Supporting information

Engineering the core shell structure CoMnOx@OTS cubic catalyst with excellent water resistant for low-temperature catalytic combustion of VOCs

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1. Catalyst Characterizations

The morphology structure of the precursors and samples was verified by a scanning electron microscope (SEM) and Transmission electron microscopy (TEM) analysis. Among, SEM image was recorded on a JSM-6701F emission scanning electron microscopy, and TEM image was carried out on a JEOL JEM-2010 transmission electron microscope equipped with an Oxford energy dispersive X-ray (EDX) spectrometer attachment operating at 200kV. For TEM analysis, the samples were uniformly dispersed in the ethanol solution, which were in further installed on double sided adhesive tape.

To determine the types of organic functional group, the existing form of polymer bonds and the structure of the samples, Fourier transform infrared spectroscopy (FTIR) spectrum were conducted on the Thermo Nicolet Avatar 380 FTIR spectrometer. Moreover, the samples surface was saturated with NH_3 to separate the Brønst and Lewis acid sites.

X-ray diffraction (XRD) analysis was conducted to explore the crystal phase of samples, which was recorded on a Rigaku D/MAX-RB X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å) and run in the range of 10-90 ° with 60 kV and 55 mA.

N_2 adsorption-desorption was conducted on a Micromeritics ASAP 2010 instrument, and the specific surface area of the sample was determined by nitrogen adsorption in accordance with the Brunauer Emmett and Teller (BET) method. Before measurements, the sample was degassed at 150 °C for 6 h, and BET surface area determination was calculated through six measurements at relative pressures of N_2 in

the range of 0.05-1.00.

H_2-Temperature program reduction (H_2-TPR) was performed by automatic multi-function adsorption apparatus. The mixed gas of 5 vol.% H_2 and 95 vol.% N_2 was introduced into the quartz tube reactor. After that, 50 mg sample was put in the quartz tube reactor. Before test, the sample was purged with pure N_2 gas at 400 °C for 2 h, and then the test was conducted from 30 °C to 800 °C with a heating rate of 10 °C min^{-1}.

X-ray photoelectron spectroscopy (XPS) analysis was carried on a VG ESCALAB 210 Electron Spectrometer using Mg Ka radiation (hv= 1253.6 eV) to determine the chemical states of elements in these samples.

To explore the formation of defect structure, A RM 2000 microscope confocal Raman spectrometer (Renishaw PLC) with 532 nm laser was used.

Besides, in order to investigate the effect of acidity, NH_3-Temperature program desorption (NH_3-TPD) was conducted by automatic multi-function adsorption apparatus. The 80 mg samples were put in the quartz tube reactor and purged with pure N_2 gas at 400 °C for 2 h, and then the adsorbing gas of 5 vol. % NH_3 and 95 vol. % N_2 was passed into the quartz tube reactor. Finally, the experiment was conducted from 30 ºC to 850 °C.

O_2-Temperature program desorption (O_2-TPD) was used to investigate the types of oxygen species in these samples. Firstly, 50 mg samples were putted into the quartz tube reactor, and then they were purged with pure N_2 gas at 400 °C for 2 h. After that, the mixture gas of 5 vol.% O_2 and 95 vol.% N_2 was introduced at 30 ºC for 1h, and then the pure He gas was used to remove the unabsorbed O_2 molecules at 30 ºC for 30 min.

Ultimately, the samples were heated from 30 ºC to 900 ºC.

In situ diffuse reflectance infrared fourier transform spectroscopy (in situ DRIFTS) was collected on Bruker V70. The powder samples were degassed in N_2 gas with 25 mL/min gas volume at 400 °C for 30 min. After that, the samples were cooled to room temperature. Accordingly, a background spectrum was respectively gathered at 100, 150, 200, and 250 °C. Toluene is introduced continuously by a bubbling method with N_2 as a carrier gas at 200°C for 30 min. To remove the weakly adsorbed toluene molecule, the samples were purged with He gas for another 30 min. Thereafter, a pure N_2 gas and a mixture reaction gas of 20 vol % O_2/N_2 (25 mL/min) were respectively introduced into the in suit cell to react with toluene as requires. Finally, the samples were further heated to 100, 150, 200 and 250°C to collect the corresponding spectra, respectively.

2. Catalytic activity measurements

Tests of activity and stability were essential for probing catalytic performance, mainly with the help of fixed-bed reactor. By pressing and sieving (40-60 mesh), it was possible to obtain 0.4 g of sample, to which 0.7 g of silica (SiO_2) was subsequently added. The catalyst and SiO_2 were mixed well and poured into the thermostatic zone of the reaction tube, which was stuffed with cotton. The catalyst was exposed to a mixture of toluene (3000 ppm) and air with a flow rate of 200 mL/min and a weight hourly space velocity (WHSV) of 30 000 mL·g^{-1}·h^{-1}. An on-line gas chromatograph (GC-6820, Agilent, USA) equipped with a flame ionization detector (FID) was used to detect the concentration of the reactants. Usually, the activity was distinguished by the reaction

temperature when the toluene conversion was 90%. The toluene conversion was calculated as follows:

$$Conversion\ of\ toluene = \frac{Toluene_{in} - Toluene_{out}}{Toluene_{in}} \times 100\%$$

Generally, to test the stability of the catalyst, it is necessary to keep the reaction temperatures at high/low conversion of toluene for about 15 hours. And the concentration of the reactants was measured every hour to calculate the toluene conversion. In general, the specific equation for carbon balance was as follows and the error of carbon balance is about ±3%:

$$Carbon\ balance\ (\%) = \frac{Mole\ of\ the\ overall\ carbon\ fed\ (mol)}{Mole\ of\ the\ outflowed\ carbon\ (mol)}$$

3. The calculation of r (reaction rate) and E_a (Activation energy):

The catalytic performance could also be identified by apparent activation energy (E_a), which was measured as follows [S1]:

$$\ln r = \frac{-E_a}{RT} + C \tag{1}$$

In equation (1), r represented the reaction rate (mol·s^{-1}), T referred to the reaction temperatures, and C was a constant term.

$$r = \frac{F \times X_{toluene}}{W} \tag{2}$$

In equation (2), $X_{toluene}$ denoted the conversion of toluene, F indicated the feeding rate (mol·s^{-1}), and W corresponded to the mass of catalyst. Therefore, the plot of lnr and 1000/T yielded the E_a value.

We performed a kinetic study of the catalysts. The specific toluene reaction rates through the catalyst's specific surface area (R_s) and the catalyst's mass (R_m) were

calculated required the following equation [1]:

$$R_S = \frac{F \times \eta_{toluene}}{S_{BET}}$$

$$R_m = \frac{F \times \eta_{toluene}}{W}$$

$$\eta_{toluene} = \log \frac{1}{1 - \frac{X_{toluene}}{100}}$$

4. The calculation of Turnover frequency (TOF):

Turnover frequency (TOF), defined as the number of toluene molecules converted

per active site per second, is calculated according to the equation:

$$\text{TOF} = \frac{F_T * X_T}{\frac{(m_{cat} * w_{Co})}{M_{Co}} * d_{Co}} \tag{3}$$

Where F_T is the toluene flow rate (mol/h), X_T is the conversion of toluene, m_{cat} is

the mass of the catalyst (g), w_{Co} is the mass percentage of Co in the catalysts, M_{Co} is

the molar mass of Co (58.93 g/mol), and d_{Co} is the Co dispersion. And d_{Co} is calculated

based on the ratio of the area occupied by the active site in the XPS spectrum.

Table S1 TOF and r for benzene degradation over $CoMnO_x$ and $CoMnO_x@OTS$ catalysts.

Catalysts	r_s (μmol/s^{-1} m^{-2})	TOF_{Co} (h^{-1}) at 320 °C
$CoMnO_x$	2.58	0.84
$CoMnO_x@OTS$-1	3.06	1.79
$CoMnO_x@OTS$-2	3.29	2.06
$CoMnO_x@OTS$-3	2.71	1.47

Table S2 The amount and percentage of surface acid sites.

Catalysts	Weak[a] peak areas	Moderate[b] Peak areas	Strong[c] peak areas	(Moderate+Strong)[d] peak areas
CoMnO$_x$	76.40	8.15	15.45	23.60
CoMnO$_x$@OTS-1	35.12	0	64.88	64.88
CoMnO$_x$@OTS-2	30.21	10.26	59.53	69.79
CoMnO$_x$@OTS-3	33.25	15.32	51.43	66.75

[a] Desorption peak areas of weak acid.

[b] Desorption peak areas of moderate acid.

[c] Desorption peak areas of strong acid.

[d] Desorption peak areas of moderate and strong acid.

Table S3 Surface atom ratios of $CoMnO_x$ and $CoMnO_x@OTS$ catalysts.

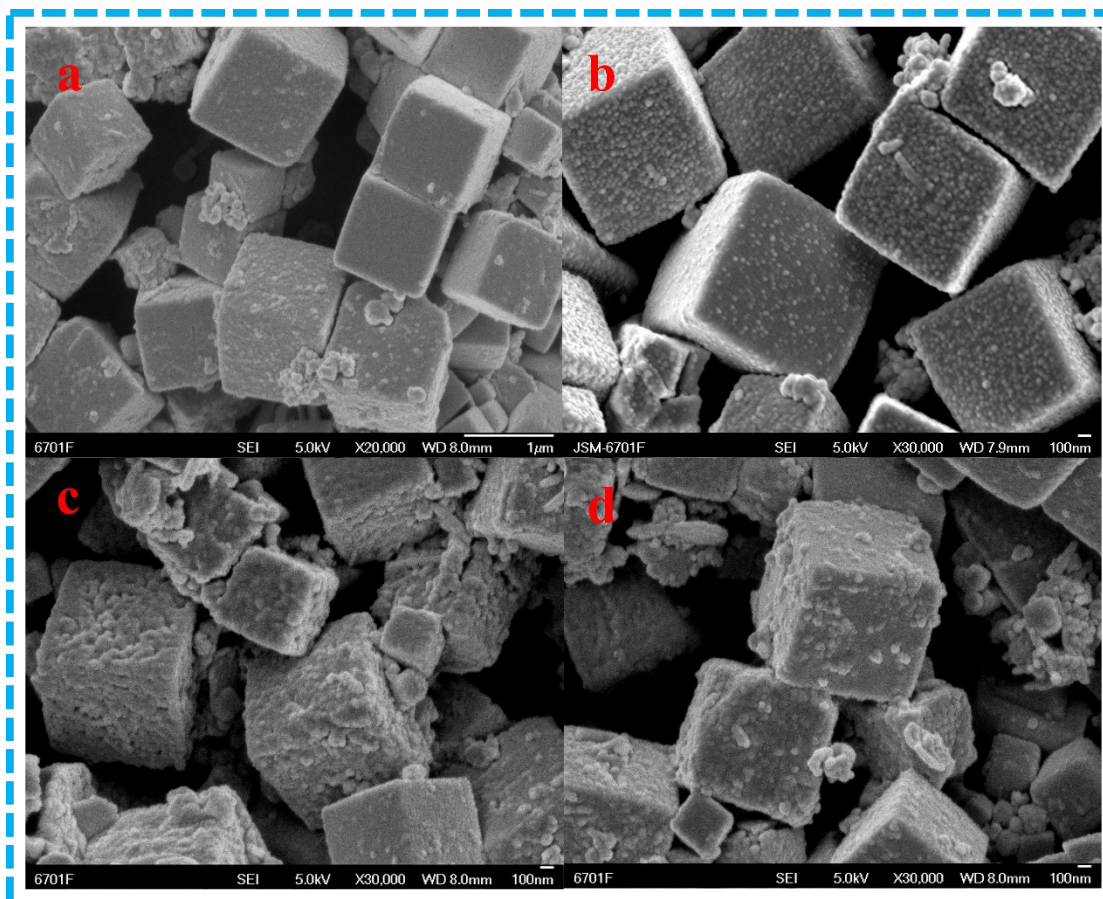| Catalysts	Co (%)	Mn (%)	Mn/Co (atomic ratio)
$CoMnO_x$	29.95	5.52	0.15
$U-CoMnO_x$	25.31	3.98	0.13
$CoMnO_x@OTS-1$	23.76	6.32	0.22
$U-CoMnO_x@OTS-1$	17.05	2.06	0.10

Fig. S1. FE-SEM images of (a) CoMnO$_x$, (b) CoMnO$_x$@OTS-1, (c) CoMnO$_x$@OTS-2 and (d) CoMnO$_x$@OTS-3.
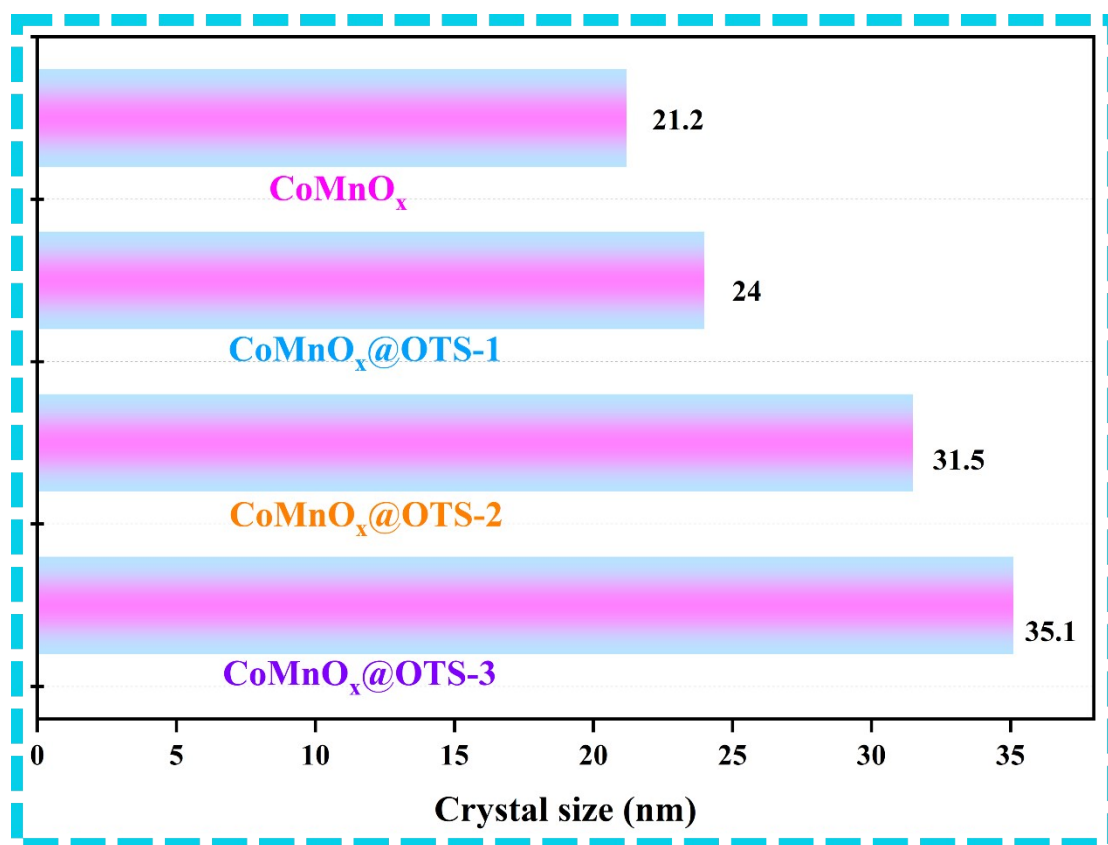
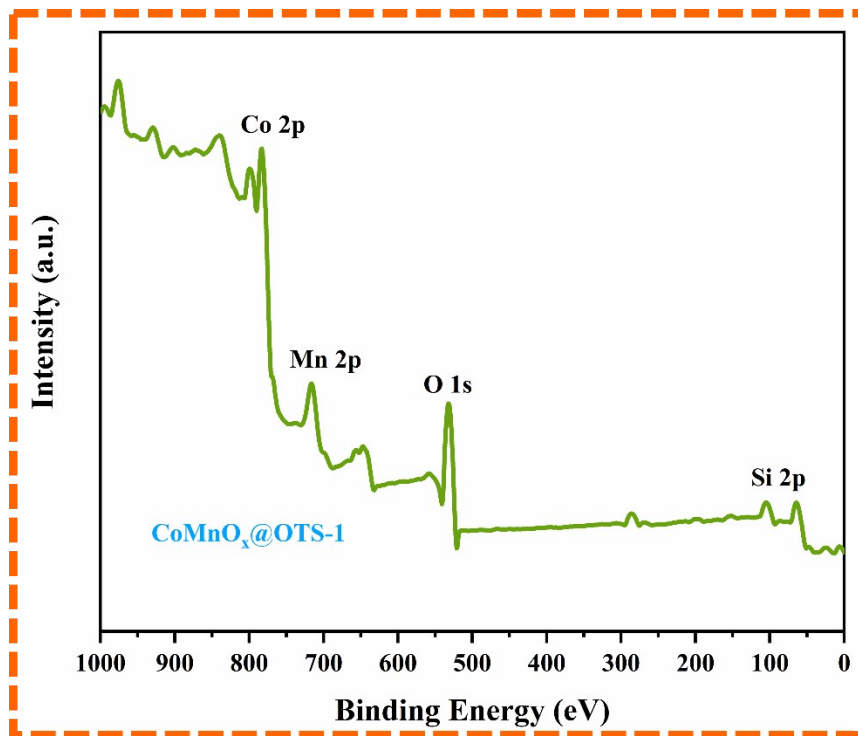**Fig. S2.** Crystal size of $CoMnO_x$ and $CoMnO_x$@OTS catalysts.

Fig. S3. Survey XPS Spectroscopy of CoMnO$_x$@OTS-1 catalysts

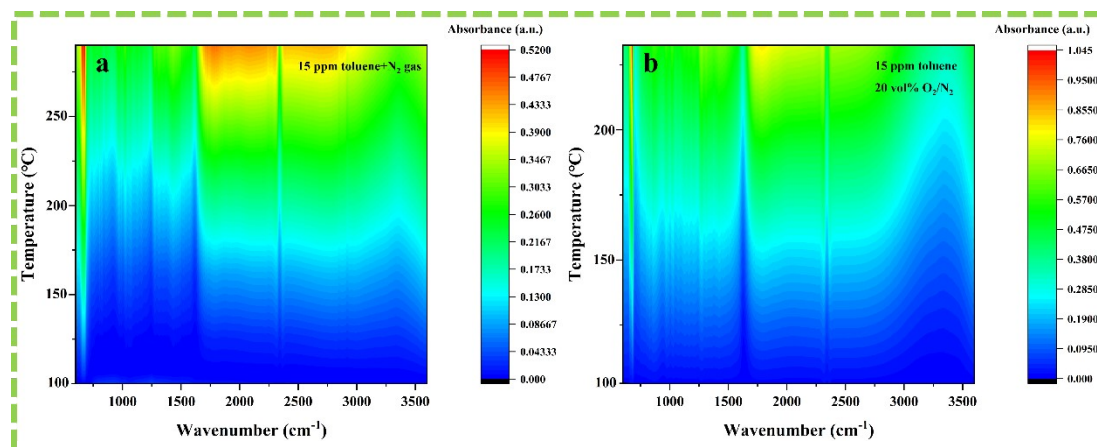**Fig. S4.** (a) In-situ FTIR spectra for adsorption exposure to 15 ppm toluene in N_2 gas,

(b) the flow of 15 ppm toluene and 20% O_2/N_2 gas and