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Multi-walled carbon nanotubes functionalized with a palladium(II)-Schiff base complex: A recyclable and heterogeneous catalyst for the copper-, phosphorous- and solvent-free synthesis of ynones

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ABSTRACT

The air-moisture stable and reusable multi-walled carbon nanotubes (MWCNTs) functionalized with a palladium(II)-Schiff base complex was synthesized by covalently anchoring a hydroxyl functionalized palladium(II)-Schiff base complex to modified MWCNTs. This heterogeneous catalyst exhibited effective catalytic activities by affording ynones in excellent yields from coupling reactions of acid chlorides with terminal alkynes under copper-, phosphorous- and solvent-free conditions in air.

1. Introduction

During the last decade, studies on the isolation, characterization, and catalytic activity of functionalized carbon nanotubes (CNTs) have attracted particular attention because of their specific catalytic applications as compared to homogeneous complexes. Metal nanoparticles as well as various transition metal complexes such as polymers and porphyrins have been used for carbon nanotubes' functionalization [1–5]. Schiff bases, which are an important class of ligands with extensive applications in different fields [6], have also showed excellent catalytic activity when grafted on CNTs [7,8].

In recent years, conjugated alkynyl ketones, best known as ynones, have received considerable synthetic interest due to their occurrence in a wide variety of bioactive molecules and natural products [9]. Moreover, they have been extensively utilized as synthetic intermediates for the synthesis of important biologically active heterocyclic compounds [10–13].

Different protocols have been reported for the synthesis of α,β-acetylenic ketones which include: (a) oxidation of alkynes [14–16], (b) oxidation of propargylic alcohols [17], which are usually obtained by nucleophilic addition of acetylides to aldehydes, (c) reaction of terminal alkynes with nitriles [18], (d) cross-coupling reaction of terminal alkynes with organic halides in the presence of carbon-monoxide gas [19–21], and finally the most efficient method is (e) the reaction between terminal alkynes and carboxylic acid derivatives such as acid chlorides, acid anhydrides, esters, and acyl cyanides [22]. Strong bases such as *n*-BuLi [23,24] and elements such as silver [25], silicon [26], zinc [27], gallium [28], tin [29], lithium [30], indium [31], boron [32], palladium [33] and copper [34] could be used in these reactions. However, the above synthetic methods suffer from serious disadvantages such as high temperatures [35,36], long reaction times [37], use of air and moisture sensitive catalysts such as phosphorous containing catalysts [38–41], use of copper catalysts which are very much prone to form diyne side products, use of hazardous organic solvents [42], use of toxic carbon-monoxide gas and need for special instruments [43]. Taking these constraints into account, the development of new, mild, simple and efficient copper- and phosphorous-free synthetic procedures would have significant value. In this paper, MWCNTs-Pd-Schiff base complex was used as a reusable and heterogeneous catalyst for the synthesis of α,β-acetylenic ketones under aerobic conditions (Scheme 1).

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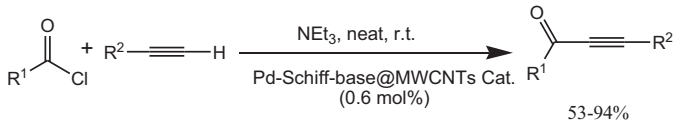

Scheme 1.

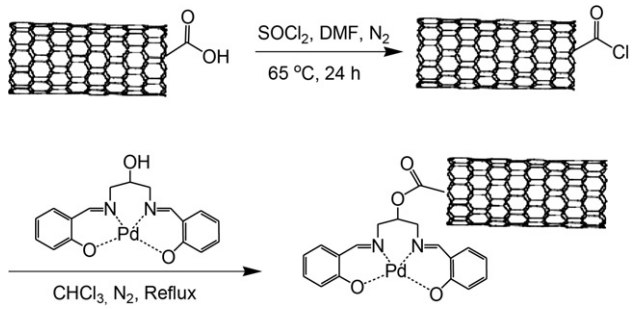

Fig. 1. Preparation of Pd-Schiff base@MWCNTs.

2. Results and discussion

2.1. Synthesis and characterization of MWCNTs-Pd-Schiff base catalyst

Carboxylic acid multi-walled carbon nanotubes (CO_2H-MWCNTs) used in this study were purchased from Times company (China) with outer diameters ranging from 10 to 20 nm, internal diameters varying from 5 to 10 nm, lengths about 30 μm and purity of >95%. They were then chlorinated using $SOCl_2$ in DMF at 65 °C for 24 h. Pd(II)-Schiff base complex which had been previously prepared was then anchored to the MWCNTs-COCl after 20 h of heating under N_2 (Fig. 1).

The Pd(II)-Schiff base complex covalently anchored to modified MWCNTs was characterized by different techniques. Attenuated total reflection infrared spectroscopy (ATR) was used to ensure the esterification step, with disappearance of the characteristic peak of the acid chloride (C=O, 1750 cm^{-1}) and the appearance of the peak at 1708 cm^{-1} associated with C=O stretch of the ester. Moreover, the metal content of the complex was found to be 16.20 ppm using inductive coupled plasma (ICP) and the ratio of Pd/N in the catalyst was obtained to be 1.82%. In fact, the X-ray diffraction (XRD) pattern of the catalyst which is presented in Fig. 2 confirms the presence of graphite at around 26° [44] and also the palladium metal at 39.9°, 47.4° and 82.0°.

Also, Raman spectroscopy showed four bands which are characteristic of CNTs (Fig. 3) including tangential stretching G-band (1567 cm^{-1}), D-band (1331 cm^{-1}), second harmonic D*-band (2678 cm^{-1}) and radial breathing band (RBM) (288 cm^{-1}) [45,46].

Further evidence for the modification of MWCNTs came from the X-ray photoelectron spectroscopy (XPS) of the complex (Fig. 4). The peaks at 290.8, 344.6 and 539.2 eV are attributed to C, N and O

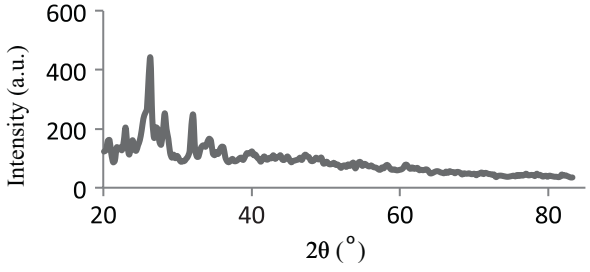

Fig. 2. XRD pattern of Pd-Schiff base@MWCNTs.

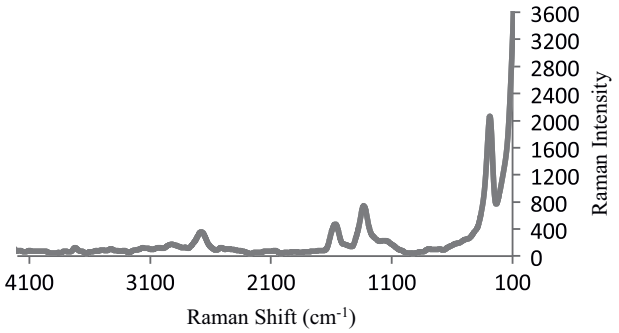

Fig. 3. Raman specrtum of Pd-Schiff base@MWCNTs.

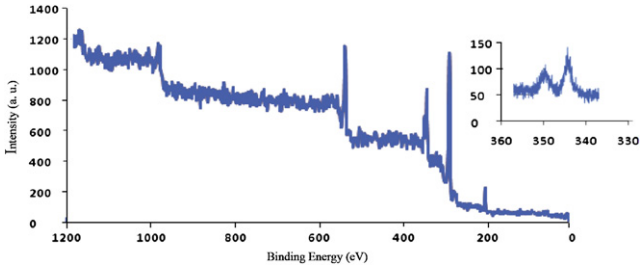

Fig. 4. XPS spectrum of Pd-Schiff base@MWCNTs with expansion.

atoms, respectively [44]; palladium $3d_{3/2}$ and $3d_{5/2}$ peaks appear at 349.8 and 344.4 eV, respectively (inset) [47,48].

Thermogravimetric-differential thermal analysis (TG-DTA) showed that the significant mass loss happened at 200–320 °C within two steps (Fig. 5). The surface grown Pd-Salen groups were lost at this temperature range [44].

In addition, transmission electron microscopic (TEM) images of the purchased CO_2H-MWCNTs and Pd-Schiff base@MWCNTs were also taken (Fig. 6). In fact, making a comparison between these images could confirm the presence of the Schiff base complex (black dots). Besides, obviously the layered structure of the MWCNTs had remained largely intact, which indicated that the MWCNTs had not been damaged during the functionalization process [44].

2.2. Catalytic performance of MWCNTs-Pd-Schiff base catalyst for the synthesis of ynones

The coupling between phenyl acetylene (1.5 mmol) and benzoyl chloride (1 mmol) in the presence of NEt_3 (2 mmol) in air and at ambient temperature was chosen as a model reaction to find

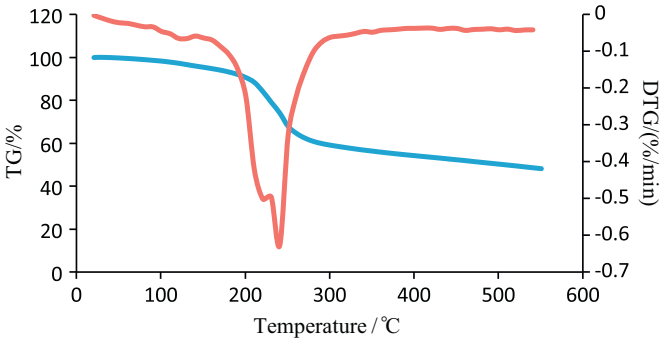

Fig. 5. TG-DTA curve of the Pd-Schiff base@MWCNTs.