Supporting Information

Highly selective phenol production from benzene on platinum-loaded tungsten oxide photocatalyst with water and molecular oxygen: Selective oxidation of water by holes for generating hydroxyl radical as predominant source of hydroxyl group

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Figure S1. Time course of hydroxylation and oxidation of benzene over (a) Pt/WO$_3$-Y and (b) Pt/TiO$_2$-R photocatalysts in aerated aqueous solutions of benzene (18.8 μmol) under ultraviolet and visible light irradiation (300 < λ < 500 nm).

Figure S2. Time course of photocatalytic oxidation of benzene over (a) Pt/TiO$_2$-P and (b) Pt/TiO$_2$-A photocatalysts in aerated aqueous solutions of benzene (18.8 μmol) under visible light irradiation (400 < λ < 500 nm).
Figure S3. Influence of Pt amount on the amount of conversion, phenol selectivity, and amount of CO$_2$ on (a) Pt/WO$_3$-K and (b) TiO$_2$ photocatalyst during hydroxylation of benzene (irradiation time 1 h).

Figure S4. Time course curves of H$_2$O$_2$ and CO$_2$ generation over (a) Pt/WO$_3$-Y and (b) Pt/TiO$_2$-R photocatalysts suspended in AcOH solution under ultraviolet and visible light irradiation (300 < $\lambda$ < 500 nm).
Figure S5. Dependence of photocatalytic hydroxylation of benzene on pH for use of Pt/WO$_3$-K photocatalyst.
Figure S6. Time course of photocatalyzed phenol production from benzene on Pt/WO$_3$-K and Pt/TiO$_2$-P samples. Reactions were conducted in H$_2^{16}$O-H$_2^{18}$O mixed solvent containing benzene and normal molecular $^{16}$O$_2$.

Figure S7. Time course of photocatalyzed phenol production from benzene on Pt/WO$_3$-Y and Pt/TiO$_2$-R samples. Reactions were conducted in $^{18}$O-enriched water (98% H$_2^{18}$O) containing benzene and normal molecular $^{16}$O$_2$. 

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Figure S8. Time course of photocatalyzed phenol production from benzene on Pt/\textit{WO}_3-Y and Pt/TiO\textsubscript{2}-R samples. Reactions were conducted in normal water (H\textsubscript{2}^{16}O) containing benzene and molecular \textsuperscript{18}O\textsubscript{2}.

Figure S9. Amount of phenol produced from hydroxylation of benzene in the presence of IPA over Pt/\textit{WO}_3-K and Pt/TiO\textsubscript{2}-P photocatalysts.
Figure S10. FT-IR subtraction spectra of benzene on photocatalysts.

Figure S11. Influence of initial concentration of benzene on the amount of phenol, di-hydroxylated benzene and CO$_2$ on (a) Pt/WO$_3$ and (b) TiO$_2$ photocatalysts during hydroxylation of benzene (Pt: 0.1 wt.%).
Figure S12. XRD pattern of WO₃ samples obtained from tungstic acid (H₂WO₄, TA) as the W precursor.
Figure S13. IR spectra of WO$_3$ samples obtained from tungstic acid (H$_2$WO$_4$, TA) as the W precursor.

Table S1. Direct hydroxylation of benzene to phenol on WO$_3$-TA (prepared by calcination of tungstic acid powder) in normal water (H$_2$O) containing benzene and molecular $^{18}$O$_2$.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Calcination temperature / K</th>
<th>Content of labeled phenol (%)</th>
<th>Amount of phenol produced / µmol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1 h</td>
<td>8 h</td>
</tr>
<tr>
<td>1</td>
<td>573</td>
<td>95.1 (0.6)</td>
<td>95.2 (2.5)</td>
</tr>
<tr>
<td>2</td>
<td>773</td>
<td>94.4 (1.2)</td>
<td>92.0 (3.8)</td>
</tr>
<tr>
<td>3</td>
<td>973</td>
<td>96.3 (1.3)</td>
<td>93.3 (4.9)</td>
</tr>
<tr>
<td>4</td>
<td>1173</td>
<td>94.9 (0.9)</td>
<td>94.0 (2.2)</td>
</tr>
</tbody>
</table>

Initial concentration of benzene : 500 µmol, Amount of solvent : 1.0 mL
Light source : 300 W Xe lamp (300 < λ < 500 nm)