# **Electronic Supplementary Information**

Promoting the Toluene Oxidation by Engineering the Octahedra Units via Oriented Insertion of Cu Ions in Tetrahedral Sites of MnCo Spinel Oxide Catalysts

Yu Chen‡, Jiang Deng‡, Bo Yang, Tingting Yan, Jianping Zhang, Liyi Shi and Dengsong Zhang\*

Department of Chemistry, Research Center of Nano Science and Technology, State Key Laboratory of Advanced Special Steel, Shanghai University, Shanghai 200444, China. †These authors contributed equally to this work. \*whom correspondence should be addressed. E-mail: dszhang@shu.edu.cn

Phone: +86-21-66132793

## **Chemicals and materials**

All the reagents for the preparation of catalysts were A.R. grade and were used directly without further purification. (Mn(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O), (Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O), polyvinylpyrrolidone (PVP, K-30), K<sub>3</sub>Co(CN)<sub>6</sub>, ethanol and toluene were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

## Synthesis of Catalysts

The Cu doped MnCo Prussian blue analogues was synthesized by means of a modified method reported by our previous work.<sup>1</sup> A 1.5 g of PVP, 0.22 g of Mn(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O and Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (the Cu doping amount is added according to the molar ratio of  $n_{Cu}/(n_{Mn} + n_{Co})$  (x% = 0%, 0.5%, 1.5%, 2.5%) were dissolved into 90 ml of the mixed solvent which contain deionized water and ethanol  $V_{H_2O}/V_{C_2H_5OH} = 1:2$ , and then magnetic stirred to form a transparent solution. Subsequently, 60 mL of an aqueous solution of K<sub>3</sub>Co(CN)<sub>6</sub> (0.16 g) was added dropwise into the above solution under magnetic stirring. Then, the mixed solution was maintained under ambient conditions. After aging for 24 h, the as-obtained sample, named as xCuMnCo-PBA (x% =  $n_{Cu}/(n_{Mn} + n_{Co}) = 0\%$ , 0.5%, 1.5%, 2.5%), was washed by deionized water and absolute ethanol several times, and finally dried at 60 °C for 12 h. In order to obtain the porous nanocages shape, the as-synthesized Prussian blue analogues were annealed in air at 450 °C for 2 h with a slow heating rate of 1°C·min<sup>-1</sup>, the retained powder was named as xCuMnCoO (x% =  $n_{Cu}/(n_{Mn} + n_{Co}) = 0\%$ , 0.5%, 1.5%, 2.5%).

The Cu doped MnCo oxides by co-precipitation method is depicted as follow. Briefly,  $Co(CH_3COO)_2 \cdot 4H_2O$  (1.0 g), and  $Mn(CH_3COO)_2 \cdot 4H_2O$  (1.5 g) and  $Cu(NO_3)_2 \cdot 3H_2O$  (  $x\% = n_{Cu}/(n_{Mn} + n_{Co}) = 1.5\%$ ) were firstly dissolved into 60 mL deionized water under magnetic stirring to form a transparent solution. Then, 30 mL of NH<sub>4</sub>OH was quickly added into the above solution under magnetic stirring, followed by 15 min stirring. After that, the suspension was transferred into a 100 mL autoclave, sealed and maintained at 150 °C for 8 h. After the reaction was completed, the precipitate was filtered and washed several times with deionized water and absolute ethanol. Finally, the obtained product was dried at 60 °C for 12 h and annealed in air at 450 °C for 2 h with a heating rate of 1 °C·min<sup>-1</sup>, the retained powder is labeled as 1.5CuMnCoO-cop.The MnCoO-cop is synthesized by the same method without the addition of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O.

#### **Characterization of Catalysts**

In this work, the nanostructures of all samples were studied by X-ray diffraction (XRD) (3KW D/MAX2200V PC, Cu Kα as the radiation source, Rigaku, Japan). The scanning speed was 8 °·min<sup>-1</sup>. The morphology and structure of the catalysts were characterized by field-emission scanning electron microscopy (FESEM, SIGMA-300), transmission electron microscopy (TEM, JEOL JEM-200CX), and high-resolution transmission electron microscope (HRTEM, JEOL JEM-2100F). The surface properties were studied by X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB250Xi). Raman spectra were recorded on the Lab RAM HR Evolution Raman spectrometer (HORIBA) and a 785 nm laser acted as an excitation source. The Fourier transform infrared (FTIR) spectrum was conducted by FT-IR spectrophotometer (Nicolet is 50). The UV-vis spectra were conducted on the Cary Series UV-Vis-NIR Spectrophotometer (Agilent). The nitrogen adsorptiondesorption isotherms of the samples were measured with ASAP 2460 Surface Area and Porosity Analyzer (Micromeritics, USA). H<sub>2</sub> temperature programmed reduction (H<sub>2</sub>-TPR) was performed on AutoChem II 2950 adsorption apparatus (Micromeritics, USA) equipped with TCD detector. Prior to H<sub>2</sub>-TPR experiment, 30 mg of catalyst was pretreated with He atmosphere with a total flow rate of 50 mL·min<sup>-1</sup> at 300 °C for 0.5 h, then cooled down to room temperature in the He atmosphere. Finally, the reactor temperature was raised to 600 °C at a constant heating rate of 10 °C ·min<sup>-1</sup> in a flow of 10 %  $H_2/Ar$  (50 mL·min<sup>-1</sup>). The H<sub>2</sub> consumption during the experiment was monitored by a TCD. O<sub>2</sub> temperature programmed desorption (O2-TPD) was performed on AutoChem II 2920 adsorption apparatus (Micromeritics, USA).50 mg of catalyst was first treated under He flow at 300 °C for 0.5 h. After cooled down to room temperature, the sample was exposed to a flow of 2 vol% O<sub>2</sub>/He for 1 h, followed by He purging (50 mL min<sup>-1</sup>) for 1 h to remove weakly adsorbed  $O_2$ . Then the sample was heated from 50 to 900 °C under He flow. Toluene temperature programmed desorption (Toluene-TPD) was tested on a Tianjin XQ TP-5080 automatic adsorption equipped with TCD detector and mass spectrometer (OMNISTARTM). 50 mg of catalyst was first treated under the flow of He flow at 300 °C for 0.5 h. After cooled down to room temperature, the sample was exposed to a flow (50 mL·min<sup>-</sup> <sup>1</sup>) of 1000ppm toluene/N<sub>2</sub> for 1 h, followed by He purging (30 mL  $\cdot$  min<sup>-1</sup>) for 1 h. Then the sample was heated from 50 to 300 °C under the flow of He. The inductively coupled plasma atomic emission spectroscopy (ICP-AES) analyses of the samples were carried out using a Thermo IRIS spectrometer to identify the amount of each element in as-obtained catalyst. In situ DRIFTS experiments were performed on an FTIR spectrometer (Nicolet is50) equipped with a Harrick DRIFT cell and a MCT/A detector. All the DRIFTS spectra were collected by accumulating 64 scans at a 4 cm<sup>-1</sup> resolution. To observe the intermediate products, the off-gas was captured by stainless steel conditioned tubes (Marks International, USA) for 10 min under 230 °C and analyzed using a calibrated GC/MS system (Agilent Technology, USA, 7890B GC System and 5977B MSD).

# **Catalytic Performance Tests**

300 mg of the sample with 20-40 mesh was used to evaluate the catalytic oxidation of toluene in a continuous flow fixed-bed tube micro reactor ( $\Phi = 6.0$  mm). The toluene vapor was generated and injected using a bubbler in a thermostatic bath at 0 °C, which passed through a container filled with

liquid toluene. The reactant mixture (volumetric composition) consisted of 1000 ppm toluene and air with a total flow of 200 mL·min<sup>-1</sup>. The equivalent of a space velocity (WHSV) was approximately 40000 mL·g<sup>-1</sup>·h<sup>-1</sup>. At the beginning of each test, the catalyst was pretreated at 300 °C in air for 1 h. The performances at steady states (typically after 30 min for every 10 °C) were used for discussion. The concentrations of outlet toluene were monitored in real time by gas chromatograph (GC-2014C, Shimadzu, Japan) equipped with flame ionization detectors (FID) and the CO<sub>2</sub> concentration was monitored by an infrared online gas analyzer.

The toluene conversion  $(X_{Toluene})$  was calculated by the following formula:

$$X_{Toluene} = \frac{[Toluene]_{in} - [Toluene]_{out}}{[Toluene]_{in}} * 100\%$$
(1)

 $[Toluene]_{in}$  was the inlet toluene concentration,  $[Toluene]_{out}$  was the outlet toluene concentration. The reaction rate (r, mol·g<sup>-1</sup>·s<sup>-1</sup>) was calculated as follow.

$$r = \frac{X * V}{W_{cat}}$$
(2)

Where  $W_{cat}$  represents the catalyst weight (g), V is the toluene gas flow rate (mol·s<sup>-1</sup>).

The activation energies are calculated for toluene conversions lower than 20%, and estimate using the following Arrhenius relationship:

$$\ln r = -\frac{E_a}{RT} + C \tag{3}$$

The activation energy  $({}^{E_a})$  can be obtained from the slope of the resulting linear plot of  $\ln r$  versus 1/T.



Fig. S1. FESEM images of (a) MnCo-PBA, (b) 0.5CuMnCo-PBA, (c) 1.5CuMnCo-PBA, (d) 2.5CuMnCo-PBA, (e) MnCoO, (f) 0.5CuMnCoO, (g) 1.5CuMnCoO and (h) 2.5CuMnCoO.

The morphology of the as-synthesized samples were characterized by field emission scan electron microscopy (FESEM), with the results shown in Fig. S1. Apparently, skeletons of Prussian blue analogues precursor is maintained either after being annealed in air nor upon the incorporation of copper. After annealing, the cubic structure still retained but the rough surfaces composed with particle clumps indicated the low crystallization during the calcination process. Additionally, the increase of copper content makes MnCoO particle size smaller, aroundly from  $1~2 \mu m$  to 60~170 nm, which is coincidence with XRD results. The cubic morphology maintained but the size decreased when Cu ion was introduced in MnCo spinel oxides.



Fig. S2. TEM images of (a) MnCo-PBA, (b) MnCoO, (c) 1.5CuMnCo-PBA, and (d) 1.5CuMnCoO. The TEM images of MnCo-PBA, 1.5CuMnCo-PBA, MnCoO, 1.5CuMnCoO were presented in Fig. S2, It can be observed that the xCuMnCo-PBA shows solid nanocubes, nevertheless, due to the kirkendall effect, the sample annealed show hollow xCuMnCoO nanocages morphology, which may be benefitial to the gas mass transfer.



**Fig. S3.** HRTEM images of (a) MnCoO, (b) 1.5CuMnCoO and (c) 2.5CuMnCoO. The inset is the corresponding SEAD image.

As show in Fig. S3, the intraplanar distance of (311) becomes smaller with increase of Cu content, and it can be observed that 2.5CuMnCoO show CuO (200) facets. The corresponding selected-area electron diffraction (SAED) patterns reveals that the addition of Cu into MnCoO lead to the lower crystallinity.



**Fig. S4.** (a) XRD patterns of xCuMnCoO-PBA ( $x=0\sim2.5$ ). (b) The enlarged image of XRD patterns at the 2 theta degree ranging from 14 to 20 degree.

It is perfectly synthesized MnCo Prussian blue analogues precursor, as shown in Fig. S4a. The diffraction peaks of MnCoO-PBA (x=0) can be readily indexed to the structure  $Mn_3[Co(CN)_6]_2 \cdot 9H_2O$  (JCPDS card no. 51-1898). All the diffraction patterns retain the structure after Cu insertion. Fig. S4b shows the enlarged drawing of XRD patterns from 14 to 20 degree. An increase of Cu content displaces the diffraction peak toward high angle indicating successful pre-doping Cu to MnCo-PBA.

 Table S1. Textural property of all synthesized catalysts.

Sample	a (Å) <sup>a</sup>	c (Å) <sup>a</sup>	V (Å) <sup>a</sup>	D <sub>XRD</sub>	FWHM <sup>a</sup>	Cu content	<i>CoO</i> <sub>4</sub>	MnO <sub>4</sub>	$MO_4$
				(nm) <sup>a</sup>		(mol%) <sup>b</sup>	<i>CoO</i> <sub>6</sub>	$\overline{MnO_6}$	$\overline{MO_6}$
							с	c	c
MnCoO	8.0847	9.2077	601.84	5.1824	0.588	-	0.99	0.55	1.54
0.5CuMnCoO	8.0922	9.2240	604.02	5.137	0.680	0.64 (0.5)	0.83	0.58	1.41
1.5CuMnCoO	8.1027	9.2723	608.76	5.1235	0.684	1.83 (1.5)	0.59	0.54	1.13
2.5CuMnCoO	8.0834	9.2651	605.40	5.1519	0.614	2.88 (2.5)	0.62	0.63	1.25

[a] From XRD analysis. Lattice parameter and the full width at half maximum are calculated in the MDI jade software and average crystallite size is obtained by Scherrer's formula.

[b] From ICP analysis.

[c] From Raman analysis. MO<sub>4</sub>/MO<sub>6</sub> presents the integrated ratio of (MnO<sub>4</sub>+CoO<sub>4</sub>)/(MnO<sub>6</sub>+CoO<sub>6</sub>).



**Fig. S5.** (a) Raman spectra of xCuMnCoO ( $x = 0 \sim 2.5$ ). (b) The enlarged image of Raman spectra at the Raman shift from 600 to 700 cm<sup>-1</sup>.

Raman spectra of xCuMnCoO catalysts was collected and shown in Fig. S5. From Raman spectrum of pure MnCoO catalyst, the peaks at 679, 652, 191 and 172cm<sup>-1</sup> correspond to octahedral sites of CoO<sub>x</sub> spinel phase, octahedral sites of MnO<sub>x</sub>, tetrahedral sites of MnO<sub>x</sub>, tetrahedral sites of  $CoO_x$ , respectively.<sup>2-5</sup> Moreover, the ratio of  $A_{679}/A_{191}$  and  $A_{652}/A_{172}$ , intuitively representing the ratio of octahedral sites to tetrahedral sites, were calculated to show the change of electronic structure of active sites. It can be observed that the substitution of Cu result in more metal cation in octahedral sites. In addition, the enlarged image of Raman spectra at the range from 600 to 700 cm<sup>-1</sup> are shown in Fig. S5b. With the increasing amount of Cu, the Raman spectra shift towards lower frequency and the peaks gradually broaden, suggesting that Cu incorporation has led to the increased disorder of MnCoO and more O vacancies (residual stress or lattice distortion). Namely, the M-O bond has been weaken by doping copper which facilitate the mobility of surface lattice oxygen and decrease formation energy of oxygen vacancies. It can conclude that the insertion of Cu to MnCoO can regulate electronic structure of active sites with more octahedral metal ion which is beneficial to gas adsorption weaken Metal-oxygen bond improving mobility surface and the of lattice oxygen.

**Table S2.** Physical characterization, catalytic activities and surface elemental ratio of Mn 2p, Co 2p and O 1 s from XPS.

XPS				Toluene					
				$\mathbf{S}_{\text{BET}}^{a}$	V <sub>pore</sub> <sup>a</sup>	conv	version	(°C)	E <sub>a</sub>
Sample	Co <sup>3+</sup> /Co <sup>2+</sup>	$Mn^{3+}/Mn^{4+}$	Oads/Olatt	(?	$(cm^{3} \cdot g^{-1})$	T <sub>10%</sub>	T <sub>50%</sub>	T <sub>90%</sub>	(kJ·mol <sup>-1</sup> )
	(%)	(%)	(%)	(m² • g					
				1)					
x=0	0.62	0.43	0.46	40.9	0.23	207	228	256	232.0
x=0.5	0.64	0.52	5.21	83.8	0.32	203	220	235	63.9
x=1.5	0.66	0.66	7.98	68.5	0.32	192	210	219	13.1
x=2.5	0.60	0.63	17.7	62.7	0.33	201	222	235	76.6

[a] From  $N_2$  adsorption-desorption measurement.  $S_{BET}$  presents BET specific surface area.



**Fig. S6.** XPS spectra of Cu 2p over xCuMnCoO (x=0.5, 1.5, 2.5).



Fig. S7. Toluene-TPD over (a) 2.5CuMnCoO, (b) 1.5CuMnCoO, (c) 0.5CuMnCoO, and (d) MnCoO.

Fig. S7 show the result of Toluene-TPD with TCD and MS signal from 50 to 300 °C. The all curve of TCD signal show a broad peak around 100 °C, which may be assigned to physically adsorbed toluene and other oxidation product. From the curve of toluene MS signal, there is a tendency that, with the increase of Cu content, desorption temperature of physically adsorbed toluene over xCuMnCoO (x=0-2.5) shift towards high region, indicating the improvement of toluene adsorption capability. Obviously, there is a small peak in the curve of TCD signal belong to xCuMnCoO (x=0.5-2.5), which keep consistent with the curve of CO<sub>2</sub> MS signal. It is indicated that the introduction of Cu facilitate the reactivity of lattice oxygen. And the 1.5CuMnCoO show the lowest CO<sub>2</sub> desorption temperature (215 °C) than 2.5CuMnCoO (233 °C) and MnCoO (240 °C) which is in line with the trend of toluene oxidation performance. All the result show that the Cu dopant can make MnCo spinel oxides strong toluene adsorption capability and high-reactive lattice oxygen.



Fig. S8. Two independent catalytic tests of 1.5CuMnCoO spinel catalyst for toluene oxidation. Fig. S8 show the results of two independent catalytic test of the most active 1.5CuMnCoO catalyst for toluene oxidation. It can be observed that the repeated test results reproduced well demonstrating its reproducibility.

Samples	VOC type	VOC concentration	WHSV	T <sub>50%</sub>	T <sub>90%</sub>
		(ppm)	$(mL \cdot g^{-1} \cdot h^{-1})$	(°C)	(°C)
$\gamma$ -MnO <sub>2</sub> -SR <sup>6</sup>	Toluene	2000	120000	242	252
Mn-Co (1:1) <sup>7</sup>	Toluene	1000	30000	236	249
Co <sub>1</sub> Mn <sub>1</sub> BHNCs <sup>8</sup>	Toluene			232	248
MOF-Mn1Co19	Toluene	500	96000	226	240
OM-CoMn0.5 <sup>10</sup>	Toluene	1200	60000	217	258
1Cu1Co/H 30% <sup>11</sup>	Toluene	600	60000	276	298
MnCuAl600 <sup>12</sup>	Toluene	800	75000	258	307
1.5CuMnCoO (This work)	Toluene	1000	40000	210	219

**Table S3.** Catalytic performance of toluene oxidation reported by other references.



**Fig. S9.** (a) Catalytic performance (The feed gas consisted of 1000 ppm toluene diluted by air , and WHSV was 40000 mL·g<sup>-1</sup>·h<sup>-1</sup>). (b) XRD images of xCuMnCoO-cop (x = 0, 1.5) prepared by a co-precipitation method. (c) N<sub>2</sub> adsorption and desorption curve of MnCoO-p and 1.5CuMnCoO-p. (d) The reaction rates normalized by the surface area of as-synthesized catalyst (MnCoO, 1.5CuMnCoO, MnCoO-p, and 1.5CuMnCoO-p).

Catalytic performance for toluene oxidation of different prepared by different method show in Fig. S9a. xCuMnCoO prepared by pyrolysis of Prussian blue analogues pre-doped with Cu show superior activity than prepared by co-precipitation.  $T_{50\%}$  are always used to evaluate catalytic performance of catalyst. Comparing the  $T_{50\%}$  of all catalysts mentioned above, the1.5CuMnCoO (210 °C) is 18 °C lower than that of MnCoO (228°C), While 1.5CuMnCoO-p (240 °C) is only 6 °C lower than that of MnCoO-p (246 °C). This result confirms the advantages of this pre-doping strategy. As

shown in Fig. S9b, the XRD pattern of xCuMnCoO synthesized by co-precipitation method are also indexed to complex spinel structure [Mn,Co][Mn,Co]<sub>2</sub>O<sub>4</sub> (JCPDS card no.18-0408). Compared with MnCoO-p, the (311) diffraction peak shift towards high angle, indicating Cu is doped into MnCo spinel successfully. Figure S9c show the N<sub>2</sub> adsorption and desorption curve of MnCoO-p and 1.5CuMnCoOp. It can be seen that xCuMnCoO prepared by pyrolysis of Prussian blue analogues possess bigger surface area than the catalysts prepares by co-precipitation. From the Figure S9d, xCuMnCoO (x = 0, 1.5) show better catalytic performance than xCuMnCoO-p (x = 0, 1.5), even eliminating the effects of specific surface area, which fully confirm the advantages of synthesis method used in this work.



**Fig. S10.** Plots of (a) Xylene, (b) benzene, (c) 2-octanol conversion and versus reaction temperature over 1.5CuMnCoO catalysts.

As shown in Fig. S10, xylene, benzene, 2-octanol were chosen as representatives of diversified VOCs to research the practicality of 1.5CuMnCoO catalysts. For the different aromatic VOCs, the  $T_{90\%}$  were 187 °C, 258 °C and 329 °C for 2-octanol, xylene, and benzene, respectively. The results show that 1.5CuMnCoO catalyst possess competitive catalytic performance for diversified VOCs, which demonstrate its practicality and versatility.



**Fig. S11.** (a) Toluene oxidation over 1.5CuMnCoO catalyst with 3 times cyclic experiment. (b) 2octanol oxidation over 1.5CuMnCoO catalyst with 3 times cyclic experiment. (c) Raman spectra of 1.5CuMnCoO before and after 3 times cyclic test.

The reusability of catalyst is an issue of concern. Researchers often evaluate the stability of catalysts in two aspects: long-term stability and recyclability. The result of long-term stability test, even the water-resistant test, about the most active 1.5CuMnCoO spinel catalyst was provided in Fig. 3c. It can be observed that 1.5CuMnCoO shows excellent thermal stability and strong tolerance against water vapour in toluene oxidation. Additionally, the cyclic catalytic test was carried out to supplementary to further confirm the stability of the most active 1.5CuMnCoO catalyst (Fig. S11a&b). It can be observed that the catalytic performance is maintained at a very similar level after 3 times cyclic experiment both for toluene oxidation and 2-octanol oxidation, indicating the recyclability of the as-synthesized catalyst. Raman spectra of the catalyst before and after 3 times cyclic test were collected and shown in Fig. S11c. Compared to the fresh 1.5CuMnCoO catalyst, no new Raman peaks appear at the Raman results of the used 1.5CuMnCoO catalyst after 3 times cyclic test, indicating there are no CuO<sub>x</sub> leaching or clustering. However, the intensity of Raman peaks of the used 1.5CuMnCoO catalyst decrease after cyclic test, which may result from that the catalyst interacted with the reactant, causing the crystal defects, reducing the crystallinity.



**Fig. S12.** *In situ* DRIFTS spectra in a flow of 500 ppm toluene diluted by air as a function of temperature (160 °C, 200 °C, 220 °C, 240 °C, 260 °C, 300 °C) from 3800 to 2700 cm<sup>-1</sup> and 2400 to 1800 cm<sup>-1</sup> over (a,b) 1.5CuMnCoO and (c,d) MnCoO.

Fig. S12 show the *in situ* DRIFTS spectra under simulated reaction condition from 3800 to 2700 cm<sup>-1</sup>. The bands between 3100 cm<sup>-1</sup> to 3000 cm<sup>-1</sup> is assigned to the C-H stretching vibration of toluene aromatic ring.<sup>13</sup> For both 1.5CuMnCoO (Fig. S12b) and MnCoO (Fig. S12d),The peak at ~3067 cm<sup>-1</sup> shows a small increase from 160 °C to 200 °C and then a decrease above 200 °C, corresponding to significant decomposition of the phenyl species.<sup>14</sup> However, both MnCoO and 1.5CuMnCoO show the bands at 2931 cm<sup>-1</sup> and 2875 cm<sup>-1</sup> at lower temperature assigned to the C-H symmetric or asymmetric stretching of methylene (rather than methyl in 2970-2950 cm<sup>-1</sup> region), which implies that the -CH<sub>3</sub> of toluene is partly oxidized by the surface active oxygen species from catalyst, resulting in the formation of alkoxide specie.<sup>15</sup> The bands at 1966, 1920, 1815, and 1303 cm<sup>-1</sup> are ascribed to maleic anhydrides which implies the further benzoate species oxidation at lower temperature.<sup>16</sup> (Fig. S12a, c)



**Fig. S13.** CO<sub>2</sub>-TPD profiles equipped with TCD detector and Mass spectrometer over xCuMnCoO (x=0, 1.5).

Fig. S13 show the result of CO<sub>2</sub>-TPD with MS signal from 50 to 300 °C. The all curve of MS signal of CO<sub>2</sub> show a broad peak around 110 °C, which may be assigned to physically adsorbed CO<sub>2</sub>. And the all curve of MS signal of CO<sub>2</sub> show other broad peak above 180 °C, which may attributed to the decomposition of carbonate species. Obviously, after the addition of Cu, desorption temperature of CO<sub>2</sub> shift towards low region, indicating the improvement of CO<sub>2</sub> desorption capability.



**Fig. S14.** *In situ* DRIFTS spectra of the transient reactions at 240 °C between (a) pre-adsorbed toluene and (b) air as a function of time over (I) 1.5CuMnCoO and (II) MnCoO.

*In situ* DRIFTS spectra of toluene adsorption over MnCoO (I) and 1.5CuMnCoO (II) at 240 °C are shown in Figure S14a. Prior to experiment, all catalysts was pre-treated by N<sub>2</sub> for 1 h at 300 °C to eliminate the effects of surface oxygen species. With the extended time, the characteristic peaks corresponding to benzaldehyde (1689 and 1644 cm<sup>-1</sup>)<sup>4</sup> can be detected both on MnCoO and 1.5CuMnCoO, and these peaks intensity decrease, while the peak intensity corresponding to benzoate (1558, 1390 cm<sup>-1</sup>)<sup>17</sup> increase which may due to the oxidation of benzaldehyde. This phenomenon indicate toluene can be oxidized to benzaldehyde which then rapidly transform to benzoate. The accumulation of benzoate species indicates it's hard to be cracked on these spinel catalyst. The deep toluene oxidation is carried out in the absence of O<sub>2</sub> as the appearance of CO<sub>2</sub>. These phenomenon demonstrate that toluene can be oxidized deeply by O<sub>latt</sub> in the absence of gaseous O<sub>2</sub> and benzoate is a key intermediates during the process.<sup>18</sup> After the adsorption of toluene, air is added into the IR cell at same temperature, and the results shown in Figure S14b. Notably, both over 1.5CuMnCoO (I) and MnCoO (II) sample, the intensity of the peaks corresponding to benzoate clearly decrease with the rising time, which indicate that gaseous O<sub>2</sub> can accelerate the process to crack benzoate to CO<sub>2</sub>. The

accumulation of benzoate during pre-adsorption of toluene and its degradation as the introduction of air suggest the importance of the replenishment of  $O_2$  corresponding to the MVK mechanism. It is concluded that toluene oxidation depend on  $O_{latt}$  and can be accelerated by  $O_2$ .



Fig. S15. GC-MS analyses on the intermediate products catalytic oxidation of toluene over 1.5CuMnCoO.

Retention time (min)	Molecular formula	Name of compound	Molecular structure
1.545	$CO_2$	Carbon dioxide	0 <b>—</b> c <b>—</b> 0
1.641~1.770	$C_2H_4O$	Acetaldehyde	<b>∽</b> ⁰
1.812	$C_2H_2O_4$	Oxalic acid	HO OH
1.876	$CH_2O_2$	Formic acid	HO
1.995	$C_3H_6O_4$	Propionic acid, 2,3-dihudroxy-	HO
2.076	$C_2H_4O_2$	Acetic acid	Он
2.712	$C_6H_6$	Benzene	$\bigcirc$
3.198	$C_6H_{12}O$	Hexanal	$\wedge \wedge \wedge \diamond_{0}$
3.307~3.554	$C_7H_{14}$	2-Heptene	$\frown \frown \frown$
3.854~4.117	$C_4H_8O_2$	Butanal,3-hydroxy-	HOPHON
3.921	$C_5H_{10}O$	Pentanal	
3.998	$C_6H_8O_2$	1,2-Cyclohexanedione	<u>گ</u> ے
4.458	$C_7H_8$	Toluene	
7.046	$C_7H_{14}O$	Heptanal	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
7.169	C <sub>5</sub> H <sub>6</sub> O	Furan,3-methyl-	
8.162	C <sub>7</sub> H <sub>6</sub> O	Benzaldehyde	
8.403	C <sub>6</sub> H <sub>8</sub> O	2-Cyclohexen-1-one	
8.513	C <sub>6</sub> H <sub>6</sub> O	Phenol	OH
9.477	C <sub>7</sub> H <sub>8</sub> O	Benzyl alcohol	HO
10.133	$C_3H_6O_3$	1,2-ethanediol, monofomate	o OH

**Table S4.** Possible intermediate products in catalytic oxidation of toluene over 1.5CuMnCoO detected

by GC-MS.<sup>a</sup>

10.641	$C_7H_{14}O$	2-Hepten-1-ol,(E)-	ОН
11.529	$C_7H_6O_2$	Benzoic acid	HO

[a] Both the Direct Match and Reverse Match are greater than 600.

The off-gas from activity evaluation of 1.5CuMnCoO at 230 °C was captured using a GC-MS spectrometer (Fig. S15 and Table S4, ESI<sup>†</sup>). Additionally, the C7 chain alkanes (2-Heptene, Heptanal, 2-Hepten-1-ol, (E)-) generated in this process is indicative of another reaction pathway of toluene oxidation via directly opening the aromatic ring without demethylation. But the weak peak suggests its secondary status.



**Scheme S1** Proposed reaction mechanism over the xCuMnCoO catalyst. (Red atom: Oxygen; Yellow atom: Oxygen vacancy; Purple atom: Metal; Blue atom: Copper; Pink atom: Mobile oxygen; Grey atom: Carbon; White atom: Hydrogen).

## Analysis Details of in situ DRIFTs for toluene oxidation

In Fig. 4a, all *In situ* DRIFTS curves of 1.5CuMnCoO show the aromatic ring out-plane and inplane vibrations at 1595, 1495, 1449 cm<sup>-1</sup>. The typical bands at 1560, 1537 and 1398 cm<sup>-1</sup> are characteristic of benzoate species. Additionally, the  $\Delta v$  of asymmetric (1560 cm<sup>-1</sup>) and symmetric (1398 cm<sup>-1</sup>) vibration of a benzoate species is 162 cm<sup>-1</sup>, which means benzoate complex exists on 1.5CuMnCoO by the bridging structure. And the bands at 1303 cm<sup>-1</sup>, only showing in the curve below 240 °C, are ascribed to maleic anhydrides which implies the further benzoate species oxidation.<sup>19</sup> The band at 1355 cm<sup>-1</sup> attributed to deformation vibration of -CH<sub>2</sub> and the peaks in the range from 1180 cm<sup>-1</sup> to 1000 cm<sup>-1</sup> are attributed to benzyl alcohol. There are several reduced typical bands at 1687 and 1650 cm<sup>-1</sup> from 160 to 220 °C which is attributed to C=O stretching vibration of benzaldehyde due to the existence of corresponding bands at 2931 and 2875 cm<sup>-1</sup> (Fig. S12). However, when temperature rise above 240 °C, The similar bands at 1689 and 1653 cm<sup>-1</sup> can be ascribed to benzoquinone with the absence of the bands at the region of 2800–3000 cm<sup>-1</sup>, of which the intensity suddenly and then decrease with the increasing temperature.<sup>20</sup>

In Fig. 4b, the skeletal stretching vibration of aromatic ring at 1600, 1492, and 1447 cm<sup>-1</sup> are observed among all curves, and the intensity of this band increase firstly and then reduce with the increasing temperature, implying the breakage of aromatic ring. The bands at 1684 cm<sup>-1</sup> and 1651 cm<sup>-1</sup> attribute benzaldehyde due to the presence of the accompany bands at 2915 and 2847 cm<sup>-1</sup>, of which the intensity also monotonically decrease with the increasing temperature.<sup>20</sup> Simultaneously, The bands at 1561, 1543 and 1396 cm<sup>-1</sup> are characteristic of typical carboxylate group, indicating the formation of benzoate species, and their relative position ( $\Delta v$ = 165 cm<sup>-1</sup>) is close to the free ion values, which indicate a bridging structure benzoate complex on MnCoO. Apparently, benzoate is a key

intermediate in toluene oxidation. The band at 1180 cm<sup>-1</sup> to 1000 cm<sup>-1</sup> identified the appearance of benzyl alcohol. The band centered at 1396 and 1350 cm<sup>-1</sup>, which are respectively assigned to symmetric -COO- stretching vibration and deformation vibration of -CH<sub>2</sub>, are declined from 160 °C to 240 °C, but strangely strengthen with the increasing temperature from 240 °C to 300 °C, which indicates the formation of new species located at similar bands. And it is reported that the peaks at 1396 cm<sup>-1</sup> and 1350 cm<sup>-1</sup> also can be assigned to the deposition of carbonate species covering the active site.<sup>4, 16</sup> We can reasonably speculate that the adsorption of carbonate species is one of the reasons causing the sluggish catalytic performance for toluene oxidation over MnCoO.

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