**Supporting Information**

**High catalytic performance of the thermally treated Mn-rich Limonite for catalytic oxidation of toluene**

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*Details of catalyst preparation*

Previous studies have shown that limonite is the weathering product of Fe-sulfide minerals, Fe-carbonate minerals, and Fe-enriched silicate minerals. It is usually composed of iron oxides (including goethite and ferrihydrite) and quartz, and is a mineral assemblage that is widely distributed in supergene environments (Kaneko *et al.*, 2002; Chen. *et al.*, 2018). Morphologically, goethite is present as intersecting nanoneedles and sheets, forming an open nanopore structure (Chen *et al.*, 2017). The natural Mn-rich limonite used in this work was collected from the Yeshan district of Tongling City, Anhui Province, China, and labeled as YL. The XRF result showed that the limonite contained Fe2O3 58.75 wt%, MnO 17.50 wt%, SiO2 4.01 wt%, Al2O3 2.09 wt%, and loss on ignition 15.73 wt%.

The Mn-rich limonite sample was first crushed and sieved to obtain 40-60 mesh particles. After that, the obtained Mn-rich limonite particles were calcined in a tube furnace (OTF-1200X, Kejing, China) at 300, 400, 500, and 600 °C for 2 h, respectively, and the heating rate was 10 °C/min. The final prepared catalysts were marked as YL-X (where X denoted the temperature of thermal treatment), and YL-Raw represented the natural limonite. For comparison, the Fe2O3 and MnOx samples were also prepared.

*Catalyst Characterization*

The X-ray diffraction (XRD) patterns of the catalysts were performed an X-ray Diffractometer (Haoyuan-DX-2700, Dandong, China) equipped with a Cu-Kα radiation (100 mA, 50 kV). The tube current and tube voltage were set as 40 mA and 40 kV and at the range from 10°2θ to 70°2θ. The sample was ground to a powder (200 mesh), and an appropriate amount of the powder was placed on a slide while ensuring that the powder's surface was even and smooth. The slide was placed on the sample stage of the X-ray diffractometer, and the X-ray diffraction scan was started to record the diffraction pattern of the sample.

Raman spectra of the catalysts were calculated on a Raman spectrometer (LabRAM HR Evolution, France) by employing the excitation wavelength of the 532 nm line of an argon-ion laser. Similar to the XRD test, the sample to be tested was ground to powder (200 mesh) and placed on a quartz slide, ensuring a smooth surface, starting the Raman spectrometer, and recording the Raman spectral data.

X-ray fluorescence (XRF) analysis was performed by an X-ray fluorescence spectrometer (LAB CENTER XRF-1800, SHIMADZU, Japan). The catalyst prepared in the section "*Details of catalyst preparation*" was ground into powder (200 mesh) and dried at 105 °C. The powder samples (3 g) were processed in a hydraulic press, and the pressed samples were put into the sample box and put into the instrument for testing to get the corresponding data.

Hydrogen temperature-programmed reduction (H2-TPR) and oxygen temperature-programmed desorption (O2-TPD) experiments were conducted using a chemisorption instrument (Auto Chem II 2920, Micromeritics, USA) equipped with a TCD detector (Micromeritics Instrument Corp). The sample for the H2-TPR and O2-TPD tests were 40-60 mesh, the same as for the catalytic performance tests.

Before the H2-TPR experiment, all samples were pretreated under an Ar atmosphere with a heating rate of 5 °C/min at 150 °C for 30 min and then cooled to room temperature. After pretreatment, a 100 mg sample was reduced to 30 mL/min in a 10% H2-90% Ar atmosphere with temperatures ranging from 50 °C to 800 °C and a heating rate of 10 °C/min. For O2-TPD, 100 mg of sample was pretreated under He atmosphere (50 mL/min) at 150 °C for 60 min. After cooling down to room temperature, the sample was exposed to a flow of 3% O2-97% for 60 min, followed by He pouring (50 mL/min) for 30 min to remove weakly adsorbed O2. The signal was recorded from 50 °C to 800 °C with a heating rate of 10 °C/min.

The oxygen vacancies of the catalysts were detected on Bruker EMX-PLUS (Germany) spin-trapping electron paramagnetic resonance spectrometer (EPR). The prepared catalysts (40-60 mesh) were placed in the EPR spectrometer, making sure that the catalysts were oriented in the same direction as the magnetic field. The EPR spectrometer was started, and the data were recorded.

Transmission electron microscopy (TEM, JEOL, Japan) images were carried out on a JEOL JEM-2100 instrument equipped with an energy dispersive X-ray (EDX) capability. The catalyst prepared in the section "*Details of catalyst preparation*" was ground into powder (200 mesh). An appropriate amount of powder was taken in anhydrous ethanol and ultrasonically dispersed (5 min) to form a suspension, which was sucked on top of the copper mesh, dried naturally, and then placed in a transmission electron microscope to observe the microstructure.

The specific surface area and pore size distributions of the catalysts were measured by N2 adsorption-desorption static using a Quantachrome Nova 3000e (USA) instrument. The catalyst prepared in the section "Details of catalyst preparation" was ground into powder (200 mesh). An appropriate amount (100 mg) of the above powder was taken into a sample tube, which was loaded into a degassing station, and the sample was heated and vacuum degassed. The sample tubes were transferred to the analysis station and cooled in liquid nitrogen. Nitrogen adsorption tests were then performed, adsorption isotherms were recorded, and the data were analyzed and processed.

Surface chemical compositions and chemical states were obtained by the ESCALAB 250Xi X-ray photoelectron spectroscopy (Thermo, USA), equipped with an Al Kα radiation source, and the binding energy was calibrated by the C 1s peak (284.6 eV) of contamination carbon. The catalyst prepared in the section "Details of catalyst preparation" was ground into powder (200 mesh). The powder samples were fixed on the sample stage to ensure that they were clean and free from contamination. After the calibration of the instrument was completed, the sample stage was placed into the XPS instrument, the spectral peaks were tested, and the data were recorded.

In situ DRIFTS experiments were carried out on an FTIR spectrometer (VERTEX 70, Bruker, Germany) in the range of 400-4000 cm-1. For the temperature-dependent in situ DRIFTS, the catalyst was pretreated under Ar flow (100 mL/min) at 105 °C for 30 min, the system was cooled to room temperature, and the background was collected. Then, 300 ppm toluene was introduced into the system and Ar was switched to air. The DRIFTS spectra were collected and continuously recorded for 60 min to realize the adsorption equilibrium at different temperatures (30-260 °C). The time-dependent in situ DRIFTS were also collected at different times.

*Details of the catalyst activity evaluation*

The catalytic activity of toluene oxidation was performed in a continuous-flow fixed-bed reactor (internal diameter is 8.0 mm). Typically, 400 mg of catalyst (40-60 mesh) was placed in the center of a quartz reactor, which was supported by quartz wool. Toluene (Analytical Grade, Sinopharm, China) and water vapor were generated at the required concentrations by syringe pumps (TYD01, LEADFLUID, China) and injected into the reactor, respectively. The reactant mixture, comprising 1000 ppm of toluene and balanced air (composed of 21% O2 and 79% N2), was fed into the reactor and subsequently flowed through the catalyst bed at a total flow rate of 100 mL/min. This flow rate corresponded to a weight hourly space velocity (WHSV) of 15,000 mL/(g⋅h), and WHSV was calculated by the following equation:

(1)

where WHSV stands for weight hourly space velocity (mL/(g⋅h)), m is the mass of the catalyst (g), Q is the volume of gas per unit time (mL/h).

The range of temperature was 30 to 300 °C. In addition, a heating tape with a temperature of 60 °C was attached to all reaction gas lines to avoid the condensation of water vapor and toluene. At the beginning of each test, toluene, water vapor, and balanced air were evenly mixed and then passed through the reactor.

A gas chromatograph (GC-9790II, FULI, China) equipped with a flame ionization detector (FID) was employed for online detection of toluene in both the inlet and outlet gases. Continuous monitoring of the CO2 concentration in the outlet gas was performed using a CO2 analyzer (gxh3010E1, Hua Yun, China). Toluene conversion (η, %) and CO2 yield (YCO2, %) are calculated according to the following equations:

(2)

(3)

where [C7H8]in and [C7H8]out represent the inlet and outlet concentrations of toluene, respectively, and [CO2]out denotes the concentration of CO2 in the outlet gas. This equation is derived from the molar ratio of toluene (C7H8) to CO2 (1:7).



Figure S1. The schematic diagram of the experimental system for toluene oxidation



Figure S2. (a) Toluene conversion and (b) CO2 yield of YL-300, Fe2O3, and MnOx catalysts. Reaction conditions: catalyst 0.4 g, toluene 1000 ppm, total flow rate = 100 mL/min, WHSV = 15,000 mL/(g·h), and 21% O2/N2 balance gas



Figure S3. (a) Toluene conversion and (b) CO2 yield reusability tests over YL-300. Reaction conditions: catalyst 0.4 g, toluene 1000 ppm, total flow rate = 100 mL/min, WHSV = 15,000 mL/(g⋅h), and 21% O2/N2 balance gas



Figure S4. Toluene conversion as a function of reaction temperature over YL-300 under (a) different WHSV and (b) different toluene concentrations. Reaction conditions: (a) catalyst 0.4 g, toluene 1000 ppm, and 21% O2/N2 balance gas, (b) catalyst 0.4 g, total flow rate = 100 mL/min, WHSV = 15,000 mL/(g⋅h), and 21% O2/N2 balance gas



Figure S5. (a) Toluene conversion and (b) CO2 yield as a function of reaction temperature over YL-300 under different relative humidity. Reaction conditions: catalyst 0.4 g, toluene 1000 ppm, total flow rate = 100 mL/min, WHSV = 15,000 mL/(g⋅h), and 21% O2/N2 balance gas



Figure S6 Exclude the effect of external and internal diffusion on YL-300. (a) external diffusion experiment and (b) influence of the catalyst size in toluene conversion. Reaction conditions: (a) catalyst 0.15 g, toluene 1000 ppm, size = 0.15-0.18 mm, and 21% O2/N2 balance gas, (b) catalyst 0.15 g, toluene 1000 ppm, WHSV = 40,000 mL/(g⋅h), and 21% O2/N2 balance gas

Table S1. The assignment information for various intermediate species adsorbed on the catalyst

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| Peaks/cm-1 | Vibration mode | References |
| ~3068 | υ(C-H) stretching vibration | methyl species (Li et al., 2017) |
| ~1594 | υ(C=C) skeleton stretching vibration | benzene ring (Shen et al., 2023) |
| ~1493 | skeleton vibration of phenyl group | absorbed toluene (Lu et al., 2019) |
| ~1452 | υ(C=C) skeleton stretching vibration | benzene ring (Shen et al., 2022) |
| ~1414,  ~1543 | υ(C-O) symmetric stretching vibration  υ(C-O) asymmetric stretching vibration | benzoate species (Shen et al., 2022)  benzoate species (Shen et al., 2022) |
| ~1081 | stretching vibration of υ(C-O) | benzyl alcohol (Mo et al., 2020) |
| ~1304 | υ(-CH2) stretching vibration | anhydride (Liu et al., 2022) |
| ~1178 | υ(C-O) asymmetric stretching | benzyl alcohol (Dong et al., 2019) |

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