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Pd nanoparticles immobilized on PAMAM-grafted MWCNTs hybrid materials as new recyclable catalyst for Mizoraki–Heck cross-coupling reactions

Mohammad Reza Nabid*, Yasamin Bide, Seyed Jamal Tabatabaei Rezaei

Department of Chemistry, Shahid Beheshti University, G.C., P.O. Box 1983963113 Tehran, Iran

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ABSTRACT

Polyamidoamine (PAMAM) dendrimers up to the third generation (G) were grown onto the surface of functionalized multiwall carbon nanotubes (MWCNTs-NH_2) by a divergent method, the PAMAM-grafted-MWCNTs (PAMAM-g-MWCNTs) hybrid materials were obtained. Because of the surface modification of the multiwall carbon nanotubes with PAMAM dendrimers, these hybrid materials are not only soluble in aqueous medium but also are able to trap water soluble metal ions such as Pd^{2+} via complex formation of PAMAM dendrimer with metal ions. The reduction of trapped palladium ions in the dendritic shell of PAMAM-g-MWCNTs by sodium borohydride led to immobilized palladium nanoparticles on the surface of MWCNTs. Thus, palladium nanoparticles were immobilized by PAMAM-g-MWCNTs hybrid materials (PdNs-PAMAM-g-MWCNTs) and their application as a new nanocatalyst toward Heck reaction in different conditions was investigated. The G3 and G2 hybrid materials were found to be very active in cross-coupling reactions of aryl iodides, bromides and also chlorides with olefinic compounds in Heck reactions with short reaction time duration and high yields. The catalyst can be recycled several times without loss in activity.

1. Introduction

Since their discovery by Iijima [1], carbon nanotubes (CNTs) have attracted great interest in the most fields of science due to their unique physical and chemical properties [2,3]. Owing to their unique structure and interesting properties such as large surface area, CNTs are excellent supporting materials for catalysts, especially in heterogeneous catalysis [4,5]. Although CNTs supported metal nanoparticles exhibit greater catalytic efficiency than their bulk counterparts, because of high surface-to-volume ratio [6], there are some difficulties in dispersing metal nanoparticles on the surface of pristine CNTs due to their hydrophobic nature as well as their tendency for agglomeration. In order to overcome these problems and to favor a high loading of nanoparticles, grafting well-defined polymers known as dendrimers can act as macromolecular coupling agents carrying multiple binding sites [7–16].

Dendrimers are nanosized, highly branched molecules, with very well-defined chemical structures, engineered precisely to carry molecules encapsulated in their interior void spaces or attached to their surface. These unique abilities of dendrimers led to the design of novel dendritic materials for a variety of advance applications [17]. Chemical attachment of dendrimers to the surface of CNTs can be performed by either “convergent” or “divergent” methods. In convergent method prefabricated dendrimers are connected to functionalize CNTs through chemical reaction. The convergent synthesis strategy is characterized by low grafting density because of the hindrance of the dendrimer branches which react with CNTs [18–20]. The divergent method involves the growth of dendrimers from the surface of CNTs by first covalently attaching of appropriate functional groups. In contrast to convergent route this method leads to the higher grafting density and control over the dendrimer growth with the possibility of designable structures [21,22].

Palladium has been recognized as an indispensable catalyst for carbon–carbon and carbon-heteroatom bond forming reactions and there is a great deal of literature on its properties in many reactions [23–31]. Recently, palladium nanoparticles supported on insoluble solids have received considerable attention as a new generation of heterogeneous catalysts in various scientific fields because of their superior catalytic performance, good stability, ease of separation and satisfactory reusability in comparison to the traditional homogeneous $Pd(OAc)_2$, $PdCl_2$ catalysts [32–57]. Because of these reasons and also as a part of our ongoing research program on the application of catalysts for the development of useful new synthetic methodologies [58–61], herein, we report the synthesis of a heterogeneous palladium nanocatalyst supported on PAMAM-grafted-MWCNTs and its efficiency in the promotion of the Heck coupling reaction.

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* Corresponding author. Tel.: +98 21 29902800; fax: +98 21 22431586.
E-mail address: m-nabid@sbu.ac.ir (M.R. Nabid).

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Table 1
Amount of $-NH_2$ groups and Pd(0) on each generation of the PdNs-PAMAM-g-MWCNTs hybrid materials.

Entry	Generation	$-NH_2$ content[a]/mmol g^{-1}	$-NH_2$ content[b]/mmol g^{-1}	Amount of Pd(0)[c]/mmol g^{-1}	Loading efficiency (%)
1	0	0.17	0.16	0.31	4.13
2	1	0.33	0.31	0.51	6.80
3	2	0.65	0.59	1.20	16.0
4	3	1.33	1.29	2.00	26.6

[a] Determined by Titration method.
[b] Determined by TGA.
[c] Determined by AAS.

2. Experimental

2.1. Materials

The used MWCNTs were prepared by chemical vapor deposition procedure in the presence of Co/Mo/MgO as catalyst at 900 °C. The outer diameter of MWCNTs was between 20 and 40 nm. All solvents and reagents were purchased from Aldrich or Merck and used without further purification unless otherwise stated. 3-Azidopropylamine was prepared according to the reported procedures in relevant literature [62].

2.2. Instruments and characterization

^1H NMR spectra were recorded with a BRUKER DRX-300 AVANCE spectrometer, and D_2O or $CDCl_3$ were used as solvents. IR spectra were recorded on a Bomem MB-Series FT-IR spectrophotometer. Transmission electron microscopy (TEM) analyzes were performed by LEO 912AB electron microscope. XPS analysis was performed using a VG multilab 2000 spectrometer (ThermoVG scientific) in an ultra high vacuum. Catalysis products were analysed using a Varian 3900 GC (GC conversions were obtained using n-decane as an internal standard based on the amount of arylhalide employed relative to authentic standard product). Ultrasonic bath (EUROSONIC® 4D ultrasound cleaner with a frequency of 50 kHz and an output power of 350 W) was used to disperse materials in solvents. Thermogravimetric analysis (TGA) was carried out using STA 1500 instrument at a heating rate of 10 °C min^{-1} in air. X-ray powder diffraction (XRD) data were collected on an XD-3A diffractometer using Cu Kα radiation.

2.3. Preparation of amino functionalized MWCNTs

MWCNTs (2 g) were refluxed under stirring in the mixture of 1:3 (v/v) HNO3 and H2SO4 at 90 °C for 24 h. The mixture was cooled and diluted by distillated water and then filtrated. The product (MWCNTs-COOH) was washed by distillated water and dried at 70 °C for 1 day under reduced pressure. Subsequently, in a 50 mL flask with a magnetic stirring bar, the obtained carboxylated MWCNTs (0.5 g) was dispersed in anhydrous dichloromethane. Then, appropriate quantities of propargyl alcohol and 4-(dimethylamino) pyridine (DMAP) were added to the above mixture. After the flask was cooled to 0 °C, a diluted solution of *N*,*N*′-dicyclohexyl carbodiimide (DCC) was added dropwise over 2 h. The reaction mixture was warmed to room temperature and stirred for 48 h. The propargyl functionalized MWCNTs obtained from the reaction was separated and washed carefully with methanol, deionised water and again with dry methanol and dried at 50 °C under reduced pressure. The amino-functionalized MWCNTs (MWCNTs-NH_2) was synthesized by “click” reaction between propargyl-functionalized MWCNTs and 3-azidopropylamine. Typically, propargyl-functionalized MWCNTs were dispersed in the mixture of 1:4 (v/v) H_2O and THF by sonication for 10 min, and the reacted with excess of 3-azidopropylamine in the presence of $Cu(OAc)_2$ and sodium ascorbate catalysts at room temperature for 48 h. The attachment of amino group onto the MWCNTs was established by FT-IR.

2.4. Preparation of PAMAM-grafted-MWCNTs hybrid materials

First-, second- and third-generation PAMAM dendrimers were synthesized on the amino functionalized MWCNTs. The amino-functionalized MWCNTs (1 g, 0.17 mmol $-NH_2$ groups) were added in portions at ambient temperature with stirring to methyl acrylate (8.8 mL, 100 mmol) and methanol (10 mL) in a 100-mL round-bottomed flask. The reaction mixture was stirred at ambient temperature under nitrogen atmosphere for 5 day. After the reaction, excess reactants and solvent were removed under vacuum. The ester-functionalized MWCNTs were washed with methanol, dichloromethane and acetone (3 mL × 20 mL). It was dried under vacuum for 24 h. Then, the ester-functionalized MWCNTs were added in small fractions with stirring to a mixture of ethylenediamine (6.4 mL, 100 mmol) and methanol (20 mL) in a round-bottomed flask and then cooled to 0 °C in an ice–salt bath. The reaction mixture was stirred at 0 °C for 1 h, the temperature was allowed to rise to ambient temperature, and the mixture was stirred at ambient temperature for 4 day to ensure reaction completion. It was filtered under vacuum, washed with methanol, acetone and diethyl ether (3 mL × 20 mL) and dried under vacuum for 24 h. Repetition of the above steps gave second- and third-generation PAMAM dendrimers attached on the surface of MWCNTs. After the synthesis, titration method [63] was used to calculate the amount of free primary amines in the periphery of the dendrimers (Table 1). Typically, 0.2 g of PAMAM-grafted-MWCNTs hybrid materials was suspended in 40 mL of 0.01 mol L^{-1} HCl aqueous solution and stirred at ambient temperature for 24 h. The hybrid materials was filtered and washed well with distilled water. The filtrate and washings were collected. The unreacted HCl was determined by titration against a standard Na_2CO_3 solution with use of methyl orange indicator. A blank titration was also carried out. From these values, the amount of amino groups per gram of the hybrid materials was calculated.

2.5. Preparation of PdNs-PAMAM-g-MWCNTs

Aqueous solution of $PdCl_2$ (0.26 g in 3 mL) and PAMAM-grafted-MWCNTs (0.2 g in 10 mL) were mixed and placed in an ultrasonic bath (50 KHz) for 10 min to well disperse metal ions in the dendritic shell of hybrid material. Mixture was stirred at room temperature for 8 h and the reduction was carry out by the addition 0.08 mL of aqueous solution of $NaBH_4$ (0.01 M) to the mixture and stirring at room temperature for 1 h. It was filtered under vacuum, washed well with ethanol and water (2 mL × 20 mL) and dried under vacuum at 50 °C for 4 h.

2.6. General procedure for the catalytic tests

The coupling reaction was carried out in a glass batch reactor. At first aryl halide (1 mmol) and methyl acrylate or styrene (1 mmol)