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### 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.

Keywords: Click reaction, Nickel nanoparticle, Heterogenous catalyst, Hiyama cross-couplig

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#### Introduction

Metal-mediated cross-coupling reactions have become routine method for the preparation of carboncarbon bonds in synthetic organic chemistry.<sup>1</sup> Organomagnesium (Kumada-Corriu), organozinc (Negishi), organotin (Stille) and organoboron (Suzuki-Miyaura) derivatives are among the most common nucleophilic partners for these reactions.<sup>2-5</sup> 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.<sup>6</sup> 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 nonprecious transition-metal based catalysts.<sup>7</sup> Recently, nickel-based catalytic systems have been enthusiastically investigated as a viable alternative to palladium in this field.<sup>89</sup> 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.<sup>10-12</sup> 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.<sup>13,14</sup>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.<sup>15</sup> 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.<sup>16</sup> 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.<sup>17</sup> Thus, the "click" strategy has emerged as an ingenious approach for the efficient introduction of new chemically modification onto magnetic nanocomposites backbone.<sup>18</sup> Recently, Khalafi-Nezhad *et al.* reported a new synthetic pathway for the synthesis of new materials based on silica and MNPs using opening of oxiran groups with different nucleophiles for the preparation of catalytic sites on the surface.<sup>19-21</sup> In this study, in continuation of our previous endeavors toward the extension of new efficient synthetic pathways to provide heterogeneous catalysts,<sup>22-31</sup> we would like to introduce a 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.<sup>32</sup> Silica encapsulation of MNPs (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>) was prepared using a known procedure,<sup>33</sup> 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<sub>2</sub>O<sub>2</sub> to produce the MNP-oxiran (MNPO) substrate. Ring-opening of the oxirane rings with N<sub>3</sub> 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  $NiCl_2.6H_2O$  in the presence of hydrazine hydrate as reducing agent to produce the final catalyst (scheme 1).

### Scheme 1

The progress of the chemically modification of MNPs was confirmed by FT-IR Spectroscopy (Fig. 1). FT-IR spectra of the Fe<sub>3</sub>O<sub>4</sub> @ SiO<sub>2</sub> 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<sup>-1</sup> 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<sup>-1</sup> and 1250 cm<sup>-1</sup> 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<sub>3</sub> absorption band at 2104 cm<sup>-1</sup> in Fig. 1e, which completely was disappeared during the click reaction between 2-ethynylpyridine and N<sub>3</sub>-MNPs.

## Fig.1

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-<sup>1</sup> 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 20 =  $30.1^{\circ}$  (220),  $35.5^{\circ}$  (311),  $43.1^{\circ}$  (400),  $47.2^{\circ}$  (331),  $53.5^{\circ}$  (422),  $57.0^{\circ}$  (511),  $62.6^{\circ}$  (440),  $75.1^{\circ}$  (622),  $82.0^{\circ}$  (551),  $86.8^{\circ}$  (642) and  $89.8^{\circ}$  (731), correspond to the cubic spinel phase of Fe<sub>3</sub>O<sub>4</sub> {JCPDS 01-075-0033}. The strongest peak at  $20 = 23^{\circ}$  attributed to SiO<sub>2</sub> and other characteristic diffraction peaks 20 of  $44.5^{\circ}$ ,  $51.8^{\circ}$  and  $76.7^{\circ}$  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.

#### Fig.4

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<sup>-1</sup>. The magnetization value for  $Fe_3O_4$  is 63.5 emu g<sup>-1</sup>.<sup>34</sup> 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  $H_2O/EtOH$  (1:1, V/V) was found to be the best solvent. The temperature as another factor was also studied and it seems that 70 °C is suitable for this cross-coupling reaction. Finally, we explored the effect of catalyst loading on the conversion by employing different amounts of catalyst. Accordingly, the best result was achieved using 0.2 mol% of catalyst. To investigate the scope of this method, various aryl halides with triethoxyphenylsilane were subjected to the protocol under optimal reaction conditions (Table 2). In general, the reactions are performed well with various aryl halides carrying either electron-withdrawing or

electron-releasing substituents and also ortho-substituted aryl halides and heteroaryl bromides. Aryl iodides and aryl bromides were rapidly converted into the desired products in high yields. Also, the generality of this method for the coupling reaction of some aryl chlorides (for more available and cheaper than aryl iodides and bromides) with triethoxyphenylsilane was also scrutinized. Compared with aryl bromides, the less active aryl chlorides give lower conversion and needed little more reaction times to obtain relatively good yields. Various electron-donating and electron-withdrawing groups on aryl halides are converted to the corresponding product with high conversions. As expected, 2-bromoacetophenone is found to be less reactive and only 54% conversion is obtained, probably due to an increase in steric hindrance of ortho substituents. Also, heteroaryl bromides underwent successful couplings to give the desired products in good conversion. This result suggests that our present catalytic system is equally efficient for catalyzing both aryl halides as well as heteroaryl halides.

#### Table 1

#### Reusability and heterogeneity test

The recycling of the catalyst is highly preferable theme, especially for its industrial applications. In order to investigate this property, the reusability of this system was examined by using 4iodoanisole and triethoxyphenylsilane under optimal reaction conditions. For this, when the reaction was complete, the catalyst material was separated using a magnetic bar, washed and save for the subsequent runs. The recycling experiment revealed that the catalyst was effectively used in six subsequent reactions (Fig. S6). Indeed, the isolated yield of the product for six run was 86 %, which clearly disclose the high catalytic activity of this system. This result was further supported by TEM, SEM, XRD and ICP analysis of the recovered catalyst. Comparison of TEM and SEM images of used catalyst with fresh catalyst showed that the morphology and size of the catalyst does not change considerably after eight times of recycling (Fig. S7). The XRD pattern of

the recovered catalyst was also investigated. As shown in Fig. S8. the pattern of the recovered catalyst is nearly the same as that of the fresh catalyst. No obvious drop in the intensity was detected, and the characteristic peaks attributed to  $Fe_3O_4$  and Ni (0) still present in pattern of the recovered catalyst. So, these observations approved that the structure of the this magnetic catalyst as well as metallic state of nickel nanoparticles were kept after the catalytic reaction during the reaction process, giving further explanation for its stable catalyst using ICP after six times of reuse and the observation revealed that only 0.091 ppm of Ni was removed from the catalyst. To probe the nature of the active species, i.e., surface or leached Ni, a hot-filtration test was also accomplished by coupling of 4-iodoanisole and triethoxyphenylsilane and the result of ICP analysis revealed that the leaching of Ni species from the solid surface into the solution was lower than 0.053 ppm, which indicate the heterogeneous manner of the prepared catalyst.

#### Table 2

#### 3. Conclusions

In summary, we have established an efficient strategy to modification of MNPs surface with azide group *via* the ring opening of oxiran groups and its further functionalization using click reaction for the immobilization of Ni nanoparticles. The newly designed material was used as an economical and practical heterogeneous organocatalyst for the Hiyama cross-coupling reaction under fluoride-free conditions. Furthermore, the high catalytic activity, ease of recovery, reusability and the use of an inexpensive nickel metal makes the reported protocol valuable from industrial and environmental viewpoint. Moreover this is the first report based on the design of Ni-containing magnetically separable organocatalyst for performing Hiyama cross-coupling reaction between a variety of aryl halides and triethoxyphenylsilane.

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Scheme



Fig.1 FT-IR spectra of Fe<sub>3</sub>O<sub>4</sub> (a), Fe<sub>3</sub>O<sub>4</sub>@ SiO<sub>2</sub> (b), VMNPs (c), MNPO (d), N<sub>3</sub>- MNPs (e), triazole modified MNPs (f)



Fig.4 TEM and SEM images of catalyst

A CERTINAN

1		Additive	T(°C)	Yield
1	DMF	TBAF	90	77
2	DMF	KF	90	-/
3	DMF	CsF	90	Ó
4	DMF	NaOH	90	57
5	DMF	КОН	90	84
6	CH <sub>3</sub> CN	КОН	80	71
7	EtOH	КОН	78	86
8	H <sub>2</sub> O: EtOH	КОН	70	96
9	H <sub>2</sub> O: EtOH	КОН	60	82
10 <sup>c</sup>	H <sub>2</sub> O: EtOH	КОН	70	84
<sup>a</sup> Reaction triethoxyp of catalys yield. <sup>c</sup> Tl	h conditions: 4-io ohenylsilane (1.2 at (0.2 mol%), tim he amount of cata	doanisole (1.0 mmol), additiv e (7 h) and solv alyst reduced to	mmol), e (2.0 mmo vent (5.0 ml) 0.1 mol%.	l), amou ). <sup>b</sup> GC

 Table 2 Hiyama cross-coupling reaction of various aryl

Entry	(Hetero) Ar	X	Time (h)	<b>Yield</b> $(\%)^{b}$
1	Н	Ι	6	97
2	Н	Cl	12	84
3	Н	Br	7	88
4	4-CH <sub>3</sub>	Cl	15	76
5	4-CH <sub>3</sub>	Ι	7	93
6	4-CH <sub>3</sub>	Br	10	84
7	4-CH <sub>3</sub> O	Br	9	87
8	4-CH <sub>3</sub> O	Ι	7	96
9	4-CH <sub>3</sub> O	Cl	15	78
10	2-COCH <sub>3</sub>	Br	12	54
11	4-COCH <sub>3</sub>	Br	7	85
12	3-NO <sub>2</sub>	Br	7	88
13	4-NO <sub>2</sub>	Cl	10	87
14	4-NO <sub>2</sub>	Br	6	92
<mark>15</mark>	Thiophene	2-Br	11	82
<mark>16</mark>	Pyridine	3-Br	8.5	86
<mark>17</mark>	Pyridine	2-Br	10	83

triethoxyphenylsilane (1.2 mmol), additive (2 mmol), solvent (4 ml), catalyst (0.2 mol%), 70 °C

## Highlights

- MNPs supported Ni catalyst
- Efficient catalyst for Hiyama reaction
- Several times recoverable magnetically catalyst

Scherch MMM