



Short communication

Multi walled carbon nanotubes supported N-heterocyclic carbene–cobalt (II) as a novel, efficient and inexpensive catalyst for the Mizoroki–Heck reaction

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ARTICLE INFO

Article history:

Received 23 November 2015

Received in revised form 23 December 2015

Accepted 24 December 2015

Available online 29 December 2015

Keywords:

MWCNTs

NHC ligand

Mizoroki–Heck

Heterogeneous catalyst

ABSTRACT

In this paper, an N-heterocyclic carbene–cobalt complex (NHC–Co²⁺) was immobilized onto the surface of multi-walled carbon nanotubes (MWCNTs) via direct grafting amination approach for the first time. The resultant composite (Co–NHC@MWCNTs) was characterized by FT-IR, TGA, XRD, ICP-OES, FE-SEM, TEM and CHN analyses. It was demonstrated that Co–NHC@MWCNTs can act as an efficient and inexpensive catalyst for Heck reactions in normal conditions which provided the corresponding products in moderate to good yields. More importantly, this phosphine and palladium-free catalyst can be reused for at least six successive runs without any discernible decrease in its catalytic activity and no remarkable changes were observed in catalyst structure.

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1. Introduction

The formation of C–C bonds is a fundamental reaction in organic synthesis for its many vast applications in the synthesis of natural products, numerous drugs and high-performance modern materials. The Mizoroki–Heck coupling received considerable attention as one of the most important C–C bond forming reaction [1]; therefore, a number of efficient catalytic systems have been developed for these transformations [2]. The standard Heck reaction contains palladium salt and phosphine ligands, which suffers from limitations that have so far precluded many industrial applications [3]. In addition, due to the high cost and toxicity of palladium; researchers are interested in Heck reaction catalyzed by inexpensive transition metals such as Ni [4], Cu [5], Fe [6] and Co [7–8]. To overcome other disadvantages of traditional methods such as using expensive, toxic and unrecoverable phosphine ligands and complicated recovery, several types of nitrogen-based ligands such as N-heterocyclic carbene (NHC) metal complexes have been developed by immobilizing them on solid supports [9–10].

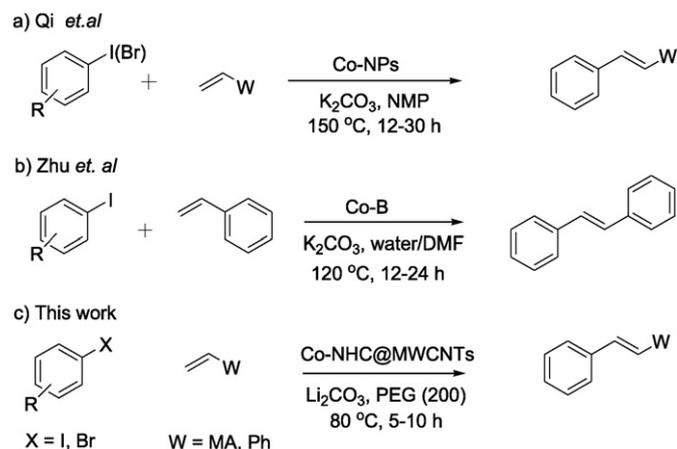
Multi-walled carbon nanotubes (MWCNTs) are one of the hottest nanomaterials in synthesis, characterization, and applications because of their unique thermal, mechanical and chemical properties [11–15]. Furthermore, MWCNTs can be used as wonderful catalyst support because of their high surface area and their insolubility in most solvents.

In this regard, diamines are the more favorite molecules, which could behave as a medium in attaching miscellaneous compounds to MWCNTs. Actually, the diamines consist of two amino groups (–NH₂): one could attach on MWCNTs, and one is available for bonding to other functional groups [16–18]. Actually, the described method is one of the most remarkable pre-functionalized strategies, which allows the covalent binding of different groups on the surface of MWCNTs. Inspired by the widespread successful applications of NHC catalytic systems [19] and disadvantages of palladium complexes, we decided to improve more cost-effective and environmentally heterogeneous palladium-free catalyst for C–C coupling reaction by immobilizing first-row transition metal–NHCs complex on MWCNTs.

Recently, cobalt-catalyzed organic synthesis has attracted much attention; because cobalt is readily available, non-toxic, low-cost, stable in air and exhibits powerful catalytic activities [20–22]. Studies on the structure of Co–NHC complex have been reported [23]; but, to the best of our knowledge, olefin arylation reactions employing such complexes were not reported previously. In the field of C–C bond formation using cobalt catalysts, the reductive coupling reactions of alkyl halides with aryl Grignard are active topics in organic synthesis [24–25]. However, the reactions between aryl halides and olefins in the presence of a base (Heck reaction) using a cobalt catalyst are rare and as we know, only a few reports refer to the application of cobalt catalysts in this coupling reaction [26–29]. For example, in 2009, Qi et al. reported Heck reaction using cobalt nanoparticles during long reaction time at extremely high temperature (150 °C, Scheme 1a) [26]. Application of uniform Co–B amorphous alloy nanoparticles as catalyst in C–C

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Scheme 1. Heck reaction using various types of cobalt catalytic systems under different conditions.

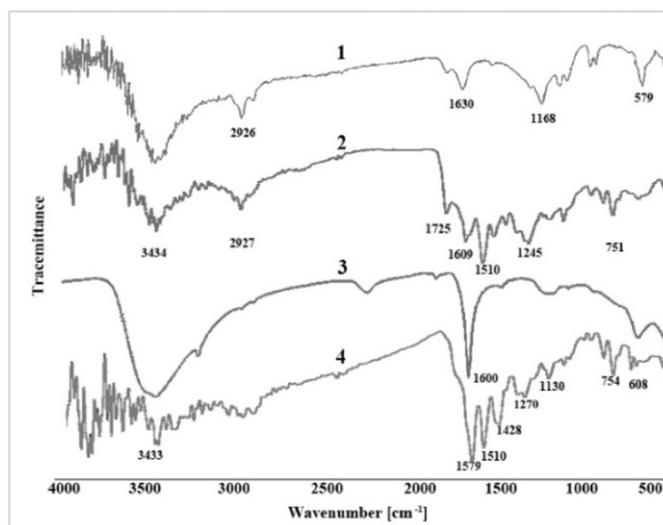


Fig. 1. FT-IR spectra of products of catalyst preparation steps.

coupling reaction was also described by Zhu and his co-workers in 2012 (at 120 °C using DMF/water as solvent and during 12–24 h, [Scheme 1b](#)) [27]. These reported cobalt catalysts have various advantages such as good mechanical and excellent chemical stabilities and better economic and ecological properties compared to palladium catalysts. In contrast, they exhibited lower activity in Mizoroki–Heck reaction in an expanded range of aryl halides, in spite of spending high temperature and long reaction time. Therefore, to overcome these problems, more convenient approaches using a cobalt catalyst are required. In continuation of our recent investigations on the application of heterogeneous catalytic systems in cross-coupling reaction [30–32]; in this report, NHC–Co(II) complex was supported on MWCNTs via direct grafting amination approach for the first time and its catalytic activity was demonstrated by employing the Mizoroki–Heck coupling reaction. Using our catalytic system, the reaction conditions can be improved and it accelerated the Heck reaction without using palladium and phosphine under mild conditions in the present polyethylene glycol as green solvent ([Scheme 1c](#)).

2. Experimental

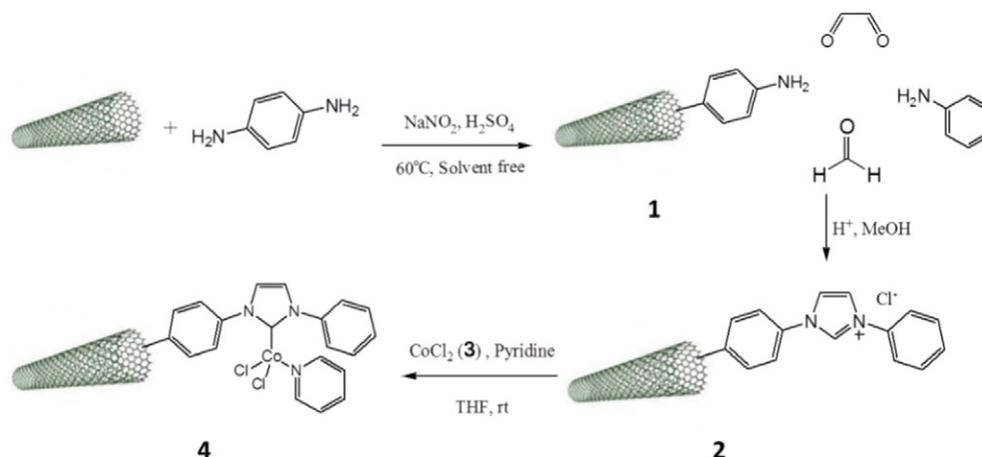
2.1. Catalyst preparation

The Co–NHC@MWCNT catalyst was prepared using multistep synthesis process which was demonstrated in [Scheme 2](#). Detailed procedures are included in the supporting information.

2.2. Characterization

The products of each step were characterized by FT-IR ([Fig. 1](#)). The FT-IR spectrum of 4 is shown with absorption bands at 2927 cm^{-1} (C–H), 3433 cm^{-1} (N–H stretching vibration) and 1579 cm^{-1} (C = C), shifting peak (in a comparison of 2 with 4 spectrum) indicates a successful modification of the NHC precursor [33]. Additionally, several signals (1130 and 608 cm^{-1}) are exposed to the chloride group bonds of 4 clearly.

The nitrogen content of the support was 6.1%. According to this value, the amount of NHC ligand which is available in the catalyst is 1.55 mmol/g. The Co loading of catalyst was measured by ICP and it was about 2.2% (0.35 mmol/g). The structural properties of catalyst were analyzed by X-ray diffraction (XRD). The resulted curve was compared with the pure MWCNTs. All peaks demonstrate the structure of this Co (II) complex ([Fig. S1](#), supplemental data), a similar XRD pattern observation was reported before for Co (II) complex [34]. The thermal stability of compound 4 was also evaluated by TGA, and the thermograms are given in [Fig. S2](#). According to these curves, the weight loss below 300 °C is 2%. This observation can be attributed to the formation of a stable cobalt complex. The degree of functionalization on the MWCNTs could be calculated from the weight loss between 200 °C and 800 °C on TGA and elemental analyses. The observed total weight loss for the catalyst is 67%, on the basis of this value, the amount of



Scheme 2. The preparation of Co–NHC@MWCNTs catalyst.

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