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

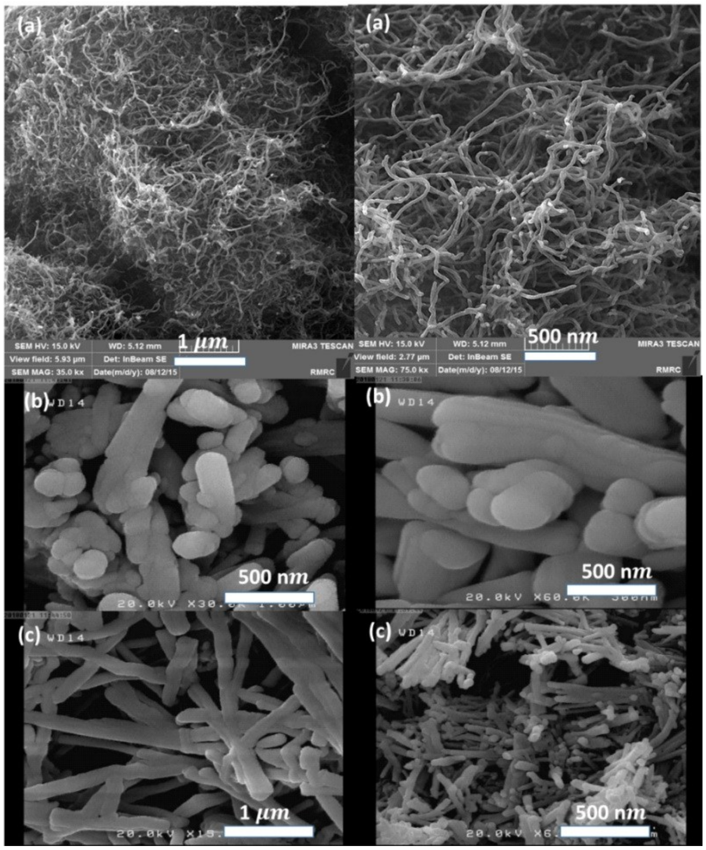


Figure S1. SEM images of (a) pure CNTs, (b) Co-out-CNTs, (c) Co-in-CNTs (II)

1.2 BET:

Table S1. The BET surface area of the catalysts and multiwalled CNTs measured by N_2 chemisorption

Catalyst	Co-out-CNTs	Co-in-CNTs (I)	Co-in-CNTs (II)	CNTs (end opened)
BET Surface Area (m^2/g)	198.6	201.4	202.2	210.2

1.3 XRD:

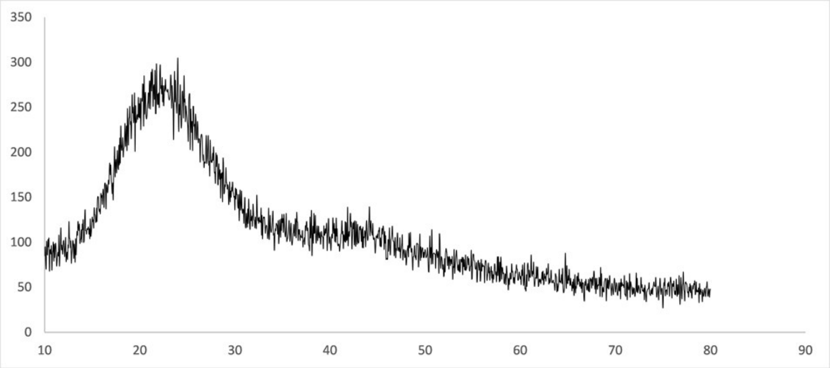


Figure S2. XRD patterns of Co-out-CNT the range of 10-80 degree.

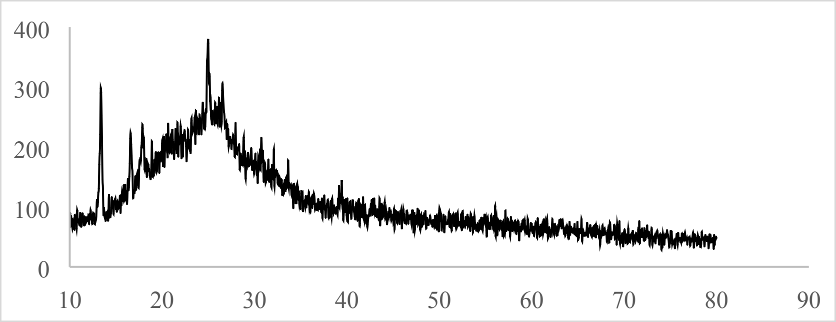


Figure S3. XRD patterns of Co-in-CNTs (II).

1.5 ICP & size of NPs:

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

catalyst	Average Pt particles size[a] (nm)	Metal dispersion[b] (wt%)
Co-out-CNTs	25	10
Co-in-CNTs (I)	21	0.5
Co-in-CNTs (II)	9	5

[a]From TEM histogram

[b]Measured by ICP

1.6 XPS & EDX:

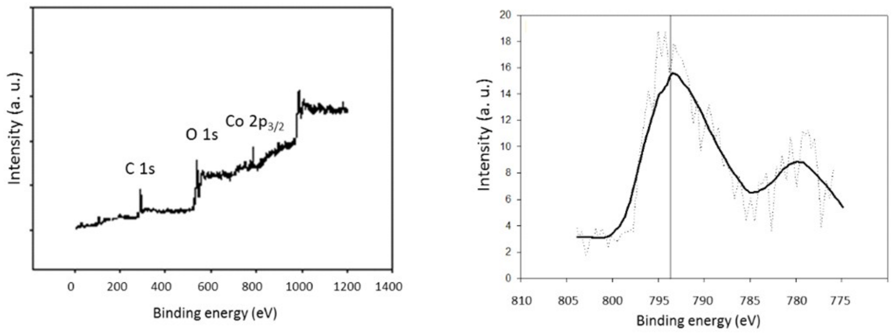


Figure S4. XPS spectrum of Co-in-CNTs (II)

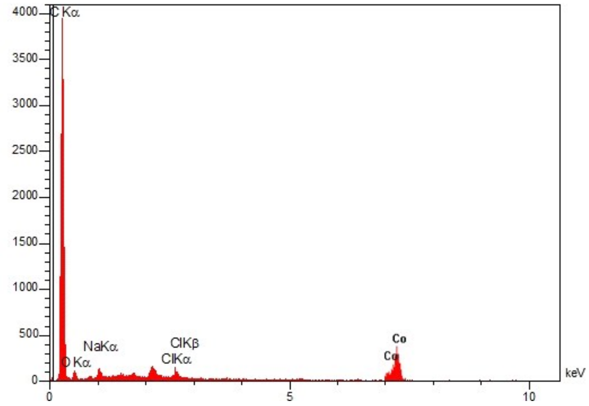


Figure S5. EDX spectrum of Co-in-CNTs (II)

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.[1] 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 ($NaBH_4$ (1 mol%)). The obtained solution was ultrasonicated for 1h and after that mixed for 3h at 45 ℃. 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 ℃. 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 ℃. It was activated by reduction using $NaBH_4$ 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.

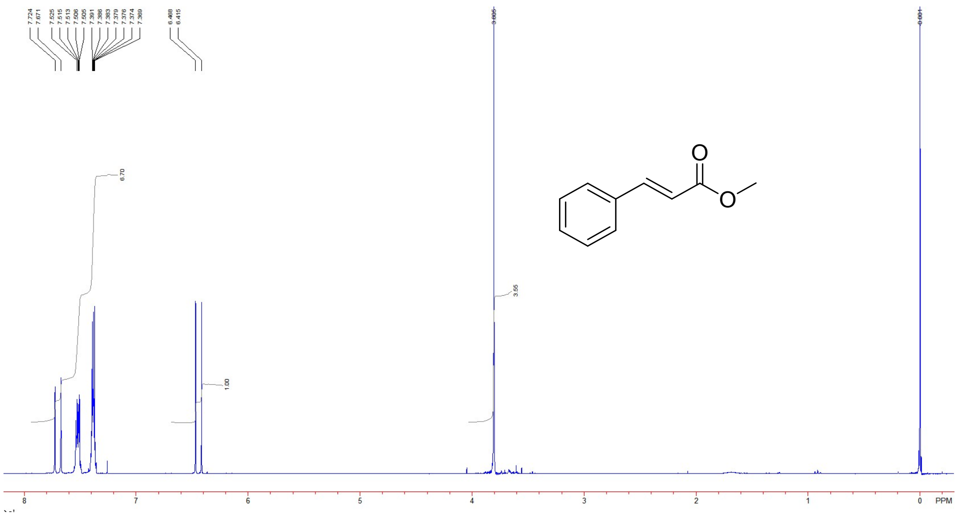
General procedure for the Heck reaction

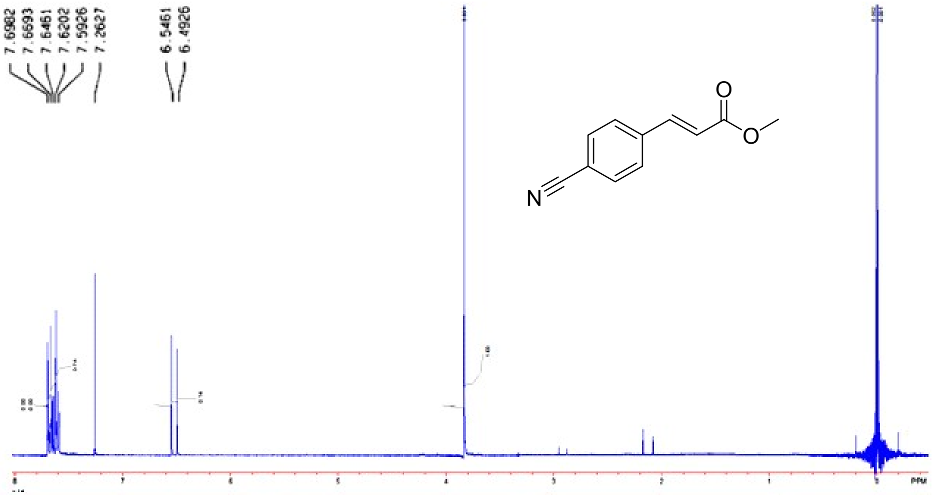
In a round-bottom flask equipped with a mechanical stirrer, a mixture of K_2CO_3 (2 equiv.), olefin (1.2 mmol), and aryl halide (1 mmol) in PEG (2 mL) was added to 20 mg of catalyst and the flask was equipped with a condenser for refluxing. The abovementioned mixture was heated at 60 °C in an oil bath. The progress of the reaction was monitored by TLC (hexane/EtOAc, 80 :

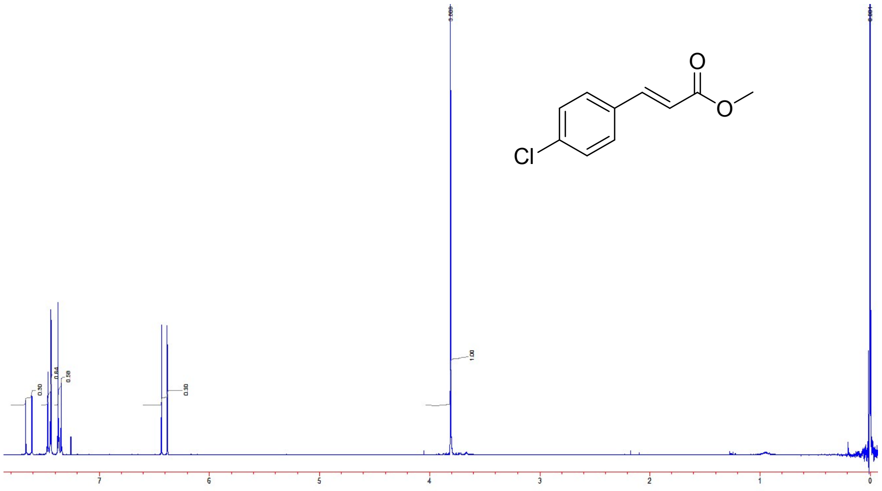
20) and gas chromatography (GC). After the completion of the reaction, the mixture was diluted with dichloromethane and water. The organic layer was washed with brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography. The products were characterized by comparing their physical properties, such as m.p., IR, ^1H, and ^{13}C NMR spectra, with those reported in literature.

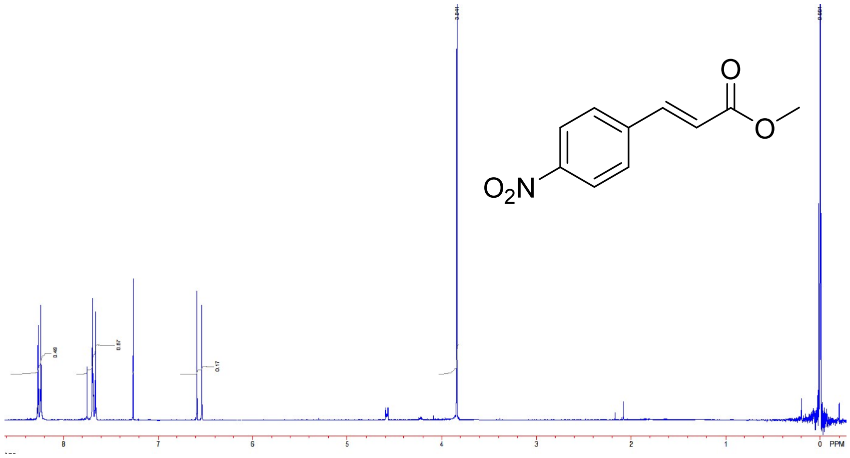
3. NMR spectra of products

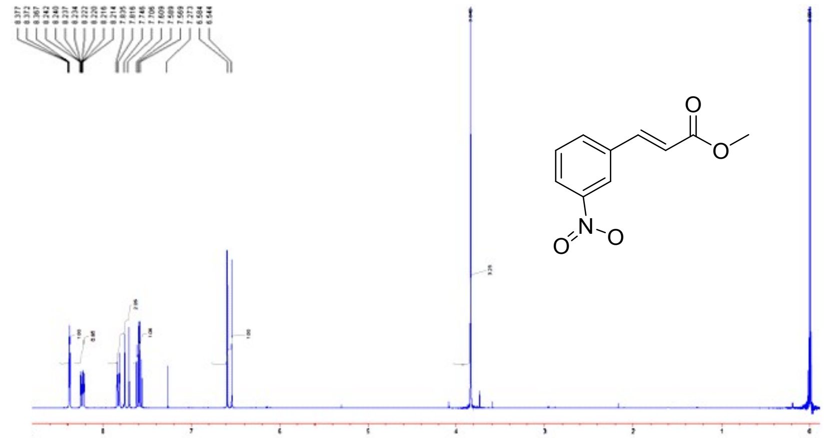
The products were characterized by comparing their physical properties m.p., IR, ^{1}H, ^{13}C NMR spectra with those found in the literature [1-5].






Cl
O
O
0.30
0.64
0.59
0.30
1.00
7
6
5
4
3
2
1
0


O
O
O_2N
0.48
0.57
0.17
8
7
6
5
4
3
2
1
0
PPM


8.377
8.372
8.367
8.242
8.240
8.237
8.234
8.222
8.220
8.216
8.214
7.835
7.816
7.745
7.706
7.609
7.589
7.569
7.273
6.584
6.544
O
O
N
O
O
1.00
8
7
6
5
4
3
2
1
0

References:

1. Y. T. Shieh, G. L. Liu, H. H. Wu, C. C. Lee, *Carbon*, 2007, 45, 1880-1890.