Supplementary Information

Rare-earth element doping promoted toluene low-temperature combustion over mesostructured CuM CeO\(_x\) (\(M = Y, \text{Eu}, \text{Ho}, \text{and Sm}\)) catalysts: The indispensable role of \textit{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 20 range of 20-80° (scanning rate of 4°/min).

N₂ 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 N₂ 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 Utrabld instrument (Kratos, UK) with Mg-Kα radiation ($hν = 1253.6$ 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 $5 \times 10^{-8}$ 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 1s = 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:

$$\text{H}_2 \text{ consumption rate} = \frac{S_{\text{cat}} \times n_{\text{CuO}} \times 1000}{S_{\text{cat}} \times m_{\text{cat}}}$$  \hspace{1cm} (S1)

where $S_{\text{cat}}$ is the fitting peak area of H$_2$ consumption for prepared catalysts; $S_{\text{CuO}}$ represents the fitting peak area of H$_2$ consumption for CuO standard sample; $n_{\text{CuO}}$ is the amount of CuO standard sample (mol); $m_{\text{cat}}$ 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 \( \text{N}_2 \) for 1 h. The toluene feed (900 ppm) was generated by using a \( \text{N}_2 \) bubbler in thermostatic bath at 30 °C and mixing with air (79% \( \text{N}_2 \) + 21% \( \text{O}_2 \)). The total flow rate was kept at 200 mL·min\(^{-1}\) (GHSV = 50,000 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 \( \text{CO}_2 \) 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 \( \mu \text{m} \). The conversion of toluene (\( X_{\text{toluene}} \)) was calculated as Eq (S2),

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

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

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

\[
r_{\text{toluene}} = \frac{X_{\text{toluene}} \cdot V_{\text{toluene}}}{W_{\text{cat}}}
\]

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

When the conversion of toluene is < 15%, a dependence of the reaction rate (\( r_{\text{toluene}} \)) on the products of \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) may be ignored and the empirical kinetic expression of the reaction rate equation of toluene oxidation can be described as Eq (S4),

\[
r_{\text{toluene}} = A \exp\left(-\frac{E_a}{RT}\right)P_{\text{toluene}}^{\alpha}P_{\text{O}_2}^{\beta}
\]

Taking the natural logarithm of Eq (S4), Eq (S5) can be obtained.
ln \( r \) = \( \ln A + \alpha \ln P_{\text{toluene}} + \beta \ln P_{O_2} - E_a / (RT) \) \hspace{1cm} (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),

\[
\ln r = -\frac{E_a}{RT} + C
\] \hspace{1cm} (S6)

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

\textbf{In-situ DRIFTS study}

\textit{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.
Fig. S1 (A) N$_2$ adsorption-desorption isotherms and (B) pore size distribution of all samples.
Fig. S2 O$_2$-TPD profiles of (a) CuCeO$_x$, (b) CuSmCeO$_x$, (c) CuEuCeO$_x$, (d) CuHoCeO$_x$, and (e) CuYCeO$_x$. 
Fig. S3 Atomistic computer simulation of the optimistic structure for reactants adsorbed over CuHoCeOₓ catalyst (green, red, faint yellow, bronzing, gray and white spheres represent Ho, O, Ce, C and H atoms, respectively).
Table S1 Summary of some active catalysts for toluene oxidation reported in the literature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reaction conditions</th>
<th>$T_{50}$ ($^\circ$C)</th>
<th>$T_{90}$ ($^\circ$C)</th>
<th>$E_a$ (kJ·mol$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuHoCeO$_x$</td>
<td>900 ppm of toluene, GHSV = 50,000 h$^{-1}$</td>
<td>206</td>
<td>224</td>
<td>92.5</td>
<td>This work</td>
</tr>
<tr>
<td>MnO$_x$</td>
<td>1000 ppm of toluene, GHSV = 15,000 h$^{-1}$</td>
<td>212</td>
<td>230</td>
<td>n.g.</td>
<td>S1</td>
</tr>
<tr>
<td>Mn$_2$O$_4$ nanorod</td>
<td>1000 ppm of toluene, GHSV = 30,000 h$^{-1}$</td>
<td>235</td>
<td>242</td>
<td>n.g.</td>
<td>S2</td>
</tr>
<tr>
<td>La$<em>{0.6}$Sr$</em>{0.4}$CoO$_3$$\delta$</td>
<td>1000 ppm of toluene, GHSV = 20,000 h$^{-1}$</td>
<td>235</td>
<td>240</td>
<td>n.g.</td>
<td>S3</td>
</tr>
<tr>
<td>LaMnO$_3$</td>
<td>1000 ppm of toluene, GHSV = 15,000 h$^{-1}$</td>
<td>205</td>
<td>213</td>
<td>71</td>
<td>S4</td>
</tr>
<tr>
<td>Mn$<em>{0.85}$Ce$</em>{0.15}$</td>
<td>1000 ppm of toluene, GHSV = 32,000 h$^{-1}$</td>
<td>207</td>
<td>&lt; 220</td>
<td>n.g.</td>
<td>S5</td>
</tr>
<tr>
<td>Meso-TiMnCeO$_x$</td>
<td>1000 ppm of toluene, GHSV = 32,000 h$^{-1}$</td>
<td>162</td>
<td>180</td>
<td>n.g.</td>
<td>S6</td>
</tr>
<tr>
<td>Hollow LaCoO$_3$</td>
<td>1000 ppm of toluene, GHSV = 20,000 h$^{-1}$</td>
<td>220</td>
<td>237</td>
<td>n.g.</td>
<td>S7</td>
</tr>
<tr>
<td>5%LaMnO$_3$/Y$_2$O$_3$-ZrO$_2$</td>
<td>1000 ppm of toluene, GHSV = 100 mL·h$^{-1}$</td>
<td>233</td>
<td>247</td>
<td>n.g.</td>
<td>S8</td>
</tr>
</tbody>
</table>

n.g.: Not given in the literature.
Reference


