Supporting Information

Facet control of manganese oxides with diverse redox abilities and acidities for catalytic removing the hazardous 1,2-dichloroethane

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**S1. Preparation**

**α-MnO₂**: 1.35 g of KMnO₄ and 3.0 mL of HCl (37 wt%) were added to deionized water. After stirring for 30 min, the solution was transferred to a Teflon-lined stainless-steel autoclave, sealed, and maintained at 120 °C for 12 h in an electric oven.

**β-MnO₂**: The mixture of 1.69 g MnSO₄ and 2.28 g (NH₄)₂S₂O₈ was added to deionized water with stirring for 30 min. Then, the solution was transferred to a Teflon-lined stainless-steel autoclave, sealed, and maintained at 140 °C for 12 h.

**γ-MnO₂**: The mixture of 6.32 g MnSO₄ and 8.56 g (NH₄)₂S₂O₈ was added to deionized water. After stirring for about 30 min, the solution was transferred to a Teflon-lined stainless-steel autoclave, sealed, and maintained at 90 °C for 24 h in oven.

**δ-MnO₂**: 1.35 g of KMnO₄ and 1.0 mL of HCl (37 wt%) were added to deionized water. After stirring magnetically for about 30 min, the solution was transferred to a Teflon-lined stainless-steel autoclave and crystallized at 100 °C for 12 h.

After the hydrothermal reaction, the autoclave was cooled to room temperature. The sediment was centrifuged, washed with distilled water and ethanol several times, dried at 80 °C for 12 h, and then calcined at 300 °C for 8 h to obtain the corresponding samples.

**S2. Characterization**

The crystallographic information of sample was investigated by X-ray diffraction using a diffractometer equipped with Cu Kα radiation (λ = 0.15406 nm, D8FOCUS, Bruker). Diffractograms were collected in the 2θ range between 10° and 80° by step of 0.1°. Phase identification was made by a comparison with JCPDS database.

The information of specific surface area (S_{BET}) was collected by N₂ sorption isotherm using a Quanta chrome Autosorb IQ analyzer at liquid N₂ temperature (-196 °C). Before analysis, samples were outgassed at 300 °C under vacuum for 10 h. Brunauer-Emmett-Teller (BET) surface area was calculated using experimental points at a relative pressure of P/P₀ = 0.05~0.35.

H₂-TPR experiment was carried out in a chemisorption device. Prior to the measurement, the samples were degassed under flowing nitrogen (30 ml/min) at 300 °C for 1 h. After cooling in nitrogen to 100 °C, a 5% H₂/N₂ flow of 30 ml/min was introduced to pass through a quartz reactor containing the sample (100 mg). The consumption of H₂ along with heating temperature was online recorded by a thermal conductivity detector (TCD, Huasi, China) and the signals of TCD were collected.
from 100°C to 600°C in nitrogen flow.

Temperature-programmed desorption of O\(_2\) (O\(_2\)-TPD) was also analyzed with an online mass spectrometer. The concentrations of O\(_2\) and CO\(_2\) were determined using m/z=32 and m/z=44, respectively. For the O\(_2\)-TPD, 0.1 g of catalyst was pretreated at 200 °C with Ar for 30 min, and then 10% O\(_2\)/Ar was introduced on the surface of the catalyst for 60 min at 100 °C. Next, the sample was purged with Ar for 1 h to remove the exterior adsorbed molecular oxygen and the catalyst was cooled down to ambient temperature. Finally, the microreactor was heated from ambient temperature to 650 °C with a heating rate of 5 °C·min\(^{-1}\) under Ar flow.

The NH\(_3\) temperature programmed desorption (NH\(_3\)-TPD) experiment was taken on a device with a thermal conductivity detector (TCD, Huasi, China). The sample (100 mg) was first pretreated at 300°C under nitrogen flow for 0.5 hr. After cooling to 100°C, the sample was saturated in 10% NH\(_3\)/N\(_2\) atmosphere for 1 h and then exposed in nitrogen atmosphere for 0.5 h to eliminate the influence of physisorbed NH\(_3\). Finally, the signals of TCD were collected from 100°C to 600°C in nitrogen flow.

A S-4800 (Hitachi, Japan) scanning electron microscope (SEM) was employed to characterize the morphology of the prepared MnO\(_2\) solids (the accelerating voltage is 5.0 kV). The powders were coated onto a conductive tape. Besides, a JEM-2100 (Jeol, Japan) high-resolution transmission electron microscopy (HRTEM) was also employed to observe the crystal lattice fringe and internal microstructure (the operating voltage is 200 kV).

X-ray photoelectron spectroscopy (XPS) instrument (Shimadzu, Japan) equipped with a monochromatic Mg/Al K\(\alpha\) was used to analyze the superficial layer properties. The binding energy was calibrated by the C 1s peak (B.E.=284.8eV) as a reference. The surface composition and chemical state were determined according to the position and areas of binding energies of Mn 2p, Mn 3s and O 1s peaks.

The in situ DRIFTS experiments were performed using an infrared spectrometer (TENSOR 27, BRUKER) that was configured with liquid N\(_2\)-cooled highly sensitive mercury cadmium telluride (MCT) detector. The reaction chamber (Praying Mantis, Harrick) as a diffuse reflection accessory included a diffuse reflectance cell (Harrick) with CaF\(_2\) windows and a heating cartridge that could control the desired temperatures. Before the test, about 50mg finely ground samples were padding in the in situ
chamber and heated under flowing Ar at 300 °C for 1 h to remove water from the surface and pores of the catalyst, the samples were then cooled to 50°C in Ar atmosphere. After that, the gaseous mixture of Ar + O₂ +1, 2-DCE with a flow rate of 40 mL/min and 400 ppm 1, 2-DCE, 20% O₂ in Ar was introduced into the chamber. The spectra were collected in 64 scans at a resolution of 4 cm⁻¹ within 850–3800 cm⁻¹. The sample was tested in the range of 50–300 °C.

S3. Temperature-programmed oxygen isotopic exchange (OIE) reaction

This experiment is performed on an oxygen isotope device, which includes a vacuum pump, a circulation pump, a heating furnace, an U-shaped micro-reaction tube (V = 70 cm³), and many gas pipelines, the signals of reactants were recorded by mass spectrometer (OmniStar, Germany). The sample (100 mg) was pretreated in O₂ atmosphere by heating to 300°C. When the temperature dropped to 200°C, redundant ¹⁶O₂ was removed under the condition of dynamic vacuum for 30 min. Then, 65.0 ± 1.5 mbar of pure Oxygen isotopic (¹⁸O₂) was introduced into the reaction system for OIE reaction, and the catalyst was heated to 600°C and the mass spectrometer is turned on at the same time. The concentration changes of ¹⁸O₂ (P₃₆), ¹⁶O₂ (P₃₂), and ¹⁶O¹⁸O (P₃₄) during the oxygen exchange reaction were recorded by mass spectrometer. Besides, N₂ (m/z=28) was also recorded in order to detect possible vacuum system leaks. Figure S1 shows a schematic diagram of an oxygen isotopic exchange device.

Figure S1: Schematic diagram of the oxygen isotopic exchange experiment

S4. Computational details
Spin-polarized Periodic Density Functional Theory (DFT) calculations were accomplished with the Vienna simulation package VASP \[^{S1}\]. The projector augmented plane wave (PAW) approach \[^{S2-S3}\] was applied to the electron-ion interaction together with generalized gradient GGA-PW91 \[^{S4}\].

**S5. Catalytic activity and products yield**

The following equations were used to calculate the conversion of 1,2-DCE as well as the CO, CO\(_2\) and HCl yields:

1. **1,2-DCE conversion (%)**
   \[
   \text{1,2-DCE conversion (\%)} = \left( \frac{[1,2-\text{DCE}]_{\text{in}} - [1,2-\text{DCE}]_{\text{out}}}{[1,2-\text{DCE}]_{\text{in}}} \right) \times 100
   \]

2. **CO yield (%)**
   \[
   \text{CO yield (\%)} = \frac{[\text{CO}]}{[\text{CO}] + [\text{CO}_2] + x[\text{C}_x\text{H}_y\text{Cl}_z]} \times 1,2-\text{DCE conversion} \times 100
   \]

3. **CO\(_2\) yield (%)**
   \[
   \text{CO}_2 \text{ yield (\%)} = \frac{[\text{CO}_2]}{[\text{CO}] + [\text{CO}_2] + x[\text{C}_x\text{H}_y\text{Cl}_z]} \times 1,2-\text{DCE conversion} \times 100
   \]

4. **HCl yield (%)**
   \[
   \text{HCl yield (\%)} = \frac{[\text{HCl}]}{[\text{HCl}] + 2[\text{Cl}_2] + z[\text{C}_x\text{H}_y\text{Cl}_z]} \times 1,2-\text{DCE conversion} \times 100
   \]

5. **C\(_x\)H\(_y\)Cl\(_z\) yield (%)**
   \[
   \text{C}_x\text{H}_y\text{Cl}_z \text{ yield (\%)} = \frac{x[\text{C}_x\text{H}_y\text{Cl}_z]}{[\text{CO}] + [\text{CO}_2] + x[\text{C}_x\text{H}_y\text{Cl}_z]} \times 1,2-\text{DCE conversion} \times 100
   \]
Figure S2: Yields of (a) CO, (b) cis-1,2-C₂H₂Cl₂, (c) trans-1,2-C₂H₂Cl₂, (d) C₂H₃Cl, (e) 1,1-C₃H₆Cl₂, (f) CCl₄ and (g) 1,1,2-C₃H₃Cl₃ over α-, β-, γ- and δ-MnO₂ samples.

Figure S2 shows the byproduct yields of 1,2-dichloroethane (1,2-DCE) combustion.
over α-, β-, γ- and δ-MnO₂ samples. α-MnO₂ presents a gradual increasing trend for CO yield, and cannot observe a decreasing trend. β-MnO₂ exhibits the highest CO yield, owing to the poor redox ability. γ-MnO₂ shows a trend of increasing first and then decreasing, which means CO can be further oxidized at high temperatures. Similar to the α-MnO₂, δ-MnO₂ also displays the same trend because of the production of too many chlorined byproducts, which hinders CO further transformation. No obvious chlorined byproducts are found on α- and γ-MnO₂, but there are many chlorined byproducts are found on β- and δ-MnO₂, especially on δ-MnO₂. Vinyl chloride (C₂H₃Cl) (Fig. S2 d) is produced due to the removal of 1,2-DCE by HCl elimination at 300°C. Then at 400 °C, an electrophilic substitution reaction between HCl and vinyl chloride was followed to form cis-dichloroethylene and trans-dichloroethylene (cis-1,2-C₂H₂Cl₂ and trans-1,2-C₂H₂Cl₂) (Fig. S2 b and c), some of which also become 1,1-dichloroethene (1,1-C₂H₂Cl₂) (Fig. S2 e), part of 1,2-DCE breaks the C-H and C-C bond, gradually becomes CCl₄ (Fig. S2 i), and this part of the polychlorinated byproducts was formed at last without further transformation, the results show that the yield of HCl at high temperature (> 400°C) was very low. Similar to δ-MnO₂, the overall yield of HCl from β-MnO₂ was also low, and several reaction products (such as cis-1,2-dichloroethene, trans-1,2-dichloroethene, 1,1-dichloroethene and tetrachloromethane) are found to be identical to δ-MnO₂. Notably, the presence of 1,1,2-trichloroethane (1,1,2-C₃H₃Cl₃) (Fig. S2 g) was noticed on the β-MnO₂, indicating that the dehydrochlorination and chlorination of vinyl chloride might take place.
**S7. Cl mass balance of all these products**

**Figure S3.** The chlorine mass balance during the 1, 2-DEC oxidation over (a) α-, (b) β-, (c) γ- and (d) δ-MnO₂

It can be found that the sum of the yields of different detected Cl-containing substances is close to 100% (Figure S3).

**S8. Catalytic stability test**

**Fig. S4.** Stability test of γ-MnO₂
The stability of the best-performing $\gamma$-MnO$_2$ catalyst is investigated as shown in Fig. S4. This catalyst was tested for 1, 2-DCE oxidation at 400 °C for 40 h. After long-term test, the 1, 2-DCE conversion decreased from 89% to 74%. It is speculated that the accumulation of chlorine over surface caused this deactivation in activity. In general, the investigated sample of $\gamma$-MnO$_2$ exhibited certain stability during activity test.

**S9. Blank experiment**

![Figure S5](image)

**Figure S5.** The blank experiment tested for decomposition 1, 2-DCE without catalysts.

A blank experiment in the absence of catalyst under the same experimental atmosphere for 1, 2-DCE oxidation was also conducted (Figure S5). The conversion of 1, 2-DCE was 40% at 500 °C with C$_2$H$_3$Cl as the main product, whose yield increased with temperature and reached 35% at 500 °C. In addition, the HCl and CO$_2$ yield were 23% and 2.15%, respectively. Therefore, it is necessary to further eliminate C$_2$H$_3$Cl using a suitable catalyst as well as improve the HCl and CO$_2$ yields.
References


