Highly Efficient α-Mn₂O₃@α-MnO₂-500 nanocomposite for Peroxymonosulfate Activation: Comprehensive Investigation of Manganese Oxides

Aimal Khan^a, Huabin Wang^b, Yong Liu^b, Ali Jawad ^{a,b}, Jerosha Ifthikar^a, Zhuwei Liao^b,

Ting Wang^a and Zhuqi Chen^a*

^a Key laboratory of Material Chemistry for Energy Conversion and Storage, Ministry of

Education; Hubei Key laboratory of Material Chemistry and Service Failure, School of

Chemistry and Chemical Engineering, Huazhong University of Science and Technology,

Wuhan 430074, PR China;

^b School of Environmental Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, PR China,

* Corresponding author:

E-mail address: zqchen@hust.edu.cn (Zhuqi Chen);

Supporting Information

Text S1.

Materials : Potassium permanganate (KMnO₄), maleic acid (C₄H₄O₄), manganese sulfate monohydrate (MnSO₄•H₂O), ammonium persulfate ((NH₄)₂S₂O₈), 80% hydrazine solution, sodium hydroxide (NaOH), tert-butyl alcohol (TBA), ethanol (CH₃CH₂OH), sodium sulfate (Na₂SO₄), sodium perchlorate (NaClO₄), potassium dihydrogen phosphate (KH₂PO₄), methanol of HPLC grade, phenol (C₆H₅OH), H₂O₂ (30%) and potassium peroxodisulfate (PDS), phenol, 4-chlorophenol (4-CP), 2,4-Dichlorophenol (2,4-DCP), 2,4,6-Trichlorophenol (2,4,6-TCP), p-Hydroxybenzoic acid (PHBA) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). MnO₂ was purchased from Xiya Reagent, 2,2,6,6-tetramethyl-4-piperidinol (TMP, 99%) and sodium azide (NaN₃) were purchased from Sigma-Aldrich, oxone (2KHSO₅•KHSO₄•K₂SO₄) and 5, 5dimethyl-1-pyrolene-N-oxide (DMPO) (98%) were purchased from Adamas Reagent Co., Ltd. These chemicals were used as received without further purification.

Catalytic degradation of phenol

Phenol degradation experiments were conducted with 25 ppm phenol solution (20 mL) in a 50 mL conical flask. 0.003 g catalyst and 1 mM PMS were both added into the solution to initiate the reaction at 25°C with water bath and constant magnetic stirring at 200 rpm. Samples were taken from the reaction mixture with an interval of 10 min, and were analyzed to determine the amount of phenol. Similarly, quenching experiments were conducted under identical conditions with the addition of extra quenching agents such as such as ethanol (EtOH), tert-butyl alcohol (TBA) and sodium azide (NaN₃) for radicals. For the recycle tests, nanorod catalyst of α -Mn₂O₃@ α -MnO₂ was filtered, washed with

deionized water dried at 90 °C for 12 h, and used for recycle test in the next round under identical conditions.

Thermodynamic tests

First order kinetic model (equation 1) was used for the curve fitting of oxidative degradation, whereas k was the first order rate constant, C was the detected concentration after certain reaction time (t), and C_0 was the initial concentration.

$$\ln\left(\frac{C}{C_0}\right) = -kt \tag{1}$$

Kinetic rate constants of phenol degradation by α -Mn₂O₃@ α -MnO₂ were measured separately under different temperatures of 25, 35 and 45 °C, respectively. The correlation between constants and temperatures was fitted by the Arrhenius relationship, based on which the activation energy was calculated.

Analysis of samples

The concentration of phenol was determined by high performance liquid chromatography (HPLC FL-2200) with C18 column (250 mm× 4.6 mm) and UV detector at λ = 220 nm. The mobile phase was taken by the combination of 70% methanol (HPLC grade) and 30% water (70:30, v/v) for phenol, 4-CP, 2,4-DCP and 2,4,6-TCP; methanol and 0.03 M acetic acid (40:60 v/v) with λ = 270 nm for PHBA. Furthermore, after the degradation of phenol, concentration of leached metal ions was determined by atomic absorption spectroscopy (AAS) ICE 3000 (USA).

The experimental method in situ characterization of the catalyst.

Fourier transform infrared (FTIR) spectra of the samples were carried out on VERTEX 70 FTIR spectrometer in the range of 400-4000 cm⁻¹. α -Mn₂O₃@ α -MnO₂ nanocatalyst (50 mg) was added into 10 mL of Milli-Q water (pH 6.5) or PMS solution (20mM) and pH of

the solution was fixed to 6.5 by addition of aqueous NaOH in glass tubes before analysis.

In situ Raman analysis of the catalyst surface in presence and absence of PMS was conducted using a confocal microscopic Raman spectrometer (Lab RAMHR800 Horiba JobinYvon) instrument with a 532 nm laser light irradiation. α -Mn₂O₃@ α -MnO₂ nanocatalyst was dispersed with Milli-Q water (pH 6.5) or PMS solution (20 mM) and pH of the solution was fixed to 6.5 with addition of aqueous (NaOH) afterward, it was dropped onto the slice. Then, the slice was scanned from 800 to 1200 cm⁻¹. The irradiation didn't cause PMS decomposition in the solution.

The redox features of the catalyst were determined by means of temperatureprogrammed reduction experiments (TPR). In the TPR measurement, about 50 mg of sample was loaded and subject to a heat treatment (10 °C/min) from 50 °C to 950 °C in a gas flow (30-35 ml/min) containing a mixture of H₂: Ar (18: 82). Signal was detected a TCD detector of Gas chromatograph.

Electron paramagnetic resonance (EPR) spectrometry studies was conducted as follows: a solution of 0.15 g/L catalyst, 1 mM PMS and different spin-trapping reagent was mixed and analyzed by EPR spectrometer (JEOL FA200, Japan) at room temperature. Conditions: sweep width: 100 G; microwave frequency: 9.87 GHz; modulation frequency: 100 GHz; and power: 18.11 mW.

Boehm titration is conducted as follows: 0.1g catalyst was dispersed in 20 mL 0.01 mol·L⁻¹ HCL solutions at 25°C, and the suspension was stirred for 4 h. Then catalyst was filtrated from the solution, and supernatants are titrated with 0.01 mol·L⁻¹ NaOH solution.

Cyclic voltammetry (CV) was conducted using CHI760 electrochemical workstation (CH Instrument Company, Shanghai, China) with a standard three electrodes system. The glass carbon electrode (mixed solution of $0.1 \text{ mol} \cdot L^{-1} \text{ Na}_2 \text{SO}_4$ and PMS as the electrolyte) acted as the working electrode and the counter electrode, respectively. As the reference electrode, an SCE reference electrode was inserted into the electrolytic cell. The scan rate is 100 mV·s⁻¹ and scan range is from -0.4 to 1 V.

List of Figures and tables

Fig. S1. XRD pattern of (a) Mn_3O_4 , (b) δ -MnO₂, (c) γ -MnO₂, (d) β -MnO₂

Fig. S2. H₂-TPR profiles (a) α -MnO₂, (b) α -Mn₂O₃

Fig. S3. First order kinetic model of α -Mn₂O₃@ α -MnO₂ nanocomposite phenol reactions

Fig. S4. Effect of temperature and First order kinetic model of α -MnO₂ catalytic phenol reactions. Reaction conditions:

Fig. S5. Effect of temperature and First order kinetic model of α -Mn₂O₃ catalytic phenol reactions. Reaction conditions:

Fig. S6. Effect of α -Mn₂O₃@ α -MnO₂ nanocomposites loading on phenol removal

Fig. S6. Removal of various pollutants on α -Mn₂O₃@ α -MnO₂ nanocomposite. Reaction conditions: Catalyst 0.15 g/L, PMS 1 mM, contaminants (Phenol, 4-CP, 2, and 4,-DCP = 25 ppm, 2, 4, 6-TCP and PHBA =10 ppm)

Fig. S7. Phenol degradation on various oxidants

Fig. S8. (a) Effect of α-Mn₂O₃@α-MnO₂ nanocomposites loading on phenol removal,
(b) Effect of PMS concentration on phenol removal

Table. S1. Phenol removal for various catalysts in the presence of PDS or H_2O_2 .

Fig. S9. Stability of α -Mn₂O₃@ α -MnO₂ nanocomposites

Fig. S10. (a) Inhibition of sodium azide (NaN₃), ethanol (EtOH) and tert-butyl alcohol (TBA) on phenol degradation by PMS/ α -Mn₂O₃@ α -MnO₂ nanocomposites. Fig. S10 (b) EPR spectra of ¹O₂ using TMP at 5 min reaction time. Fig. S10 (C) EPR spectra of DMPO-OH and DMPO-SO₄ adduct at 10 min reaction time.

Fig. S11. Photos of α -Mn₂O₃@ α -MnO₂ nanocomposites (30 mg in the reaction tube) in

10 mL Milli-Q water and 10 mM PMS solution (adjusted to pH 6.5 with NaOH):

(d). Photo of the α -Mn₂O₃@ α -MnO₂ nanocatalyst (20 mg in the glass bottle) in 10 mL

(Milli-Q water) and 100 mM PMS solution (adjusted to pH 7.0 with NaOH):

Fig. S12. Raman spectra of the PMS solution alone, the α -Mn₂O₃@ α -MnO₂ nanocomposites in water and the α -Mn₂O₃@ α -MnO₂ nanocomposites in the PMS solution

Fig. S13. Wide survey XPS spectra of α -Mn₂O₃@ α -MnO₂ nanocomposites

Fig. S14. Absorption spectra of hexaammoium heptamolybdate as H₂O₂ detector.

Fig. S15. XRD patterns of samples that calcinated from the MnO2 precursor at different temperatures.

Fig. S16. (a) SEM image of α -Mn₂O₃@ α -MnO₂-500, and (b) SEM image of sample treated at 750 °C.

















Reaction condition: Catalyst 0.15 g/L, PMS 1 mM and phenol 25 ppm





Reaction condition: Catalyst 0.15 g/L, PMS 1 mM and phenol 25 ppm





Time (70 min)





Reaction conditions: Catalyst 0.15 g/L, oxidant 1 mM, phenol 25 ppm, and temperature: 25 $^\circ\text{C}.$

Table. S1. Phenol removal for various catalysts in the presence of PDS or H_2O_2 .

Entry	Catalyst	Phenol removal with PDS	Phenol removal with H_2O_2
1	α -Mn ₂ O ₃ @ α -MnO ₂ -500	83%	3%
5	α-MnO ₂	59%	3%
7	α -Mn ₂ O ₃	21%	2%

Reaction conditions: Catalyst 0.4 g/L, oxidant 6.5 mM, phenol 25 ppm, reaction time 180 min and temperature 25 $^{\circ}$ C.





Reaction conditions: (a) PMS 1 mM, phenol 25 ppm, and temperature: 25 °C. (b) Catalyst 0.15 g/L, phenol 25 ppm, and temperature: 25 °C.



Reaction conditions: Catalyst 0.15 g/L, PMS 1 mM, phenol 25 ppm, and temperature: 25 °C.





Fig. S10. (a) Inhibition of sodium azide (NaN₃), ethanol (EtOH) and tert-butyl alcohol (TBA) on phenol degradation by PMS/ α -Mn₂O₃@ α -MnO₂ nanocomposites. Fig. S10 (b) EPR spectra of ¹O₂ using TMP. Reaction conditions: Catalyst 0.15 g/L, PMS 1 mM, phenol 25 ppm, TMP 3 mM, 5 min, 25 °C. Fig. S10 (c) EPR spectra of DMPO-OH and DMPO-SO₄ adduct . Reaction conditions: Catalyst 0.15 g/L, PMS 1 mM, phenol 25 ppm, DMPO 30 mM, 25 °C:

Fig. S11







Reaction Conditions: Initial pH of the pure water was 6.5; initial pH of the PMS solution was adjusted to 6.5 with NaOH.

Fig. S13



Fig. S14



Fig. S15.





