalysts.

sample	H ₂ consumption (mmol/g)		
	Mn ³⁺	Mn ⁴⁺	Mn ³⁺ / Mn ⁴⁺
MnO _x -Ac/PCS	0.686	0.352	1.95
MnO _x -N/PCS	0.592	0.333	1.78
MnO _x -Cl/PCS	0.538	0.420	1.28

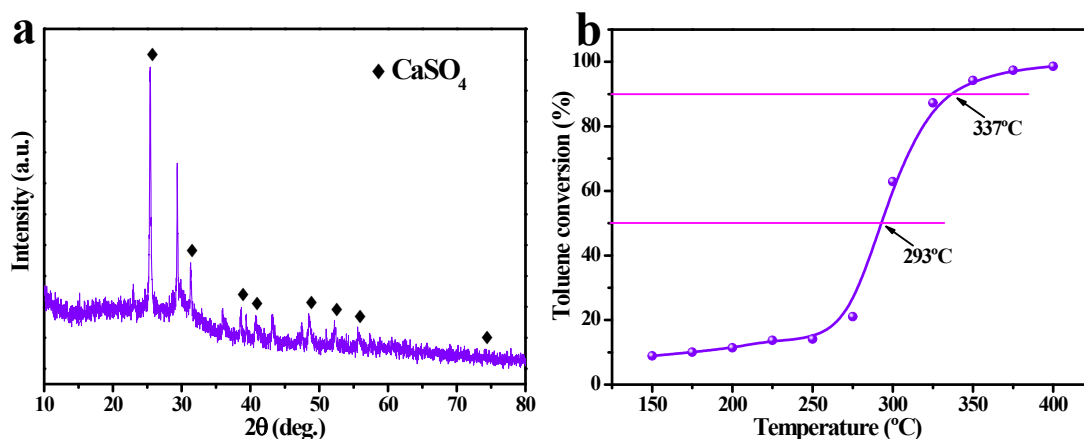


Fig.S5. The powder XRD patterns (a) and the toluene catalytic activity (b) of the MnO_x-S/PCS catalyst

We prepared MnO_x-S/PCS catalyst using manganese sulfate as the precursor and the powder XRD patterns is shown in **Fig. S5(a)**, the diffraction peaks at 25.4°, 31.4°, 38.6°, 40.8°, 48.7°, 52.2°, 55.7° and 74.2° are correlated with the standard CaSO₄ (PDF#37-1496), which is maybe due to the reaction between PCS and Mn(SO₄)₂·H₂O during the preparation of the catalyst, it has a toxic effect on the catalyst, leading to the worst catalytic performance, we can see from the **Fig. S5(b)** that the T_{50} was 293°C and the T_{90} was 337°C, respectively. Therefore, manganese sulfate is not suitable as catalyst precursor in this work.

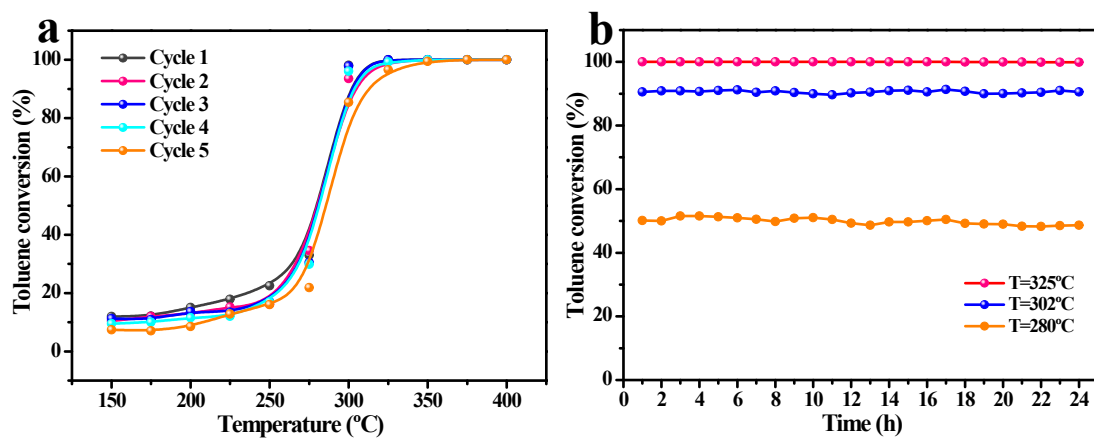


Fig.S6. The toluene catalytic oxidation performance during five consecutive cycles experiment (a) and the thermal stability during continuous online reaction experiment at 280, 302 and 325°C (b). (The WHSV of 30000 ml/(g h) and the toluene concentration of 1000 ppm)