Catalytic Degradation of Toluene over MnO$_2$/LaMnO$_3$: Effect of Phase Type of MnO$_2$ on Activity

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Experimental details

Text S1. Chemicals and materials

All the reagents for the preparation of catalysts were A.R. grade and were used directly without further purification. Potassium permanganate ($KMnO_4$), manganese sulfate monohydrate ($MnSO_4 \cdot H_2O$), lanthanum nitrate hexahydrate ($LaMnO_3 \cdot 6H_2O$), and toluene were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

Text S2. Characterization

The crystal structures of the samples were analyzed by powder X-ray diffraction (XRD, LabX XRD-6000, Cu Kα, λ=1.5406 Å, Shimadzu, Kyoto, Japan). The surface morphology was checked using field emission scanning electron microscopy (SEM, MIRA3-LHM, TESCAN Czech & BRUKER, Hamburg, Germany). X-ray photoelectron spectroscopy (XPS) was carried out on an RBD upgraded PHI-5000C ESCA system (Perkin-Elmer, Waltham, MA, USA) with Mg Ka radiation (h_v=1253.6 eV). Hydrogen temperature-programmed reduction (H_2-TPR) experiments were carried out on a chemical adsorption analyzer (Autochem II 2920, Micromeritics, Norcross, GA, USA) under H_2/Ar gas flow at a rate of 10 °C/min up to 600 °C. Before TPR measurement, the samples were pre-treated at 300 °C for 1 hr in Ar (50 ml·min^{-1}) to remove impurities adsorbed on the surface. A rare content of other byproducts in gas due to incomplete VOC mineralization was

detected by a thermal desorption/gas chromatograph mass spectrometer (TD/GC–MS) instrument. N_2 adsorption-desorption isotherms and Brunauer–Emmett–Teller (BET) specific surface area were obtained on Autosorb-iQ surface aperture adsorption instrument (Quantachrome Corporation, Boynton Beach, FL, USA) by N_2 physisorption at -196 °C. The pore size distributions were evacuated using the Barrett-Joyner-Halenda (BJH) method.

The reactant intermediate that occurred on the catalyst was investigated by in situ diffuse reflectance infrared Fourier transform spectroscopy (Nicolet 6700, Tübingen, Germany) (DRIFTS) experiment.

Text S3. Preparation of LaMnO$_3$

LamMnO$_3$ was prepared by direct calcination without adding water as a solvent of metal salts and citric acid. The specific preparation process was as follows: 5 mmol of $Mn(Ac)_2 \cdot 4H_2O$, 5 mmol of $La(NO_3)_3 \cdot 6H_2O$, and 5 mmol of citric acid were mixed directly. Then, the mixed liquid was raised to 750 °C at 2 °C/min in air and maintained at 750 °C for 2 h.

Text S4. Preparation of MnO$_2$ with different crystal phases

1. Preparation of α-MnO$_2$

The typical preparation procedure of α-MnO$_2$ was as follows: 1.25 g of $KMnO_4$ and 0.53 g of $MnSO_4 \cdot H_2O$ were added to 80 mL deionized water and

agitated for 30 min at room temperature. The above-mixed solution was transferred to a 100 mL PTFE kettle, and the hydrothermal reaction was carried out at 160 °C for 12 h. The filtered precipitate was dried overnight at 80 °C and then calcined at 400 °C in a muffle furnace for 4 h.

2. Preparation of δ-MnO$_2$

The typical preparation procedure of δ-MnO$_2$ was as follows: 1.50 g of KMnO$_4$ and 0.28 g of MnSO$_4$·H$_2$O were added to 80 mL deionized water and agitated for 30 min at room temperature. The above-mixed solution was transferred to a 100 mL PTFE kettle, and the hydrothermal reaction was carried out at 160 °C for 12 h. The filtered precipitate was dried overnight at 80 °C and then calcined at 400 °C in a muffle furnace for 4 h.

3. Preparation of β-MnO$_2$

The typical preparation procedure of β-MnO$_2$ was as follows: 1.69 g of MnSO$_4$·H$_2$O and 2.28 g of (NH$_4$)$_2$S$_2$O$_8$ were added to 80 mL deionized water and agitated for 30 min at room temperature. The above-mixed solution was transferred to a 100 mL PTFE kettle, and the hydrothermal reaction was carried out at 160 °C for 12 h. The filtered precipitate was dried overnight at 80 °C and then calcined at 400 °C in a muffle furnace for 4 h.

4. Preparation of γ-MnO$_2$

The γ-MnO$_2$ was synthesized via the redox reaction of KMnO$_4$ and MnSO$_4$ in an acidic aqueous. The preparation procedure was as follows: 0.3169 g of MnSO$_4$ was dissolved in 60 ml of deionized water. Under vigorous

stirring at 80 °C in a water bath, 1 ml of concentrated H_2SO_4 and 60 ml of 0.1 mol/L $KMnO_4$ were added by dripping. After additional stirring at 80 °C for 24 h. Afterward, the as-obtained black precipitate was washed and then dried at 60 °C, and the γ-MnO_2 sample was prepared.

Text S5. Normalized reaction rate equation

The specific surface area plays an important role in catalyst reaction activity. To rule out its impact as far as possible, the normalized reaction rate (r, $mol \cdot m^{-2} \cdot s^{-1}$) is derived from the following formula [45–47]:

$$r = \frac{C_{in} \cdot F}{m_{cat} \cdot S_{BET}} \cdot \ln\left(\frac{1}{1-X}\right) \qquad \text{(eq. S1)}$$

where r is the normalized reaction rate in a unit of $mol \cdot m^{-2} \cdot s^{-1}$; C_{in} is the toluene concentration in the inlet gas streams, zero dimension (ppm/1 000); F is the flow rate of toluene in a unit of $mol\ s^{-1}$; m_{cat} is the amount of catalyst, g; S_{BET} is the surface area calculated by N_2 physisorption results obtained at P/P_0 = 0.05–0.30, $m^2\ g^{-1}$; X is the toluene conversion efficiency.

The apparent reaction rates of prepared catalysts are calculated at low reaction efficiency (< 10%) [2] to reflect their inherent catalytic activities, where 210 °C was chosen as the basic calculation condition.
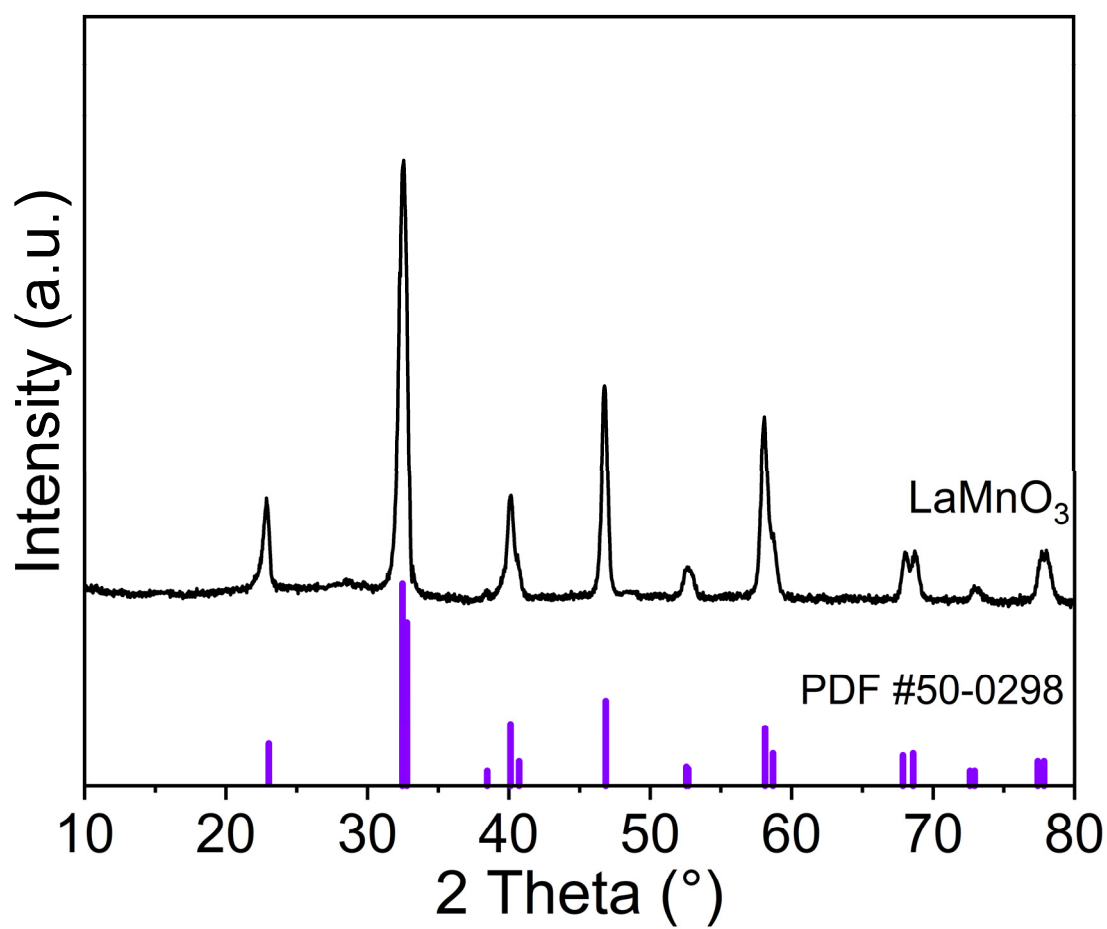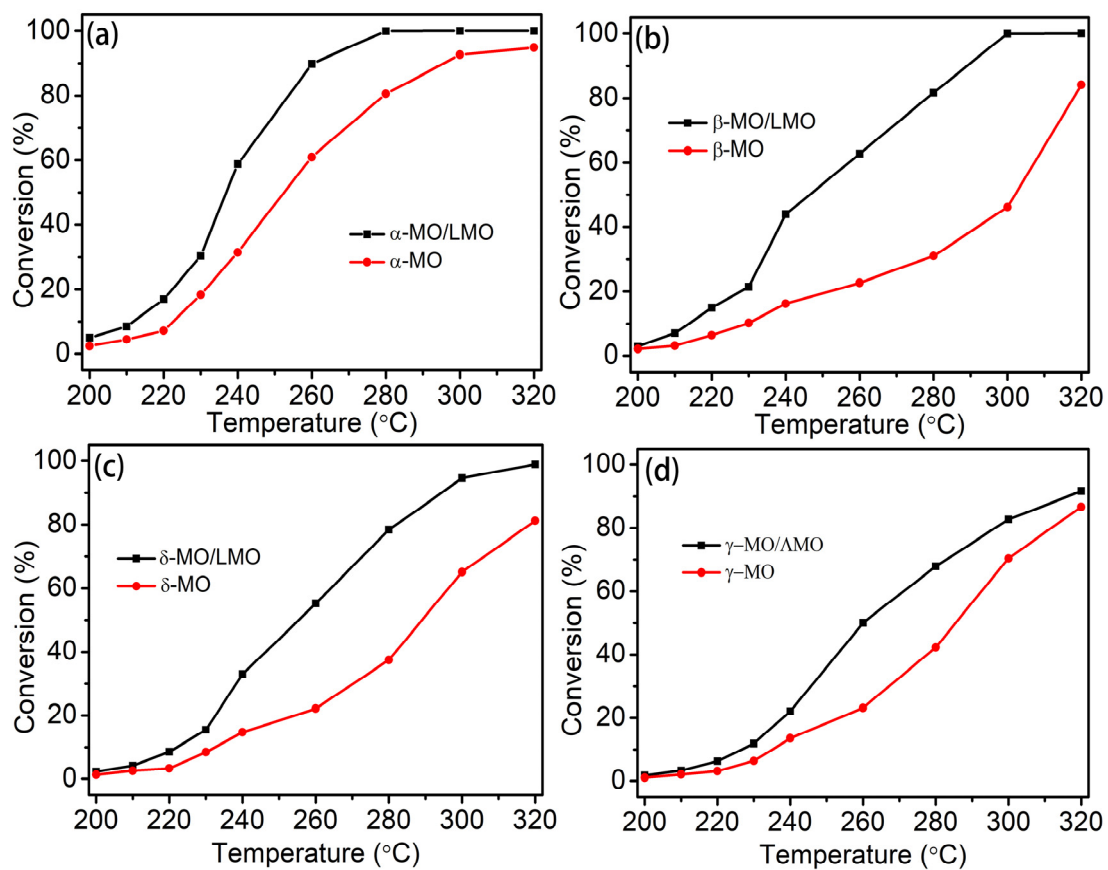
Figure S1. XRD patterns of LMO.

Figure S2. Toluene oxidation over of (**a**) α-MO and α-MO/LMO, (**b**) β-MO and β-MO/LMO, (**c**) δ-MO and δ-MO/LMO, (**d**) γ-MO and γ-MO/LMO