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Excellent porous environmental nanocatalyst: Tactically integrating size-confined highly-active MnO_x in nanospace of mesopore enables promotive catalytic degradation efficiency of organic contaminants

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Characterizations

The XRD patterns of all of the samples were collected using Smartlab TM 9 KW (Rigaku Corporation, Tokyo, Japan) equipped with a rotating anode and Cu K α radiation ($\lambda = 0.154178$ nm).

The N₂ adsorption-desorption tests were carried out using BELSORP-MINI volumetric adsorption analyzer (BEL Japan, Osaka, Japan). The resulting samples were outgassed in vacuum at 150 °C for 3 h and before measurements. The specific surface areas and pore size distribution were calculated through Brunauer-Emmet-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively.

Diffused Reflection UV-Vis spectra of samples were obtained in the range of 200-800 nm by Lambda 950 spectrophotometer (PerkinElmer, Waltham, MA, USA).

Fourier Transform Infrared (FT-IR) spectra of the samples were collected on Bruker VECTOR22 resolution (Bruker, Germany) based on a quantitative powder experiment.

Field emission scanning electron microscopic (FESEM) images were obtained from a Hitachi S4800 Field Emission Scanning Electron Microscopy (Hitachi, Tokyo, Japan). The elemental distribution of materials was determined with energy-dispersive X-ray spectroscopy (EDX).

High-resolution transmission electron microscopy (HRTEM) images were collected on a JEM-2010 EX microscope (JEOL, Tokyo, Japan) equipped with EDX.

The X-ray photoelectron spectra (XPS) were collected on a PHI 5000 Versa Probe X-ray photoelectron spectrometer (ULVAC-PHI, Kanagawa, Japan) equipped with Al K α radiation (1486.6 eV). The binding energy of C1s at 284.6 eV was utilized as the reference.

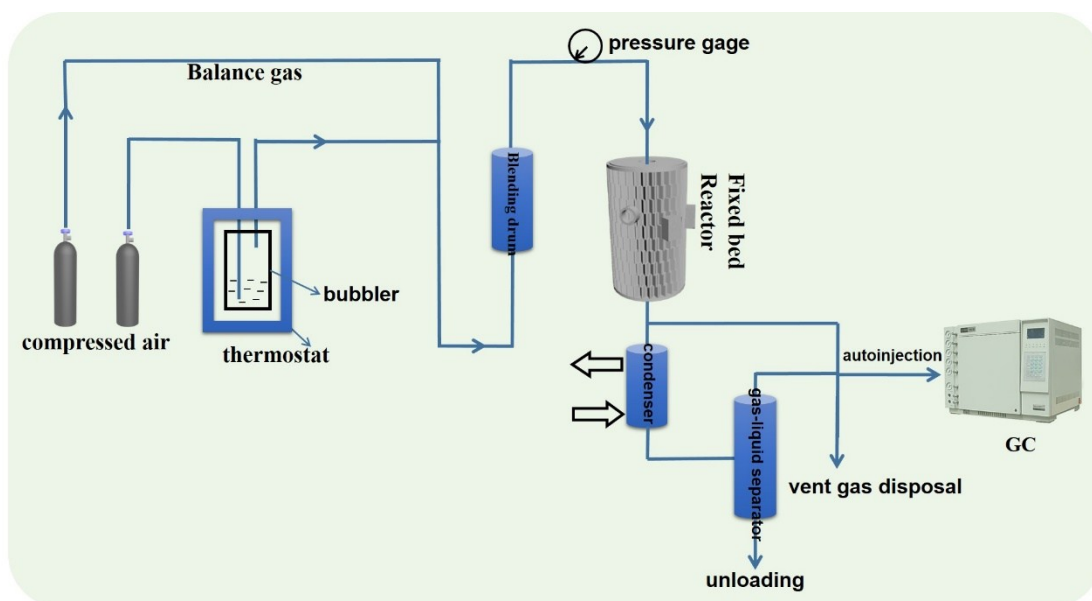
The manganese contents in the catalysts were examined using a PE Optima 2000DV Inductively Coupling Plasma emission spectrometer (ICP) (PerkinElmer, Waltham, MA, USA). All the samples were pretreated and completely dissolved with hydrofluoric acid.

Hydrogen temperature-programmed reduction (H₂-TPR) were conducted in a fixed-bed reactor from 20 °C to 800 °C with 10% H₂ atmosphere flow (Ar as balance

gas) and a heating rate of 10 °C/min. Prior to the analysis, the samples were treated by flowing 30 ml/min argon at 300 °C for 1 h, then cooling to room temperature. The consumption amount of H₂ was recorded continuously using a thermal conductivity detector (TCD).

The EPR signals of the solid sample were collected with the settings of center field of 3515.0 G, microwave frequency of 9.86 mW, receiver gain of 20 dB, the scan time of 60 s, and scan number of 2. The EPR signals of liquid samples were obtained with the settings of center field = 3515.0 G, microwave frequency = 18.57 mW, receiver gain = 30 dB, scan time 155 = 30 s, and scan number = 2. 5, 5-dimethyl-1-pyrroline n-oxide (DMPO) was used as radical trapping agent for capturing the free radicals in the solution identified by their hyperfine splitting constants of $\alpha_N=14.9\text{G}$, $\alpha_H=14.9\text{ G}$ for DMPO-OH, and $\alpha_N=13.2\text{ G}$, $\alpha_H=9.6\text{ G}$, $\alpha_H=1.48\text{G}$, $\alpha_H=0.78\text{ G}$ for DMPO-SO₄.

The *in-situ* DRIFTS study was conducted via FTIR spectrometer (Nicolet 6700) equipped with a DRIFTS cell in the range of 1100-4000 cm⁻¹. Firstly, prior to the test, the sample loaded in the IR cell was pretreated, followed by the standard procedure that heating to 300 °C for 30 min in the N₂ atmosphere to remove the surface adsorbed species, and then decreased to 225 °C to collect the background. Then, 100 mL/min of toluene gas balanced by N₂ was introduced to the reaction cell at 225 °C for 60 min. Afterward, N₂ was inlet about 1 h to remove physically-absorbed toluene. Finally, 20% of O₂/N₂ was inlet to the *in-situ* cell to record the spectrum.



Scheme S1 Catalytic reactor flow for toluene combustion.