Electronic Supplementary Information

In situ Synthesis of Ultrafine Metal Clusters triggered by Dodecaborate Supramolecular Organic Frameworks

Bin Qi, Xin Li, Liang Sun, Bo Chen, Hao Chen, Chenchen Wu, Haibo Zhang* and Xiaohai Zhou*

*College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, China.
Figure S1. FT-IR spectrum of pure Cs2[closo-B12H12], CB[7] and Cs2[closo-B12H12]@CB[7] assemblies........................................................................................................................................3
Figure S2. Views of the CB6/B12H122- complex XRD structure........................................................................................................................................4
Figure S3. Views of the CB7/B12Cl122- complex XRD structure........................................................................................................................................4
Figure S4. The photographic images of the obtained final metal/BOFs products..................................................................................................................................................4
Figure S5. XRD results of CBn-BOFs and Au/CBn-BOFs........................................................................................................................................5
Figure S6. The survey XPS spectra (a) and high-resolution XPS Au 4f spectra (b) of Au-BOFs.................................................................................................................................5
Figure S7. XRD results of CBn-BOFs and Pd/CBn-BOFs........................................................................................................................................6
Figure S8. The survey XPS spectra (a) and high-resolution XPS Pd 3d spectra (b) of Pd-BOFs.................................................................................................................................6
Figure S9. XRD results of Ag/ BOFs................................................................................................................................................7
Figure S10. The survey XPS spectra (a) and high-resolution XPS Ag 3d spectra (b) of Ag/BOFs.................................................................................................................................7
Figure S11. XRD results of Pt/ BOFs................................................................................................................................................8
Figure S12. The survey XPS spectra (a) and high-resolution XPS Pt 4f spectra (b) of Pt/BOFs.................................................................................................................................8
Figure S13. The GC standard curves of (a) toluene and FAL, (b) toluene and FOL.................................................................................................................................9
Figure S14. The GC spectrum of the conversion of FAL to FOL treated with various Au/BOFs and BOFs catalysts................................................................................................................9
Figure S15. The GC spectrum of the recycling tests of FAL to FOL treated with Au/CB7-BOFs catalysts.........................................................................................................................9
Figure S16. The TEM image and powder XRD pattern of the Au/CB7-BOFs catalysts after 15th round of catalysis......................................................................................................................10
Table S1. Comparison of the catalytic performances of Au/BOFs catalyst with already reported catalysts towards the selective reduction of FAL with FOL.................................................................................................................................10
1H NMR and 13C NMR spectra for the products listed in Table 2 of the main text.................................................................................................................................11
Reference........................................................................................................................................................................20
Figure S1. FT-IR spectrum of pure $\text{Cs}_2[\text{closo-B}_{12}\text{H}_{12}]$, $\text{CB}[7]$ and $\text{Cs}_2[\text{closo-B}_{12}\text{H}_{12}]@\text{CB}[7]$ assemblies.

Figure S2. Views of the $\text{CB}_6/\text{B}_{12}\text{H}_{12}^+\text{ complex XRD structure.}$
Figure S3. Views of the CB7/B$_{12}$Cl$_{12}^{2-}$ complex XRD structure.

Figure S4. The photographic images of (a) the metal/BOFs reaction systems standing for 0.5 h, (b) the obtained final metal/BOFs products.
Figure S5. XRD results of CBn-BOFs and Au/CBn-BOFs.

Figure S6. The survey XPS spectra (a) and high-resolution XPS Au 4f spectra (b) of Au-BOFs.
Figure S7. XRD results of CBn-BOFs and Pd/CBn-BOFs.

Figure S8. The survey XPS spectra (a) and high-resolution XPS Pd 3d spectra (b) of Pd-BOFs.
Figure S9. XRD results of Ag/BOFs.

Figure S10. The survey XPS spectra (a) and high-resolution XPS Ag 3d spectra (b) of Ag/BOFs.
Figure S11. XRD results of Pt/ BOFs.

Figure S12. The survey XPS spectra (a) and high-resolution XPS Pt 4f spectra (b) of Pt/BOFs.
Figure S13. The GC standard curves of (a) toluene and FAL, (b) toluene and FOL. A represented the integral value in the GC spectrum.

Figure S14. The GC spectrum of the conversion of FAL to FOL treated with various a) b) c) d) Au/BOFs and e) BOFs catalysts.
Figure S15. The GC spectrum of the recycling tests of FAL to FOL treated with Au/CB7-BOFs catalysts.

Figure S16. The TEM image (a) and powder XRD pattern (b) of the Au/CB7-BOFs catalysts after 15th round of catalysis.

Table S1. Comparison of the catalytic performances of Au/BOFs catalyst with already reported catalysts towards the selective reduction of FAL with FOL.

<table>
<thead>
<tr>
<th>catalyst</th>
<th>solvent</th>
<th>H2 pressure (bar)</th>
<th>temperature (°C)</th>
<th>time (h)</th>
<th>FOL yield (%)</th>
<th>Publication date</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(acac)3</td>
<td>/</td>
<td>30</td>
<td>120</td>
<td>9</td>
<td>98.1</td>
<td>2018[1]</td>
</tr>
<tr>
<td>Cu/AC–SO3H</td>
<td>2-propanol</td>
<td>4</td>
<td>100</td>
<td>3</td>
<td>47.3</td>
<td>2017[2]</td>
</tr>
<tr>
<td>SO42-/SnO2–APG</td>
<td>/</td>
<td>1</td>
<td>170</td>
<td>0.33</td>
<td>93.1</td>
<td>2017[3]</td>
</tr>
<tr>
<td>Pt-NPs@SiO2</td>
<td>heptane</td>
<td>40</td>
<td>80</td>
<td>4</td>
<td>87</td>
<td>2017[4]</td>
</tr>
<tr>
<td>LaCu0.67Si1.33</td>
<td>methanol</td>
<td>30</td>
<td>120</td>
<td>3</td>
<td>99</td>
<td>2017[5]</td>
</tr>
<tr>
<td>Ru-NNS</td>
<td>2-propanol</td>
<td>30</td>
<td>80</td>
<td>1</td>
<td>99</td>
<td>2017[6]</td>
</tr>
<tr>
<td>m-PhPZr</td>
<td>iPrOH</td>
<td>1</td>
<td>120</td>
<td>2</td>
<td>99</td>
<td>2017[7]</td>
</tr>
<tr>
<td>Co-Ru/C</td>
<td>2-propanol</td>
<td>1</td>
<td>150</td>
<td>4</td>
<td>100</td>
<td>2016[8]</td>
</tr>
<tr>
<td>Fe-Ru NPs@SILP</td>
<td>/</td>
<td>20</td>
<td>120</td>
<td>18</td>
<td>99</td>
<td>2016[9]</td>
</tr>
<tr>
<td>Ir@CN</td>
<td>H2O/HCOOH</td>
<td>1</td>
<td>100</td>
<td>18</td>
<td>99</td>
<td>2015[10]</td>
</tr>
<tr>
<td>Au/BOFs</td>
<td>2-propanol</td>
<td>1</td>
<td>45</td>
<td>1</td>
<td>99</td>
<td>This work</td>
</tr>
</tbody>
</table>
$^1$H NMR and $^{13}$C NMR spectra for the products listed in Table 2 of the main text
References