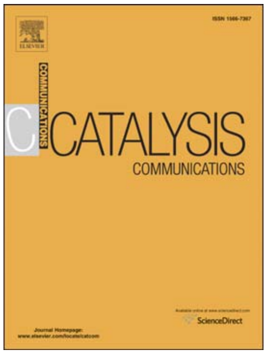

Multi walled carbon nanotubes supported N-heterocyclic carbene–cobalt () as a novel, efficient and inexpensive catalyst for the Mizoroki–Heck reaction

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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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Abstract

In this paper, an N-heterocyclic carbene–cobalt complex (NHC-Co^{2+}) 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 analysis. 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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Key words: MWCNTs, NHC ligand, Mizoroki–Heck, heterogonous catalyst

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 have received considerable attention as one of the most important C-C bonds forming reaction [1]; therefore, a number of efficient catalytic systems have been developed for this transformations [2]. The standard Heck reaction contains palladium salt and phosphine ligands suffers from limitations that have so far precluded many industrial applications [3]. In addition to, 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 carbenes (NHCs) metal complexes have been developed by immobilizing them on solid supports [9-10].

Multi walled carbon nanotubes (MWCNTs) are one of the hottest nano materials in the 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 high surface area and their insolubility in the most solvents. In this regard, diamines are more favorite molecules, which could behave as a medium to attach miscellaneous compounds to MWCNTs. Actually, the diamines consist of two amino groups (–NH_2): 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 NHCs 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 have 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 did not report previously. In the field of C–C bond formation using cobalt catalysts, the reductive coupling reaction 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 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 in compared to palladium catalysts. In contrast, they exhibited lower activity in Mizoroki–Heck reaction in 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 accelerated the Heck reaction without using palladium and phosphine under mild conditions in present poly ethylene glycol as green solvent (Scheme 1c).

Scheme 1

2. Experimental

2.1. Catalyst preparation

The Co-NHC@MWCNTs catalyst was prepared using multistep synthesis process which demonstrated in Scheme 2. Detailed procedures are included in the supporting information.

Scheme 2

2.2. Characterization

The products of each step was characterized by FT-IR (Figure 1). The FT-IR spectrum of 4 is shown 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}) is exposed the chloride group bonds of 4 clearly.

Fig. 1

The nitrogen content of the support was 6.1 %. According to this value, the amount of NHCs ligand which is available in 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 was 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), the similar XRD pattern observation were reported before for Co (II) complex [34]. The thermal stability of compound 4 was also evaluated by the TGA, and the thermograms are given in Fig. S2. According to these curves, the weight loss below 300 ºC 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 analysis. The observed total weight losses for catalyst is 67 %, on the basis of this value, the amount of organic moieties was about 1.73 mmol/g of catalyst. A good agreement was observed between elemental analysis and TGA data for these conversions. The morphology of the surfaces of MWCNTs and catalyst were studied by field emission scanning electron microscopy (FE-SEM). As can be seen the nanotubes are aggregated and has retained their nanotube nature upon functionalization (Fig. S3). In Figure 2, the transmission electron microscopy (TEM) images of catalyst 4 clearly show the immobilization of cobalt complex on MWCNTs. Moreover, the large metal nanoparticles which appear in TEM images could be related to some aggregating [35].

Figure 2

3. Results and Discussion

To explore the activity of the nanocatalyst, we applied it in the Mizoroki–Heck cross-coupling reaction. A model reaction of iodobenzene with methyl acrylate was used to optimize the reaction conditions. The activity of the catalyst in different amounts, using various base, solvent and reaction temperature was studied (Table 1). According to the optimization results and the goals of green chemistry, all the reactions were carried out in poly ethylene glycol (PEG) at 80 ºC. Table 1

Encouraged by our initial studies; the generality and versatility of this catalyst have been examined. The results are shown in Table 2. Aryl halides with electron-donating groups, in comparison with aryl halides with electron-withdrawing groups, showed better conversions in shorter reaction times. Table 2

Interestingly; as shown in Table 2, the supported NHC-cobalt (II) nanocatalyst was compatible with a wide range of functional groups and exhibited good activity in the Mizoroki–Heck reaction using PEG as a solvent in mild conditions. Our catalyst was successfully reused at least six times without any significant losing of its activity (Table 3). The scale of the reaction was increased to 10.0 mmol, keeping the reaction stoichiometry intact. The reaction was found to proceed successfully, and the corresponding product was obtained in 78% yield via described method respectively. Table 3

The recovered catalyst was analyzed using TEM and FT-IR (Fig. S4, S5). According to these results no remarkable changes were observed in catalyst structure. To explore the leaching of the catalyst, the Heck coupling in model reaction was studied. After 30% of the coupling reaction had proceeded, the catalyst was separated with a centrifuge and ICP analysis of the remaining solution revealed that there was no cobalt in the reaction mixture. These results suggested that the cobalt was not being leached out from the solid surface of the catalyst during the coupling reaction and clearly demonstrated that this novel catalyst was heterogeneous in nature.

4. Conclusions

In summary, cobalt supported on direct functionalization MWCNTs as NHCs precursor was fabricated for the first time. The prepared Co-NHC@MWCNTs catalyst exhibited high catalytic activity for the Mizoroki–Heck reaction. The current strategy is a novel, environmentally friendly and economical way for the Heck reaction using significantly low cobalt loading. It could be recycled and reused six times without obvious cobalt leaching. Further applications of the catalytic system in other reactions are under investigation in our laboratory.

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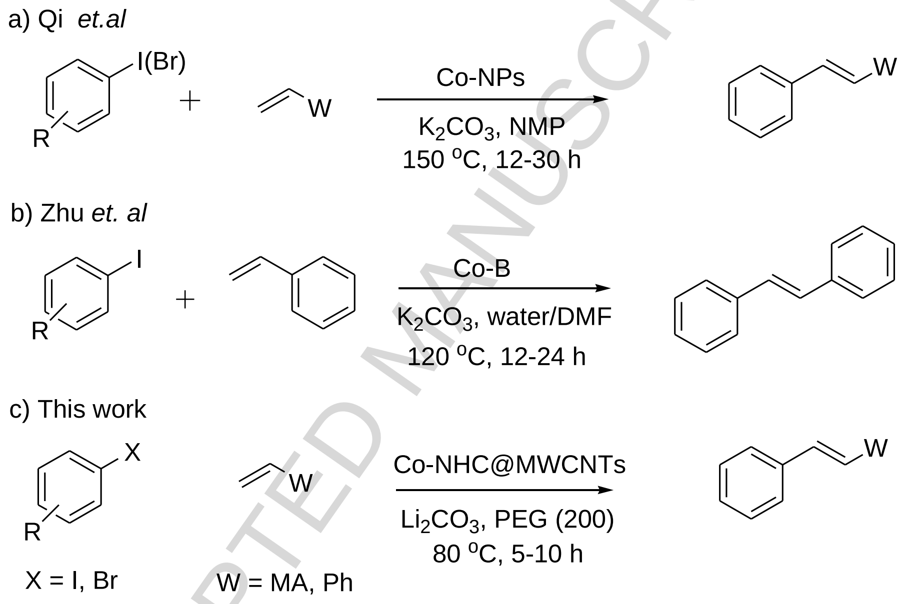
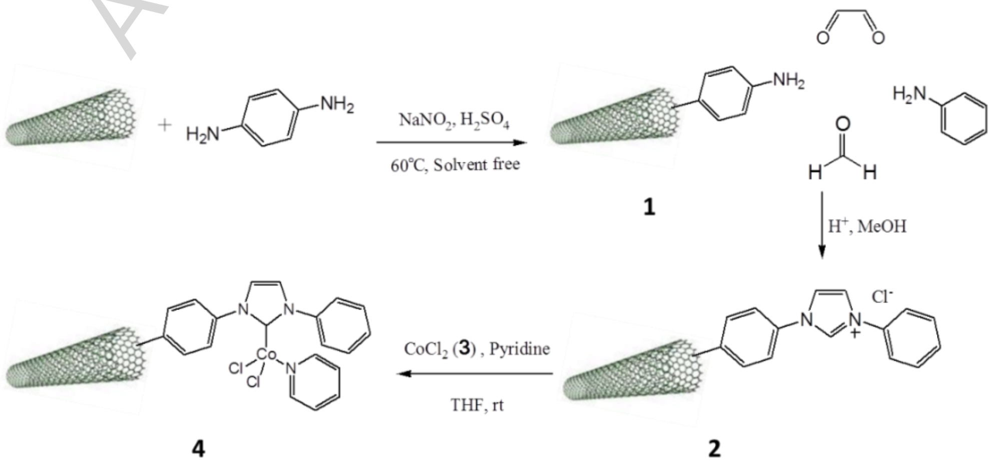
Legend for Scheme

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

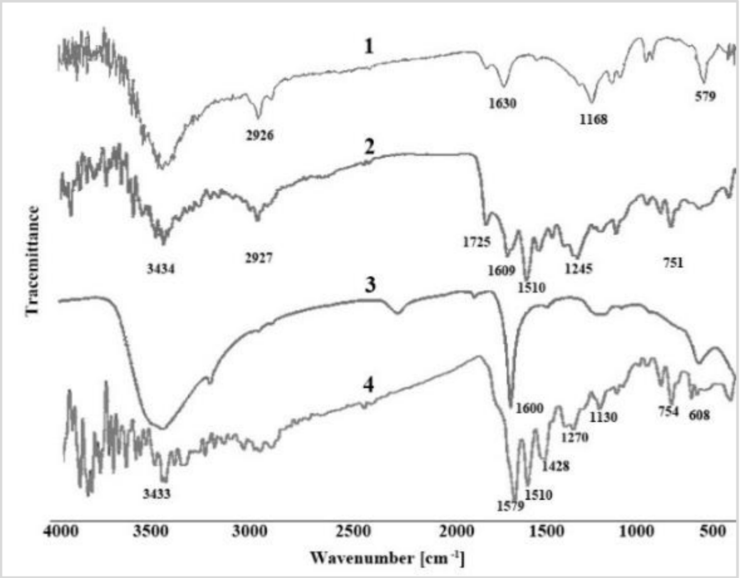


Scheme 2. The preparation of Co-NHC@ MWCNTs catalyst



Legend for Figure

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



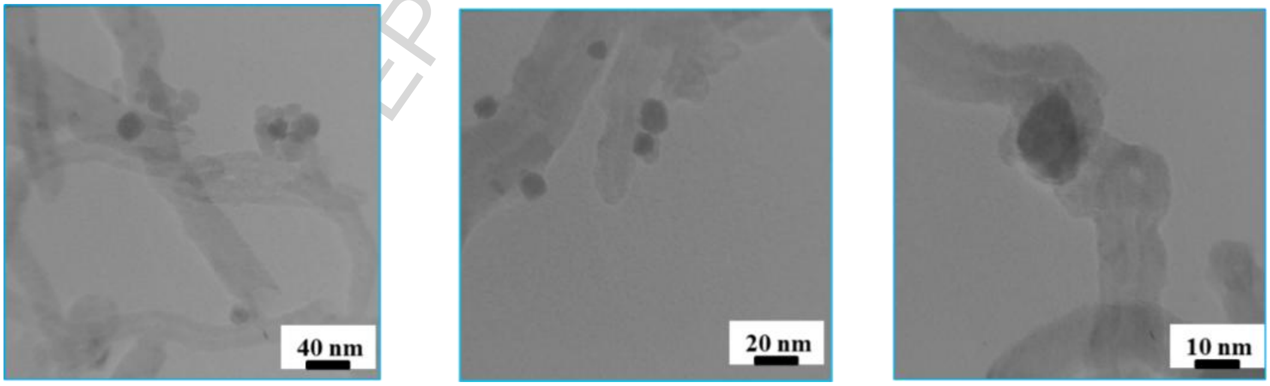
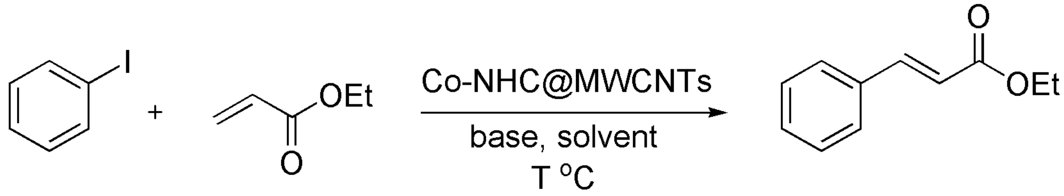


Fig. 2.TEM image of Co-NHC@MWCNTs

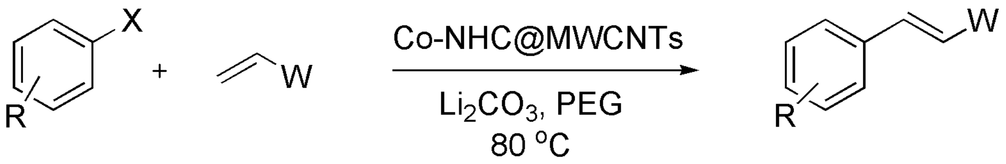
Table 1. Optimization of reaction conditions[a]



Entry	Solvent	Base (equiv.)	Cat (mg)	T (ºC)	Yield[b] (%)
1	PEG (200)	K_2CO_3 (2)	10	100	71
2	PEG (200)	KOH (2)	10	100	68
3	PEG (200)	LiOH (2)	10	100	73
4	PEG (200)	Li_2CO_3 (2)	10	100	78
5	PEG (200)	Li_2CO_3 (3)	10	100	82
6	PEG (200)	Li_2CO_3 (4)	10	100	86
7	PEG (200)	Li_2CO_3 (1.5)	10	100	76
8	DMSO	Li_2CO_3 (4)	10	100	74
9	NMP	Li_2CO_3 (4)	10	100	69
10	Toluene	Li_2CO_3 (4)	10	100	54
11	EtOH	Li_2CO_3 (4)	10	100	58
12	PEG (200)	Li_2CO_3 (4)	5	100	79
13	PEG (200)	Li_2CO_3 (4)	20	100	89
14	**PEG (200)**	**Li_2CO_3 (4)**	**10**	**80**	**85**
15	PEG (200)	Li_2CO_3(4)	10	60	61

[a]Reaction conditions: iodobenzene (1 mmol, 120 μL), MA (1.5 equiv., 136 μL), base, solvent (3 mL); [b]GC conversion.

Table 2. Heck reactions of aryl halides with olefin catalysed by 4



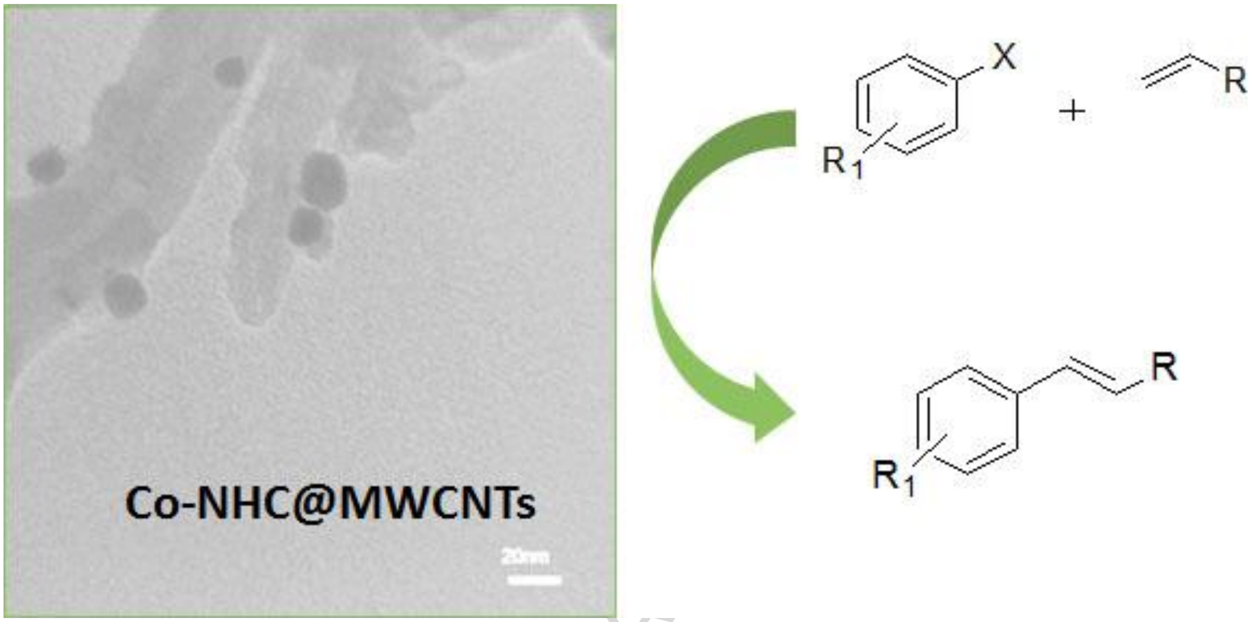
Entry	X	R	Olefin	Time (h)	Yield[b](%)
1	I	H	MA	5	85
2	I	4-OMe	MA	5	92
3	I	4-NO_2	MA	5	87
4	I	3-NO_2	MA	5	81
5	Br	H	MA	6	77
6	Br	4-NO_2	MA	6	74
7	Br	4-OMe	MA	6	80
8	Br	4-Cl	MA	6	76
9	Br	4-CN	MA	6	73
10	Br	4-$COCH_3$	MA	6	64
11	I	H	EA	5	82
12	I	4-NO_2	EA	5	77
13	I	3-NO_2	EA	5	79
14	I	4-OMe	EA	5	81
15	Br	H	EA	6	72
16	Br	4-NO_2	EA	6	65
17	Br	4-OMe	EA	6	63
18	Br	4-Cl	EA	6	58
19	Br	4-CN	EA	6	60
20	I	H	Styrene	8	78
21	I	4-OMe	Styrene	8	82
22	I	4-NO_2	Styrene	8	74
23	Br	H	Styrene	10	67
24	Br	4-NO_2	Styrene	10	61

[a] GC conversion**.**

Table 3. Reusability of the catalyst

Run	Yield [a] (%)	Run	Yield[a] (%)
1	85	4	81
2	85	5	80
3	83	6	80

[a]Isolated yield



Graphical abstract

Highlights

- The first time report of N-heterocyclic carbene–cobalt complex (NHC-Co2+) immobilized onto the surface of multi-walled carbon nanotubes (MWCNTs) via direct grafting amination approach.
- The introduced catalyst is air stable, highly active and reusable without toxic ligands.
- This paper presents a facility and high efficiency strategy for the Heck reaction using green solvents and mild conditions.