# Supplemental Information

# Exploration of the interaction mechanism in the synergistic degradation of benzene and toluene over $MnCoO_x$ catalysts

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## 1. Detailed procedures of catalyst preparation

### 1.1 Chemicals and raw materials

Sodium dodecyl sulfate (SDS, 99%), methyl methacrylate (MMA, 99%), ammonium persulfate (APS, 98%), anhydrous sodium carbonate ($Na_2CO_3$, 99%) and ammonia hydroxide ($NH_3 \cdot H_2O$, 25%) were obtained from Sinopharm Chemical Reagent (Shanghai, China), Maxemul™ 5011, a non-ionic reactive surfactant, was from Croda (Britain). Manganese nitrate solution ($Mn(NO_3)_2$, 50wt.%) and cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, 99%) was from Macklin technology (Shanghai, China). All the chemicals were used as received. Deionized water was self-made in laboratory.

### 1.2 Synthesis of catalysts

#### 1.2.1 Synthesis of poly methyl methacrylate nanospheres

PMMA microspheres were prepared by soap free emulsion method. The preparation process was as follows: 0.9 g SDS and 0.6 g Maxemul™ 5011 were mixed in 100 mL of deionized water and put into a three necked flask, and the above solution was heated to 70°C while stirring, then 30 mL MMA was added to the solution and stirred for emulsification for 1 h. Finally, 0.225 g of APS

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and 10 mL of deionized water were mixed and added into above flask for polymerization reaction over 3 h.

### 1.2.2 Preparation of $Mn_aCo_bO_x$ catalyst

$Mn(NO_3)_2$ and $Co(NO_3)_2·6H_2O$ (Mn: Co = 1:2, 1:1, 2:1 molar ratio) were added to a beaker with 400 mL of deionized water as precursor solution A. 50 mL ammonia solution (25%) was diluted with 200 mL deionized water as precursor solution B. 47.6 g PMMA emulsion was dispersed into the solution B to form a precipitant. Then, the precursor solution A was dropped into the precipitant at room temperature for 8 h and keep stirring. After finishing the dropping, another 20 mL ammonia solution (25%) was added into the mixture solution, and heated to 80°C for 3 h. The obtained precipitate was filtered and washed by deionized water. Finally, the sediment was dried at 80°C for 12 h and then the dried precipitate was decomposition at 600°C for 3 h in air. Additionally, the Mn–Co derived mixed oxides were denoted as $Mn_aCo_bO_x$ (a: b = 1:2, 1:1 and 2:1), the specific synthesis process of the material were shown in Figure S1.

### 1.2.3 Synthesis of $MnO_x$ and $CoO_x$

0.05 mol $Co(NO_3)_2·6H_2O$ and 200 mL of deionized water were added to a beaker under vigorously stirring. 1 mol/L of $Na_2CO_3$ was prepared and dropwise added to the beaker, and the pH of this solution was controlled to reach 9.0. After 3 h of aging, the precipitate was subsequently washed and filtered. Finally, the resulting sample was dried in oven at 80°C for 12 h, and the $CoO_x$ catalyst was obtained by calcining at 600°C for 3 h. Moreover, the $MnO_x$ catalyst was obtained by the same method.

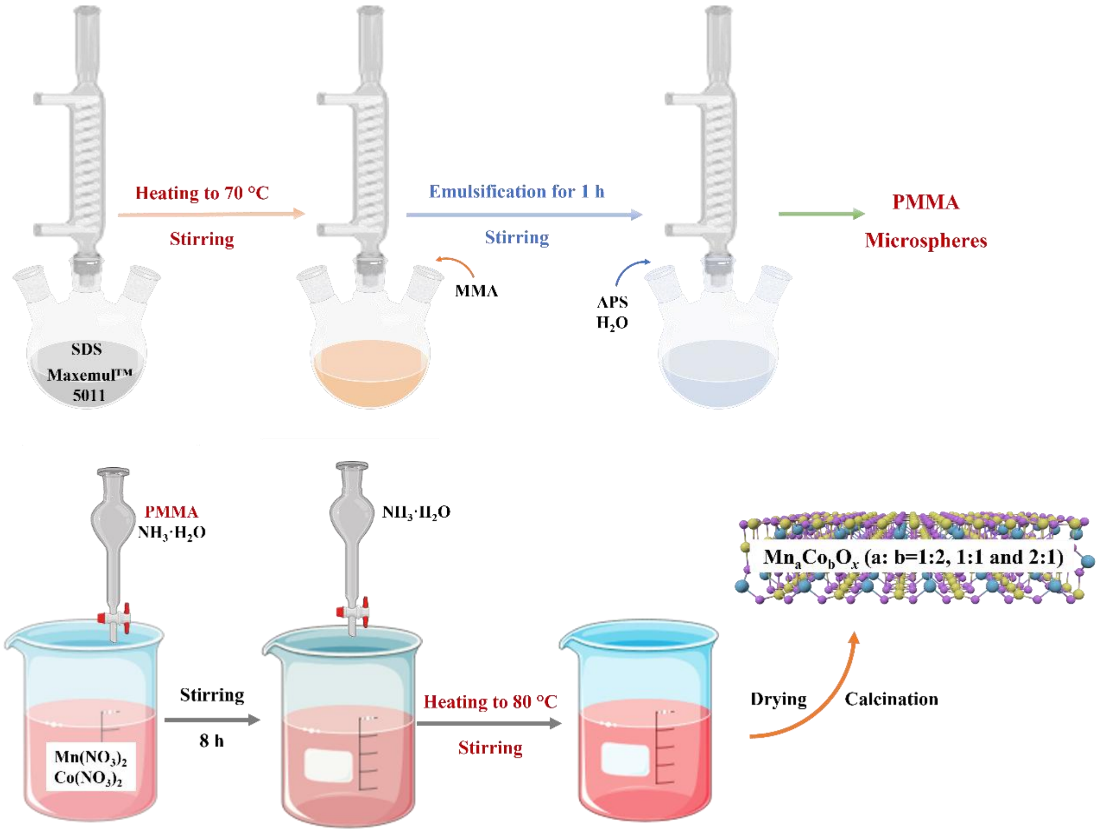

**Fig. S1** the material synthesis process diagram.

# 2. Catalyst Characterization

X-ray diffraction (XRD, Bruker D8 Advance, Germany) patterns were recorded on an X'Pert PRO (PANalytical) diffractometer equipped with a Cu Kα radiation source (λ = 0.15418 nm). A continuous mode was used for collecting data in the 2θ range from 10° to 80° at a scanning speed of 5°/min.

Nitrogen adsorption and desorption isotherms were measured by the Micromeritics ASAP 2020 (micromeritics, USA) gas sorption analyzer. The special surface area was calculated using the Barret-Joyner-Halenda method. The total pore volume was estimated from the amount adsorbed at a relative pressure of about 0.99. The samples were degassed in vacuum chamber for 3h at 300°C before the measurement.

The Raman scattering measurements were performed with a laser micro-confocal Raman spectrometer (InVia Reflex, Renishaw, Britain). The solid-state diode laser (532 nm) was used as an excited source. The measurements were performed in the range of 100-1000 $cm^{-1}$ and the spectral resolution was 1 $cm^{-1}$. All measurements were taken at room temperature.

$H_2$ temperature-programmed reduction ($H_2$-TPR) experiments were accomplished on a Micromeritics Chemisorb 2950 (micromeritics, USA) apparatus. Prior to each TPR run, the catalysts were pre-heated in He flow from room temperature to 300°C and held for 1h. TPR profiles were obtained by passing a 5% $H_2$/Ar flow (50 mL/min) through the pretreated catalyst (about 50 mg). Reduction temperature was increased from room temperature to 800°C at a rate of 10°C/min. Hydrogen concentration in the effluent was continuously monitored by a thermal conductivity detector.

The temperature-programmed desorption of ammonia ($NH_3$-TPD) was conducted in a Micromeritics Chemisorb 2950 (micromeritics, USA) apparatus. Prior to each TPD run, the catalyst (100 mg) was pretreated in a helium flow at 300°C for 1 h in a quartz reactor, and then the temperature of the quartz reactor was lowered to room temperature. The catalyst adsorbed $NH_3$ for 30 min under an $NH_3$ flow of 50 mL/min. Then, helium gas was fed into the reactor at 50 mL/min for 30 min to purge any residual ammonia. The catalyst was then heated to 900°C at a constant heating rate of 10°C/min under a helium flow of 50 mL/min. The desorbed ammonia was monitored using a thermal conductivity detector (TCD).

X-ray photoelectron spectra (XPS) were investigated with a Japan SHIMADZU Axis Supra (600W) instrument using Al Kα radiation. The base pressure was $5 \times 10^{-8}$ Pa. Binding energies were calibrated using the C (1s) peak of contaminant carbon (BE = 285 eV) as the standard and quoted with a precision of ± 0.2 eV.

In situ diffuse reflectance infrared Fourier transform spectra (DRIFTS) was recorded on a Bruker INVENIO S spectrometer (Germany), equipped with an MCT detector and a diffuse reflection accessory including a high temperature reaction chamber. The catalyst is placed into the diffuse reflectance cell fitted with $BaF_2$ windows positioned in a heating chamber that allows the temperature of sample to be stabilized at the desire temperature. Prior to the recording of an IR spectrum, the catalyst sample was degassed for 1 h at 500°C to eliminate weakly adsorbed species. The background at each temperature point was taken as the background while the sample was cooled to room temperature under vacuum. Then a mixture gas stream containing 250 ppm of benzene and toluene, with or without 20 vol % $O_2$, in $N_2$ were introduced to the chamber. Meanwhile, the DRIFTS spectra were sequentially recorded by accumulating 100 scans at a spectra resolution of 4 $cm^{-1}$.

**Table S1** Textual properties data of $CoO_x$, $MnO_x$ and $Mn_aCo_bO_x$ catalysts.

| Samples | SSA ($m^2/g$) | Pore volume ($cm^3/g$) | BJH Desorption average Pore size (nm) |
|---|---|---|---|
| $CoO_x$ | 1.23 | 0.017 | 31.99 |
| $MnO_x$ | 5.70 | 0.023- | 21.94 |
| $MnCoO_x$ | 19.43 | 0.10 | 21.20 |
| $MnCo_2O_x$ | 20.20 | 0.12 | 23.34 |
| $Mn_2CoO_x$ | 17.34 | 0.088 | 18.94 |

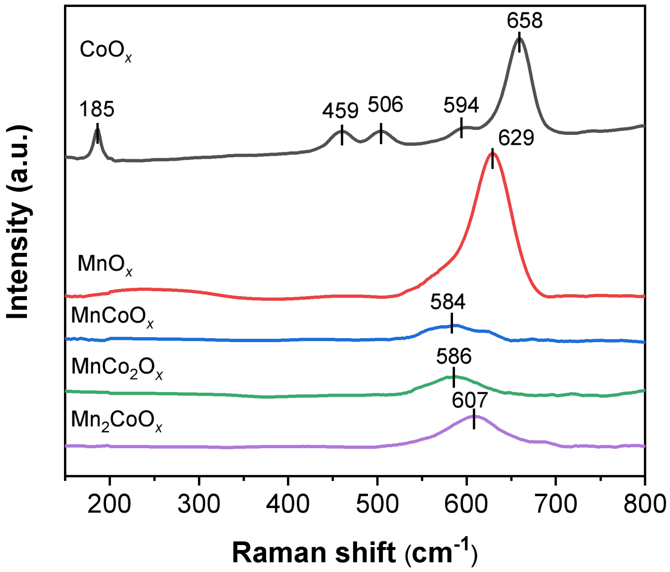

**Fig. S2** Raman spectra of $CoO_x$, $MnO_x$ and $Mn_aCo_bO_x$ (a:b = 1:1, 1:2 and 2:1).

# 3. The catalytic stability of $MnCoO_x$

The catalytic performance of exhaust containing water vapor may result in the deactivation of catalysts in practical application. Hence, the investigation of the effect of $H_2O$ on the catalytic stability of $MnCoO_x$ is worthwhile. The durability behavior of $MnCoO_x$ sample at 300°C was shown in Fig. S3. The conversion of benzene and toluene remained constant at nearly 100% with the reaction proceeding continuously for 50 h. At this time, 10 vol% $H_2O$ was controlled to enter the reaction system through a mass flow meter. It was found that after introducing 10% water vapor, the conversion of benzene and toluene rapidly decrease, with the conversion of benzene and toluene decreasing from 100% to about 80% and 84%, respectively. After cutting off the water vapor, the conversion rate of benzene and toluene returned to 100%. These results indicate that the presence of water vapor could have a negative impact on reaction performance, which may be attributed to the competitive adsorption of pollutant molecules and water molecules on the surface of catalyst.

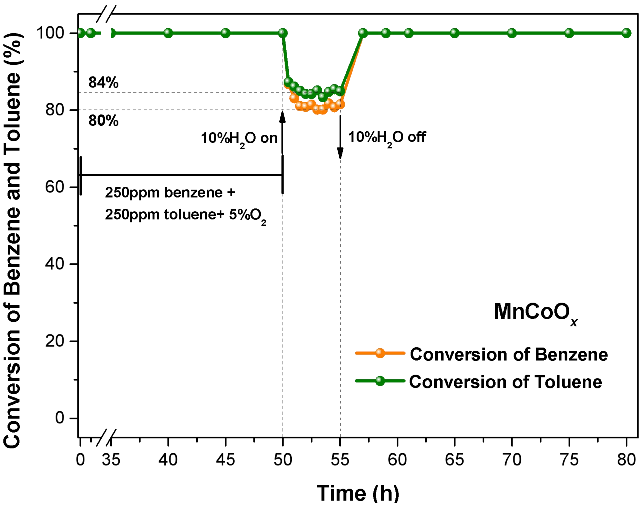

**Fig. S3** Time on stream behavior of the $CuMn_2O_4$ catalyst (reaction conditions: 250ppm benzene, 250ppm toluene, 5%$O_2$, 10% $H_2O$, $N_2$ as balance gas, $t = 300°C$, GHSV = 18000 $h^{-1}$).