

Novel Carbon Nanofibers Supported Ni(0) Nanoparticles Catalysed Heck Reaction under Ligand-Free Condition

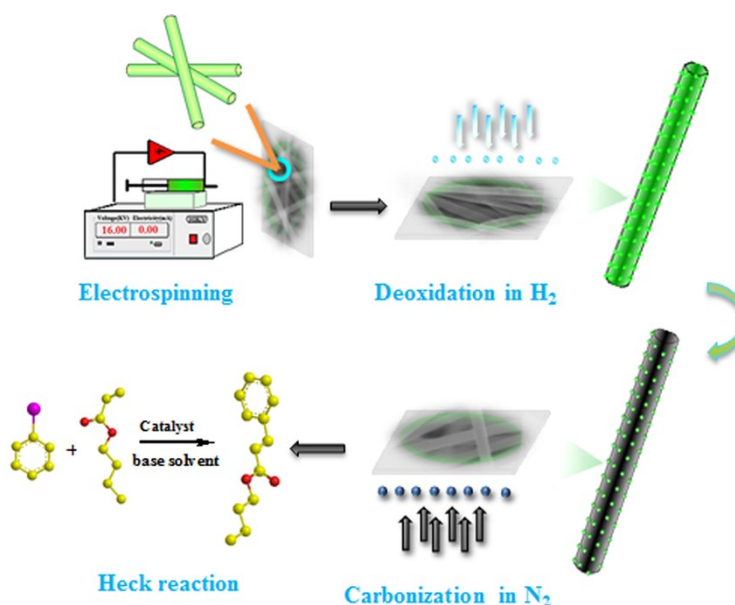
EXPERIMENTAL SECTION

Materials

Polyacrylonitrile (PAN, Mw=80000 g/mol) was provided by Kunshan Hongyu Plastics Co., Ltd.. N,N-dimethyl formamide (DMF, AR, 99.5%) and N-methylpyrrolidone (NMP, AR, 99%) were from Tianjin Gaungfu Fine Chemical Co., Ltd.. Dimethyl sulfoxide (DMSO, AR, 99%) and dimethylacetamide (DMAC, AR, 99.5%) were purchased from Tianjin Fuyu Fine Chemical Co., Ltd.. Nickel(II) acetylacetonate (Ni(acac)₂, 99.5%), iodobenzene (AR, 97%), n-butyl acrylate (AR, 98%) and triethylamine (Et₃N, AR, 99%) were bought from Sinopharm Chemical Reagent Co., Ltd.. All of these reagents were used without additional purification, but all solvents needed deoxygenation.

Preparation of Ni(0)/CNFs

As is shown in Scheme 1, the clear and straightforward flowchart reflects the whole process. Electrospun precursor solution of 8% was prepared by dissolving PAN into DMF with stirring at room temperature for 24 h, then added to Ni(acac)₂ (AN and Ni(acac)₂ at the molar rate of 20:1) and continuously stirred for 24 h. The homogenous solution was electrospun into nanofiber membranes through a glass dropper under an applied voltage of 16 KV which was provided from a high-voltage power supply. The best distance between the glass dropper and the aluminum foil as a receiver was 18 cm. Taking advantage of H₂ deoxidized Ni/NFs at 120 °C for 10 h in the 2 MPa H₂ atmospheres. After deoxidation, nanofibers needed the process of carbonization to get more stable catalyst. Carbonization of Ni(acac)₂/PAN nanofibers was as following: (1) The stabilization of the precursor nanofibers was at 250 °C for 2 h in vacuum tube furnace; (2) The carbonization and formation of Ni nanoparticles was at 600 °C for 2 h and then the samples were cooled to RT automatically, and finally carbon nanofibers loaded Ni nanoparticles were obtained. Whole process was in N₂ atmosphere.



Scheme 1. Scheme of the process of preparation Ni(0)/CNFs and catalyst Heck reaction.

Characterization of Catalysts

The morphology of the Ni(0)/CNFs and nanoparticles were observed by scanning electron microscopy (SEM, Hitachi S-3400N, Japan), energy dispersive X-ray and transmission electron microscopy (EDS and TEM, F20 S-TWIN, Tecnai). Structural characterization could be got from fourier transform infrared spectroscopy (FTIR, Shimadzu, Japan). Though H₂ deoxidation, temperature-programmed reduction (TPR, Chembet Pulsar TPR/TPD, Quantzchrome, USA)

analysis was an effective way to identify whether specified nickel element has been reduced to zero valence. To acquire more information about the Ni(0)/CNFs, especially to the surface composition and electronic properties, X-ray photoelectron spectra (XPS, Escalab 250xi, ThermoFisher Scientific USA) was used.

Heck reaction by Ni(0)/CNFs

In a typical Heck reaction, in nitrogen atmosphere, iodobenzene, n-butyl acrylate, trimethylamine and solvent were added into the parallel quartz reactor with the Ni(0)/CNFs in the heating and stirring. Then more than once vacuuming replace air with nitrogen in quartz tube. Finally, the mixed solution was heated to expected temperature for designated time. As a result, the solution was filtered, extracted and subsequently monitored by gas chromatograph (GC2010 Plus, Shimadzu, Japan). The whole catalyst was retrieved and washed by distilled water and ethanol for reusing.