Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary Information

Insight into the pH effect over the oxygen species and Mn chemical valence of Co-Mn catalysts for the total toluene oxidation

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Experimental section

Catalyst characterizations

X-ray diffraction (XRD) was characterized on Bruker D8 advanced X-ray diffractometer, scanning from 5 to 90° with a scan rate of 8° min^{-1}.

The morphology of samples was characterized by scanning electron microscopy (SEM, JEOL, JSM-7800F) operated at 5 kV. Transmission electron microscopy (TEM), and elemental mapping were collected by a Talos F200S microscope operating at 200 kV.

Raman spectra were obtained on a WI Tec Alpa 300R spectrometer equipped with an ion-argon laser ($\lambda = 514$ nm) and a CCD detector. A twenty seconds acquisition time was used for each spectrum and five spectra were accumulated from 100 to 1000 cm^{-1}.

Prior to N_2 adsorption, the samples were degassed at 250 °C for 6 h. The specific surface areas were calculated by the Brunauer–Emmett–Teller (BET) equation. The pore volumes and pore size distributions were determined by the Barrett–Joyner–Halenda (BJH) method from the desorption branches of the isotherms.

X-ray photoelectron spectroscopy (XPS) data were obtained using a spectrometer (ESCALAB250, Thermo Fisher Scientific) performed with a monochromatic Al Ka X-ray source. The emission lines were calibrated with the C 1s signal at 284.8 eV.

Electron paramagnetic resonance (EPR) profile spectra was obtained by JEOL JES-FA300 (ESR/EPR) spectrometer at room temperature.

Positron annihilation lifetime spectra (PALS) were measured using AMETEK PLS-SYSTEM system at room temperature. The sample powder was pressed into a disk (diameter: 10.0 mm, thickness: 1.0 mm). A 10^6 Bq ^{22}Na positron source was sandwiched between two identical sample disks. Each spectrum contained 1.0×10^6 and 4×10^6 counts for PATFIT and MELT, respectively. The positron lifetime spectrum containing 10^6 counts was analyzed by the PATFIT program to be decomposed into several lifetime components, while the spectrum containing 4×10^6 counts was analyzed by the MELT program which resolved the continuous distribution of the ortho-positronium (*o*-Ps) lifetime.

The catalyst reducibility was examined by temperature programmed reduction with hydrogen (H_2-TPR) on a Shanghai HX chromatography GC-950 chemisorption analyzer equipped with a thermal conductivity detector (TCD). Prior to the test, the catalysts were firstly pre-treated at 300 °C for 1 h with a He flow (50 mL min^{-1}), and then cooled down to room temperature. 10 *vol.* % H_2/Ar with a flow rate of 50 mL min^{-1} as the reducing gas was introduced and the reactor was heated from 50 °C to 800 °C with a rate of 10 °C min^{-1}. The water produced in the reduction process was trapped into a cold trap.

Oxygen temperature programmed desorption (O_2-TPD) experiment was performed in a U-shaped quartz reactor and the signal of desorption O_2 was simultaneous recorded on a Hiden Analytical QIC-20 chemisorption analyzer equipped with a thermal conductivity detector (TCD) to measure the amount of O_2 desorption. Briefly, 10 mg of catalyst was placed into a U-shaped quartz reactor, heated to 300 °C with a rate of 10 °C min^{-1} and held at this temperature for 1 h under a He flow (50 mL min^{-1}). Then, when the temperature was reduced to room temperature, 5 *vol.* % O_2/Ar with a flow rate of 50 mL min^{-1} as the adsorbing gas was introduced into and contacted the catalyst for 0.5 h. After that, the sample was continued to purge a He flow (50 mL min^{-1}) for 0.5 h, and then the desorption gas signal was recorded between 50 °C to 900 °C with a rate of 10 °C min^{-1}.

In situ diffuse reflectance infrared Fourier transform spectroscopy (in situ DRIFTS) experiments were performed on an FTIR spectrometer (Nicolet 6700) equipped with a Harrick DRIFT cell and an MCT/A detector in the range of 650 ~ 4000 cm^{-1} with 32 scans at a resolution of 4 cm^{-1}. Prior to each experiment, the sample was pretreated at 300 °C in a gas flow of N_2 for 0.5 h and then cooled to target temperature under N_2 flow. Background spectra were recorded in the N_2 flow and automatically subtracted from the corresponding spectra. Afterward, 500 ppm of toluene balanced with N_2 was introduced to the cell under a flow rate of 30 mL min^{-1} at 210 °C, and then DRIFTS spectra were recorded. After physisorbed toluene was removed by flushing wafer with N_2 for 2 h, subsequently 21 % O_2/N_2 was introduced to investigate the reactivity of preadsorbed toluene with $N_2 + O_2$ at 210 or 240 °C. In addition, a mixture 500 ppm of toluene/air (21 % O_2 /N_2) /5 *vol.* % water vapor was introduced into the system under a flow rate of 34.1 mL min^{-1} at 240 °C, and then DRIFTS spectra were recorded.

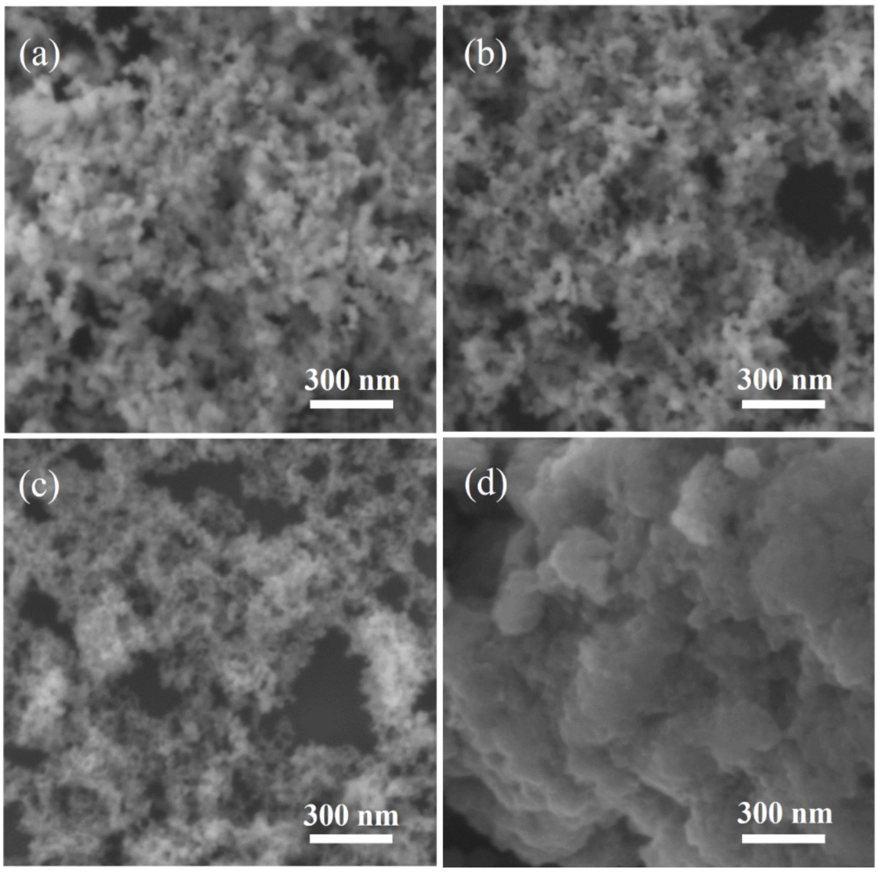

Fig. S1. SEM images of (a) Co-Mn-2, (b) Co-Mn-7, (c) Co-Mn-12 and (d) Co-Mn-14 catalysts.

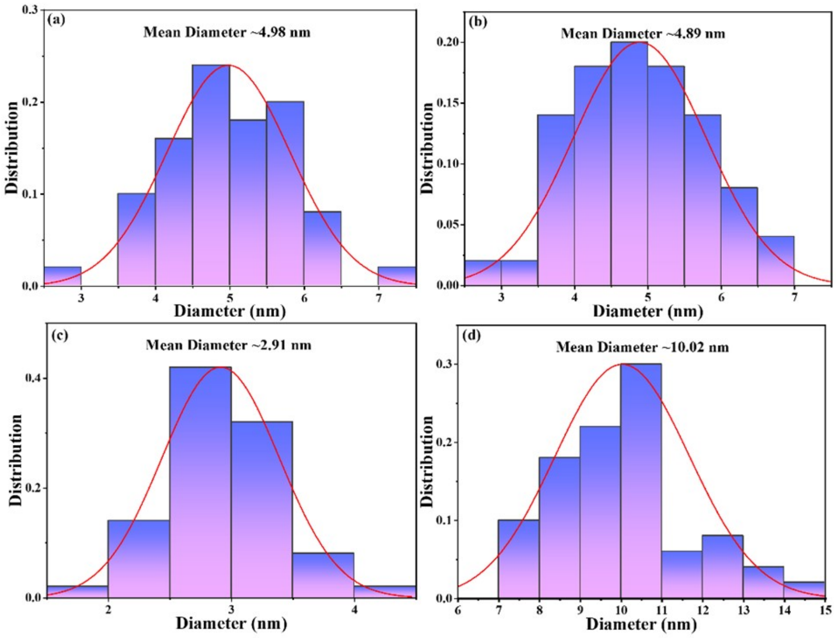

Fig. S2. The size distribution of (a) Co-Mn-2, (b) Co-Mn-7, (c) Co-Mn-12 and (d) Co-Mn-14.

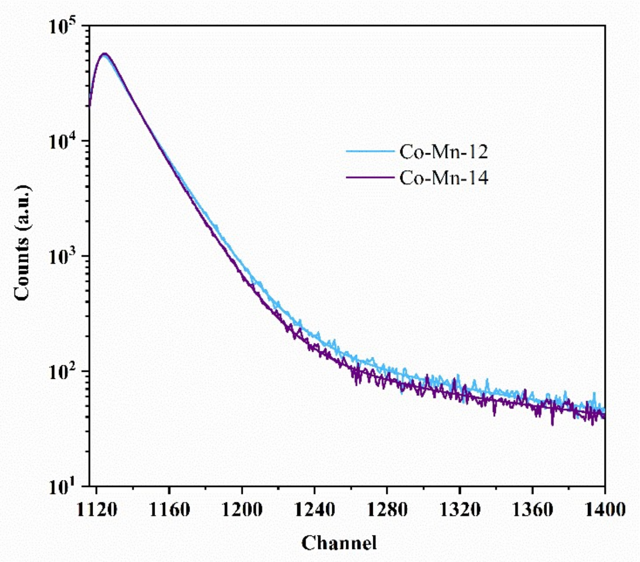

Fig. S3. The lifetime spectra of Co-Mn-12 and Co-Mn-14 samples.

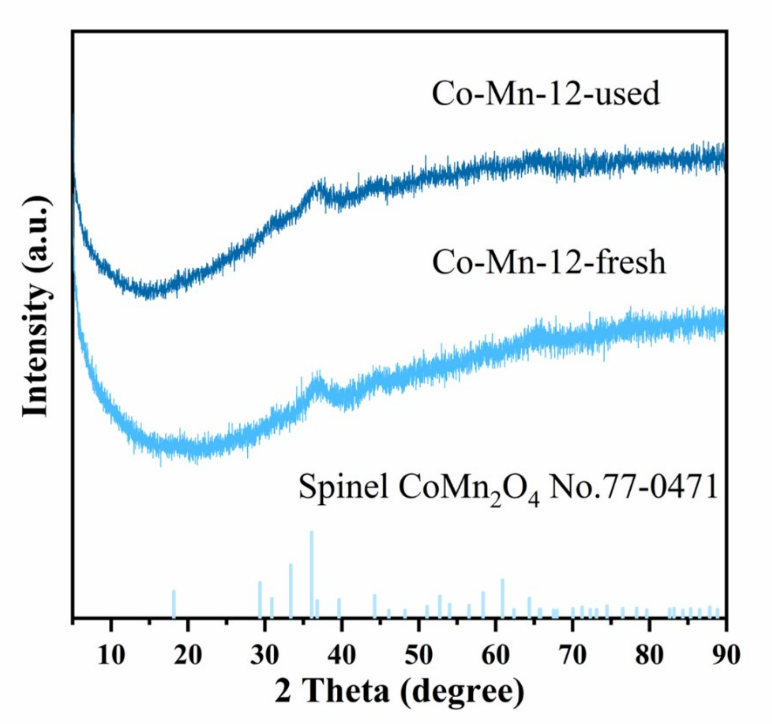

Fig. S4. XRD patterns of fresh and used Co-Mn-12.

Table S1 Catalytic performance of different Co-Mn catalysts for toluene removal

Catalyst	Preparation Method	Conc. ppm/ppmv	WHSV $cm^3\ g^{-1}\ h^{-1}$	T_{50} °C	T_{90} °C	Stability h	Ref.
Ce-Co CXN 1:2	Exotemplating	266	60 000 (h^{-1})	225	241	/	1
HW-$Mn_xCo_{3-x}O_4$	Pyrolysis	3 000	30 000	159	188	30	2
Mn-Co oxides	Pyrolysis	500	96 000	226	240	25	3
$CoMn_2O_4$	Co-precipitation	500	22 500	202	210	12	4
Mn-Co (1:1) / CZ	Co-precipitation	1 000	30 000	222	242	50	5
OM-$CoMn_{0.5}$	Co-precipitation	1 200	60 000	217	258	/	6
Mn-Co (1:2)	Hydrothermal	1 000	30 000	225	238	/	7
5Co1Mn	Hydrothermal	1 000	60 000	232	247	24	8
$Co_{2.25}Mn_{0.75}O_4$	Hydrothermal	1 000	8 016	210	214	70	9
Mn2Co1 oxides	Agar-gel	1 000	60 000	228	236	50	10
C3M1-R	Redox- precipitation	500	67 500	169	189	50	11
Co-Mn-12	Redox- precipitation	1 000	20 000	203	208	60	This work
Co-Mn-12	Redox- precipitation	1 000	60 000	214	224	/	This work
Co-Mn-12	Redox- precipitation	1 000	100 000	220	248	/	This work

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