



Short communication

Nickel embedded on triazole-modified magnetic nanoparticles: A novel and sustainable heterogeneous catalyst for Hiyama reaction in fluoride-free condition

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ABSTRACT

An interesting MNPs -supported nano-nickel catalyst was successfully synthesized through “click” reaction of azide-functionalized magnetic nanoparticles with 2-ethynylpyridine followed by immobilization of nickel nanoparticles. In deed, the azide group was introduced into the magnetic nanoparticles surface *via* ring-opening of exist oxirane rings on the surface. The catalytic activity of this catalyst was then evaluated for Hiyama cross-coupling reaction under fluoride-free conditions. Besides, the as-prepared nanocatalyst can be reused easily by an external magnet for several times.

1. Introduction

Metal-mediated cross-coupling reactions have become routine method for the preparation of carbon-carbon bonds in synthetic organic chemistry [1]. Organomagnesium (Kumada-Corriu), organozinc (Negishi), organotin (Stille) and organoboron (Suzuki-Miyaura) derivatives are among the most common nucleophilic partners for these reactions [2–5], but each of these reagents has inherent limitations for the practical applications, such as low stability, high toxicity and poor biocompatibility of the reagent. Recently, silicon-derived compounds have emerged as attractive alternatives reagents for cross-coupling reactions (Hiyama coupling reaction) due to their low toxicity, low cost, broad availability, environmentally benign nature and high chemical stability [6]. While a number of strategies have been developed employing a range of palladium complexes, increasing demands for effective palladium-free systems are highly sought after, owing to the robust request of palladium and its limited resources. On the other hand, a recent surge of regard is growing up for using less expensive, easily available and non-precious transition-metal based catalysts [7]. Recently, nickel-based catalytic systems have been enthusiastically investigated as a viable alternative to palladium in this field [8,9]. Despite the upsurge of interest towards the development of Ni-based catalytic systems aimed at pragmatic cross-coupling reactions, a common feature involves the combination of homogeneous nickel-catalysts and various ligands in organic solvents [10–12]. However, the greatest obstacle to the wider use of homogeneous active metal salts is

the difficulty in separation and recovery of these catalysts. Recently, heterogenization of the existing homogeneous complexes has received tremendous attention as an ideal alternative in organic synthesis [13,14]. Among the numerous of insoluble supports explored so far, functionalized magnetic nanoparticles have attracted immense interest as practical alternatives to conventional solid matrices to use as high surface area supports, stable, cheap, readily available with an inherent low toxicity in catalytic transformations. Most importantly, these materials can be conveniently separated from the reaction system using an external magnetic field without filtration techniques [15]. Consequently, by the functionalisation of magnetic nanoparticles with a range of different organic groups and metal nanoparticles it is possible to design of highly active for an efficient heterogeneous catalyst [16]. In the past few years, the copper-catalyzed azide-alkyne cycloaddition (CuAAC), known as the “click reaction”, have in particular opened up new horizons in the field of catalytic research owing to its high quantitative yield, simple procedure, mild experimental conditions with no side products [17]. Thus, the “click” strategy has emerged as an ingenious approach for the efficient introduction of new chemically modification onto magnetic nanocomposites backbone [18]. Recently, Khalafi-Nezhad et al. reported a new synthetic pathway for the synthesis of new materials based on silica and MNPs using opening of oxirane groups with different nucleophiles for the preparation of catalytic sites on the surface [19–21]. In this study, in continuation of our previous endeavors towards the extension of new efficient synthetic pathways to provide heterogeneous catalysts [22–31], we would like to introduce a

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new synthetic pathway to graft azide group through the ring opening of oxiran groups on the MNPs surface and its further functionalization using click reaction for the preparation of Ni nanoparticles. The obtained catalyst was evaluated as an efficient and recyclable nanocatalyst in Hiyama cross-coupling reaction. To the best of our knowledge, it is the first report of applying Ni-based heterogeneous catalyst for performing of Hiyama cross-coupling reaction between a variety of aryl halides and heteroaryls with triethoxyphenylsilane under fluoride-free conditions.

2. Results and discussion

2.1. Preparation and characterization of the catalyst

The first step towards the preparation of this catalytic system is the synthesis of magnetic nanoparticles by codeposition method according to the reported procedure in the literature [32]. Silica encapsulation of MNPs ($\text{Fe}_3\text{O}_4@ \text{SiO}_2$) was prepared using a known procedure [33], which is subsequently treated with trimethoxy (vinyl) silane to introduce a vinyl group on the surface of magnetic nanoparticles (VMNP). Thereafter, vinyl group was oxidized using H_2O_2 to produce the MNP-oxiran (MNPO) substrate. Ring-opening of the oxirane rings with N_3 group was resulted the introduction of azide moiety on the surface, which was later reacted with 2-ethynylpyridine *via* click reaction. Ultimately, the immobilization of nickel nanoparticle was carried out by the reduction of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in the presence of hydrazine hydrate as reducing agent to produce the final catalyst (Scheme 1).

The progress of the chemically modification of MNPs was confirmed by FT-IR Spectroscopy (Fig. 1). FT-IR spectra of the $\text{Fe}_3\text{O}_4 @ \text{SiO}_2$ particles display the characteristic vibration for Fe–O–Fe, Si–O–Si and O–H groups. As shown in Fig. 1c, the peak positioned at 1558 cm^{-1} is attributed to the stretching of C=C, which revealed the successful immobilization of vinyl groups on the surface. In Fig. 1d, the bands appear at 3054 cm^{-1} and 1250 cm^{-1} are attributed to the characteristic absorptions of the oxirane ring, which could be assigned to C–H and C–O–C bond. Also the presence of azide group on the surface was confirmed by the appearance of the N_3 absorption band at 2104 cm^{-1} in Fig. 1e, which completely was disappeared during the click reaction between 2-ethynylpyridine and N_3 -MNPs. (See Fig. 2.)

The existence of elements of C, N, O, Si and Ni in the catalyst was also confirmed by EDX analysis (Fig. S1). Also, the quantitative amount of azide group on the MNPs substrate was identified to be 0.37 mmol g^{-1} using elemental analysis. Meanwhile, the quantitative determination of the nickel content was ascertained by ICP analysis and was identified to be 1.43% for this catalyst. According to XRD patterns of the catalyst, the observed diffractions at $2\theta = 30.1^\circ$ (220), 35.5° (311), 43.1° (400), 47.2° (331), 53.5° (422), 57.0° (511), 62.6° (440),

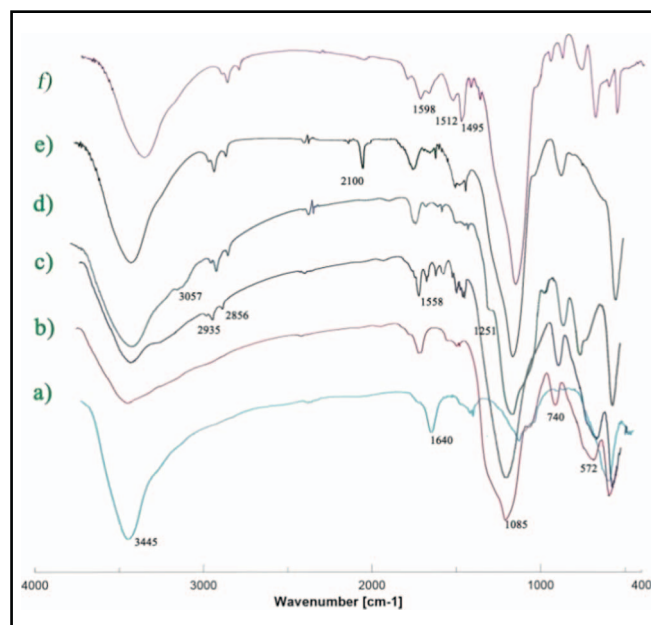


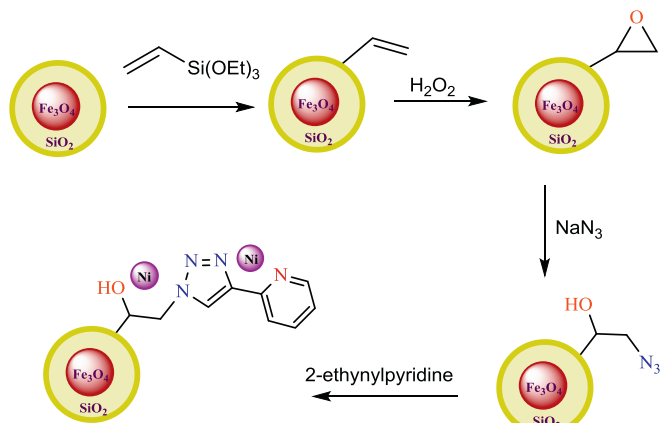
Fig. 1. FT-IR spectra of Fe_3O_4 (a), $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ (b), VMNPs (c), MNPO (d), N_3 -MNPs (e), triazole modified MNPs (f).

75.1° (622), 82.0° (551), 86.8° (642) and 89.8° (731), correspond to the cubic spinel phase of Fe_3O_4 {JCPDS 01-075-0033}. The strongest peak at $2\theta = 23^\circ$ attributed to SiO_2 and other characteristic diffraction peaks 2θ of 44.5° , 51.8° and 76.7° are indexed as the (111), (200) and (220) crystal planes of Ni (0) (JCPDS, no. 03–1051) (Fig. S2). The nano feature, shape and morphology of the synthesized catalyst were studied by transmission electron microscopy (TEM) micrographs and Scanning electron microscopy (FE-SEM). Considering the TEM and SEM images, the nanoparticles were observed in spherical shape with nearly good arranged mode. TEM images also established the core-shell structure of nanoparticles. According to the DLS analysis, the average size of nanoparticles is estimated around 14 nm, which are appropriate for catalytic purposes.

Magnetic measurements of catalyst were measured using a vibrating sample magnetometry (VSM). As shown in Fig. S5, the saturation magnetization of the obtained catalyst is saturated up to 42 emu g^{-1} . The magnetization value for Fe_3O_4 is 63.5 emu g^{-1} [34]. This drop in magnetic strength can be attributed to the surface coating on magnetic particles.

2.2. Catalytic performances

The catalytic activity of the prepared catalyst was then evaluated for the Hiyama cross-coupling reaction. As a model reaction, we initially examined the coupling reaction of 4-iodoanisole with triethoxyphenylsilane in the presence of tetrabutylammonium fluoride (TBAF) as an activator of the organosilane in DMF with 0.2 mol% of catalyst at 90°C , which delivered the corresponding product in 77% yield within 7 h (Table 1, entry 1). In order to reach the highest catalytic activity, the reaction conditions were studied by means of changing solvent, additive, reaction temperature and catalyst loading. On the basis of the preliminary result, we therefore turned our attention to the scrutiny of other fluoride source such as KF, NaF, CsF and also KOH and other inorganic bases as additives. It was found that the reaction never proceeded with the use of metal fluorides, while replacement of TBAF as an additive by KOH improved the reaction efficiency. The next set of experiments was focused on the effect of solvent on the model reaction. Among the tested solvents, a mixture of $\text{H}_2\text{O}/\text{EtOH}$ (1:1, V/V) was found to be the best solvent. The temperature as another factor was also



Scheme 1. The nanocatalyst preparation.

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