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Supplementary Information

Rare-earth element doping promoted toluene low-temperature combustion over mesostructured CuMCeO$_x$ (M = Y, Eu, Ho, and Sm) catalysts: The indispensable role of *in-situ* generated oxygen vacancy

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Table S1 Summary of some active catalysts for toluene oxidation reported in the literature.

Catalyst characterizations

XRD measurements were performed using a powder diffractometer (PANalytical, Netherlands) with Cu-Ka radiation. The tube voltage was 40 kV, and the current was 40 mA. XRD diffraction patterns were obtained in the 2θ range of 20-80° (scanning rate of 4°/min).

N_2 sorption isotherms were measured at 77 K on a Builder SSA-6000 apparatus. Prior to the measurements, the samples were evacuated for 4 h under vacuum at 473 K. The total pore volume was estimated from the amount of nitrogen adsorbed at a relative pressure (P/P_0) of *ca.* 0.99. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method, and the pore size distribution was derived from the adsorption branch of the N_2 isotherm using the Barrett-Joyner-Halenda (BJH) method.

Field emission scanning electron microscopy (FE-SEM) images were recorded on a JEOL 7800F (Japan) microscope. High resolution transmission electron microscopy (HR-TEM) and high-angle annular dark-field imaging in scanning transmission electron microscopy (HAADF-STEM) images were collected on a G2F30 microscope (FEI, America) operating at an acceleration voltage of 300 kV.

X-ray photoelectron spectroscopy (XPS) experiments were carried out on an AXIS ULtrabld instrument (Kratos, UK) with Mg-Kα radiation ($h\nu$ = 1253.6 eV). The X-ray anode was run at 250 W, and the high voltage was maintained at 14.0 kV with a detection angle at 54°. The pass energy was fixed at 93.90 eV to ensure sufficient resolution and sensitivity. The base pressure of the analyzer chamber was approximately 5×10^{-8} Pa. The entire spectra (0 to 1100 eV) and narrow spectra of all elements were both recorded with extremely high resolution by using a RBD 147 interface (RBD Enterprises, USA) through the XPS Peak4.1 software. Binding energies were calibrated using the containment carbon (C 1*s* = 284.6 eV).

H_2-TPR experiments were performed on a PCA-1200 (Builder, China) equipped with a TCD, using 50 mg of the catalyst samples, which were pretreated at 200 °C (10 °C/min) for 2 h under N_2 at a flow rate of 30 mL/min. Then the samples were reduced from room temperature to 250 °C at 10 °C/min under a mixture of 5 vol.% H_2/Ar at a flow rate of 30 mL/min. Hydrogen consumption was measured using a thermal conductivity detector (TCD). The initial H_2 consumption rate (mmol/g) of prepared samples is calculated based on the fitting peak area of H_2 consumption from H_2-TPR profiles, as follows:

$$\mathrm{H_2\ consumption\ rate} = \frac{S_{\mathrm{cat}} \times n_{\mathrm{CuO}} \times 1000}{S_{\mathrm{cat}} \times m_{\mathrm{cat}}} \tag{S1}$$

where S_{cat} is the fitting peak area of H_2 consumption for prepared catalysts; S_{CuO} represents the fitting peak area of H_2 consumption for CuO standard sample; n_{CuO} is the amount of CuO standard sample (mol); m_{cat} represent the weight of catalyst (g).

Temperature programmed desorption of O_2 (O_2-TPD) was performed on a PCA-1200 equipped with a TCD. Typically, 0.1 g of the catalyst was pre-treated in a pure N_2 flow (40 mL/min) at 400 °C for 1 h and then cooled to room temperature (25 °C) prior to adsorption of O_2 for 2 h. After being saturated with O_2, the catalysts were flushed with pure N_2 flow (40 mL/min) for 1 h at room temperature. The desorption profile of O_2-TPD was recorded online at a heating rate of 10 °C/min.

Raman spectra in the range of 300-1200 cm^{-1} were obtained on a RM2000 laser Raman spectrometer by employing excitation wavelength of 532 nm line of Ar ion laser and recorded on a LabRam spectrometer (JobinYvon Horiba). The wavelength was calibrated using Si signal at 520 cm^{-1}.

Catalytic activity

The performance of each material for toluene oxidation was investigated in a continuous-flow fixed-bed reactor consisting of a steel tube (6 mm, i.d.) at atmospheric pressure. In each test, 0.40 g of catalyst (40-60 mesh) was placed into the tube reactor. Prior to testing, the catalyst was pretreated at 200 °C with N_2 for 1 h. The toluene feed (900 ppm) was generated by using a N_2 bubbler in thermostatic bath at 30 °C and mixing with air (79% N_2 + 21% O_2). The total flow rate was kept at 200 $\mathrm{mL \cdot min^{-1}}$ (GHSV = 50,000 $\mathrm{h^{-1}}$). The catalyst bed was subsequently set to the desired temperature and left to equilibrate for 30 min before online sampling was initiated. The concentrations of toluene, CO, and CO_2 were measured by an on-line gas chromatography (GC-9890B; Linghua, China) equipped with a flame ionization detector (FID) and HT-Wax column in 30 m × 0.32 mm (ID) × 0.5 μm. The conversion of toluene (X_{toluene}) was calculated as Eq (S2),

$$X_{\text{toluene}}(\%) = \frac{[\text{toluene}]_{\text{in}} - [\text{toluene}]_{\text{out}}}{[\text{toluene}]_{\text{in}}} \times 100\% \qquad \text{(S2)}$$

where $[\text{toluene}]_{\text{in}}$ and $[\text{toluene}]_{\text{out}}$ represent the toluene concentrations in the inlet and outlet gas, respectively.

The reaction rate (r_{toluene}, $\mathrm{mmol \cdot g^{-1} \cdot s^{-1}}$) was calculated as Eq (S3),

$$r_{\text{toluene}} = \frac{X_{\text{toluene}} \cdot V_{\text{toluene}}}{W_{\text{cat}}} \qquad \text{(S3)}$$

where W_{cat} represents the catalyst weight (g) and V_{toluene} is the toluene gas flow rate ($\mathrm{mol \cdot s^{-1}}$).

When the conversion of toluene is < 15%, a dependence of the reaction rate (r_{toluene}) on the products of CO_2 and H_2O may be ignored and the empirical kinetic expression of the reaction rate equation of toluene oxidation can be described as Eq (S4),

$$r_{\text{toluene}} = A\exp\left(-\frac{E_{\text{a}}}{RT}\right)P_{\text{toluene}}^{\alpha}P_{O_2}^{\beta} \qquad \text{(S4)}$$

Taking the natural logarithm of Eq (S4), Eq (S5) can be obtained.

$$\ln r = \ln A + \alpha \ln P_{\text{toluene}} + \beta \ln P_{O_2} - E_{\text{a}} / (RT) \tag{S5}$$

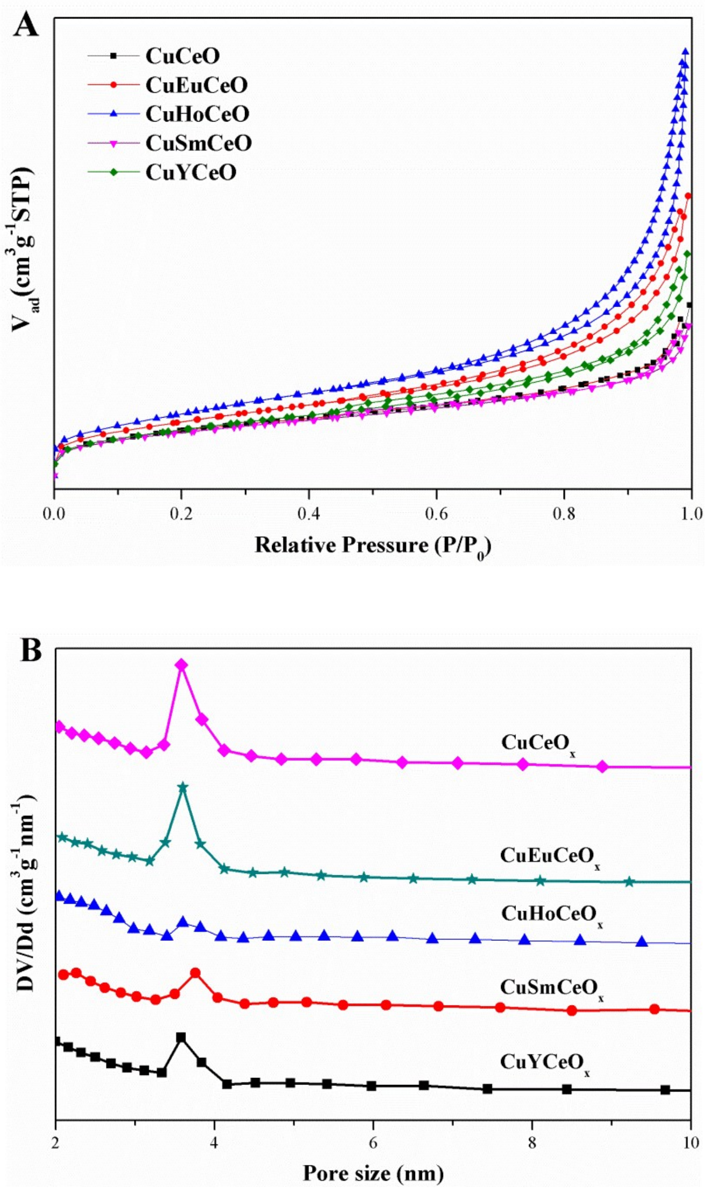
The components of the reactant gas feed undergo minor changes during the kinetics data testing, and the conversion of toluene is < 15%. Therefore, $\ln A$, $\alpha \ln P_{\text{toluene}}$, and $\beta \ln P_{O_2}$ can be supposed to be approximately constant, and Eq (S5) can be simplified to Eq (S6),

$$\ln r = -\frac{E_{\text{a}}}{RT} + C \tag{S6}$$

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

In-situ DRIFTS study

In-situ DRIFTS of toluene oxidation was performed using a Bruker Tensor 37 infrared spectrometer, equipped with a mercury cadmium telluride (MCT) detector cooled by liquid nitrogen. A Harrick reaction cell was fitted with KBr windows and connected to a purging and adsorption gas control system. The total flow rate was controlled by a mass flow meter. Prior to the catalytic oxidation of toluene, the catalyst samples were pre-treated under N_2 at 500 °C for 1 h to remove the surface impurities. In each case, a spectrum corresponding to the catalyst powder was recorded at selected reaction temperatures under an N_2 flow. This spectrum was then subtracted from the corresponding spectrum of the catalyst and reaction mixture in the cell. For the toluene oxidation experiment, the catalysts were exposed to a gas mixture consisting of 900 ppm toluene/20% O_2/N_2 at temperatures in the range of 180-240 °C. The system reached a steady state in about 20-25 min, as verified by the stabilized MS peak intensities. All spectra were collected at a resolution of 4 cm^{-1} with 100 scans.



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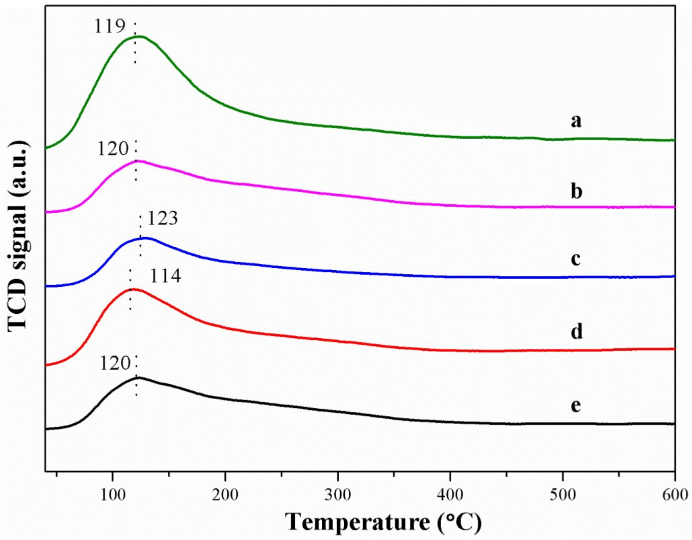

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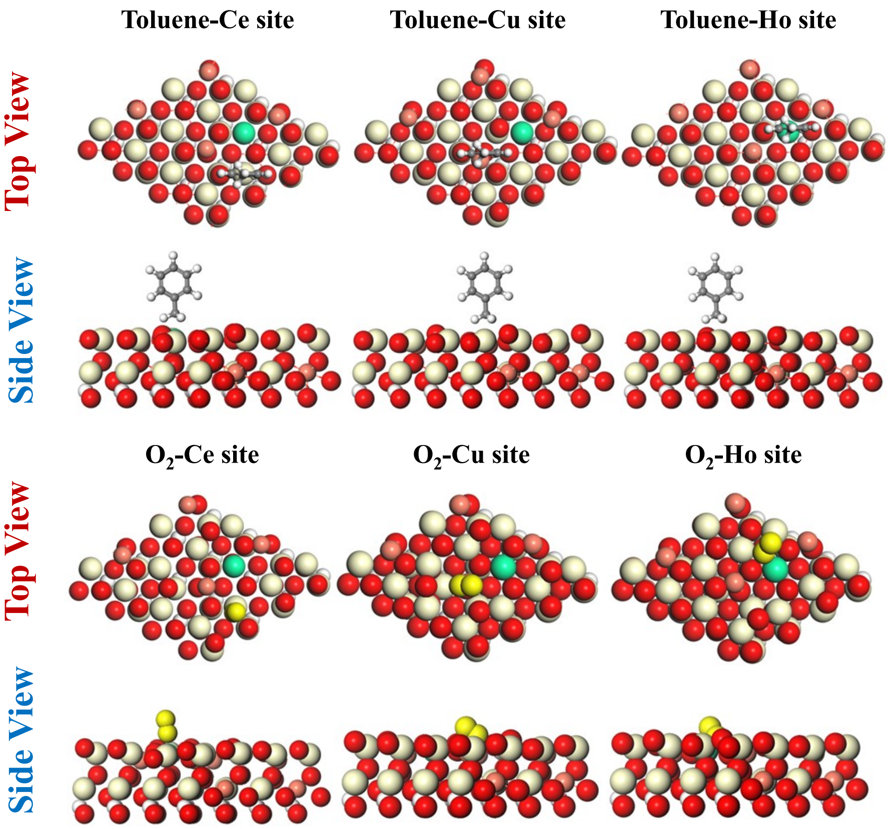

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Sample	Reaction conditions	T_{50} (°C)	T_{90} (°C)	E_a (kJ·mol^{-1})	*Ref.*
$CuHoCeO_x$	900 ppm of toluene, GHSV = 50,000 h^{-1}	206	224	92.5	*This work*
MnO_x	1000 ppm of toluene, GHSV = 15,000 h^{-1}	212	230	n.g.	S1
Mn_3O_4 nanorod	1000 ppm of toluene, GHSV = 30,000 h^{-1}	235	242	n.g.	S2
$La_{0.6}Sr_{0.4}CoO_{3-\delta}$	1000 ppm of toluene, GHSV = 20,000 h^{-1}	235	240	n.g.	S3
$LaMnO_3$	1000 ppm of toluene, GHSV = 15,000 h^{-1}	205	213	71	S4
$Mn_{0.85}Ce_{0.15}$	1000 ppm of toluene, GHSV = 32,000 h^{-1}	207	< 220	n.g.	S5
Meso-$TiMnCeO_x$	1000 ppm of toluene, GHSV = 32,000 h^{-1}	162	180	n.g.	S6
Hollow $LaCoO_3$	1000 ppm of toluene, GHSV = 20,000 h^{-1}	220	237	n.g.	S7
5%$LaMnO_3$/Y_2O_3-ZrO_2	1000 ppm of toluene, GHSV = 100 mL·h^{-1}	233	247	n.g.	S8

n.g.: Not given in the literature.

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