Supporting Information

In Situ Synthesis of Carbon Nanotube-Encapsulated Cobalt Nanoparticles by a Novel and Simple Chemical Treatment Processes: Efficient and Green Catalysts for Heck Reaction

- Abdol R. Hajipour* Zahra Khorsandi and Hossein Farrokhpour*
1. Catalyst characterization

1.1. SEM

**Figure S1.** SEM images of (a) pure CNTs, (b) Co-out-CNTs, (c) Co-in-CNTs (II)

1.2 BET:

**Table S1.** The BET surface area of the catalysts and multiwalled CNTs measured by N\textsubscript{2} chemisorption

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Co-out-CNTs</th>
<th>Co-in-CNTs (I)</th>
<th>Co-in-CNTs (II)</th>
<th>CNTs (end opened)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET Surface Area (m\textsuperscript{2}/g)</td>
<td>198.6</td>
<td>201.4</td>
<td>202.2</td>
<td>210.2</td>
</tr>
</tbody>
</table>
1.3 XRD:

Figure S2. XRD patterns of Co-out-CNT the range of 10-80 degree.

Figure S3. XRD patterns of Co-in-CNTs (II).

1.5 ICP & size of NPs:

Table S2. The average Co particles sizes and the amount of cobalt

<table>
<thead>
<tr>
<th>catalyst</th>
<th>Average Pt particles size (nm)</th>
<th>Metal dispersion (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-out-CNTs</td>
<td>25</td>
<td>10</td>
</tr>
<tr>
<td>Co-in-CNTs (I)</td>
<td>21</td>
<td>0.5</td>
</tr>
<tr>
<td>Co-in-CNTs (II)</td>
<td>9</td>
<td>5</td>
</tr>
</tbody>
</table>

a From TEM histogram
b Measured by ICP
1.6 XPS & EDX:

**Figure S4.** XPS spectrum of Co-in-CNTs (II)

**Figure S5.** EDX spectrum of Co-in-CNTs (II)
2. Experimental

*Synthesis of Cobalt Nanoparticle Catalyst Supported on the Internal Surface of MW-CNTs (method I).*

A solution (20 mL) of concentrated nitric acid (68–70%, Sigma-Aldrich Co.) and sulfuric acid (40%) was prepared and 0.5 g multiwalled carbon nanotubes (MW-CNTs, purity > 95%, i.d. = 5-10 nm, o.d. =20-30 nm, Specific surface area >200 (m2/g)) was suspended in it; and refluxed at 110 °C for 5 h. The black solid was filtrated and washed with deionized water several times to pH 7 then dried in an oven at 100 °C overnight. The solid (opened end MW-CNTs (Figure 1a)) was redispersed in aqueous solution of 1.0 g cobalt(II) chloride hexahydrate (>98%, Sigma-Aldrich Co.) and reducing agent (NaBH₄ (1 mol%)). The obtained solution was ultrasonicated for 1h and after that mixed for 3h at 45 °C. The loading amount was~0.5 wt % as measured using inductively coupled plasma atomic emission spectroscopy (ICP-AES). The black product filtrated and dried at 80 °C overnight in an oven. The Co-in-MW-CNTs was formed and as shown in Figure 1c the cobalt nanoparticles filled internal surface of MW-CNTs.

*Synthesis of Cobalt Nanoparticle Catalysts Supported on the Internal Surface of MW-CNTs (method II).*

Other methods was tested to synthesized these materials: A solution (20 mL) of concentrated nitric acid (68–70%, Sigma-Aldrich Co.) and sulfuric acid (40%) was prepared and 0.5 g multiwalled carbon nanotubes (MW-CNTs, purity > 95%, i.d. = 5-10 nm, o.d. =20-30 nm, Specific surface area >200 (m2/g)) was suspended in it, and refluxed at 110 °C for 5 h. The black solid was filtrated and washed with deionized water several times to pH 7 then dried in an oven at 100 °C overnight. The solid (opened end MW-CNTs) was redispersed in aqueous solution of
1.0 g cobalt(II) chloride hexahydrate (>98%, Sigma-Aldrich Co.). The obtained solution was ultrasonicated for 3h at 35 °C. The loading amount was~5 wt % as measured using inductively coupled plasma atomic emission spectroscopy (ICP-AES). The black product filtrated and dried at 80 °C overnight in an oven. To forming the reactive Co-in-MW-CNTs catalyst, the precursor was activated by reduction using NaBH4 (1 mol%) at 80 °C for 2 h, the cobalt nanoparticles was tagged on internal walls of MW-CNTs, more density of NPs and more smaller NPs compared to previous technic was achieved (Figure 1b).

**Synthesis of Cobalt Nanoparticle Catalysts Supported on External Surfaces of MW-CNTs.**

A solution (20 mL) of concentrated nitric acid (68–70%, Sigma-Aldrich Co.) and sulfuric acid (40%) was prepared and 0.5 g multiwalled carbon nanotubes (MW-CNTs, purity > 95%, i.d. = 5-10 nm, o.d. =20-30 nm, Specific surface area >200 (m2/g)) was suspended in it and refluxed at 110 °C for 5 h. The black solid was filtrated and washed with deionized water several times to pH 7 then dried in an oven at 100 °C overnight. The solid (opened end MW-CNTs) was redispersed in aqueous solution of 1.0 g cobalt(II) chloride hexahydrate (>98%, Sigma-Aldrich Co.). After ultrasonication for 1 h, the solution was mixed for 5 h at 140 °C. It was activated by reduction using NaBH4 at 80 °C for 2 h. The loading amount was~10 wt % as measured using inductively coupled plasma atomic emission spectroscopy (ICP-AES). The Co-out-MW-CNTs was gave which its TEM was shown in Figure 1d.

**General procedure for the Heck reaction**

In a round-bottom flask equipped with a mechanical stirrer, a mixture of K₂CO₃ (2 equiv.), olefin (1.2 mmol), and aryl halide (1 mmol) in PEG (2 mL) was added to 20 mg of catalyst and the flask was equipped with a condenser for refluxing. The abovementioned mixture was heated at 60 °C in an oil bath. The progress of the reaction was monitored by TLC (hexane/EtOAc, 80 :
20) and gas chromatography (GC). After the completion of the reaction, the mixture was diluted with dichloromethane and water. The organic layer was washed with brine, dried over anhydrous MgSO$_4$, and concentrated under reduced pressure. The residue was purified by column chromatography. The products were characterized by comparing their physical properties, such as m.p., IR, $^1$H, and $^{13}$C NMR spectra, with those reported in literature.
3. NMR spectra of products

The products were characterized by comparing their physical properties m.p., IR, $^1H$, $^{13}C$ NMR spectra with those found in the literature $^1$-$^5$. 
References: