Supporting Information for

δ-MnO₂ with ultrahigh Mn⁴⁺ fraction: highly active and stable for catalytic wet air oxidation of phenol under mild conditions

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Preparation of MnO₂

The synthetic procedure for self-reactivated δ -MnO₂ as follows: 0.91 g of Manganous nitrate solution (Sinopharm 49-51 wt. %) was mixed with 1.0 g of potassium permanganate (Sinopharm 99.5%) in 20 mL of deionized water. In another container, 0.78 g of potassium hydroxide (Guanghua 85%) was dissolved in 44 mL of deionized water. The above solutions were mixed together and stirred for 30 min. After stirring, the mixed solution was transferred into a 100 mL Teflon-lined stainless autoclave and heated up to 160 °C for 12 h. Once the autoclave was cooled to room temperature, the precipitates were washed and filtrated by deionized water. The obtained precipitates were dried at 100 °C for 12 h. The α -MnO₂ was synthesized exactly the same as δ -MnO₂, only without the addition of potassium hydroxide.

The amorphous α -MnO₂ was synthesized according to Kang.¹ The preparation procedures as follows: 1.58 g of potassium permanganate (Sinopharm 99.5%) and 3.68 g of manganese acetate (Sinopharm 99 wt. %) were individually dissolved in 50 mL of deionized water. After stirring for 30 min, manganese acetate solution was drop-wisely added into potassium permanganate solution under stirring. The pH of the solution was then adjusted to 4 by hydrochloric acid (Sinopharm 36-38 wt. %). The solution was stirred for 4 h, and the precipitates were filtered and washed by deionized water. The collected precipitates were dried in oven at 85 °C for 12 h.

X-ray diffraction patterns (XRD)

XRD patterns for manganese oxide catalysts were collected on a Rigaku X-ray diffractometer. Cu K_a radiation was used as the X-ray source. The voltage and current were set to 40 kV and 30 mA. The samples were scanned in the range of 10 °C to 70 °C at a scanning speed of 10 ° min⁻¹.

N2 adsorption-desorption experiments

 N_2 adsorption-desorption experiments were performed at 77 K using Micromeritics ASAP 2020 instrument. All samples were degassed at 200 °C for 2 h in vacuum. The specific surface areas were calculated using Brunauer-Emmett-Teller (BET) method.

Catalytic wet air oxidation (CWAO) of phenol

The CWAO process was carried out in a 50 mL autoclave reactor with a magnetic mixer. Typically, 20 mL of phenol solution (1000 ppm) and 0.1 g of catalysts (5gL⁻¹) were added into the reactor. The reactor was purged using N₂ and raised to 70 °C. When the desired temperature was reached, 2 MPa of oxygen was charged into the reactor. The reactor was kept at 70 °C for 3 h, and then cooled to room temperature. The reacted solution was withdrawn, the phenol concentration was analyzed by an Agilent 1100 high performance liquid chromatography (HPLC) using a C₁₈ column. Total organic carbon (TOC) was measured by a Shimadzu TOC-L analyzer. The leached Mn was measured using a Shimadzu AA-6880 atomic absorption spectroscopy (AAS). The pH of phenol solutions were measured using Eutech pH 700.

Temperature-programmed reduction by H₂ (H₂-TPR)

The H₂-TPR was performed using a thermal conductivity detector (TCD). 30 mg of sample was pretreated in argon (AR, 99.999%) at 250 °C for 1 h with a flow rate of 30 mL min⁻¹. After the sample was cooled to 40 °C, the gas was switched to 10% H₂/Ar gas, and the flow rate was set to 60 mL min⁻¹. The temperature was allowed to reach to 800 °C at a ramp of 10 °C min⁻¹.

Temperature-programmed desorption of oxygen (TPD-O₂)

The TPD-O₂ profiles of each catalyst were measured using Micromeritics Auto Chem II 2920. Typically, 100 mg of catalyst was loaded into a U-shaped quartz tube. The sample was saturated with oxygen (O₂, 99.999%) at 250 °C for 1 h. After cooled to 100 °C, the gas was switched to helium (He, 99.999%) for 1 h. The catalyst was then raised to 900 °C at a ramp of 10 °C min⁻¹. The desorption of O₂ was detected using a mass spectrometer.

X-Ray Photoelectron Spectra (XPS)

XPS were collected from the PHI Quantum 2000. Al K_{α} radiation was used as the x-ray source (1846.6 ev). The binding energy of each spectrum was calibrated with the reference to C1s peak at 284.6 eV.



Fig. S1 XRD pattern of amorphous α -MnO₂.



Fig. S2 TOC conversion using different MnO₂ based catalysts. Reaction conditions: 100 mg of catalyst, 20 mL of phenol solution (1000 ppm), 70 °C, 2 MPa O₂, 3 h.



Fig. S3 Mn 2p XPS spectra of the MnO₂ catalysts



Fig. S4 O 1s XPS spectra of the MnO_2 catalysts



Fig. S5 The XRD patterns of fresh and used $\delta\text{-MnO}_2$ catalysts.



Fig. S6 pH values of the reacted phenol solutions using δ -MnO₂ and α -MnO₂ as catalysts.

References

1. C. Wei, C. Xu, B. Li, H. Du, D. Nan and F. Kang, J. Power Sources, 2013, 234, 1-7.