† Electronic Supporting Information

Novel Nickel Nanoparticles Stabilized by Imidazolium-Amidinate Ligands for Selective Hydrogenation of Alkynes


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S1. TEM of Ni@L3

Figure S1. TEM images of Ni@L3 showing the polydispersity of the nanoparticles.

S2. HRTEM of Ni@L1

Figure S2. HRTEM image of Ni@L1 (left, right bottom) and the Fourier Transform Analysis (right, top) with planar reflections.
S3. WAXS analysis of Ni@L1, Ni@L2 and Ni@L3.

Figure S3. WAXS analysis of Ni@L1 (blue), Ni@L2 (green) and Ni@L3 (red), which shows crystalline Ni NPs (fcc) with a coherence length close to 3 nm.

S4. AAS analysis for Ni@L1, Ni@L2 and Ni@L3

<table>
<thead>
<tr>
<th>Ni NP[^a]</th>
<th>Size (nm)</th>
<th>% Ni[^a]</th>
<th>Ni:L Ratio</th>
<th>Niₓ:Lᵧ[^b]</th>
<th>Ni(s)[^c]</th>
<th>Ni(s)ₓ/Lᵧ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni@L1</td>
<td>2.8 (0.4)</td>
<td>75.9</td>
<td>25:1</td>
<td>1070:43</td>
<td>401</td>
<td>9.3</td>
</tr>
<tr>
<td>Ni@L2</td>
<td>2.8 (0.5)</td>
<td>71.1</td>
<td>21:1</td>
<td>1070:52</td>
<td>401</td>
<td>7.7</td>
</tr>
<tr>
<td>Ni@L3</td>
<td>3.4 (2.0)</td>
<td>45.5</td>
<td>7:1</td>
<td>1865:269</td>
<td>597</td>
<td>2.2</td>
</tr>
</tbody>
</table>

[^a] % of Ni obtained by Atomic Absorption Spectroscopy (AAS) [^b] The total number of atoms is determined, calculating the unit cell of Ni (fcc) per NP base on the diameter measured by TEM. [^c] Number of surface atoms. Approximate values obtained from ChemCatChem 2011, 3, 1413-1418.
S5. Catalytic profile for semi-hydrogenation of 3-hexyne using Ni@L2 and Ni@L3

![Ni@L2 and Ni@L3](image)

**Figure S4.** Time course of the product yield in the semi-hydrogenation of 3-hexyne using Ni@L2 (left) and Ni@L3 (right) as catalysts. Reaction conditions: 0.5 mmol of 3-hexyne, 3 mmol% catalyst, 0.75 mL toluene, 1 bar H₂.

S6. TEM after catalytic recycling experiments with Ni@L1

After the recycling experiments in the semi-hydrogenation of 3-hexyne, the isolate nanoparticles were analyzed by TEM according to the above mentioned procedure.

![TEM images](image)

**Figure S5.** TEM images of Ni@L1 after catalytic recycling (after 3 cycles) experiments.
**Figure S6.** TEM images of Ni@L1 after catalytic recycling (after 5 cycles) experiments.

**S6. NMR**

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>A</th>
<th>B</th>
<th>C</th>
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</thead>
<tbody>
<tr>
<td>3-hexyne</td>
<td>1.11 ppm (6H)</td>
<td>2.15 ppm (4H)</td>
<td></td>
</tr>
<tr>
<td>Hexene</td>
<td>0.89 ppm (6H)</td>
<td>1.27 ppm (2H)</td>
<td>1.29 ppm (2H)</td>
</tr>
<tr>
<td>cis-hexene</td>
<td>0.96 ppm (9H)</td>
<td>2.03 ppm (4H)</td>
<td>5.33 ppm (2H)</td>
</tr>
<tr>
<td>trans-hexene</td>
<td>0.96 ppm (9H)</td>
<td>2.03 ppm (4H)</td>
<td>5.41 ppm (2H)</td>
</tr>
</tbody>
</table>

**Figure S7.** $^1$H NMR spectrum after hydrogenation of 3-hexyne with Ni@L1 (5h, 1 bar H$_2$, r.t., toluene).