Electronic Supplementary Information

Tuning the Interlayer Cations of Birnessite-Type MnO₂ to Enhance Its Oxidation Ability for Gaseous Benzene with Water Resistance

Yang Liu *, Wenjing Zong *, Hao Zhou *, Dingsong Wang *, Ranran Cao b, Jingjing Zhan a, Lifen Liu a, Ben W.-L. Jang c*

a. Key Laboratory of Industrial Ecology and Environmental Engineering (Ministry of Education), School of Food and Environment, Dalian University of Technology, Panjin 124221, China

b. School of Environment, Tsinghua University, Beijing 100084, China

c. Department of Chemistry, Texas A&M University-Commerce, PO Box 3011, Commerce, TX 75429, USA

* Corresponding authors. Fax: +86-427-2631799 (Y. Liu), +1-903-468-6020 (B.W.-L. Jang).
E-mail addresses: liuyang20180129@dlut.edu.cn (Y. Liu), Ben.Jang@tamuc.edu (B.W.-L. Jang).
Details of Catalyst characterization

The weight percentage of K element in the samples was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES, 730, Agilent, USA).

The X-ray diffraction (XRD) experiments were carried out on a Shimadzu 7000S X-ray diffractometer. The scan rates were $6^\circ \cdot \text{min}^{-1}$ and $0.5^\circ \cdot \text{min}^{-1}$ for the regular scan and step scan, respectively.

Raman spectra were acquired on the Renishaw inVia Raman Microscope. The laser power was fixed at 2.5 mW produced by an excitation source with a wavelength of 532 nm. About 0.05 g of catalyst powder was pressed into thin wafer and then mounted onto the sample holder for observation.

Fourier-transform infrared (FT-IR) spectra of the samples were collected on an FT-IR spectrometer (Nicolet 870, Thermo, USA) by potassium bromide pellet method. The spectra were obtained at a resolution of 4 cm$^{-1}$ averaged over 32 scans.

The specific surface area ($S_{\text{BET}}$) of the catalysts was measured using the N$_2$ adsorption BET method at $-196 \ ^\circ \text{C}$ (Autosorb-iQ-C, Quantachrome, USA). The sample was first degassed at 100 $^\circ \text{C}$ for 4 h before measurement.

The particle morphology was observed by scanning electron microscopy (SEM, Nova NanoSEM 450, FEI, USA) and transmission electron microscopy (TEM, Tecnai G$^2$ F20, FEI, USA). The lattice images were taken using high-resolution TEM (HRTEM). The distributions of Mn, O, K, Ce and Cu elements on the surface of the catalysts were provided by the energy dispersive X-ray spectrometry (EDS) mapping.
The X-ray photoelectron spectroscopy (XPS) was used to analyze the chemical states of surface elements on an X-ray photoelectron spectrometer (ESCALAB 250Xi, Thermo Fisher, USA). The XPS spectra were calibrated by referencing the C 1s signal at 284.6 eV.

Temperature programmed reduction by hydrogen (H₂-TPR) was carried out on Chemisorption Analyzer (Autochem II 2920, Micromeritics, USA). First, ~0.05 g of catalyst was pretreated in 50 mL·min⁻¹ of helium stream at 100 °C for 30 min, and cooled down to room temperature in the same atmosphere afterwards. Then the catalyst was purged by 50 mL·min⁻¹ of 5 vol.% H₂/Ar until the baseline of the thermal conductivity detector (TCD) became stable. The temperature was linearly increased to 700 °C with a heating rate of 5 °C·min⁻¹ for reduction. An isopropyl alcohol / liquid nitrogen slurry, which was placed upstream of the TCD, was used as cold trap (-80 °C) to condense any formed water before the outlet gas entered the detector.

Temperature programmed desorption of O₂ (O₂-TPD) was also performed on the Chemisorption Analyzer with ~0.05 g of catalyst. After pretreated in the same conditions as those of H₂-TPR, the catalyst was switched to 50 mL·min⁻¹ of 5 vol.% O₂/He for 0.5 h, which was followed by purging with 50 mL·min⁻¹ of helium for 0.5 h to remove the physisorbed O₂. The O₂ desorption was carried out in 50 mL·min⁻¹ of helium from room temperature to 850 °C with a heating rate of 5 °C·min⁻¹. The cold trap of isopropyl alcohol / liquid nitrogen slurry was also used during O₂ desorption stage.