Supplemental Information

Efficient synergistic oxidation of multi-component VOCs over bimetallic MOF-derived CuMn oxide catalysts

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Table of Contents

1. Experimental section

1.1 Chemical reagents

1.2 Preparation of catalyst

1.3 Characterization of catalysts

1.4 DFT calculation method

1.5 Catalytic performance tests

Table S1 Textual properties of CuO_x, MnO_x and Cu_aMn_b (a/b=1/1, 1/2, 2/1) samples

Table S2 The apparent activation energies (Ea) of Cu_1Mn_2 catalyst

Fig. S1 Raman spectra of CuO_x, MnO_x and Cu_aMn_b (a/b=1/1, 1/2, 2/1)

Fig. S2 Arrhenius plots for the catalytic oxidation of benzene and toluene

Fig. S3 Time on stream behavior of the Cu_1Mn_2 catalyst (reaction conditions: 250ppm benzene, 250ppm toluene, 5%O_2, 10% H_2O, N_2 as balance gas, T=300 °C, GHSV=18,000 h^{-1})

Fig. S4 O_2-TPD results of CuO_x, MnO_x and Cu_aMn_b (a/b=1/1, 1/2, 2/1)

References

1. Experimental section

1.1 Chemical reagents

The manganese nitrate solution ($Mn(NO_3)_2$, 50wt.%), ethanol, and N,N-Dimethylformamide (DMF) were obtained from Macklin Technology (Shanghai, China). Cupric nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$, 99%) was purchased from Tianjin Tianli Chemical Reagent (Tianjin, China). Benzene-1,3,5-tricarboxylic acid was obtained from Sinopharm Chemical Reagent (Shanghai, China). All the chemicals were used as received without further purification. Deionized water was prepared in-house in the laboratory.

1.2 Preparation of catalyst

Cu-BTC, Mn-BTC, and Cu-Mn-BTC were synthesized via a solvothermal method. Typically, benzene-1,3,5-tricarboxylic acid was dissolved in a mixed solvent of dimethylformamide (DMF, 60 mL) and ethanol (60 mL) under ultrasonication for 30 min to obtain solution A. A predetermined amount of $Cu(NO_3)_2 \cdot 3H_2O$ and $Mn(NO_3)_2$ was dissolved in 60 mL of deionized water to prepare solution B. Solutions A and B were then combined and magnetically stirred for 30 min. The resulting mixture was transferred into a Teflon-lined stainless-steel autoclave, sealed, and heated at 100 °C for 10 h. After naturally cooling to room temperature, the solid product was collected by centrifugation (4000 rpm, 5 min) and washed three times with DMF and ethanol. The obtained solid was then dried overnight at 90 °C to yield a blue powder, denoted as Cu-Mn-BTC-n (where n represents the molar ratio of Cu to Mn, n = 1/1, 1/2, 2/1). Cu-BTC and Mn-BTC were synthesized following the same procedure.

The Cu-Mn oxide catalysts were obtained by pyrolyzing the Cu-Mn-BTC-n (n = 1/1, 1/2, 2/1) precursors. The samples were placed in a muffle furnace and heated in air to 400 °C at a ramp rate of 5 °C min^{-1}, held for 2 h, and then cooled to room temperature, yielding Cu_aMn_b (a/b = 1/1, 1/2, 2/1). Similarly, the Cu-BTC and Mn-BTC precursors were decomposed into CuO_x and MnO_x, respectively, under identical conditions.

1.3 Characterization of catalysts

The crystalline phases of the catalysts were analyzed by X-ray diffraction (Bruker D8 Advance, Germany) at a scanning rate of $5° \cdot min^{-1}$ over a 2θ range of 10°-80°. Textural properties were determined from N_2 adsorption-desorption isotherms (Micromeritics ASAP 2020), after degassing the samples at 300 °C for 6 h.

Thermogravimetric analysis (TGA) was carried out on a STA6000 simultaneous thermal analyzer to investigate the thermal stability and decomposition behavior of the samples. Raman spectra were recorded on a LabRam HR Evolution spectrometer with a 532 nm excitation wavelength over a frequency range of 100-1000 cm^{-1}. H_2 temperature-programmed reduction (H_2-TPR) and NH_3 temperature-programmed desorption (NH_3-TPD) measurements were performed on a Micromeritics Chemisorb 2920 instrument to evaluate the redox properties and surface acidity of the catalysts. X-ray photoelectron spectroscopy (XPS) measurements were conducted using an Axis Supra (600 W) instrument to investigate the elemental composition and chemical states on the catalyst surface. Electron paramagnetic resonance (EPR) measurements were carried out at 77 K using an X-band Bruker EMX spectrometer. In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was performed on a Bruker INVENIO S spectrometer equipped with an MCT detector and a Harrick Praying Mantis diffuse reflectance accessory coupled with a high-temperature reaction cell. The catalyst was loaded into the diffuse reflectance cell with BaF_2 windows, and the sample temperature was precisely controlled and stabilized at the target value. Before spectral collection, the sample was pre-treated by degassing at 350 °C for 1 h to remove surface weakly adsorbed impurities. After cooling to room temperature, the background spectrum was recorded at corresponding temperatures. Subsequently, mixed gas consisting of 250 ppm benzene or toluene balanced with nitrogen was introduced into the reaction chamber. Notably, pure nitrogen atmosphere was adopted for adsorption experiments without oxygen addition, whereas 5 vol% O_2 was introduced for catalytic oxidation tests. All spectra were acquired with 100 scans at a resolution of 4 cm^{-1}.

1.4 DFT calculation method

All the spin-polarized DFT calculations were conducted based on the Vienna Ab initio Simulation Package (VASP)[1-2]. The exchange-correlation potential was described by the Perdew−Burke−Ernzerhof (PBE) generalized gradient approach (GGA)[3]. The electron-ion interactions were accounted by the projector augmented wave (PAW)[4]. All DFT calculations were performed with a cut-off energy of 400 eV, and the Brillouin zone was sampled with a 3 × 3 × 1 k-point grid. The energy and force convergence criteria of the self-consistent iteration were set to 10^{-4} eV and 0.02 eV $Å^{-1}$, respectively. Besides, the DFT + U correction for Cu and Mn atoms was taken into account, and the U-J value of 7.0 for Cu, and 4.0 eV for Mn. DFT-D3

method was used to describe van der Waals (vdW) interactions[5]. VESTA software was used to visualize the results[6].

The adsorption energies (E_{ads}) of the reactive intermediates are calculated by

$E_{ads} = E_{*A} - E_A - E_{sub}$

where E_A and E_{*A} represent the energies before and after the adsorption of A molecule on the substrate, respectively. E_{sub} is the energy of clean surface.

1.5 Catalytic performance tests

Catalytic performance tests were evaluated using a fixed-bed quartz setup under ambient-pressure conditions. The reactor was operated with a gas flow rate of 150 mL min^{-1}, which corresponds to a gas hourly space velocity (GHSV) of 18000 h^{-1}. The catalytic activity was investigated across temperatures from 100 to 600 °C. For each test, about 0.5 mL of sample particles (40-60 mesh) was measured and filled into a quartz tube having an internal diameter of 6 mm. The reactant stream consisted of 250 ppm benzene, 250 ppm toluene, and 5% O_2, with N_2 serving as the balance gas. The concentrations of reactants and products were analyzed online using a portable gas chromatograph (GC 7960 Plus, Allen Analyzer, China) equipped with a flame ionization detector (FID). The corresponding experimental results were calculated using Eqs. (1)-(3):

$$Benzene\ conversion\ (\%) = \frac{benzene\ (in) - benzene\ (out)}{benzene\ (in)} \times 100 \quad (1)$$

$$Toluene\ conversion\ (\%) = \frac{toluene\ (in) - toluene\ (out)}{toluene\ (in)} \times 100 \quad (2)$$

$$CO/CO_2\ selectivity\ (\%) = \frac{CO/CO_2\ (ppm)}{Total\ product\ C\ (ppm)} \times 100 \quad (3)$$

Table S1 Textual properties of CuO_x, MnO_x and Cu_aMn_b (a/b=1/1, 1/2, 2/1) samples

Catalysts	SSA (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
CuO_x	2.04	0.032	25.66
MnO_x	21.28	0.049	19.03
Cu_1Mn_1	9.21	0.020	26.67
Cu_1Mn_2	8.62	0.019	20.96
Cu_2Mn_1	6.02	0.014	18.36

Table S2 The apparent activation energies (Ea) of Cu_1Mn_2 catalyst

Reactant	Ea(kJ/mol)
Benzene	11
Toluene	16
Toluene in benzene+toluene	24

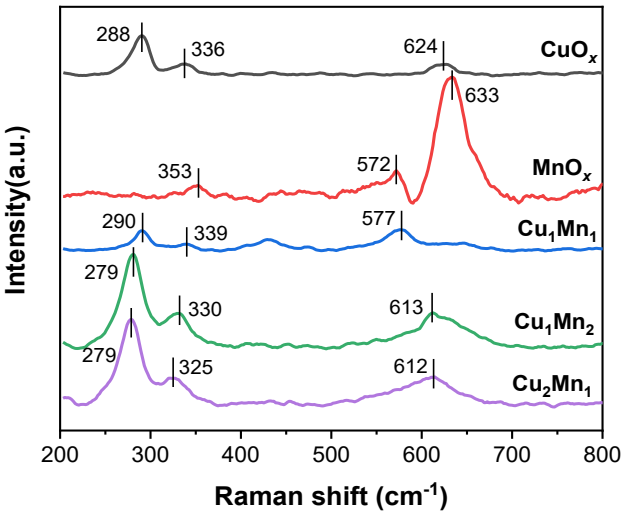


Fig. S1 Raman spectra of CuO_x, MnO_x and Cu_aMn_b (a/b=1/1, 1/2, 2/1)

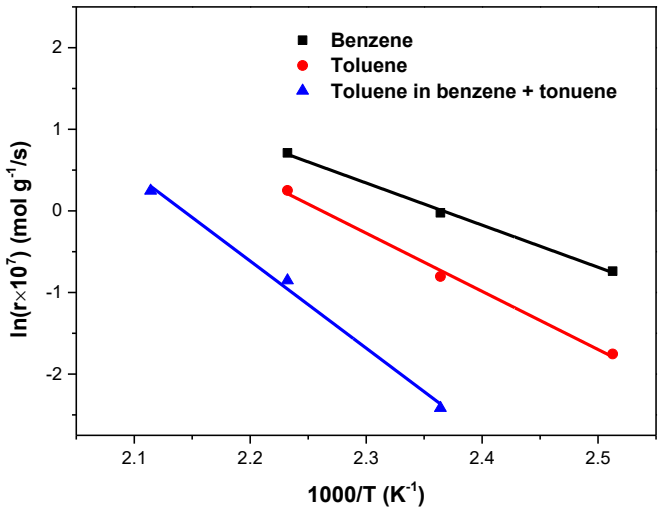


Fig. S2 Arrhenius plots for the catalytic oxidation of benzene and toluene

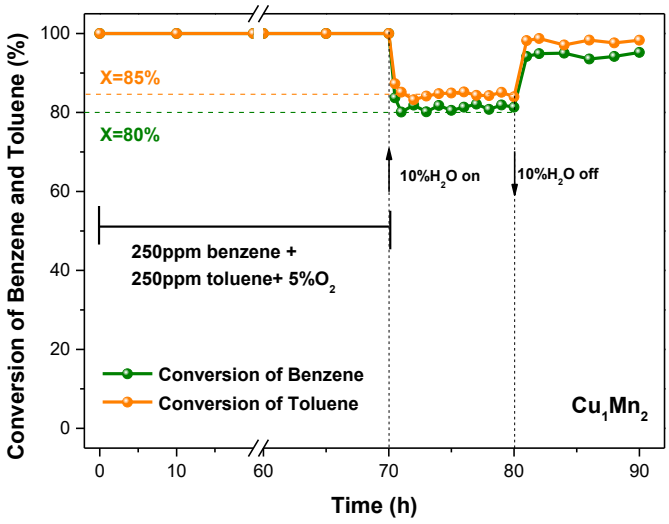


Fig. S3 Time on stream behavior of the Cu_1Mn_2 catalyst (reaction conditions: 250ppm benzene, 250ppm toluene, 5%O_2, 10% H_2O, N_2 as balance gas, T=300 °C, GHSV=18,000 h^{-1})

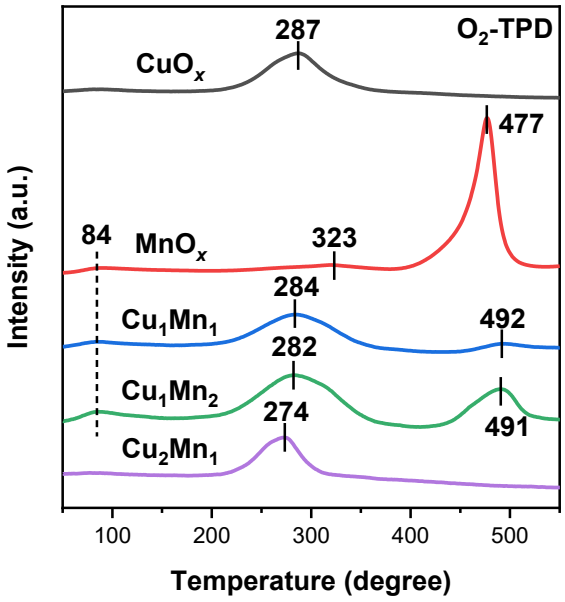


Fig. S4 O_2-TPD results of CuO_x, MnO_x and Cu_aMn_b (a/b=1/1, 1/2, 2/1)

As shown the O_2-TPD profiles **(Fig. S4)**, a low-temperature desorption peak at approximately 84 °C is observed, which can be assigned to physically adsorbed oxygen species on the catalyst surface. The desorption peaks located in the range of 270-330 °C are attributed to chemically adsorbed oxygen species, while the high-temperature peaks above 400 °C are associated with lattice oxygen species. Among the investigated catalysts, Cu_1Mn_2 exhibits a pronounced chemically adsorbed oxygen desorption peak, indicating the presence of abundant surface oxygen species. This result is in good agreement with the O 1s XPS analysis, where Cu_1Mn_2 shows the

highest O_{ads} content (36.5%). Therefore, the O_2-TPD results provide additional experimental evidence supporting the assignment of the O 1s peak at 530.8 eV to surface adsorbed oxygen species rather than hydroxyl or carbonate species.

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