



Green-Synthesized Nickel Nanoparticles on Reduced Graphene Oxide as an Active and Selective Catalyst for Suzuki and Glaser-Hay Coupling Reactions

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A mild and benign methodology to syntheses biaryls and 1,3-diynes has been demonstrated using the nickel nanoparticles supported on reduced graphene oxide (RGO-Ni) as a heterogeneous catalyst which is prepared using green reagents. A series of substituted biaryls and 1,3-diynes has been synthesised in good to excellent yields through C-C homocoupling reaction of arylboronic acids and terminal alkynes respectively using 1,4-dioxane as a benign solvent. The present ligand-free catalytic system proceeds smoothly under mild conditions, avoids noble and stoichiometric metal reagents and tolerates sensitive functional groups. Also has a wide substrate scope and feasible with other nitrogen and sulphur containing heteroaryl boronic acids. Hot filtration test unambiguously proves the true heterogeneity of the catalyst and which support for the further reusability of the catalyst for several times without any change in the activity. The easy preparation and simple magnetic separation, stability and reusability reveal that as-prepared RGO-Ni as a versatile catalyst for the synthesis of polyaromatic compounds both in academia and industries.

Highlights

- Green-synthesized RGO-Ni nanocomposite used as a heterogeneous catalyst for Suzuki type (C-C) and Glaser-Hay (C \equiv C) homocoupling coupling reactions.
- Ligand-free catalytic system and avoids noble and stoichiometric metal reagents
- Short reaction time with a minimum catalyst (nickel) loading
- RGO-Ni nanocomposite is highly stable, reusable, and magnetically retrievable

KEYWORDS

Glaser-Hay reaction, magnetically retrievable catalysis, nickel nanoparticles, reduced graphene oxide, Suzuki coupling

1 | INTRODUCTION

Symmetrical biaryls and 1,3-diynes structural motifs have exhibited a variety of physical and chemical properties.^[1] They have been found in natural products such as fatty acids, alkaloids as well as in numerous biologically active parts of pharmaceutical and agrochemical entities, bioactive molecules,^[2] conducting polymer materials,^[3] optical light-emitting materials,^[4] and supramolecular architectures.^[5] The straightforward approach to obtain biaryls and 1,3-diynes scaffolds are the direct coupling of corresponding arylboronic acids and terminal alkynes, respectively.^[6] In this context, the formation of aryl ($C_{sp^2}-C_{sp^2}$) bond and ($C_{sp}-C_{sp}$) bond formation is an essential and challenging process to both academic and industrial catalytic community. One of the promising approaches for the production of symmetrical biaryls is transition metal-catalyzed coupling of arylboronic acids.^[7] Whereas Glaser-Hay coupling is the most widely used procedure for the synthesis of 1,3-diynes through the oxidative homocoupling of terminal alkynes. Though a number of modifications were made for the synthesis of both symmetrical and unsymmetrical diynes, still novel, and simple methodologies are continuously emerging.^[8] In general, palladium and other noble transition metals were extensively employed in such C-C coupling reactions.^[9] However, a recent search on the alternate transition metals with economic and simple experimental aspects, nickel getting more attention, owing to its elegant properties such as stability and unique catalytic response towards coupling reactions. These properties represent nickel as an ideal alternative to the existing noble metals which has already explored in coupling reactions. Nickel-based homogeneous catalysts have employed in various coupling reactions such as Kumada,^[10] Stille,^[11] Suzuki,^[12] Negishi,^[13] Chan-Lam^[14] and Glaser-Hay^[15] type reactions. However, to stabilize and sustain its oxidation states as a metal catalyst, complex ligands, additives are required, and unique or selective reaction atmosphere also essential which made the coupling reactions are more expensive and experimentally laborious. Hence, it is an immediate demand to develop a mild, operationally simple, economically viable heterogeneous and recyclable catalyst for coupling reactions.^[16]

Graphene materials are a pivotal candidate in the development of contemporary heterogeneous catalysis. It acts as a suitable support for the development of supported heterogeneous metal nanocomposite and exhibiting superior properties in catalyzed reactions, oxygen reduction reactions, drug delivery, and sensors.^[17] Most of the noble and non-noble transition metals like Au,^[18] Pt,^[19] Pd,^[20] Ag,^[21] Ru,^[22] Rh,^[23] Ir,^[23] Ti,^[24]

Mn,^[25] Fe,^[26] Co,^[27] Cu,^[28] and W^[29] had immobilized on the surface of graphene basal plane. Even some of the non-transition metals like Eu,^[30] Gd,^[31] Al,^[32] Ge,^[33] Sn^[34]- graphene composite also been studied. Although these graphene-metal nanocomposites found diverse material applications. Whereas, Pd, Cu and Au metals supported on graphene have extensively investigated as a catalyst in organic coupling reactions.^[35] More recently nickel nanoparticles (Ni NPs) has acquired growing attention for their potential utility in diverse catalytic applications.^[36] It has been immobilized on various supports^[26] to avoid the formation of large aggregates, to protect from further oxidation and its surface reactivity. Notably, Ni NPs supported on reduced graphene oxide (RGO) has shown significant advantages as a catalyst because of its distinct reactivity, ease of separation by a magnetic field and recyclability of the catalyst.^[37] The catalytic proficiency of graphene supported Ni nanoparticles were explored in very few synthetic transformations.^[38] In which, the notable reports on C-C coupling reactions like Kumado-Corriu cross-coupling,^[39] Sonogashira coupling,^[40] Silylation of the aldehyde with phenyl silanes,^[41] and C-S coupling reactions.^[42] However, still, the homocoupling of $C_{sp^2}-C_{sp^2}$ as well as $C_{sp}-C_{sp}$ are not yet investigated with graphene supported Ni nanoparticles.

In the present work, to unleash the catalytic potential of the RGO-Ni in coupling reactions under a relatively milder condition, it has been employed as a catalyst for the homocoupling of arylboronic acid to biaryls (Suzuki coupling) as well as homocoupling of terminal alkynes to 1,3-diynes (Glaser-Hay coupling) and its sustainable nature also explored. The optimization and observed results are discussed below.

2 | RESULTS AND DISCUSSION

Reduced graphene oxide supported nickel nanoparticles (RGO-Ni) has prepared by the hydrothermal process by adopting our previous report.^[43] In which 1:3 ratio of GO and $NiCl_2 \cdot 6H_2O$ were taken in water, along with 0.1 M solution of ascorbic acid. This mixture was placed in a Teflon lined autoclave in an oven at 120 °C for 16 hr. The resulting RGO-Ni nanocomposite was obtained as a black precipitate and it was characterized by various analytical tools like FT-IR, PXRD, Raman, XPS and TEM ((Figure S1- S5) for details see ESI). To explore the catalytic potential of the as-prepared RGO-Ni nanocomposite and to develop a benign and alternate methodology for coupling reactions, synthesis of the biaryl compound has taken as a prototype reaction. For that phenylboronic acid (**1a**) is considered as a model substrate to identify

the appropriate catalytic parameters such as solvent, temperature, time, base and amount of the catalyst loading. From the preliminary study, it is understood that the RGO-Ni nanocomposite catalyzes the homocoupling when using 1,4-dioxane as a solvent with K_3PO_4 as a base at 100 °C in an open vessel yield the corresponding biphenyl (**2a**) as a sole product. This encouraging result from the preliminary study, further directed to screen all the possible solvent system to choose more appropriate and compatible solvent works with RGO-Ni. The optimization results obtained from employing various solvents and diverse bases which are listed in Table 1. From the observed experimental results, it could be seen that the solvents behaved aberrantly in the presence of RGO-Ni and yield the biphenyl product in different ranges of yields. While using highly polar solvent, DMSO gives good yield meantime with another polar solvent DMF and ACN though the reaction takes place; indeed, the conversion is not impressive.

The catalyst is highly inert with the protic polar solvents, such as methanol, ethanol and water and no conversions were noted. However, in the case of non-polar

solvents such as THF, *n*-hexane and 1, 4-dioxane, no reaction was observed with THF and hexane. Among all the screened solvents the 1,4-dioxane exhibited significant superiority over the other solvents, and the reaction went to completion with a very good yield of 99% of the homocoupled product (entry 7, Table 1). To improve the greenness of the reaction, the reaction was carried out with the aqueous mixture of the 1,4-dioxane solvent system; however, the observed result was unfortunate than the normal solvent conditions and gave a poor yield of 35% (entry 12, Table 1).

Furthermore, to fix the role of the base in the homocoupling of phenylboronic acid (**1a**), various bases were screened, among which the inorganic base K_3PO_4 resulted in a better yield with RGO-Ni without any adverse effect during the product separation and no influence on the catalyst stability. Other inorganic bases such as Cs_2CO_3 , K_2CO_3 and Na_2CO_3 gave poor yield (entries 13–15, Table 1) and with the organic base triethylamine (TEA) shown inferior yield (entry 16, Table 1), and the catalyst was found to be inactive towards coupling in the absence of a base (entry 8, Table 1). In general, nickel catalysed coupling reactions required a strong base like K_3PO_4 to initiate the coupling process. To fix the exact amount of the base required in the coupling reaction, the quantity of the base was screened with the optimised conditions, and the results revealed that 2.5 equiv. (1.25 mmol) of the base is adequate for the complete conversion of the reaction with an excellent yield (Figure 1a). Similarly, though the initial reaction was performed up to 12 hr to explore the catalytic performance of the catalyst in the present coupling reaction and also for solvent and base optimisation, the exact time optimisation with the screened data shown that within 3 hr the desired coupling was formed without any byproducts. (Entry 8, Table 1). The optimised reaction time (3 hr) is minimum for the present nickel catalyzed coupling reactions when compared to the literature reports.^[44]

Similarly, in the RGO-Ni catalyzed coupling reaction, the product conversion is susceptible to temperature changes; A mild drop in temperature dramatically affects the yield (Figure 1b) within the studied time. And the temperature optimization showed that at 85 °C complete the conversion of phenylboronic acid to the corresponding coupled product. Thus, 85 °C was chosen as the optimum temperature for further reactions.

With the screened parameters, in order to know the appropriate amount of catalyst, reactions were performed with different amount of catalyst loading, since it plays a crucial role in the enhancement of product conversion and quantifies the efficiency of the heterogeneous catalyst used. Finally, the studies have shown that 50 mg of catalyst is adequate to achieve the maximum yield (99%)

TABLE 1 Reaction parameter optimization of RGO-Ni Catalyzed Homocoupling of Boronic acids^a

Entry	Solvent	Base	Yield ^b (%)
1	1,4-Dioxane	K_3PO_4	- ^c
2	Methanol	K_3PO_4	-
3	Ethanol	K_3PO_4	-
4	Water	K_3PO_4	-
5	DMSO	K_3PO_4	95
6	DMF	K_3PO_4	-
7	1,4-Dioxane	K_3PO_4	99
8	1,4-Dioxane	K_3PO_4	- ^d , 68 ^e , 82 ^f , 99 ^g
9	DCM	K_3PO_4	-
10	THF	K_3PO_4	trace
11	ACN	K_3PO_4	78
12	1,4-Dioxane: Water	K_3PO_4	35
13	1,4-Dioxane	Cs_2CO_3	-
14	1,4-Dioxane	K_2CO_3	-
15	1,4-Dioxane	Na_2CO_3	-
16	1,4-Dioxane	Et_3N	15

^aReaction Conditions: phenylboronic acid (0.5 mmol), base (1.5 mmol) and 60 mg of RGO-Ni in 2 ml of solvent at 100 °C up to 12 hr.

^bIsolated yield.

^cwithout catalyst,

^dwithout base,

Yields in

^e1 hr, ^f2 hr, and

^g3 hr.

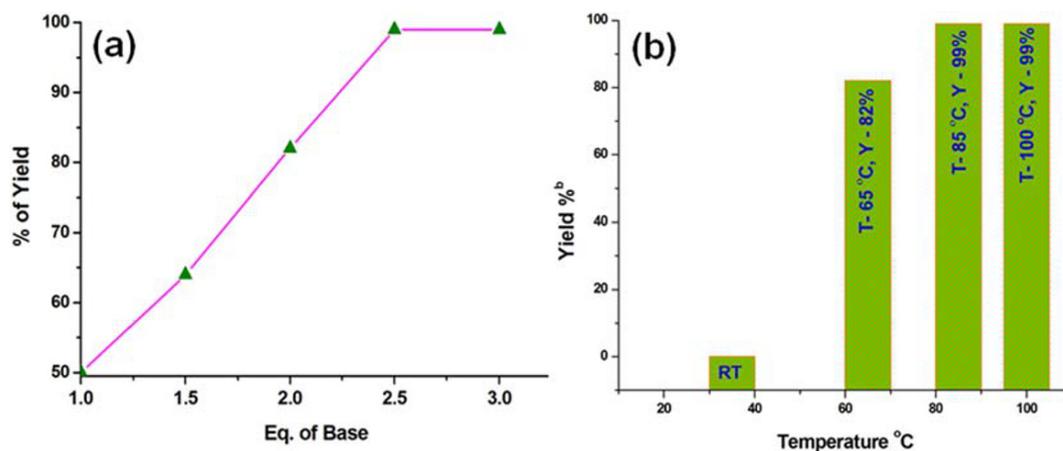


FIGURE 1 Optimization of base load (a) and temperature (b) for RGO-Ni catalysed homocoupling

of the homocoupled product with a minimum amount of nickel loading (9.5 mg, 0.16 mmol). Meanwhile, no coupling product was formed in the absence of RGO-Ni, which reveals the role of RGO-Ni catalyst towards the coupling reaction (Figure 2) (Table S1). Finally, all the above screening studies gave an optimised reaction condition such as K_3PO_4 as a base, 1,4-dioxane as a medium of solvent at 85 °C, where the RGO-Ni nanocomposite efficiently catalyses the homocoupling of phenylboronic acid and selectively promotes the homocoupled symmetrical biaryls.

With the optimum reaction conditions, the scope of the RGO-Ni nanocomposite catalysed homocoupling was extended to other arylboronic acids, and the results are presented in Table 2. A diverse arylboronic acids with either electron-donating or electron-withdrawing substituents smoothly underwent the homocoupling and gave

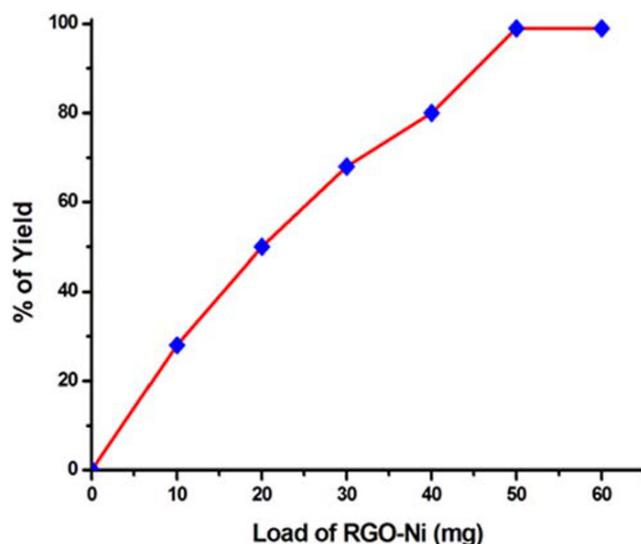


FIGURE 2 Catalyst (RGO-Ni) load optimization for homocoupling reaction

the corresponding symmetrical biaryls in 85–99% yields (**2a–2 l**, Table 2). Phenylboronic acids with electron-donating substituents such as methyl and methoxy groups facilitated the coupling and gave a better yield within the stipulated reaction time (**2b** and **2c**, Table 2).

Table 2 RGO-Ni nanocomposite catalysed homocoupling of arylboronic acid^a

^aReaction conditions: RGO-Ni catalyst (50 mg), arylboronic acid (0.5 mmol), K_3PO_4 (1.25 mmol) 1,4-dioxane (2.0 ml) at 85 °C up to 3 hr. All are isolated yields.

^bTON,

^cTOF (h^{-1}).

Meanwhile, when the same substituents present on the *meta* position of the aryl ring, a slight decrease in the yield was noted when compared to its corresponding *para*-substituted isomers (**2d** and **2e**, Table 2). On the other hand, electron-withdrawing substituents such as chloro and bromo gave good yields irrespective of their electron nature (**2f** and **2g**, Table 2). The same trend was observed with aryl-substituted phenylboronic acid with an excellent yield of 95% (**2h**, Table 2). 2,5-diphenyl substituted bulkier phenylboronic acid gave attractive yield (**2i**, Table 2). These results have shown that the catalyst is not more sensitive towards the steric nature of the substrate owing to the presence of large surface area as well as good synergy with aryl motifs. With this promising results in arylboronic acids, further attempts have been made on various nitrogen and sulfur-containing heteroaryl boronic acids, resulted with the excellent formation of symmetrical bipyridines and bithiophenes (**2j–2 l**, Table 2), which are being used as versatile building blocks in synthetic organic and material chemistry. Furthermore, the fused ring system, such as naphthyl boronic acid and oxiranes were studied for this C-C coupling reaction, gave better yields (**2m–2n**, Table 2). Based on this excellent results and formation of the coupled

TABLE 2 RGO-Ni nanocomposite catalysed homocoupling of arylboronic acids

products with various substituents, we concluded that the acidity of arylboronic acids plays a crucial role in the coupling reaction, electron-withdrawing groups increase the acidity of arylboronic acid, which gave the better yield than the electron releasing group on boronic acid.^[26]

Having these impressive results from the C_{SP}²-C_{SP}² homocoupling of arylboronic acids, further directed to extend our curiosity towards the C_{SP}-C_{SP} coupling of terminal alkynes (Glaser-Hay coupling). Initially, we performed the Glaser-Hay coupling by employing the RGO-Ni catalyst with our optimised reaction conditions. A model reaction was performed to establish the catalytic proficiency of RGO-Ni using phenylacetylene (3a), as a model substrate and K₃PO₄ as a base at 85 °C temperature. The observed results are highly encouraging, and phenylacetylene gave 99% of 1,3-diynes under the identical screened condition within the optimised time as like in arylboronic acid system. It was confirmed by GC-MS, ¹H and ¹³C NMR analysis. Changing the reaction parameters for RGO-Ni catalysed Glaser-Hay coupling has no impact on the formation of 1,3-diynes. Hence the optimised condition for homocoupling of arylboronic acids has worked smoothly for the coupling of terminal alkynes also. With the suitable reaction parameters in hand, the scope of RGO-Ni nanocomposite catalyzed synthesis of 1,3-diynes has been expanded to other terminal alkynes including aromatic and aliphatic terminal alkynes, and the results are presented in Table 3. Various aromatic terminal alkynes with electron-donating substituents smoothly underwent homocoupling and gave the corresponding 1,3-diynes in 72–99% yields (4a–4 g, Table 3).

Table 3 RGO-Ni nanocomposite catalysed Glaser-Hay coupling of terminal alkynes^a

^aReaction conditions: RGO-Ni nanocomposite catalyst (50 mg), alkynes (0.5 mmol), K₃PO₄ (1.25 mmol) 1,4-dioxane (2.0 ml) at 85 °C up to 3 hr. All are isolated yields.

^bReaction time was extended to 10 hr.

^cTON,

^dTOF (h⁻¹)

Phenylacetylene having electron-donating substituents at a *para* position such as methyl, ethyl, *tert*-butyl, methoxy and propyloxy groups were facilitates the coupling and gave a good yield of 1,3-alkynes within the

reaction time. Meanwhile, a moderate decrease in the yield (72%) was noted for the *meta*-amino substituted phenylacetylene (4 g, Table 3). On the other hand, halo substituents such as chloro and fluoro gave good yields irrespective of their position and electronic nature. From these flattering results with aromatic alkynes, further attempts have made on various aliphatic terminal alkynes, which resulted in reasonable yield. The oxidative homocoupling of aliphatic terminal alkynes yields only 38 to 42% of the corresponding 1,3-diynes (4 k–4 m, Table 3). However, the other non-aromatic terminal alkynes required a quite longer reaction time with inferior to moderate yields. Based on these experimental observations, it concluded that aryl alkynes are more reactive towards the homocoupling than aliphatic systems in RGO-Ni catalyzed Glaser-Hey coupling.

Though RGO-Ni catalyzes the homocoupling of arylboronic acid as well as terminal alkynes with a minimum Ni loading (9.5 mg, 0.16 mmol) without any external ligands, in order to understand the role of nickel nanoparticles present on the RGO surface control experiments were carried out with other catalytic systems under the similar optimized conditions and the results are listed in Table 4.

In control experiments, the precursor of RGO-Ni, such as graphite, graphene oxide and RGO were tested as catalysts in the coupling of phenylboronic acid, however, as individuals they were inactive, and no coupling or any other products were observed (entries 2–3, Table 4). Added to that, separately we performed the coupling reaction with reduced graphene oxide (RGO) and with homogeneous nickel salt NiCl₂·6H₂O under the identical optimised condition, which yields no or poor conversion even the reaction time extended up to 24 hr (entries 4–5, Table 4). Similar results again repeated while using the nickel nanoparticles as a catalyst (entry 6, Table 4). The results from the above control experiments collectively indicate that the metal and the carbon support as an individual does not possess any catalytic effect on the C-C coupling of arylboronic acid. The superior catalytic properties of the nickel and reduced graphene oxide has unleashed when it exists together as an RGO-Ni nanocomposite due to the synergy between RGO and nickel nanoparticles. Also, the high surface of the RGO and presence of aromatic graphitic basal plane facilitate the binding of the aryl moiety of the boronic acid through

TABLE 3 RGO-Ni nanocomposite catalysed Glaser–Hay coupling of terminal alkynes

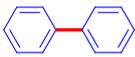
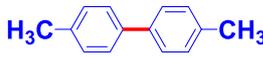
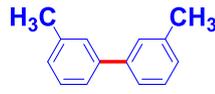
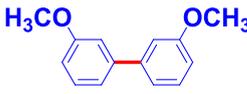
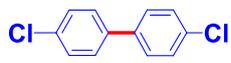
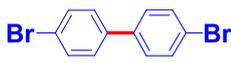
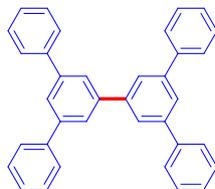
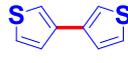
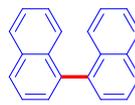
		
2a , 99% 618, ^b 206 ^c	2b , 90% 562, ^b 187 ^c	2c , 88% 550, ^b 183 ^c
		
2d , 86% 537, ^b 179 ^c	2e , 85% 531, ^b 177 ^c	2f , 88% 550, ^b 183 ^c
		
2g , 88% 550, ^b 183 ^c	2h , 95% 593, ^b 197 ^c	2i , 96% 600, ^b 200 ^c
		
2j , 88% 550, ^b 183 ^c	2k , 82% 512, ^b 170 ^c	2l , 90% 562, ^b 187 ^c
		
2m , 96% 600, ^b 200 ^c	2n , 95% 593, ^b 197 ^c	

TABLE 4 Control experiments for the catalytic efficiency of RGO-Ni in the homocoupling of phenylboronic acid^a

Entry	Catalyst	Yield ^b (%)
1	RGO-Ni	99
2	GO	-
3	Graphite	-
4	RGO	trace ^c
5	NiCl ₂ ·6H ₂ O	38,38 ^c
6	Nickel nanoparticle	75 ^d

^aReaction condition: Phenylboronic acid (0.5 mmol), K₃PO₄ (1.25 mmol) and 50 mg of catalyst in 2 ml of 1,4-dioxane at 85 °C up to 3 hr.^bIsolated yield.^cReaction carried out up to 24 hr.^d9.5 mg of catalyst.

π - π interaction which delivers the high mass transfer towards the active nickel sites.

The reusability studies investigate the sustainable nature of the catalyst and greenness of the catalytic process. In the present work, the reusability of the catalyst was assessed from the stability of catalytically active nickel sites on RGO after completion of the reaction. For this analysis, RGO-Ni used in the homocoupling of phenylboronic acid was recovered and reused under the optimised conditions (Figure 3b). Reusability results have shown that the catalyst is highly stable and withstand for several reuses. Similarly, to ascertain the stability of the catalyst after successive reuses, it was recovered by simple magnetic separation (Figure 3a) followed by washing and drying and subjected to PXRD and SEM analyses, to study the structural and morphological changes of the RGO-Ni nanocomposite before and after the catalytic reuses.

The observed results of the reused catalyst shown that there is no remarkable change in the PXRD pattern of the reused catalyst, which matches the pattern of the

freshly prepared RGO-Ni. The peak position and shape was not altered in the PXRD pattern of the fifth time reused catalyst (Figure 4a-b), indicating that the crystallinity and oxidation state of the catalyst has maintained without any oxidised impurities even after five repeated uses.

Furthermore, the morphology of the reused catalyst was demonstrated using SEM analysis. Figure 4c & 4d shows the SEM images of fresh and fifth time reused catalysts. From the images, it understands that the morphology of both RGO and the immobilized nickel nanoparticles are highly crystalline with a negligible deformation in the sheet-like morphology of RGO. It represents the highly sustainable nature of the catalyst.

Further, the heterogeneity of the catalyst was proved by the hot filtration test. It is crucial for the carbon-based heterogeneous nanocomposite-based catalyst. Because during the course of the reaction some of the immobilized nanoparticles may be leached into the solvent owing to the influence of any reaction parameters which promotes the reaction and behaves like

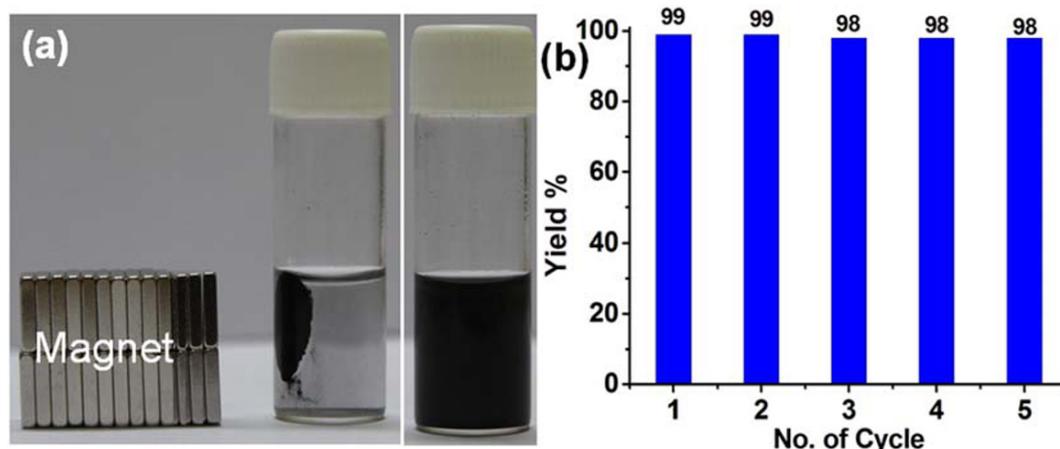


FIGURE 3 a) Magnetic separation of the RGO-Ni catalyst; (b) Reusability profile of RGO-Ni in homocoupling of phenylboronic acid. Reaction conditions: RGO-Ni catalyst (50 mg), phenylboronic acid (0.5 mmol), K_3PO_4 (1.25 mmol) 1,4-dioxane (2.0 mL) at 85 °C up to 3 hr. All are isolated yields

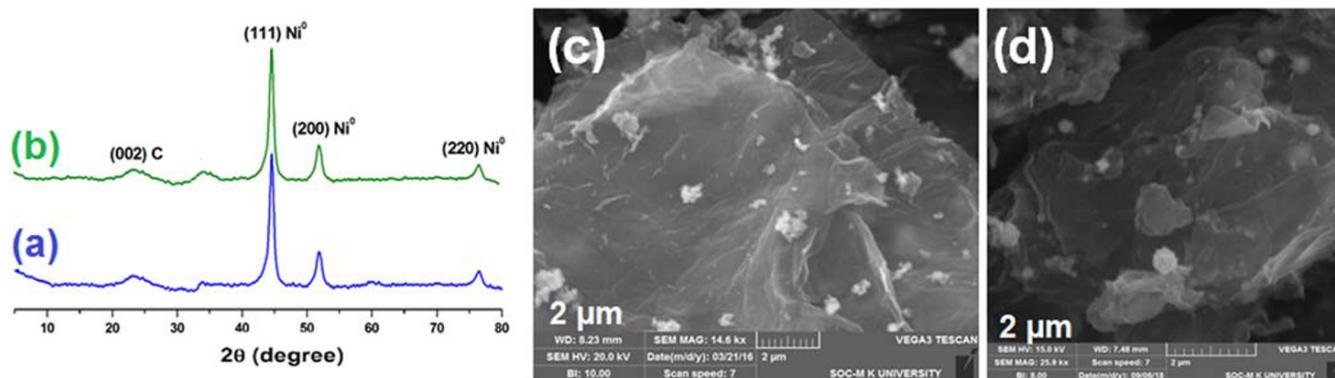


FIGURE 4 (a) Powder-XRD pattern of fresh, (b) fifth reused RGO-Ni, (c) SEM image of fresh, (d) fifth reused RGO-Ni

homogeneous system. Hence, a control experiment was carried out under the optimized conditions, in order to verify the true heterogeneity of the RGO-Ni. The control reaction was carried with phenylboronic acid under the optimized condition, and then the catalyst was removed entirely from the reaction mixture by external magnet after 1 hr at 85 °C and further the mother liquor alone was allowed to stir to for the optimized reaction time at the same temperature (Figure 5).

Before and after the removal of the catalyst, the product conversion was quantified using gas chromatography, and no further product conversion was observed even after the removal of the catalyst from the reaction medium. The hot filtration test strongly evidenced that there is no leaching of nickel nanoparticles from the RGO-Ni nanocomposite and it is stable under the developed reaction condition for the homocoupling of arylboronic acids which proved the heterogeneous manner of the catalyst. Furthermore, the analysis of the recovered solvent using inductively coupled plasma

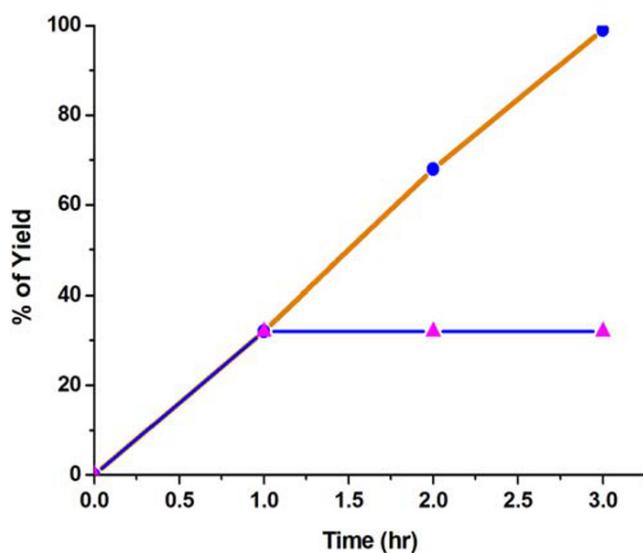


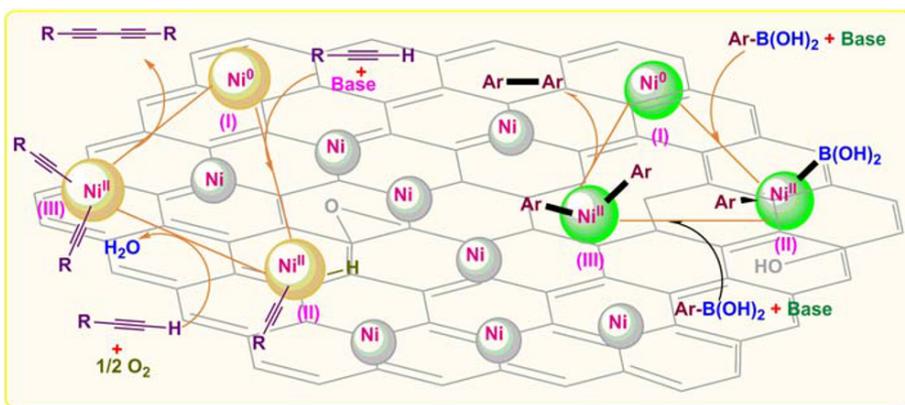
FIGURE 5 Hot filtration test for RGO-Ni catalyzed homocoupling of phenylboronic acid

optical emission spectroscopy (ICP-OES) confirms the absence of any detectable nickel species after the reaction which also supports the true heterogeneity nature of the catalyst.

Based on the experimental observations and from reported literature,^[8,27,35] a plausible mechanism has been proposed for the RGO-Ni nanocomposite catalyzed homocoupling of the arylboronic acid and for terminal alkyne which are shown in scheme 1. The presence of a high surface area exposed active sites Ni^0 on the graphene surface, and synergy between the RGO and nickel nanoparticle catalytically promotes the homocoupling. From the recent findings,^[27] the possibility of generating reversible $\text{Ni}^0/\text{Ni}^{2+}$ entities in RGO-Ni could significantly support the following proposed mechanism. Symmetrical biaryls and 1,3-diynes^[8,35] were synthesized *via* nano Ni-catalyzed homocoupling from nucleophilic aryl boronic acids and terminal alkynes respectively, in the presence of an oxidant through the oxidative coupling.

The proposed mechanism involves the oxidative addition **II** in the presence of a base K_3PO_4 and oxygen from the air. It leads to the formation of intermediate **III**, which subsequently undergoes the reductive elimination, gives the corresponding coupled product. At the end of the catalytic cycle, the catalyst gets regenerated and enters into another new catalytic cycle, which may be owing to the presence of the π -electrons cloud on the surface of RGO.

The comparison of the catalytic propensity of RGO-Ni towards the recently reported coupling reactions (Table 5) emphatically proves its better reactivity and good sustainable as well as economical nature in the synthetically important and industrially essential coupling reactions. Remarkably, its unique catalytic behavior towards both homocoupling of aryl boronic acids and Glaser-Hay coupling augments its demand as a versatile heterogeneous catalyst among the coupling reagents.



SCHEME 1 Plausible mechanism for RGO-Ni catalyzed homocoupling of arylboronic acid/aryl alkynes

TABLE 5 Comparative table for the catalytic efficiency of RGO-Ni in the coupling reactions

S. No.	Catalyst	Condition	Type of Coupling	Yield (%)	Ref
1	Ni (OAc) ₂ ·4H ₂ O and AgOTf	110 °C, DMF, 3 hr	Glaser – Hay Heterocoupling	81	[8a]
2	[Pd(η ³ -allyl)Cl (PPh ₃)]	25 °C, NaOAc, H ₂ O: Acetone,	Glaser – Hay Homocoupling	99	[8b]
3	Cu/Cu ₂ O-NPs@rGO	80 °C, Cs ₂ CO ₃ , EtOH, 8 hr	Glaser – Hay Homocoupling	99	[35b]
4	Ni nano- rGO -	120 °C, CuI, K ₂ CO ₃ , NMP, 4 hr	Sonogashira coupling	93	[40]
5	Ni-RGO 40	100 °C K ₂ CO ₃ , DMF, 4 hr	C-S Coupling	92	[42]
6	NiCl ₂ ·6H ₂ O-n-Bu ₄ NBr	120 °C, NaOH, ethyleneGlycol, 12 hr	Sonogashira coupling	91	[45]
7.	RGO - Ni	80 °C, K ₃ PO ₄ , 1,4-Dioxane, 3 hr	Homocoupling of boronic acid & Glaser – Hay coupling	99	This work

3 | CONCLUSIONS

The present work discloses the potential catalytic application of the as-prepared RGO-Ni nanocomposite in C_{sp}²-C_{sp}² Suzuki type homocoupling and C_{sp}-C_{sp} Glaser-Hay coupling reactions. A simple, efficient and greener methodology has been developed for the synthesis of both symmetrical biphenyls and 1,3-diynes using the heterogeneous nickel-based catalytic system with good to excellent yields. This multicatalytic behaviour of the RGO-Ni nanocomposite has more advantageous when compared to the existing commercial catalyst due to the utilization of a non-noble and readily available nickel metal without any ligand or additives under optimum temperature with the minimum nickel loading. Also, the RGO-Ni nanocomposite is highly stable and could be reused for five times without any significant loss in catalytic activity. The developed catalytic methodology offers to develop a commercially viable heterogeneous nanocomposite based sustainable catalytic system for synthesis of industrially demanding diverse biaryl and 1,3-diynes compounds.

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