Supporting Information

The investigations on crystal plane effect of ceria on gold catalysis in the oxidative dehydrogenation of alcohols and amines in liquid phase

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**Experimental Section**

**Synthesis of ceria**

CeO$_2$ nanorod, nanocubic and nanoparicles were prepared as reported.[1] Typically, Ce(NO$_3$)$_3$ (6 mmol) was added into a NaOH aqueous solution with appropriate concentration (120 mL, C$_{NaOH}$). This stock solution was stirred at room temperature for 10 min in a Teflon bottle and then sealed tightly in a stainless-steel autoclave. Hydrothermal treatment was carried out at different temperatures (T) for 24 h. After cooling, the white precipitates were collected, washed with deionized water, and dried at 80 °C. The dried yellow powders were calcined in air at 300 °C for 3 h. The values of C$_{NaOH}$ and T were varied according to the target crystal shape (CeO$_2$ nanorod: C$_{NaOH}$ = 6 M, T = 100 °C; CeO$_2$ nanocube: C$_{NaOH}$ = 6 M, T = 180 °C; CeO$_2$ nanoparicles: C$_{NaOH}$ = 0.1 M, T = 180 °C). CeO$_2$ nanoctahedra were prepared according to reported paper. [2] cerium(III) nitrate hexahydrate (3 mmol) trisodium phosphate hexahydrate (0.03 mmol) were dissolved in distilled water (120 mL). After being stirred at room temperature for 1 h, the mixed solution was transferred into Teflon-lined stainless autoclave and heated at 170 °C for 12 h.

**Synthesis of Au/CeO$_2$**

The deposition of Au onto the ceria substrate was conducted using deposition–precipitation (DP) method. In brief, the CeO$_2$ were dispersed in an aqueous solution of HAuCl$_4$ at a fixed pH of 10. The nominal Au loading was 1.0 wt%. The suspension was aged at room temperature for 24 h and washed with deionized water several times. The final Au containing material was obtained by calcination in air at 300 °C for 3 h. For brevity, gold supported on CeO$_2$ nanorod, nanoparticles, nancube and nano-octahedra were denoted as Au/CeO$_2$-R, Au/CeO$_2$-P, Au/CeO$_2$-C and Au/CeO$_2$-O, respectively. ICP analysis shows that the gold loading were 1.1 wt%, 1.2 wt%, 0.8 wt% and 0.9 wt% for Au/CeO$_2$-R, Au/CeO$_2$-P, Au/CeO$_2$-C and Au/CeO$_2$-O, respectively.
Oxidation of alcohols

1 mmol of alcohols, 0.05 mmol of p-xylene as internal standard, 5 mL chlorobenzene, catalyst (0.1 mol% Au) and magnetic stir were added to two-necked round bottom flask. O$_2$ were bubbled through a needle connected with a side-mouth sealed with Teflon septum. The reactor was placed into an oil bath which was thermally stabilized at the desired temperature. Aliquots were collected at intervals. The reactant and product were analyzed and quantified by gas chromatography–mass spectrometry (GC–MS) using an Agilent 7890A/5975C instrument equipped with an HP-5MS column (30 m in length, 0.25 mm in diameter). The conversion was determined using internal standard method. The selectivity was determined using area normalization method.

Hot filtration test

The benzyl alcohol oxidation mixture was quickly filtered through a Teflon-membrane filter after 1 h to another pre-heated glass reactor with Cs$_2$CO$_3$, which was placed in the same oil-bath with the previous one. The reaction was then conducted with the filtrate for another 8 hour. Four samples were collected at 3 h, 5 h, 7 h and 9 h, and analyzed.

Oxidation of amines

0.2 mmol of amines, 0.05 mmol of p-xylene as internal standard, 2 mL of 1,4-dioxane and catalyst (0.25 mol% Au) were added to stainless steel autoclave. After heating to the desired temperature, the oxygen was charged into the reactor to 0.3 MPa and the reaction was performed for 6 h under magnetic stirring. The reactant and product were analyzed and quantified by gas chromatography–mass spectrometry (GC–MS) using an Agilent 7890A/5975C instrument equipped with an HP-5MS column (30 m in length, 0.25 mm in diameter). The conversion was determined using internal standard method. The selectivity was determined using area normalization method.

Characterizations
The nitrogen sorption experiments were performed at 77 K on a Quantachrome Autosorb-1 system with micropore analysis. Prior to the measurement, the samples were outgassed at 150 °C. The Brunauer-Emmett-Teller (BET) specific surface areas were calculated using adsorption data at a relative pressure range of $P/P_0$: 0.05-0.25. The X-ray photoelectron spectroscopy (XPS) measurements were carried out on a VG ESCALAB MK2 spectrometer equipped with an AlK α X-ray source ($h\nu = 1486.6$ eV) and operating at 12.5 kV and 220 W. The binding energy (BE) was calibrated with the C1s signal (285.0 eV) as a reference. Raman spectra were recorded on a micro-Raman spectrometer (Renishaw) equipped with a CCD detector using a He/Ne laser with a wavelength of 514 nm. Microstructures of the catalysts were examined by transmission electron microscopy (TEM, JEOL JEM-2000EX) and high resolution electron microscopy (HRTEM, FEI Tecnai G2 F30 S-Twin).
**Fig. S1** XRD patterns of (a) Au/CeO₂-R, (b) Au/CeO₂-P, (c) Au-CeO₂-C and (d) Au/CeO₂-O.
Fig. S2 TEM images of (a) Au/CeO$_2$-R, (b) Au/CeO$_2$-P, (c) Au/CeO$_2$-C and (d) Au/CeO$_2$-O.
Fig. S3 Reuse of the Au/CeO$_2$-R in the benzyl alcohol oxidation. Reaction conditions: 1 mmol benzyl alcohol, 0.5 mmol p-xylene, 5 mL chlorobenzene, 20 mg catalyt, O$_2$ 1 atm, 90 °C, 8 h.
Fig. S4 Hot filtration experiment. Reaction conditions: 1 mmol benzyl alcohol, 0.5 mmol p-xylene, 5 mL chlorobenzene, 20 mg catalyst, O₂ 1atm, 90 °C, 8 h. The catalyst was filtrated at 1 h.
**Fig. S5** Raman (514 nm) characterization of the VŌ in different crystal plane after gold deposit. (a) Au/CeO$_2$-R{110}, (b) Au/CeO$_2$-O{111} and (c) Au/CeO$_2$-C{100}; (d) The comparison of the loss of VŌ after gold deposit among three samples.

**Fig. S6** The comparison of surface concentration of oxygen vacancy sites in different catalyst.
**Fig. S7** XPS characterization of the gold species of (a) Au-CeO$_2$-R, (b) Au-CeO$_2$-O and (c) Au-CeO$_2$-C.

**Table S1.** Concentration of gold species in Au/CeO$_2$ samples determined by XPS

<table>
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<tr>
<th>Catalyst</th>
<th>$\text{Au}^0/\text{Au}_\text{T}$</th>
<th>$\text{Au}^+/\text{Au}_\text{T}$</th>
<th>$\text{Au}^{3+}/\text{Au}_\text{T}$</th>
<th>$(\text{Au}^+ + \text{Au}^{3+})/\text{Au}_\text{T}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au/CeO$_2$-R</td>
<td>28.3%</td>
<td>20.3%</td>
<td>51.4%</td>
<td>71.7%</td>
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<tr>
<td>Au/CeO$_2$-O</td>
<td>52.7%</td>
<td>43.1%</td>
<td>4.3%</td>
<td>47.3%</td>
</tr>
<tr>
<td>Au/CeO$_2$-C</td>
<td>63.5%</td>
<td>36.5%</td>
<td>-</td>
<td>36.5%</td>
</tr>
</tbody>
</table>
**Fig. S8** (a) Kinetic analysis over the Au/CeO$_2$-R. (b) Arrhenius plot

**Fig. S9** Arrhenius plots for the oxidation of benzyl alcohols by (a) Au/CeO$_2$-P, $E_a = 35.1$ kJ mol$^{-1}$ and (b) Au/CeO$_2$-O, $E_a = 42.3$ kJ mol$^{-1}$.
**Fig. S10** Correlation between cationic gold percent and reaction rate for benzyl alcohol oxidation.
Reference: