† Electronic Supplementary Information (ESI)

Tailoring graphene-supported Ru nanoparticles by functionalization with pyrene-tagged N-heterocyclic carbenes

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1. TEM

**Figure S1.** TEM image and size distribution histogram of Ru@rGO/pyr-IMes$_{0.2}$.

**Figure S2.** TEM image and size distribution histogram of Ru@rGO/pyr-IMes$_{0.8}$.

**Figure S3.** TEM image and size distribution histogram of Ru@rGO/pyr-IMes$_1$. 
2. HRTEM

Figure S4. HRTEM micrographs of Ru@rGO (left, right bottom) and Fourier Transform Analysis with the planar reflections (right, top).

3. Raman

Figure S5. Raman spectrum and \( I_D / I_G \) ratio of rGO.
4. EA and BET surface area

Table S1. Elemental analysis (EA) and BET surface area of Ru@rGO/pyr-IMes$_x$. Determination of the precise number of equiv. of pyr-IMes incorporated to Ru@rGO.

<table>
<thead>
<tr>
<th>Ru@rGO/pyr-IMes$_x$</th>
<th>X = 0.2</th>
<th>X = 0.5</th>
<th>X = 0.8</th>
<th>X = 1</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>BET Surface area of Ru@rGO (nm$^2$/100 mg)</strong></td>
<td>3.32·10$^{19}$</td>
<td>3.32·10$^{19}$</td>
<td>3.32·10$^{19}$</td>
<td>3.32·10$^{19}$</td>
</tr>
<tr>
<td>EA (wt% N)</td>
<td>2.38</td>
<td>5.94</td>
<td>9.50</td>
<td>11.88</td>
</tr>
<tr>
<td>% N incorporated</td>
<td>49.61</td>
<td>52.47</td>
<td>49.58</td>
<td>50.34</td>
</tr>
<tr>
<td>pyr-IMes molecules per nm2</td>
<td>0.053</td>
<td>0.141</td>
<td>0.214</td>
<td>0.271</td>
</tr>
<tr>
<td>Actual nº equiv. of pyr-IMes</td>
<td>0.099</td>
<td>0.262</td>
<td>0.397</td>
<td>0.503</td>
</tr>
</tbody>
</table>
5. TEM of ligand-stabilized Ru NPs

Figure S8. TEM image and size distribution histogram of Ru/pyr-IMes$_{0.2}$.

Figure S9. TEM image and size distribution histogram of Ru/pyr-IMes$_{0.5}$.

6. HRTEM of ligand-stabilized Ru NPs

Figure S10. HRTEM micrographs of Ru/pyr-IMes$_{0.5}$ (left, right bottom) and Fourier Transform Analysis with the planar reflections (right, top).
7. ICP-AES

Table S2. ICP analysis for Ru/pyr-IMes$_{0.2}$ and Ru/pyr-IMes$_{0.5}$.

<table>
<thead>
<tr>
<th></th>
<th>Size (nm)</th>
<th>Ru (wt%)[a]</th>
<th>Ru$_x$:L$_y$[b]</th>
<th>Ru$_x$/L$_y$</th>
<th>Ru$_{(s)}$[c]</th>
<th>Ru$_{(s)}/L_y$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru/pyr-IMes$_{0.2}$</td>
<td>1.4 ± 0.4</td>
<td>55.7</td>
<td>91:18</td>
<td>5</td>
<td>73</td>
<td>4.06</td>
</tr>
<tr>
<td>Ru/pyr-IMes$_{0.5}$</td>
<td>1.3 ± 0.4</td>
<td>33.2</td>
<td>132:44</td>
<td>2</td>
<td>62</td>
<td>1.41</td>
</tr>
</tbody>
</table>

[a] % of Ru obtained by ICP analysis. [b] The total number of atoms was determined calculating the unit cell of Ru (hcp) per MNP, based on the mean diameter measured by TEM. [c] Number of surface atoms. Approximate values obtained from ref.1.

8. DRIFT

Figure S11. DRIFT spectra of a sample of Ru/pyr-IMes$_{0.2}$ before (blue) and after (red) exposure to CO (bubbling CO into a THF solution for 5 min).

Figure S12. DRIFT spectra of a sample of Ru/pyr-IMes$_{0.5}$ before (blue) and after (red) exposure to CO (bubbling CO into a THF solution for 5 min).
9. MAS-NMR

Figure S13. $^{13}$C($^1$H) CP-MAS NMR spectra for Ru/pyr-IMes$_{0.2}$ (a) before and (b) after exposure to $^{13}$CO (1bar, $^{13}$CO, 20h, r.t.). Asterisks mark the positions of spinning side bands (*).

Figure S14. C-MAS NMR spectra for Ru/pyr-IMes$_{0.5}$ after exposure to $^{13}$CO (1bar 13CO, 20h, r.t.). Asterisks mark the positions of spinning side bands (*).
10. XPS

Figure S15. X-ray photoelectron spectroscopy (XPS) of the Ru 3p_{3/2} signals of (a) Ru/pyr-IMes_{0.5}, (b) Ru@rGO and (c) Ru@rGO/pyr-IMes_{0.5}.

11. TEM after catalysis

Figure S16. TEM images and size histogram of Ru@rGO after catalysis.

Figure S17. TEM images and size histogram of Ru@rGO/pyr-IMes_{0.2} after catalysis.
Figure S18. TEM images and size histogram of Ru@rGO/pyr-IMes$_{0.5}$ after catalysis.

Figure S19. TEM images and size histogram of Ru@rGO/pyr-IMes$_{0.8}$ after catalysis.

Figure S20. TEM images and size histogram of Ru@rGO/pyr-IMes$_{1}$ after catalysis.

12. Ru@rGO/ICy

Figure S21. Two-step synthetic route followed for the synthesis and subsequent functionalization of Ru@rGO with ICy.
Figure S22. Hydrogenation of acetophenone using Ru@rGO/ICy, as catalysts at short (a) and long (b) reaction times.

Figure S23. TEM images and size histogram of Ru@rGO/ICy,.

Figure S24. TEM images and size histogram of Ru@rGO/ICy, after catalysis.
13. Multiple addition experiment

![Figure S25. TEM images and size histogram of Ru@rGO/pyr-IMes$_{0.5}$ after multiple addition catalysis.](image)

14. “Hot Filtration”

**Table S3.** Conversions of Ru@rGO/pyr-IMes$_{0.5}$ in acetophenone hydrogenation after thermal filtration$^a$ and in the presence of catalyst.$^b$

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>2h</th>
<th>4 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru@rGO/pyr-IMes$_{0.5}$$^a$</td>
<td>59 %</td>
<td>59 %</td>
</tr>
<tr>
<td>Ru@rGO/pyr-IMes$_{0.5}$$^b$</td>
<td>57 %</td>
<td>88 %</td>
</tr>
</tbody>
</table>

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