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Functionalized graphene oxide anchored to Ni complex as an effective recyclable heterogeneous catalyst for Sonogashira coupling reactions

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Abstract:

The Sonogashira cross coupling reaction is an applied method for preparation of diarylethyne compounds from readily available aryl halide derivatives and phenyl acetylene. The coupling reaction using nickel complex of N,N'-Bis(2-hydroxyethyl)ethylenediamine onto core shell graphene oxide (GO@SiO₂-BHED-Ni) as a catalyst was studied in this research. This heterogonous catalyst showed good thermal stability, highly efficiency and recyclability in the reaction. Moreover, the catalyst is simply separated and can be reused several times without significant loss of catalytic activity. A wide range of aryl halides was coupled successfully under palladium and phosphine free conditions. The use of this catalyst led to the formation of substituted aromatic alkynes in excellent yields and short reaction times.

Keywords: Coupling reaction, Diarylethynes, Heterogonous catalyst, Nickel chloride, Graphene oxide.

1. Introduction

The Sonogashira cross coupling reaction between alkynes and aryl halides is blooming as a general methodology for the construction of $C(sp)-C(sp^2)$ bonds [1]. Diarylethynes are versatile

compounds in organic chemistry, and therefore, several procedure for their synthesis have been investigated [2]. The carbon-carbon triple bonds are very useful in the chemical industry such as new drugs and polymers, because they can be simply functionalized through multiple addition reactions. In chemical science, polyalkyne derivatives are applied to prepare carbon-rich materials, new carbon allotropes and organic LEDs [3, 4]. Traditionally Pd or Pd/Cu complexes are used as catalysts in the Sonogashira reaction [5-7]. The use of effective palladium-free systems, including copper, zinc or iron, would obviously be much more interesting in view of modern organic synthesis owing to the lower cost and easy availability of these systems [8, 9]. Diverse heterogeneous catalytic systems based on transition metals [10] such as iron, [11] cobalt, [12] nickel [13] and silver, [14] in combination with various ligands have been investigated for coupling reactions.

A main drawback of coupling reaction is the essential application of an expensive palladium as a catalyst. Thus, the development of a mild, rapid, cheaper and environmentally friendly method to overcome these difficulties is still a notable aim for the coupling reactions. Nickel emerges the most promising for the replacement of palladium among the transition metals for that it is active for Sonogashira coupling reaction and very cheaper than palladium [15, 16].

Nowadays, different solid materials such as polymers [17, 18], mesoporous solids [19-22], metal oxides [23-25] and carbon polymorphs [26-28], have been used as catalyst supports with high performance.

Recently, graphene as a mono-atomic sheet of hexagonally arranged carbon atoms, has been extensively investigated successfully synthesized [29]. Graphene has exhibited excellent electrical conductivity and extremely high specific surface area (2600 m²/g). GO was prepared from graphite spheres using the modified Hummers' method [30]. Graphene oxide (GO)

containing oxygen-rich functional groups, such as epoxide, hydroxyls, and carboxylic acids, provide anchors for further chemical modifications, and can be used as an excellent support for heterogeneous catalysts in chemical process [24, 31-34].

Due to the importance of the C-C bond forming reactions, and in continuation of our previous studies on preparation of heterogeneous catalytic systems [24, 35, 36], Herein, we focus on synthesis, full characterization and application of GO@SiO₂-BHED-Ni as an environmentally-benign, highly efficient and reusable catalyst for the synthesis of phenylethynyl derivatives.

2. Experiment

2.1. Materials and Apparatus

All commercially available reagents were used without further purification and purchased from Merck Chemical Company in high purity. The used solvents were purified by standard procedure. Products were characterized by comparison of their physical data, IR and ¹H NMR and ¹³C NMR spectra with known samples. Fourier transform infrared (FT-IR) spectra were obtained using a Perkin-Elmer 781 spectrophotometer. The NMR spectra were recorded on a Bruker Advance DPX 400 MHz instrument spectrometer at 400 and 100 MHz in CDCl₃ as solvent in the presence of tetramethylsilane (TMS) as internal standard. Field emission scanning electron microscopy (FE-SEM) images were obtained by HITACHI S-4160. Nanostructures were characterized using a Holland Philips Xpert X-ray powder diffraction (XRD) diffractometer (Cu K α , radiation, $\lambda = 0.154056$ nm), at a scanning speed of 2 °/min from 10 ° to 100 ° (2 θ). The AFM image of catalysts was investigated using scanning probe microscopy (SPM-9600, Shimadzu). Thermo gravimetric analysis (TGA) was performed on a mettler TA4000 system

TG-50 at a heating rate of 10 K min⁻¹ under N_2 atmosphere. The purity determination of the substrates and reaction monitoring were accomplished by TLC on silica-gel polygram SILG/UV 254 plates (from Merck Company). Melting points were measured on a Yanagimoto micro melting point apparatus.

2.2. Catalyst preparation

2.2.1 General procedure for preparation of graphene oxide nanosheets

The graphene oxide nanosheets were obtained from natural graphite by the modified Hummer's method [37]. Graphite powder (5.0 g) was stirred in the presence of sodium nitrate (2.5 g) and concentrated sulfuric acid (115 mL) in a 1000 mL round-bottom flask placed in an ice bath. Afterwards, 15.0 g of potassium permanganate was slowly added to obtained solution and stirred for 2 h. The mixture solution was taken to a water bath (35°C) and stirred for 30 min. Then, 230 mL of deionized water was slowly added into the solution and the solution temperature monitored was about 98°C and stirred for 15 min. After this step, 700 mL of deionized water and 50 mL of H₂O₂ (30%) was added to the solution, respectively. The resulting materials were filtered and washed by diluted HCl (5%) and deionized water for several times. Then graphite oxide powder was dispersed in distilled water to make concentration of 0.5 mg mL⁻¹ and exfoliated by ultrasonication to obtain graphene oxide nanosheets.

2.2.2. General procedure for preparation of 3-chloropropyltrimethoxysilane-functionalized GO (GO@SiO₂)

GO (0.5 g) was dispersed in 50 mL of dry toluene using an ultrasonic irradiation (35W for 10 min). Then, 3.0 mL of 3-chloropropyltrimethoxysilane was diluted in 15 mL of dry toluene followed by dropwise addition to the GO dispersion. The reaction vessel was heated to reflux with continuous stirring for 48 h under nitrogen atmosphere. After completion of the reaction, the functionalized GO nanosheets were washed with toluene three times and ethanol two times to remove excess/non-reacted CIPTMS. The product was dried in an oven at 80°C [38].

2.2.3. General procedure for preparation of N, N'-bis(2-hydroxyethyl)ethylenediamine functionalized GO (GO@SiO₂-BHED-Ni)

In a 100 ml round-bottom flask, 0.5 g of GO@SiO₂ was added into acetonitrile (30 mL), followed by sonication (35 W) for 12 min. Then, 0.7 mL (5 mmol) of N,N'-bis(2-hydroxyethyl)ethylenediamine (BHED) was added into the round-bottom flask, and refluxed for 36 h. Then, the resulting product was centrifuged and washed three times with dichloromethane and dried at 80°C in vacuum. In the last step, the GO@SiO₂-BHED (0.5 g) and nickel chloride (0.2 mmol) was suspended in acetonitrile (25 mL) and mixed for 24 h at room temperature. The obtained solution was filtered and washed with acetonitrile in order to ensure that the excess nickel chloride was completely separated and finally, the product was dried at 70 °C under vacuum.

2.3. General procedure for the Sonogashira reaction

The quantities 1.2 mmol of phenyl acetylene, 1.0 mmol of selected aryl halide, and 2 mmol NEt₃, in the presence of 0.005g GO@SiO₂-BHED-Ni as catalyst were added to 7 mL ethanol/water (3:1) as solvent under stirring at 80 °C for an appropriate time. The progress of the reaction was monitored by thin layer chromatography (petroleum ether/ethyl acetate, 4:1). After completion of

the reaction, the catalyst was filtered under reduced pressure using vacuum pump over sinter glass (G4), washed with absolute ethanol, and dried for further use. After separation of the catalyst, the product was extracted with ethyl acetate and purified by column chromatography (Table 4).

2.4. Spectral data for diarylethyne derivatives:

1, 2-Diphenylethyne. White solid; m.p=58-60°C (Lit. [39] 60°C). IR (KBr)/ ν (cm⁻¹); 3060, 2923, 1598, 1493, 1440, 1278, 1068, 755, 688. ¹H NMR (400 MHz, CDCl₃) δ: 7.33-7.37 (m, 6H), 7.52-7.54 (m, 4H).

1-Methoxy-4-(phenylethynyl) benzene. White solid; m.p=61-63°C (Lit.[40] 60-62°C). IR (KBr)/ v (cm⁻¹); 2212, 1598, 1247, 1174, 1135, 835, 755, 690. ¹H NMR (400 MHz, CDCl₃) δ : 3.84 (s, 3H), 6.89 (d, *J* = 8.0 Hz 2H), 7.34(m, 3H), 7.49 (d, *J* = 8.5 Hz, 2H), δ = 7.52 (d, *J* = 8.4 Hz, 2H).

1-Nitro-4-(phenylethynyl) benzene. Yellow solid; m.p=112-114°C (Lit. [41] 114-116°C). IR (KBr)/ν (cm⁻¹); 2213, 1593, 1512, 1379, 1343, 855, 766, 689. ¹H NMR (400 MHz, CDCl₃) δ: 7.40 (m, 3H), 7.56 (m, 2H), 7.67 (d, *J* = 8.00 Hz, 2H), 8.23 (d, *J* = 8.00 Hz, 2H).

4-(Phenylethynyl) benzonitrile. White solid; m.p=102-104-72°C (Lit. [41] 106-107°C). IR (KBr)/ ν (cm⁻¹); 3082, 2223, 1603, 1502, 1442, 1273, 1177, 1071, 842, 761, 692. ¹H NMR (400 MHz, CDCl₃) δ: 7.43-7.51 (m, 3H), 7.59-7.61 (m, 2H), 7.66-7.74 (m, 4H).

4-(Phenylethynyl) benzaldehyde. White solid; m.p=101-103°C (Lit. [42] 98-100°C). IR (KBr)/ v (cm⁻¹); 3058, 2854, 2216, 1700, 1600. ¹H NMR (400 MHz, CDCl₃) δ: 7.34-7.37 (m, 3H), 7.52-7.53 (m, 2H), 7.67 (d, 2H, *J*=8Hz), 7.94 (d, 2H, *J*=8.4 Hz), 10.02 (s, 1H, CHO).

Methyl 4-(phenylethynyl) benzoate. Pale orange solid; m.p=112-114°C (Lit. [43] 115–116. °C). IR (KBr)/ ν (cm⁻¹); 2924, 2853, 1715, 1604, 1442, 1404, 1280, 1190, 1106, 925, 857, 765, 694. ¹H NMR (400 MHz, CDCl₃) δ: 3.93 (s, 3H), 7.36-7.42 (m, 3H), 7.54-7.60 (m, 4H), 8.01-7.03 (m, 2H).

1-(4-(Phenylethynyl) phenyl) ethan-1-one. Pale yellow solid; m.p=98-100°C (Lit. [43] 98-100°C). IR (KBr)/ ν (cm⁻¹); 3075, 2924, 2214, 1679, 1599, 1440, 1401, 1263, 1174. ¹H NMR (400 MHz, CDCl₃) δ : 2.67 (s, 3H), 7.37 (m, 3H), 7.54 (m, 2H), 7.60-7.62 (d, J = 7.6 Hz, 2H), 7.91 (d, J = 8.00 Hz, 2H).

1-Methyl-4-(phenylethynyl) benzene. Yellow solid; m.p=70-72°C (Lit. [28] 71°C). IR (KBr)/ν (cm⁻¹); 3027, 2227, 1630, 1598. ¹H NMR (400 MHz, CDCl₃) δ: 2.37 (s, 3 H), 7.17 (d, *J* = 7.2 Hz, 2H), 7.34 (m, 3 H), 7.43-7.45 (d, *J* = 7.6 Hz, 2 H), 7.53 (m, 2 H).

1-Methyl-3-(phenylethynyl) benzene. Light yellow oil; (Lit.[39]). IR (KBr)/ v (cm⁻¹); 3025, 2220, 1625, 1551. ¹H NMR (400 MHz, CDCl₃) δ: 2.44 (s, 3 H), 7.16 (d, *J* = 7.2 Hz, 1H), 7.25-7.27 (m, 1 H), 7.35-7.54 (m, 5 H), 7.54 (m, 2 H).

1-Chloro-3-(phenylethynyl) benzene. Colourless oil; (Lit. [42]). IR (KBr)/ ν (cm⁻¹); 3059, 2926, 2856, 2226, 1563, 1491, 882, 755, 540. ¹H NMR (400 MHz, CDCl₃) δ: 7.27-7.30 (m, 2 H), 7.33-7.35 (m, 3 H), 7.40-7.42 (m, 1 H), 7.52-7.66 (m, 3 H).

1-(Phenylethynyl) naphthalene. Yellow oil; (Lit. [44]). IR (KBr)/ v (cm⁻¹); 3055, 2955, 2212, 1595, 1506, 1490, 1442, 1394, 796, 796, 756, 565, 552, 432. ¹H NMR (400 MHz, CDCl₃) δ: 7.41-7.69 (m, 8H), 7.80-7.88 (m, 3H), 8.52-8.55 (d, *J*= 8.25, 1H).

1, 4-Bis(phenylethynyl)benzene. Yellow solid; m.p=165-167°C (Lit.[42] 169.3-172.4°C). IR (KBr)/ v (cm⁻¹); 2983, 2923, 2855, 1725, 1443, 1378, 1271, 1122, 1022, 915, 846, 690. ¹H NMR (400 MHz, CDCl₃) δ: 7.34 (dd, J = 5.8, 2.8 Hz, 3H), 7.51 (s, 2H), 7.51-7.53 (m, 2H).

3. Results and discussion

A brief procedure for synthesis of GO@SiO₂-BHED-Ni catalyst is schematically depicted in Scheme 1. The nanocatalyst was characterized by using AFM, XRD, SEM, EDX, FT-IR, and TGA techniques.

Scheme 1. Preparation of the GO@SiO₂-BHED- Ni

3.1. Characterization results of GO@SiO2-BHED-Ni

Figure 1 shows the FT-IR spectrum of graphite, GO, GO-SiO₂, GO@SiO₂-BHED-Ni, respectively in the range 400–4000 cm⁻¹. The FT-IR spectrum of graphite powder 1a shows peaks characteristic of C=C groups at 1570 cm⁻¹ which the peak is not sharp. The FT-IR spectrum of graphene oxide powder shows in 1b. The absorption band at 1575 cm⁻¹ is related to C=C double bonds which this peak is sharper than the graphite due to the unsymmetry of GO. The absorption peaks at 1062, 1720 and 3414 cm⁻¹ are assigned to C=O, carbonyl, and hydroxyl stretching mode of functional groups attachment to GO, respectively. Figure 1c shows the FT-IR spectrum of CIPTES-coated GO. The absorption peak at 1048 cm⁻¹ corresponds to the Si–O–C

bond. The vibrational bands at 2925 cm⁻¹ is related to CH₂ and the peak at 557 cm⁻¹ representing the C–Cl bond indicates the successful coating of the ClPTES onto GO through chemical bonding. After the reaction between N,N'-bis(2-hydroxyethyl)ethylenediamine with GO@ClPTMS, N, N'-bis(2-hydroxyethyl)ethylenediamine groups were attached to the surfaces of GO, which is evident from the appearance of the characteristic FT-IR absorption peak of C-N groups at 1370 cm⁻¹. The vibrational bands at 1168 cm⁻¹ is related to C-O groups and a typical band around 2923 cm⁻¹ should be attributed to aliphatic C–H bond stretching, the signal at 1450 cm⁻¹ indicates aliphatic CH₂ bending vibrations (Figure 1d).

Fig. 1. FT-IR spectra of a) Graphite, b) GO, c) GO-SiO₂ and d) GO@SiO₂-BHED

Figure 2 shows XRD patterns of graphite, GO and GO@SiO₂-BHED-Ni, respectively. The XRD pattern of graphite (Figure 2a) exhibits a peak at approximately $2\theta=26.5^{\circ}$, indicating that the interlayer distance was 0.335 nm. In Figure 2b, graphene oxide exhibits a peak at about $2\theta = 12.7^{\circ}$. The interlayer spacing (d-spacing) of GO was calculated 0.78 nm which revealed the formation of oxygen-containing functional groups between the layers of the graphite. The XRD patterns indicate that for two products (Fig. 1 b, c) represent the similar diffraction peaks indicating that the coating agent does not significantly affect the crystal structure of the GO. The XRD results indicate that the GO nanosheets were successfully coated with the NiCl₂.

Fig. 2. XRD patterns of (a) graphite, (b) GO and (c) GO@SiO₂-BHED-Ni

The SEM images of GO and GO@SiO₂-BHED-Ni are shown in Figure 3. As can be clearly seen in Figure 3a, the GO has layered structures with crumpled sheets. Figure 3b is indicated the SEM

image of GO@SiO₂-BHED-Ni revealing that the layered structure can be maintained in the functionalized graphene oxide after the treatments.

Fig 3. FESEM images of a) GO nanosheets and b) GO@SiO₂-BHED-Ni

Figure 4 shows the EDX spectra of GO and the GO@SiO₂-BHED-Ni nanosheets. The EDX analysis of the GO and the GO@SiO₂-BHED-Ni catalyst confirmed the presence of organosilane and NiCl₂ on support (Fig. 4a, b). Also, the catalyst was evaluated by an inductively coupled plasma (ICP) analyzer. ICP analysis indicated the presence of nickel in the catalyst and the content of Ni was measured to be 1.0 mmolg⁻¹ (7.6% W).

Fig. 4. EDX spectra of the (a), GO (b) and the GO@SiO₂-BHED-Ni

AFM was applied to determine the morphology of GO nanosheets and measure their thickness. As shown in Fig. 5, the image analysis confirms that the measured values of thickness are in the range 1–1.5 nm, indicating that exfoliated mono and dilayer graphene oxide was prepared in this research. After surface functionalization, the thickness of sheets is increased to 6.5 nm (Figure 5b). The increase in thickness of functionalized GO nanosheets is probably affected by the organic groups connected to the GO sheets.

Fig. 5. AFM images of GO nanosheets (A) and the GO@SiO₂-BHED-Ni (B)

In Figure 6, the TGA thermogram of the $GO@SiO_2$ -BHED-Ni is displayed. The thermal stability of the catalyst was studied using thermogravimetric analysis to confirm the presence of organic groups on the surface of the GO nanosheets. TGA was applied to verify the anchoring of organic

compound on the surface of GO. The initial small weight loss (10%) from the catalyst below 270 °C which could be assigned to the loss of bound water or physically adsorbed solvent. The weight loss observed (22%) at 270–700 °C in TGA curve GO@SiO₂-BHED-Ni is mainly attributed to the decomposition of organic groups grafted to the GO surface.

Fig. 6. TGA curve of GO@SiO₂-BHED-Ni

3.2. Investigation of catalyst activity

To study the catalytic activity of the GO@SiO₂-BHED-Ni and to characterize optimal performance for Sonogashira reaction, iodobenzene and phenyl acetylene was chosen as model substrates and were checked with different agents such as type and amount of catalyst, solvent, bases and the effect of temperature and the results are listed in Tables 1, 2 and 3. At first, we examined effect of the various metals in model reaction. After testing the different catalysts containing Ni, Ag, Au and Cu complex, it has been detected that the GO@SiO₂-BHED-Ni has a very high catalytic activity for synthesis of 1, 2-diphenylethyne (Table 1, entry 4). Therefore, GO@SiO₂-BHED-Ni complex was chosen for further studies. Then, we studied productivity of the several solvents such as DMF, PEG, EtOH, Toluene, DMSO, Ethanol/Water (3:1) and Water in coupling reaction. The investigation of solvent was indicated that Ethanol/Water (3:1) was the best solvent for the model reaction of phenyl acetylene and aryl halide compounds (Table 1, entry 7). In continued, the performance of the catalyst in different amounts on the model reaction was checked. The results demonstrated that in the presence of 0.005g of the GO@SiO₂-BHED-Ni catalyst, the yield increased sharply to 87% (Table 1, entry 10).

Table 1. The optimization of solvent and catalytic system for the formation of 1, 2-diphenylethyne^a.

In next step of this research, to obtain the proper base for the reaction, we tested different bases, among the different bases applied, NEt_3 was found to be the excellent base for this reaction (Table 2, entry 1).

Table 2. The optimization in the presence of different bases ^a

Afterwards, we investigated and optimized efficiency of the several temperatures in Sonogashira reaction. The effective temperature was found to be 80°C (Table 3, entry 4).

Table 3. Study of the temperature effect on the Sonogashira reaction

Finally, considering the optimal reaction condition, a broad range of structurally diverse aryl halides were reacted with Phenyl acetylene in the presence of 0.005g of GO@SiO₂-BHED-Ni nano catalyst and 2 mmol NEt₃ in Ethanol/Water (3;1) as solvent under 80 °C and the results are indicated in Table 4. As demonstrated in Table 4, in the presence of GO@SiO₂-BHED-Ni catalyst, the excellent product yields were achieved in shorter reaction time.

Table 4. Sonogashira cross-coupling of aryl halides and Phenyl acetylene in the presence of GO@SiO_2-BHED-Ni $^{\rm a}$

The obtained pure products were characterized by melting points and FT-IR, ¹H NMR spectra. The present catalytic system was compared with some literature reports for the Sonogashira reaction of 4-iodoanisole with phenyl acetylene in EtOH/Water (3:1), and the results are shown in Table 5. Obviously, the reaction conditions are different, but the most significant benefits of this work are related to the advantages of heterogeneous catalytic system such as, featuring easy

separation of product and catalyst, minimization of metal contamination, high yields of products and short reaction times, mild reaction condition and low cost [45-49].

Table 5. Comparison the reaction results of 1-methoxy-4-(phenylethynyl) benzene in this work and various reports in the literature.

3.3. The proposed reaction mechanism

The first step is the oxidative addition of Ni-(0) with aryl halide. The next step is the activation of the terminal alkyne. Because no copper salt was employed, and the bases are not strong enough to subtract a proton from the alkyne, a transmetalation step could be excluded. The terminal alkyne C-H bond activation is acomplished by the coordination of the alkyne to the ArNiX complex. Upon coordination, the C-H bond is weakened, and HX is removed from **1** in the presence of a base to form arylalkynylnickel species **2**, which undergoes reductive elimination to afford the product **3** and regenerates the catalyst.

Scheme 2. Synthesis of the GO@SiO₂-BHED- Ni.

3.4. Catalyst Reusability

One of the intended aims of this research was to design a nanocatalyst that can be easily recovered and reused. The possibility of recycling the catalyst was investigated through the reaction of phenyl acetylene and iodo benzene catalysed by GO@SiO₂-BHED-Ni under reaction conditions. Upon completion of the reaction, the catalyst was separated by filtration, washed with ethanol and dried at 70°C in an oven for 10 h and reused again in the reaction. As shown in Fig. 7, the catalytic system can be recovered and reused in this reaction for six times with considerable activity and selectivity.

Fig. 7. Reusability of catalyst for the synthesis of 1, 2-diphenylethyne

4. Conclusion

In summary, we have demonstrated a novel and highly efficient economical Sonogashira coupling reaction for preparation of diarylethyne products using the highly active GO@SiO₂-BHED-Ni as a nanocatalyst. This nanocomposite was found to be efficient in the Sonogashira coupling reaction and could be successfully recovered from the reaction mixture and reused. Furthermore, in this research, the prepared catalyst was characterized by some microscopic and spectroscopic techniques such as; SEM, EDX, AFM, FT-IR, XRD, and TGA techniques. These analysis was confirmed that the functionalization of GO was successfully carried out.

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Scheme 1. Preparation of the GO@SiO₂-BHED- Ni.

Scheme 2. Proposed reaction mechanism.

Fig. 1. FT-IR spectra of a) Graphite, b) GO, c) GO-SiO₂ and d) GO@SiO₂-BHED

Fig. 2. XRD patterns of (a) graphite, (b) GO and (c) GO@SiO₂-BHED-Ni

Fig 3. FESEM images of a) GO nanosheets and b) GO@SiO₂-BHED-Ni

Fig. 4. EDX spectra of the (a), GO (b) and the GO@SiO₂-BHED-Ni

Fig. 5. AFM images of GO nanosheets (A) and the GO@SiO₂-BHED-Ni (B)

Fig. 6. TGA curve of GO@SiO₂-BHED-Ni

Fig. 7. Reusability of catalyst for the synthesis of 1, 2-diphenylethyne

Table 1. The optimization of solvent and catalytic system for the formation of 1, 2-diphenylethyne^a

Table 2. The optimization of the presence of different bases^a

Table 3. Study of the temperature effect on the Sonogashira reaction.

Table 4. Sonogashira cross-coupling of aryl halides and Phenyl acetylene in the presence of GO@SiO₂-BHED-Ni^a

Table 5. Comparison the reaction results of 1-methoxy-4-(phenylethynyl) benzene in this work and various reports in the literature.



Scheme 1. preparation of the GO@SiO₂-BHED- Ni.







Fig. 1. FT-IR spectra of a) Graphite, b) GO, c) GO-SiO₂ and d) GO@SiO₂-BHED



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Fig. 5. AFM images of GO nanosheets (A) and the GO@SiO₂-BHED-Ni (B)







Fig. 7. Reusability of catalyst for the synthesis of 1, 2-diphenylethyne

		H Nanocomposite NEt ₃ , Solvent, 100 C	
Entry	Solvent	Catalytic system (gr)	Yield ^b (%)
1	EtOH	GO@SiO ₂ -BHED-Cu (0.008)	52
2	EtOH	GO@SiO ₂ -BHED-Ag (0.008)	28
3	EtOH	GO@SiO ₂ -BHED-Au (0.008)	23
4	EtOH	GO@SiO ₂ - BHED-Ni (0.008)	64
5	water	GO@SiO ₂ - BHED-Ni (0.008)	51
6	PEG	GO@SiO ₂ - BHED-Ni (0.008)	37
7	Ethanol/Water (3:1)	GO@SiO2- BHED-Ni (0.008)	87
8	Toluene	GO@SiO ₂ - BHED-Ni (0.008)	14
9	DMF	GO@SiO ₂ - BHED-Ni (0.008)	74
10	DMSO	GO@SiO ₂ - BHED-Ni (0.008)	55
11	Ethanol/Water (3:1)	GO@SiO ₂ - BHED-Ni (0.006)	87
12	Ethanol/Water (3:1)	GO@SiO ₂ - BHED-Ni (0.005)	87
13	Ethanol/Water (3:1)	GO@SiO ₂ - BHED-Ni (0.004)	57

Table 1. The optimization of solvent and catalytic system for the formation of 1, 2-diphenylethyne^a.

^a Reactions conditions: aryl halide (1 mmol), Phenyl acetylene (1.2 mmol), NEt₃ (2 mmol), 100°C, ^b Isolated yield

ble 2. The c	optimization in the pre	esence of different bases ^a		8
Entry	Base	Base amount	Time	Vield ^b
Linu y	Dase	(mmol)	(h)	liciu
1	NEt ₃	2	0.5	87
2	K ₃ PO ₄	2	2	53
3	NaHCO ₃	2	2.5	73
4	Na ₂ CO ₃	2	4	78
5	t-BuOH	2	3.5	42
6	КОН		3	57
7	K ₂ CO ₃	2	2.5	43
8	Li ₂ CO ₃	2	3	31
9	NEt ₃	1.5	0.5	87
10	NEt ₃	1	0.5	87

^a Reactions conditions: aryl halide (1 mmol), Phenyl acetylene (1.2 mmol), 100°C, GO@SiO₂- BHED-Ni in Ethanol/Water, ^bIsolated yield.

Entry	T (°C)	Time (h)	Yield (%) ^b
1	50	3.5	37
2	60	3	54
3	70	2	81
4	80	0.5	96
5	90	0.5	96

Table 3. Study of the temperature effect on the Sonogashira reaction.

^a Reactions conditions: aryl halide (1 mmol), Phenyl acetylene (1.2 mmol), GO@SiO2-BHED- Ni and NEt₃ (3 mmol) in Ethanol/Water, ^b Isolated yield.

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Table 4. Sonogashira cross-coupling of aryl halides and Phenyl acetylene in the presence of $GO@SiO_2$ -BHED-Ni^a



^a Reactions conditions: aryl halide (1 mmol), Phenyl acetylene (1.2 mmol), GO@SiO₂-BHED- Ni and NEt₃ (2 mmol), 80°C, ^b Isolated yield. ^c TON: mole of formed diarylethynes per mole of catalyst, ^d TOF (h⁻¹): (mmol of product/mmol of active site of catalyst)/time of the reaction (h).

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Entry	Reaction Condition	Time(h)	Yield (%) ^a	Ref.
1	GO@SiO2-BHED-Ni /	2	02	This
1	80 °C/NEt ₃	3	93	work
2	Cu(I)-PANI@MWCNT	2	85	[45]
2	KOH, DMF, 135 °C		05	
3	Cu(MeCN) ₄ ClO ₄ (5	16	83	[46]
U	mol%)dioxane, K ₂ CO ₃		00	[10]
4	CuBr/phen, n-Bu ₄ NBr	24	72	[47]
·	NaOH, H ₂ O, 120 °C		. 2	
5	CuBr/ rac-BINOL/ Cs ₂ CO ₃	30	79	[48]
6	Pd nanoparticles, K ₂ CO ₃ ,	5	91	[49]
	Water, 80°C			
^a Isolat	red yield.			

Table 5. Comparison the reaction results of 1-methoxy-4-(phenylethynyl) benzene in this work and various reports in the literature.

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Highlight Research

- ➤ The GO@SiO₂-BHED-Ni nanocatalyst was prepared via simple chemical process.
- > The catalyst was characterized using FT-IR, FE-SEM, XRD, AFM and TGA techniques.
- > The catalyst can be recovered several times without any loss of catalytic activity.
- ➤ The GO@SiO₂-BHED-Ni nanocatalyst was employed in synthesis of diarylethynes.

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