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Chitosan-Supported Ni particles: An Efficient Nanocatalyst for Direct Amination of Phenols

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1 | INTRODUCTION

The synthesis of aryl amines as an important class of building blocks widely applied in the synthesis of natural products, pharmaceuticals, agrochemicals and polymers, has attracted much attention in organic synthesis.^[1] Therefore, the discovery of efficient and practical methods for the assembly of aromatic C-N bonds is a matter of particular interest to synthetic chemists. Among many synthetic methods available for C-N bond formation, transition metal-catalyzed reactions, led by Buchwald and Hartwig amination of aryl halides^[2] and triflates,^[3] are recognized as one of the most practical used methods in chemical synthesis. Recent progress has been made toward the catalytic amination of inactive phenolic derivatives,^[4-7] which are less expensive and readily available, in the presence of inexpensive metal catalysts.^[8] What is notable herein is that, for the above method, phenolic compound as an electrophile require pre-installation of reactive functional groups (e.g., esters,^[9] carbamates,^[10] carbonates,^[11] phosphates,^[12] triflates and sulfonates^[13]) to participate in cross-coupling reactions. Indeed, this preactivation step limits wider applicability of these protocols in terms of overall yields and step economy. Undoubtedly, the direct N-arylation of phenols would be

A practical method for the direct amination of phenols using 2,4,6-trichloro-1,3,5-triazine (TCT) as an efficient promotor for the activation of phenols in the presence of an efficient and recyclable heterogeneous catalyst prepared by immobilization of nickel particles on triazole modified chitosan is described. This heterogeneous catalyst has demonstrated a promising activity for the conversion of phenolic compounds to their corresponding amine under mild conditions. Moreover, the obtained catalyst can be reused in five consecutive runs with consistent catalytic activity.

KEYWORDS

click reaction, direct amination, heterogenous catalyst, nickel nanoparticle

the best strategie to resolve such a problem and develop the diversity of functional molecules and could thus be used to create new materials. As a result, recent attention has been focused on the in situ activation of phenols as a new pathway for creation of an active partner in cross-coupling reactions.^[14] On the other hand, 2,4,6-Trichloro-1,3,5-triazine (TCT) as an efficient and mild promotor for the activation of phenols has received great attention due to its commercial availability, low cost and synthetic usage in organic transformations.^[15] In fact, this reagent can active hydroxyl group via conversion to a better leaving group (Scheme 1). Along this line, the choice of nickel complexes as a viable alternative to Pd catalyzed amination reactions has been attracting considerable interest in the recent years, due to their low cost and readily availability.^[16] However, such amination reactions applying homogeneous Ni catalytic system always suffered from separation and organic wastes which are very difficult to reuse. Moreover deactivation of soluble nickel complex catalysts is often encountered at elevated reaction temperatures and extended reaction times. These problems associated with homogenous catalyst could be principally minimized by immobilization of the catalyst in various solid-supported.^[17]Amongst the different insoluble supports, natural materials, especially bio-based



SCHEME 1 The nanocatalyst preparation

polymers, have recently engrossed immense attention as an applicable and interesting alternatives to conventional solid catalysts. As one kind of the extensively used biopolymers, chitosan is renewable, biodegradable, cheap and non-toxic polysaccharide. Furthermore, the insolubility of chitosan in common solvents explains the potential of chitosan as suitable supports for various reagents and catalysts.^[18-20] Recently, Iranpoor et al. reported amination of phenols using (TCT) as an efficient promotor under homogeneous catalytic system applying various Ni sources and ligands.^[21] We recently reported an interesting chitosan based nickel nanocatalyst which were synthesized via 'click' reaction of an alkynlated imino- thiophene ligand with azide functionalized chitosan for application in Suzuki reaction. As a part of our ongoing research work on the application of heterogeneous catalytic systems in organic synthesis,^[22k] and in order to determine the efficiency of the previously synthesized catalytic system in various organic reactions.^[23] we would like to evaluate performance of this solid catalyst for the direct nickel-catalyzed amination of phenols.

2 | RESULTS AND DISCUSSION

2.1 | Preparation and characterization of the catalyst

Triazole functionalized chitosan, were prepared in several steps from the azidated chitosan and an alkynlated ligand. These starting materials were synthetized as follows (Scheme 1): an alkynlated imino- thiophene ligand was prepared by reaction of the imino- thiophene ligand with propargyl bromide. The azide group was introduced into chitosan according to the reported procedure.^[24] Then azidated chitosan underwent a click process with alkynlated ligand in the presence of active copper (I) to give the chitosan-triazole support. Afterwards, the immobilization of Ni nanoparticles was carried out by the reduction of NiCl₂.6H₂O in the presence of hydrazine hydrate as reducing agent to afford the desired solid catalyst.

The modifications of the chitosan we followed by IR spectroscopy (Figure 1). As shown in Figure 1c, the



FIGURE 1 FT-IR spectra of alkynlated imino- thiophene ligand (a), pure chitosan (b), azidated chitosan (c), triazolemodified chitosan (d), triazole- modified chitosan-Ni (e)

absorption bond at 2100 cm^{-1} corresponds to N_3 stretching, which reveals that the azide moiety have been successfully immobilized on the surface of chitosan. As

TABLE 1Elemental analysis (EA) and inductively coupledplasma analysis (ICP) results

Sample	C% ^a	H% ^a	$N\%^a$	S% ^a	Ni% ^b
Pure chitosan	44/73	6/14	8/67		-
Azidated chitosan	42/19	5/62	10/29		-
Triazole-modified chitosan	47/21	5/13	10/32	1/14	-
Nickel content (final catalyst)					1/37

 $^{\rm a} Elemental analysis (EA) (wt%).$ $^ binductively coupled plasma analysis (ICP) (wt%).$ -WILEY-Organometallic 3 of 10 Chemistry

can be seen in Figure 1d, the band attributed to the azide groups completely was disappeared after the click reaction between alkynlated ligand and all azide groups. In addition, two new bands emerged, one of low intensity at 1613 cm⁻¹ and other of higher intensity at 1490 cm⁻¹ that were assigned to (C=N vibration) and (C=C vibration of the aryl ring) respectively. In Figure 1e, the imine group shifts to lower frequency and appears at 1578 cm⁻¹ due to the coordination of the nitrogen with the nickel.

The catalytic system was also characterized using techniques including elemental analysis (EA), inductively coupled plasma analysis (ICP), EDX, SEM, TEM, ICP and XRD analysis. The ICP analysis showed that 1.37% of Ni



FIGURE 2 TEM images of nanocatalyst (a and b), SEM photographs of catalyst (c) The particle size distribution of nanoparticles (d)

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was anchored on the catalyst. The amount of organic moieties on the chitosan surface was determined by elemental analysis, which was 0.3 mmol/g (Table 1). The particle size, shape and surface morphologies of the synthesized nanomaterial were directly visualized by Scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM) imaging techniques. As can be seen in Figure 2 (a and b), TEM image confirms that chitosan surface is decorated successfully with many welldispersed nickel nanopartices. According to DLS measurement, the average diameter of the spherical particles was about 10 nm.

The energy dispersive X-ray (EDX) spectrum in Figure 3 confirms the presence of C, N, O, S and Ni species in the structure of catalyst. X-ray powder diffraction (XRD) pattern of catalyst is shown in Figure 4. The strongest peak at $2\theta = 20^{\circ}$ is attributed to the plane of the chitosan structure and other diffraction peaks at 2θ of 44.5°, 51.8° and 76.7° representing (111), (200) and (220) was attributed to crystal planes of Ni (0), which matched well with those found in the JCPDS database (PDF No. 03–1051).^[25]

2.2 | Catalytic performances

In an initial study to obtain the proper conditions for the cross-coupling step, we surveyed the reaction of TCT under different conditions to achieve a high yield of 2,4,6-triaryloxy-1,3,5-triazine (5),^[26] because this step has a significant role on the progress of the reaction and total yield. Initially, in order to optimize conditions for this step, we selected the reaction of TCT and para-cresol as the model reaction under various circumstances such as kind of base and solvent, temperature and the effect of the molar ratio of phenol to TCT. The results are



FIGURE 3 EDX spectrum of catalyst



FIGURE 4 XRD pattern of catalyst

summarized in Table 2. Among a variety of solvents that showed satisfactory conversions (e.g., Toluene, THF and Dioxane, we chose to proceed with Toluene. In terms of base, NaH afforded the desired product with the highest yield. Other bases such as K₃PO₄, K₂CO₃ and NaHCO₃ resulted in poorer yields. It was found that increasing the temperature from 80 to 100 °C improved significantly reaction results. As shown in Table 2, the best result was obtained when the molar ratio was 3.2, while higher than this value of substrate ratios did not provide any improved percentage yields. Under these optimized conditions, we tried to apply the in situ generated aryl C-O electrophile in the cross-coupling with amines for the preparation of arylamines. Then, we explored appropriate conditions for this cross-coupling reaction using the reaction of paracresol and morpholine as model reaction. As shown in Table 3, K_2CO_3 was the most effective base. On the basis of this study, the quantitative conversion can be obtained with increasing the amount of the catalyst to 0.3 mol%. Further scrutiny of the reaction time, amount of base, temperature and amount of used morpholine showed that entry 8 has the most effective optimum conditions. To explore the scope of the protocol in the synthesis of diverse arylamines, the present study is extended to different aryl amines and phenols under the optimized conditions (Table 4). Aromatic amines including aniline, n-methylaniline and diphenylamine carrying either electron-withdrawing or electron-releasing substituents underwent coupling with phenols and desired product were synthesized in moderate to good yields. In general, both electron-donating and electron-withdrawing phenols were suitable substrates in this protocol. The feasibility of coupling o-substituted substrate was also examined using 2- methyl phenol. Of note, an increasing steric hindrance of ortho- substituted phenols can cause a decrease in the reaction yield.

TABLE 2 Optimization of reaction conditions for synthesis of 2,4,6-triaryloxy-1,3,5-triazine^a



^aReaction conditions: para-cresol (1 mmol), TCT (0.34 mmol), base (2 mmol), solvent (5 ml). ^bThe ratio of para-cresol to TCT. ^cIsolated yield. ^d2.5 mmol of base was used. ^e1.5 mmol of base was used.

2.3 | Reusability and heterogeneity test

Reusability is one of the important purposes for designing heterogeneous catalysts, which can give effective evidence about the catalytic stability along successive cycles. Thus, the potential reuse of catalyst was examined by the model reaction under optimized conditions. For this purpose, at the end of the reaction as monitored by TLC analysis, the catalyst was isolated as black powders by centrifugation, washed with water and ethanol, and dried at room temperature. The isolated catalyst was redispersed to the reaction mixture under the same conditions and reused for subsequent runs. It is notable that catalyst retains 74% of its initial activity even at the fifth run of the synthesis of desired product (Figure 5). To determine if the metal is leached out into the solution during the degradation reaction, the catalyst was collected from the solution after 13 h. The residual solution was then allowed to react, but no further progress in the conversion percentage of the reactants was observed after 24 h. Additionally, the ICP result of the solution only showed 0.061 ppm of the Ni species is leach out from the supported heterogeneous catalyst during the course

of the reaction, which indicating the truly heterogeneous nature of the nanocatalyst.

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2.4 | Plausible mechanism

The reaction mechanism for this reaction is suggested based on reported procedure.^[21] In all likelihood, the nickel metal can coordinate with ortho nitrogen atom of 2,4,6-triaryloxy-1,3,5-triazine and this conveniences the oxidative addition in which Ni inserts into the C-O bond to produce Ni (II) intermediate. In step 2, such an intermediate could react with amine in the presence of K_2CO_3 as a base to render intermediates B. Finally, the Ni (0) catalyst is regenerated by the reductive elimination of the Ni (II) compound and the expected products are formed (Scheme 2).

3 | EXPERIMENTAL

All chemical reagents were purchased from Merck Chemical Company and used without further purification. ¹H-NMR spectra were recorded on a Bruker 400 spectrometer

TABLE 3 Optimization of the coupling reaction conditions^a

	Me OH	1. TCT(0.31 mmol), NaH (2 mmol) Toluene, 90 °C, 10 h 2. catalyst, morpholine, base,Toluene, 90 °C, 8 h	Me N	
Entry	base	Catalyst (mol%)	Time (h)	Yield (%) ^b
1	K ₂ CO ₃	0.2	8	80
2	K ₃ PO ₄	0.2	8	72
3	NaHCO ₃	0.2	8	68
4	KO-t-Bu	0.2	8	67
5	КОН	0.2	8	75
6	NEt ₃	0.2	8	50
7	K ₂ CO ₃	0.1	8	64
8	K ₂ CO ₃	0.3	8	85
9	K ₂ CO ₃	0.4	8	78
10	K ₂ CO ₃	0.3	8	84 ^c
11	K ₂ CO ₃	0.3	8	85 ^d
12	K ₂ CO ₃	0.3	8	68 ^e
13	K ₂ CO ₃	0.3	8	86 ^f
14	K ₂ CO ₃	0.3	8	88 ^g

^aReaction conditions: para-cresol (1 mmol), morpholine. (1.5 mmol), base (2 mmol), and solvent (5 ml). ^bIsolated yield. ^c1.5 mmol of base were used. ^d2.0 mmol of morpholine were used. ^eAt 70 °C. ^fAt 100 °C. ^gReaction time was 24 h.

using deutrated CDCl₃ as solvent and tetramethylsilane (TMS) as internal standard. X-ray diffraction (XRD) powder patterns were obtained using an X'PERT MPD, with Cu K α radiation (40 kV, 30 mA). Transmission electron microscopy (TEM) images were obtained using a Philips CM10 microscope. FT-IR spectroscopy (JASCO FT-IR 680-Plus spectrophotometer) was employed for characterization of products. Also we used Inductive coupled plasma Perkin Elmer Optima 7300 DV, gas chromatography (GC) (BEIFIN 3420 gas chromatograph equipped with a Varian CP SIL 5CB column: 30 m, 0.32 mm, 0.25 mm), field emission scanning electron microscopy [FE-SEM, HITACHI (S-4160)], for consideration of reactions conversions. The acknowledgements come at the end of an article after the conclusions and before the notes and references.

3.1 | Synthesis of imino-thiophene ligand (1)

In a 100 ml flask equipped with mechanical stirring and condenser, 10 mmol of Thiophene-2-carbaldehyde and 25 ml of methanol were added. To this suspension was added 10 mmol p-aminophenol and solution was refluxed for 3 h. The solid was filtered and washed with mthanol and acetone and the pure product 1 was obtained. The product was characterized by ¹H NMR spectra

(Supplemental Data). Yellow crystals; ¹H NMR (400 MHz, DMSO-d6): 9.53 (s, 1H), 8.76 (s, 1H), 7.74 (d, J = 6.8 Hz 1H), 7.60 (d, J = 4 Hz, 1H), 7.17–7.21 (m, 3H), 6.79 (d, J = 11.6 Hz, 2H).

3.2 | Synthesis of propargyl iminothiophene (2)

A 50 ml flask was charged with 5 mmol of compound 1, 10 mmol K_2CO_3 and 10 ml of acetone. Then 5.2 mmol of propargyl bromide was added dropwise to this suspension. The resulting mixture was stirred at 50 °C for 24 h under a nitrogen atmosphere. After this time the solvent was removed and the crude was recrystallized from ethanol to give a brown crystalline solid. The product was characterized by ¹H NMR spectra (Supplemental Data). ¹H NMR (400 MHz, CDCl3): 8.55 (s, 1H), 7.46 (d, J = 6.8 Hz, 1H), 7.43 (d, J = 4.4 Hz, 1H), 7.2 (d, J = 8 Hz, 2H), 7.09–7.12 (m, 1H), 6.97 (d, J = 8 Hz, 2H), 4.68 (s, 2H), 3.56 (s, 1H)

3.3 | Synthesis of precursors for azidation

Trifluoromethane sulfonyl (triflyl) azide (TFA) solution was obtained according to a reported procedure.^[27]

TABLE 4 Amination of various amines with phenols

	Ĺ	1. TCT(0.31 mmol), NaH (2 mmol) Toluene, 90 °C, 10 h		
	R 1 n	2. catalyst (0.3 mol%), nmol amine (1.5 mmol), base (2 mmol), Toluene, 90 °C, 8 h	R	
Entry	Phenols	Amines	Product ^a	Yield (%) ^a
1	Me		Me	85
2	ОН			93
3	O ₂ N-OH		O ₂ N N O	98
4	ОН			92
5	O ₂ N-OH		O2N N	98
6	O ₂ N-OH	HN	O ₂ N	79
7	ОН	HN		77
8	Me OH	HN	Me Ne	72
9	O ₂ N-OH	NH ₂	O ₂ N NH	87
10	ОН	NH ₂ Me	NH NH Me	90
11	Me - OH	NH ₂	Me NH	82

(Continues)



TABLE 4 (Continued)



^aIsolated yield.



FIGURE 5 Reusability of the catalyst

3.4 | Synthesis of azide-functionalized chitosan

A 50 ml flask equipped with mechanical stirring was charged 0.5 g of chitosan, 0.5 M aqueous HCl. NaHCO₃ (9.3 mmol, 20 ml), 0.09 mmol of $CuSO_4.5H_2O$, 5.95 mmol of triflyl azide (TFA) solution and 15 ml of acetonitrile. The reaction mixture was stirred at room temperature for 5 days. Finally, the solid was filtered and washed with acetonitrile, HCl solution (5% solution in water) and then water and dried at room temperature.^[24]

3.5 | Click Reaction

In a 50 ml flask equipped with magnetic stirring containing azide functionalized chitosan (0.5 g) and compound 2 (2 mmol), CuI (0.1 mmol) in DMF/THF (1:1, V/V) solution were added and the mixture was stirred for 72 h at that temperature. Finally, the solid particles were filtered from the mixture, washed several times with Et₂O, H₂O and then acetone and dried in vacuum at 60 °C.

3.6 | Preparation of triazole-modified chitosan @ nickel (0)

At first, 0.2 g of the modified chitosan was dispersed into ethanol. Afterward, 3.4 ml of 0.1 mol L^{-1} NiCl₂/ethanol solution was added to this solution and stirred for 12 h at room temperature. Then, 2 ml of hydrazine as reducing agent was then dropwise added to the above mixture at a temperature of 60 °C. Then the catalyst was separated from the mixture washed with ethanol and water, and finally vacuum dried at room temperature.^[28]

3.7 | General procedure for direct amination of phenols

A mixture of phenol (1 mmol), and NaH (1.5 mmol) in dry toluene (4 ml) was stirred at room temperature for 2 h. Then 0.31 mmol of TCT were added to the mixture and the solution was stirred at 90 °C. The reaction monitoring was carried out by TLC. After completion of the reaction, amine (1.5 mmol), catalyst (0.3 mol%), and K₂CO₃ (2.0 mmol) were added to the reaction mixture. The progress of the reaction was checked by TLC. After the specified time, the mixture was cooled to room temperature, and the catalyst was separated from the reaction mixture by centrifugation. The reaction mixture was quenched with water and extracted with CH₂Cl₂, and the organic phase was dried over Na₂SO₄. The crude product was purified by column chromatography (hexane/ethyl acetate) to achieve the desired purity. ¹H NMR spectrum of some of the products has been given in the supporting information.



SCHEME 2 A plausible mechanism for the formation of the amination of phenols by TCT reagent

4 | CONCLUSIONS

In summary, we have applied nickel nanoparticles supported on modified chitosan as economical and efficient heterogeneous catalysts in the direct amination of phenols by 2,4,6-trichloro-1,3,5-triazine (TCT) for the activation of phenols. Additionally, broad substrate scope and the use of an inexpensive chitosan and nickel metal make it a favorable strategy from industrial view point.

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SUPPORTING INFORMATION

Additional Supporting Information may be found online in the supporting information tab for this article.

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