Supporting Information

Highly efficient catalysts of bimetallic Pt-Ru nanocrystals supported on ordered ZrO$_2$ nanotube for toluene oxidation

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S1 Experimental

Synthesis of SBA-15-OH template

In a typical fabrication, 4.00 g P123, 130 ml ultrapure water, and 20 ml concentrated hydrochloric acid (37 wt%) were mixed and stirred uniformly. Then, 8.230 g tetraethyl orthosilicate was slowly added, and stirred at 38 °C for 24 hours; then the mixture was hydrothermal at 110 °C. After reacting for 24 hours, the reaction was allowed to naturally cool to room temperature, and the mixture was suction filtered to give a precipitate which was dried at 80 °C. Next, the P123 template was removed, and the dried precipitate was placed in a 1 L flask with 120 ml concentrated nitric acid (65 wt%) and 40 ml H₂O₂. After refluxing for 3 hours at 80 °C, the mixture was naturally cooled and suction filtered to obtain SBA-15-OH, rinsed to neutral with multiple times of ultrapure water and ethanol, and dried at 50 °C.

S2 Structure and composition study

S2.1 EDX pattern and SEM EDX maps of Pt_{0.9}Ru_{0.1}/ZrO₂

![Figure S1](image)

**Figure S1.** (a) SEM EDX of Pt_{0.9}Ru_{0.1}/ZrO₂ and elemental mapping images of (b) O, (c) Zr, (d) Pt, and (e) Ru.
(c) Zr, (d) Pt and (e) Ru.

S2.2 TEM images, EDX pattern and particle size distribution of catalysts

Figure S2. Particle size distributions of Pt/ZrO$_2$, Ru/ZrO$_2$, Pt$_{0.7}$Ru$_{0.3}$/ZrO$_2$

Figure S2 shows the particle size distributions of Pt/ZrO$_2$, Ru/ZrO$_2$, Pt$_{0.7}$Ru$_{0.3}$/ZrO$_2$. Apparently, the ZrO$_2$ support displayed a well-defined ordered nanotube arrays, and Pt/Ru nanoparticles with a size of smaller than 6 nm were highly dispersed on the nanotube arrays. Moreover, for monometallic Pt/ZrO$_2$ and Ru/ZrO$_2$, the average diameter of Pt or Ru nanoparticles were about 3.91 nm and 3.02 nm, respectively. Notably, the average diameter of PtRu composite nanoparticles was 1.95 nm by making a statistic analysis on the sizes of more than 200 PtRu composite nanoparticles in the TEM image of the Pt$_{0.7}$Ru$_{0.3}$/ZrO$_2$ sample. This suggested an enhancement of active surface area in catalytic reaction for the bimetallic Pt$_x$Ru$_y$/ZrO$_2$ samples, which may be one of the important reasons of their superior activities towards the monometallic catalysts.
**Table S1.** The weight fraction of Pt/Ru composite nanoparticles with different Pt/Ru molar ratio

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Pt/ZrO₂</th>
<th>Pt₉₀Ru₁₀/ZrO₂</th>
<th>Pt₈₀Ru₂₀/ZrO₂</th>
<th>Pt₇₀Ru₃₀/ZrO₂</th>
<th>Pt₅₀Ru₅₀/ZrO₂</th>
<th>Ru/ZrO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>weight fraction of Pt-Ru (wt%)</td>
<td>1.39</td>
<td>1.22</td>
<td>1.15</td>
<td>1.10</td>
<td>1.04</td>
<td>0.74</td>
</tr>
</tbody>
</table>

**Figure S3.** HAADF-STEM images and EDX pattern of Pt₀.₇Ru₀.₃/ZrO₂.

**S2.3** XRD patterns of Pt₀.₉Ru₀.₁/ZrO₂, Pt₀.₈Ru₀.₂/ZrO₂, Pt₀.₅Ru₀.₅/ZrO₂
**Figure S4.** XRD patterns of $\text{Pt}_{0.9}\text{Ru}_{0.1}/\text{ZrO}_2$, $\text{Pt}_{0.8}\text{Ru}_{0.2}/\text{ZrO}_2$, $\text{Pt}_{0.5}\text{Ru}_{0.5}/\text{ZrO}_2$.

**S2.4** The XPS survey spectrum and spectra analysis of the catalysts

**Figure S5.** The survey scan XPS spectrum of $\text{Pt}_x\text{Ru}_y/\text{ZrO}_2$, (a) $\text{Pt}_{0.9}\text{Ru}_{0.1}/\text{ZrO}_2$, (b) $\text{Pt}_{0.8}\text{Ru}_{0.2}/\text{ZrO}_2$, (c) $\text{Pt}_{0.7}\text{Ru}_{0.3}/\text{ZrO}_2$, (d) $\text{Pt}/\text{ZrO}_2$, (e) $\text{Ru}/\text{ZrO}_2$. 
Table S2. The content of lattice oxygen (O\textsubscript{latt}), absorbed oxygen (O\textsubscript{ads}), and the ratio of O\textsubscript{ads}/O\textsubscript{latt} in the Pt\textsubscript{x}Ru\textsubscript{y}/ZrO\textsubscript{2} catalysts.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Pt\textsubscript{0.9}Ru\textsubscript{0.1}</th>
<th>Pt\textsubscript{0.8}Ru\textsubscript{0.2}</th>
<th>Pt\textsubscript{0.7}Ru\textsubscript{0.3}</th>
<th>Pt\textsubscript{0.5}Ru\textsubscript{0.5}</th>
<th>Pt/ZrO\textsubscript{2}</th>
<th>Ru/ZrO\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content of O\textsubscript{latt} (%)</td>
<td>47.9</td>
<td>46.6</td>
<td>41.7</td>
<td>47.0</td>
<td>42.7</td>
<td>63.2</td>
</tr>
<tr>
<td>Content of O\textsubscript{ads} (%)</td>
<td>52.1</td>
<td>53.4</td>
<td>58.3</td>
<td>53.0</td>
<td>57.3</td>
<td>36.8</td>
</tr>
<tr>
<td>O\textsubscript{ads}/O\textsubscript{latt}</td>
<td>1.09</td>
<td>1.15</td>
<td>1.40</td>
<td>1.13</td>
<td>1.34</td>
<td>0.58</td>
</tr>
</tbody>
</table>

Figure S6. The Pt 4f and Ru 3d XPS spectra of Pt\textsubscript{0.7}Ru\textsubscript{0.3}/ZrO\textsubscript{2} after catalytic reaction.

Table S3. The comparison of the XPS analysis of catalysts before and after catalytic reaction.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Pt (0) contents (%)</th>
<th>Ru (0) contents (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>before</td>
<td>after</td>
</tr>
<tr>
<td>Pt\textsubscript{0.9}Ru\textsubscript{0.1}/ZrO\textsubscript{2}</td>
<td>60.5</td>
<td>58.8</td>
</tr>
<tr>
<td>Pt\textsubscript{0.8}Ru\textsubscript{0.2}/ZrO\textsubscript{2}</td>
<td>62.0</td>
<td>59.1</td>
</tr>
<tr>
<td>Pt\textsubscript{0.7}Ru\textsubscript{0.3}/ZrO\textsubscript{2}</td>
<td>64.2</td>
<td>62.8</td>
</tr>
</tbody>
</table>
S2.5 ESR profiles of surface oxygen vacancies for the catalysts

![ESR profiles](image)

**Figure S7.** ESR profiles of surface oxygen vacancies for Pt$_{0.9}$Ru$_{0.1}$/ZrO$_2$, Pt$_{0.8}$Ru$_{0.2}$/ZrO$_2$ and Pt$_{0.7}$Ru$_{0.3}$/ZrO$_2$.

S2.6 UV–vis absorption spectra of Pt/ZrO$_2$ and Pt$_{0.7}$Ru$_{0.3}$/ZrO$_2$

![Absorption spectra](image)

**Figure S8.** UV–vis absorption spectra of catalysts Pt/ZrO$_2$ and Pt$_{0.7}$Ru$_{0.3}$/ZrO$_2$ before and after calcined under H$_2$ atmosphere.
S2.7 BET, and BJH properties of the catalysts

**Table S4.** BET surface areas, pore volumes and pore sizes for SBA-15-OH, ZrO₂.

<table>
<thead>
<tr>
<th>Samples</th>
<th>S\textsubscript{BET} (m\textsuperscript{2}/g)</th>
<th>Pore Size (nm)</th>
<th>Pore volume (cm\textsuperscript{3}/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBA-15-OH</td>
<td>447.2</td>
<td>7.55</td>
<td>0.84</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>192.8</td>
<td>8.97</td>
<td>0.43</td>
</tr>
<tr>
<td>Pt\textsubscript{0.7}Ru\textsubscript{0.3}/ZrO₂</td>
<td>183</td>
<td>6.56</td>
<td>0.30</td>
</tr>
</tbody>
</table>

Pt\textsubscript{0.7}Ru\textsubscript{0.3}/ZrO₂ samples.

S3 Catalytic performance and stability

S3.1 The stability of catalytic performance for the catalysts

![Figure S9](image)

**Figure S9.** Catalytic activities of the Pt\textsubscript{0.7}Ru\textsubscript{0.3}/ZrO₂, Pt\textsubscript{0.5}Ru\textsubscript{0.5}/ZrO₂, Pt/ZrO₂ and Ru/ZrO₂ samples when the reaction temperature went up (dashed line), then went down.
(solid line), and then up again (dashed line) under the conditions of toluene concentration = 50 ppm, and SV = 36000 ml/(h·g).

S3.2 The FT-IR spectra spectrum analysis

Figure S10 shows the FT-IR spectra study of the template SBA-15-OH, support ZrO₂, and the catalyst Pt₀.₇Ru₀.₃/ZrO₂ before and after catalytic oxidation of toluene. As for template SBA-15-OH, we can see apparent Si-O bond absorption band at 1090 cm⁻¹. In comparison, the ZrO₂ support has obvious Zr-O-Zr bond absorption band at about 654 cm⁻¹ and Zr-O bond absorption band at about 940 cm⁻¹ without 1090 cm⁻¹ absorption bands, indicating the template is completely removed. Moreover, the FT-IR spectra of sample Pt₀.₇Ru₀.₃/ZrO₂ before and after catalytic oxidation of toluene exhibit similar absorption bands of ZrO₂, explaining the stability of the catalyst in the catalytic oxidation process.

![FT-IR spectra study](image)

Figure S10. The FT-IR spectra study of the template SBA-15-OH, support ZrO₂, and
the catalyst Pt$_{0.7}$Ru$_{0.3}$/ZrO$_2$ before and after catalytic oxidation of toluene.