## **Supporting Information**

# Self-template synthesis of a MnCeOδ/Co3O4 polyhedral nanocage catalyst for

# toluene oxidation

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# **Supporting Information content**

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# Highlights

- A novel nanocage catalyst of a porous Mn-Ce-Co polyhedral was prepared from a Co-based zeolitic imidazolate framework as a sacrificial template.
- The novel porous catalyst has excellent low temperature oxidation activity and lower apparent activation energy for the catalytic oxidation of toluene.
- The catalyst prepared from the template method shows a high specific surface area and porous structure compared with the traditional preparation method.

## **Experimental section**

## Characterization

## XRD

XRD was applied in an AXS D8 Advance diffractometer equipped with a graphite monochromator and Cu K $\alpha$  radiation source (0.15418 nm). The diffraction scattering angle (2 $\theta$ ) was set from 5 to 80° using a scan rate of 0.02 °min<sup>-1</sup>

TGA

Thermogravimetric analysis (TGA) data were recorded on a NETZSCH STA 449F3 between 25 and 600°C at a heating rate 10 °C min<sup>-1</sup>.

#### SEM

Thermogravimetric analysis (TGA) data were recorded on a NETZSCH STA 449F3 between 25 and 600°C at a heating rate 10 °C min<sup>-1</sup>.

### BET

Scanning electron microscopy (SEM) images were obtained on a JSM-5900 instrument after precoating the samples with gold (ion sputtering apparatus, JFC-1600).

# TEM

The surface area and pore size distribution measurements were carried out on an ASAP 2020 by  $N_2$  adsorption-desorption isotherms at a liquid nitrogen temperature (-196°C) using the BET, Horvath-Kawazoe (HK) and Barrett-Joyner-Halenda (BJH) methods.

# Raman

The Raman spectra of the samples were measured using a DXR532 laser Raman spectrometer equipped with a 532 nm laser as the excitation source with 10 mW laser power.

## H<sub>2</sub>-TPR

The H<sub>2</sub>-TPR experiments using an Autochem 2920 (Micromeritics, USA) provided an automated catalyst characterization system. In these tests, 50 mg of the purged samples were used under a flow of a mixture gas (5% H<sub>2</sub>/Ar, 25 ml min<sup>-1</sup>)

with a heating ramp of 10 °C min<sup>-1</sup> from room temperature to 700°C. Prior to the runtime analyses, the samples were degassed at 350°C for 4 h.

O<sub>2</sub>-TPD

The  $O_2$ -TPD was also tested on an Autochem 2920 (Micromeritics, USA), and the samples were pretreated at 150°C under an Ar flow. The samples were then treated with 30 ml/min of mixture gas (5%  $O_2$ , 95% Ar) for 2 h at room temperature and then heated to 800°C at a rate of 10°C min<sup>-1</sup>.

## XPS

The XPS patterns were acquired on a PHI-5000C ESCA system (upgraded by RBD company, America) using a dual Mg/Al K $\alpha$  anode at 250 W and running at 14 KV in a pressure range of 10-8 Torr. The charging of the catalyst samples was corrected by setting the binding energy of adventitious carbon (C1s) to 284.5 eV.

#### **Figure captions**



Figure S2. Raman spectra of the  $Co_3O_4$  bulk,  $Co_3O_4$ -NC and  $MnCeO_{\delta}/Co_3O_4$ -NC.



Figure S.1. TG-DSC curve of the ZIF-67 crystal material.

Figure S.1 exhibits the thermogravimetric analysis (TGA) curve of the ZIF-67 precursor. It can be observed that there is almost no change in the mass of the material before 120°C, indicating that the free and anhydrous methanol in the material is almost completely removed under vacuum at 80°C. The material has a slight weight loss of 6% at 120-200°C due to the loss of water molecules from the porous framework structure. When the temperature is higher than 260°C, a significant inflection point appears, and the material quickly loses 60% of its mass. The process is basically completed at 310°C. During this period, the DSC curve showed a significant endothermic peak, a phenomenon that was attributed to the decomposition of the ZIF-67 material. Therefore, to obtain the MnCeO<sub> $\delta$ </sub> solid solution and pure Co<sub>3</sub>O<sub>4</sub>-NC, the calcination temperature of ZIF-67 from the template is 350°C.



Figure S.2. Raman spectra of the  $Co_3O_4$  bulk,  $Co_3O_4$ -NC and  $MnCeO_{\delta}/Co_3O_4$ -NC.

The Raman spectra of the three samples are shown in Figure S.2s In the case of the Co<sub>3</sub>O<sub>4</sub> bulk and Co<sub>3</sub>O<sub>4</sub>-NC catalysts, five distinct peaks are observed at approximately 195, 484, 519, 621 and 687 cm<sup>-1</sup>, which correspond to the five characteristic Raman modes ( $A_{1g} + E_g + 3F_{2g}$ ) of spinel Co<sub>3</sub>O<sub>4</sub>.<sup>1,2</sup> The MnCeO<sub> $\delta$ </sub>/Co<sub>3</sub>O<sub>4</sub>-NC catalyst shows the characteristic Raman mode ( $F_{2g}$ ) of CeO<sub>2</sub> (~462 cm<sup>-1</sup>) and five characteristic Raman modes of spinel Co<sub>3</sub>O<sub>4</sub>. Compared with the other catalysts, the MnCeO<sub> $\delta$ </sub>/Co<sub>3</sub>O<sub>4</sub>-NC catalyst shows a slight shift to lower wavenumbers and a redshift phenomenon. This finding shows that the sample has microscopic stress and disordered lattice defects.

# References

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