

Article

Nickel-Fe₃O₄ Magnetic Nanoparticles Supported on Multiwalled Carbon Nanotubes: Effective Catalyst in Suzuki Cross Coupling Reactions

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Abstract: Nickel-Fe₃O₄ nanoparticles supported on multi-walled carbon nanotubes (Ni-Fe₃O₄/MW-CNTs) were synthesized by mechanical grinding of a sample of nickel salt, Fe₃O₄ and MWCNTs using a ball-mill mixer. The preparation method allows for bulk production of Ni-Fe₃O₄ nanoparticles at room temperature without the necessity of any solvent or chemical reagent. The nanoparticles prepared by this method exhibit small particles size of 5–8 nm with uniform dispersion of nickel nanoparticles on the surface of multi-walled carbon nanotubes. The Ni-Fe₃O₄/MWCNTs demonstrated remarkable catalytic activity for Suzuki cross coupling reactions of functionalized aryl halides and phenylboronic acids with excellent turnover number and turnover frequency (e.g., 76,000 h^{−1}) using Monowave 50 conventional heating reactor at 120 °C within a very short reaction time of 15 min. The catalyst is air-stable and exhibits easy removal from the reaction mixture due to its magnetic properties, recyclability with no loss of activity, and significantly better performance than the other well-known commercial nickel catalyst. The Ni-Fe₃O₄/MWCNTs nanoparticles were fully characterized by a variety of spectroscopic techniques including X-ray Diffraction (XRD), Transmission Electron Microscopy (TEM) and X-ray Photoelectron Spectroscopy (XPS). Since nickel offers similar properties to other more expensive transition metals including the most widely used palladium counterpart in cross coupling catalysis, this work demonstrates a promising lower-cost, air-moisture stable and efficient alternative catalyst based on nickel nanoparticles for cross coupling reactions.



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Keywords: nickel; nickel-Fe₃O₄ nanoparticles; magnetic nanoparticles; Suzuki cross coupling reactions; multiwalled carbon nanotubes

1. Introduction

The versatility of the metal catalysis in organic synthesis has been demonstrated in a variety of systems over many years [1]. Among them, the transition metal catalyzed cross coupling reactions between organic electrophiles and organometallic compounds are one of the most versatile synthetic methods to construct carbon-carbon bonds [2–5]. The development of cross-coupling reactions represents one of the most significant advancements in contemporary organic synthesis. This area of chemistry has increased accessibility to the molecules of greater chemical complexity, particularly in the area of pharmaceutical drug discovery and development. In 2010 Richard Heck, Ei-Ichi Negishi and Akira Suzuki received the Nobel Prize in Chemistry for their groundbreaking work in cross coupling catalysis. While palladium complexes are the most commonly used catalyst in variety of cross coupling reactions such as Suzuki, Heck, Sonogashira, Negishi and Kumada coupling reactions [6–8], more attention has been taken recently to employ less expensive and more abundant transition metals in these reactions. In this regard, nickel is considered as one of the potential alternatives to palladium due to its similar electronic structure and the ability to undergo oxidative addition, high bonding affinity and flexibility in forming multiple

oxidation states [9,10]. Even though a variety of nickel complexes have been developed as efficient new homogeneous systems for C–C bonds [11–13], the use of these catalysts under homogeneous conditions has limited their commercial viability due to product contamination as a direct result of inability to effectively separate the catalyst from the reaction product [14–17]. The issue of product contamination is of particular importance in pharmaceutical applications where this chemistry is practiced extensively. In addition, the reaction under homogeneous conditions requires ligands to solubilize the catalyst and broaden its window of reactivity [18,19]. Ligand free heterogeneous transition metal nanocatalysts present a promising option to address this problem by easy removal from the reaction mixture, recyclability and perhaps significantly better performance [20,21]. In this approach, the metal usually in the form of nanoparticles is fixed on solid supports such as zeolites, polymers, mesoporous silica, inorganic oxides and activated carbon, graphene and carbon nanotubes (CNTs) [22–32].

Among these support systems, CNTs [33–38], including single-walled carbon nanotubes (SWCNT) and MWCNT, have emerged significant attention because of intriguing electrochemical, mechanical and thermal properties mainly associated with large surface to volume ratio and their hollow structures. The presence of sp^2 carbon atoms within the hexagonal structure of these nanomaterials with several nanometers in diameters and many microns in length provides ideal platform for electronic conductivity as well as superior electrochemical and chemical stability in different solutions [33–35]. These types of materials not only efficiently catalyze the reaction, but also leverage the reactivity and stability of these materials along with the potential advantage of separation and reusability in subsequent reactions with minimum amount of metal contamination. Furthermore, the high surface area associated with carbon nanotubes ($2600\text{ m}^2\text{ g}^{-1}$) and extended π -system provide unique properties and remarkable tunability in supporting a variety of metallic and bi-metallic systems in heterogeneous catalysis [39–43]. We recently reported the extraordinary cross-coupling catalytic activity of MWCNTs supported palladium nanoparticles (Pd/MWCNTs) which were prepared using straightforward mechanochemical mixing of palladium salt and MWCNTs under ball-mill mixing [43–45]. This catalyst system demonstrated extremely high reaction rates and product yields for Suzuki coupling reactions [45]. The preparation method allows for simple, rapid and uniform deposition of metal nanoparticles on the surface of CNTs without the use of any chemical reducing agent or solvent and high reaction temperature. In addition, this effective solventless method to enchant metal nanoparticles supported on CNTs can be readily scaled up to multi-gram quantities. Due to particularly attractive properties of the nickel and its unique reactivity in variety of chemical processes including hydrogenation, cycloaddition and coupling reactions and extremely lower price compared to palladium, we were determined to explore the preparation of nickel nanoparticles supported MWCNTs by direct ball-milling of an appropriate nickel salt and MWCNTs at ambient temperature. Moreover, the addition of Fe_3O_4 to this mixture provides a platform for preparation of a bimetallic magnetic system consists of nickel and Fe_3O_4 supported on multiwalled carbon nanotubes ($\text{Ni-Fe}_3\text{O}_4/\text{MWCNTs}$). The enhanced magnetic properties imparted by Fe_3O_4 facilitate the easy separation of the catalyst from the reaction mixture by using a strong external magnet, thus increasing the economic value of the catalyst.

Herein, we report a simple, one-step method for the preparation $\text{Ni-Fe}_3\text{O}_4$ bimetallic nanoparticles supported on multi-walled carbon nanotubes ($\text{Ni-Fe}_3\text{O}_4/\text{MWCNTs}$) under mechanical shaking in a ball-mill. Both transition metals used for making these nanocomposites are inexpensive and highly abundant. The preparation method is very fast and straightforward which does not require any chemicals, solvents, or additional ligands. The as-prepared nanoparticles demonstrated remarkable catalytic activities in Suzuki cross coupling reactions of the functionalized aryl halides and phenyl boronic acids with high turnover number and turnover frequency in a single catalytic reaction using Monowave 50 heating reactor. This reactor provided conductive heating of the sealed glass vessel under monitored temperature and pressure with continuous magnetic stirring allowing

for a more efficient and rapid reaction. Notably, all Suzuki cross coupling reactions were completed in Monowave 50 at 120 °C in a short reaction time of 15 min affording high yield of the coupling products. In addition, the solid supported nanoparticles can be easily removed from the reaction by applying an external magnet and recycled for several times without significantly losing their catalytic activities in Suzuki coupling reactions. The preparation method provides a convenient, inexpensive and scalable synthesis of nickel-iron oxide nanomaterials for catalytic applications with the goal of developing more efficient, affordable and environmentally benign CNT-based nanomaterials for industrial and pharmaceutical applications in future.

2. Results and Discussion

The preparation of (Ni-Fe₃O₄/MWCNTs) nanoparticles was achieved using our previously reported synthetic method of mechanochemical ball-mill technique. In this method, a sample of Ni(OAc)₂·4H₂O, Fe₃O₄ and MWCNTs in appropriate ratios were mixed together and subjected to ball-milling at room temperature using a zirconium vial. The method is very simple and straight forward and provide an easy access to multigram of the Ni-Fe₃O₄/MWCNTs catalyst at once. The as-prepared catalyst was characterized by XRD, TEM and XPS to elucidate further insight into the structure of these nanoparticles.

Figure 1 display the XRD pattern of Ni-Fe₃O₄/MWCNTs nanoparticles as well as the XRD patterns of the original samples of Ni(OAc)₂·4H₂O, Fe₃O₄ and MWCNTs.

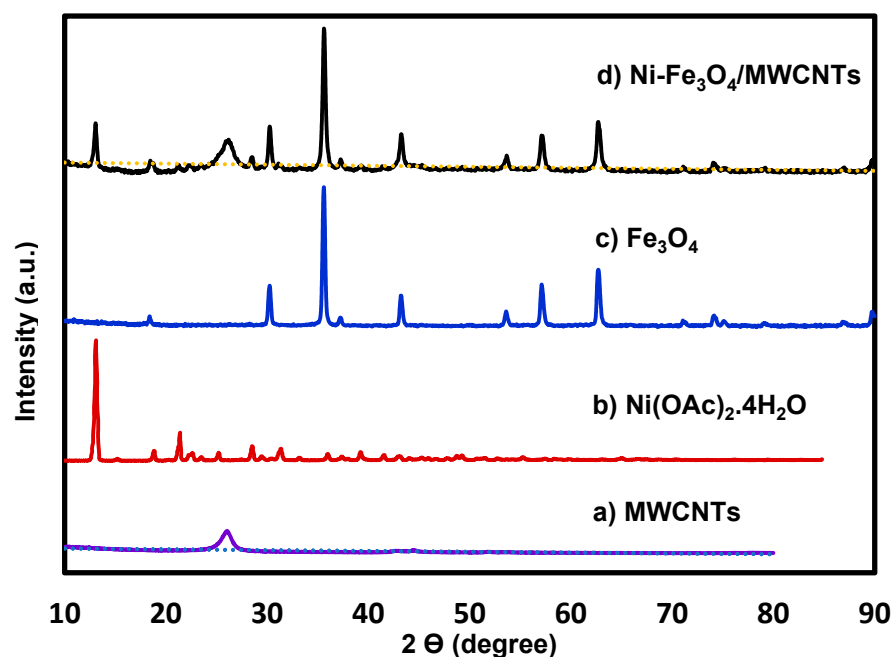


Figure 1. X-ray Diffraction (XRD) patterns of Nickel-Fe₃O₄ nanoparticles supported on multi-walled carbon nanotubes (Ni-Fe₃O₄/MWCNTs) nanoparticles and the original samples.

The XRD pattern of Ni-Fe₃O₄/MWCNTs demonstrates a strong reflection indicating the crystalline structure of these nanoparticles. The corresponding peaks at 18.3°, 30.2°, 35.5°, 43.2°, 53.7°, 57.1° and 62.8° related to the (111), (220), (311), (400), (422), (511) and (440) planes are characteristic peaks for the spinal Fe₃O₄ phase [46,47]. In addition, the XRD pattern of the residual Ni(OAc)₂·4H₂O is noticeable in the product indicating that the mechanical energy of the ball-mill may not be sufficient to completely decompose the metal salts. Nevertheless, the presence of peaks at 37.1°, 43.1°, 62.6°, 75.1° and 79.2° could be attributed to the corresponding (111), (200), (220), (311) and (222) planes for nickel oxide nanoparticles suggesting that under the ball-mill energy some of the Ni salts have been converted to NiO nanoparticles [48–52]. The broad shoulder at 45° can be identified as

small amount of Ni (111) phase. The small and broad peak at 26.3° is the characteristic diffraction of MWCNTs.

Figure 2 represents the TEM images of Ni-Fe₃O₄/MWCNTs nanoparticles. As shown, both nickel and iron nanoparticles are uniformly mixed on the surface of multi-walled carbon nanotubes. The average particle size of nickel nanoparticles calculated from several images indicate an average size of 5–10 nm for nickel in most area on MWCNTs with a consistent and uniform distribution pattern (see EDS and additional TEM images in Supplementary Material). The average particle size of Fe₃O₄ is determined between 15–25 nm with high dispersion among the Ni nanoparticles on the surface of nanotubes which imply the effect of mixing the metal salts during the mechanical shaking in the ball-mill to produce ultrafine mixture of Ni-Fe₃O₄ magnetic materials.

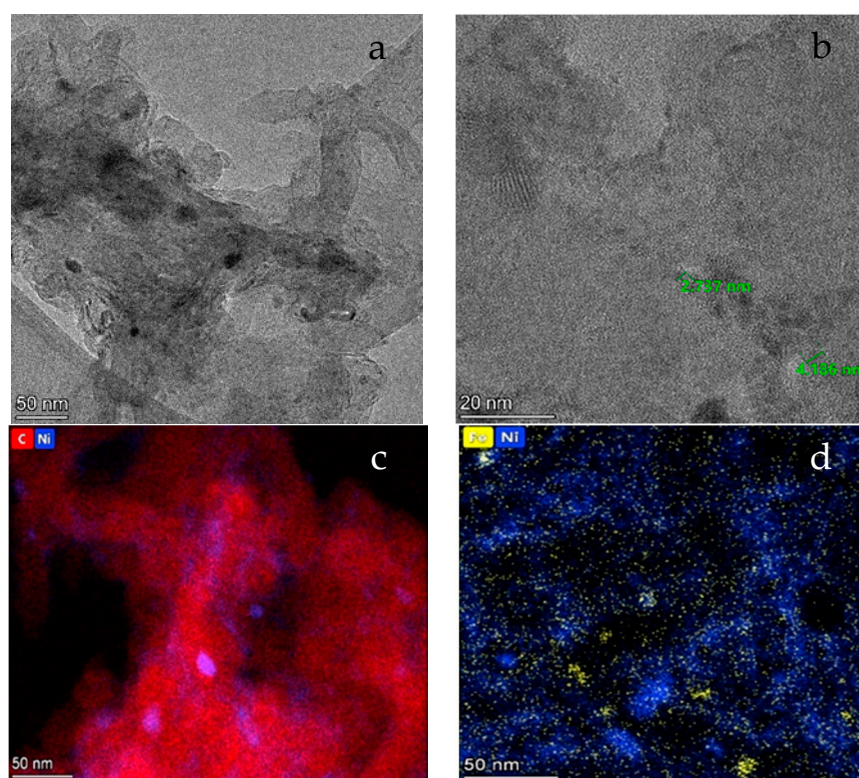


Figure 2. Transmission Electron Microscopy (TEM) images of Ni-Fe₃O₄/MWCNTs, (a) 50 nm of magnification; (b) 20 nm of magnification; (c) Elemental mapping C/Ni; (d) Elemental mapping Fe/Ni.

The composition of the nickel and iron nanoparticles on the surface was investigated using XPS analysis. Figure 3a shows the survey spectra of Ni-Fe₃O₄/MWCNTs nanoparticles including the presence of nickel, iron, carbon and oxygen. As shown in Figure 3b, the observed peaks at 709.2 eV and 723.07 eV correspond to the typical 2p_{3/2} and 2p_{1/2} binding energies for Fe in Fe₃O₄, respectively [53]. The broad characteristic of 2p_{3/2} peak at 709.2 eV attributes to the presence of both Fe(II) and Fe(III) in the catalyst. Figure 3c displays the measured binding energies of Ni 2p_{3/2} and Ni 2p_{1/2} at 856.5 eV and 874.3 eV, respectively, consistent with the dominant presence of Ni (II) in these nanoparticles [49–53]. The significant broadness of the peak at lower binding energy of around 852 eV for metallic Ni 2p_{3/2} indicates the formation of small amount Ni (0) during the ball mill process due to a partial reduction of the nickel salt [48–50].

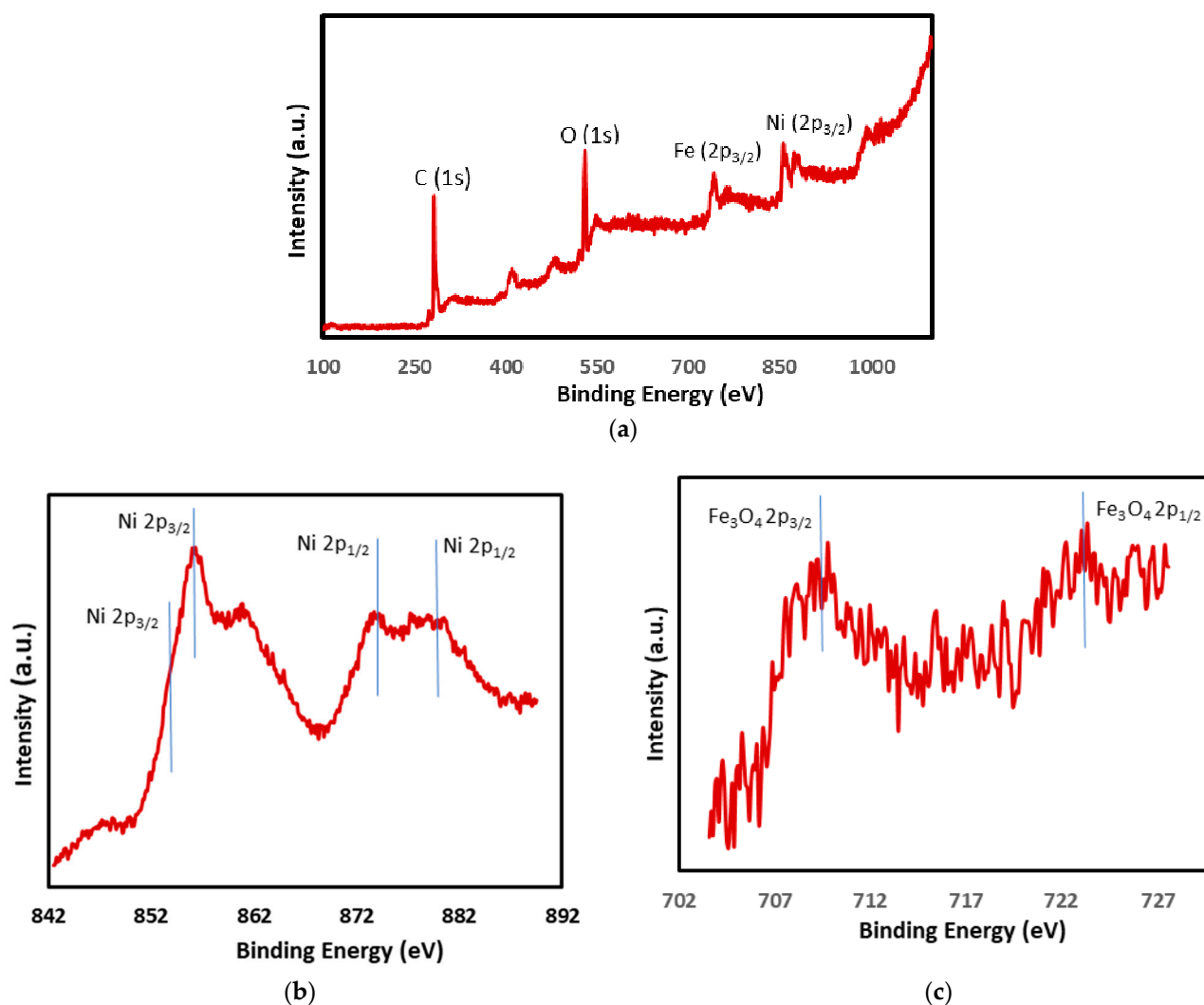


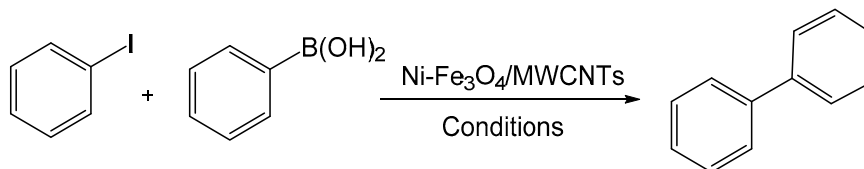
Figure 3. X-ray Photoelectron Spectroscopy (XPS) Spectra of (a) Ni-Fe₃O₄/MWCNTs (b) Ni (2p) binding energies, (c) Fe (2p) binding energies.

2.1. Application in Suzuki Cross Coupling Reactions

The catalytic activity of Ni-Fe₃O₄/MWCNTs was investigated in Suzuki cross coupling reaction of iodobenzene and phenyl boronic acid using Anton-Paar Monowave 50 heating reactor as shown in Table 1. This apparatus allows for direct heating of the reaction mixture under solvent pressure in a sealed tube using a conductive heating of a stainless-steel heating jacket [54]. The great advantages of this nonclassical heating method for various synthetic applications have been thoroughly investigated in both academic and industrial applications [55–57]. The rapid heating and cooling of the reaction mixture along with continuous stirring and temperature and pressure control are characteristic features of this conventionally heating technique. The reaction was completed to a quantitative formation of biphenyl product in only 15 min at 120 °C using 3 mol% of Ni-Fe₃O₄/MWCNTs in a mixture of H₂O:EtOH (1:1) and K₂CO₃ as the base (entry 7). The conversion was very low when DMF was used as the solvent in the presence of NEt₃ indicating that H₂O:EtOH combination with K₂CO₃ is the best possible solvents and base for this reaction. Lower reaction temperature of 100 °C produced a lower conversion of 85% (entry 6). Notably, this reaction can successfully afford a high yield of the Suzuki product (95%) with a very low concentration of the catalyst (0.005 mol%) at 120 °C in 15 min using Monowave 50 heating reactor (entry 12). These results imply a remarkable turnover number (TON) of 19,000 and turnover frequency (TOF) of 76,000 h^{−1} which reveal the efficiency of Ni-Fe₃O₄/MWCNTs

nanoparticles in catalyzing Suzuki cross coupling under the applied reaction conditions. No reactivity was observed in the absence of the catalyst, or when Fe_3O_4 or MWCNTs were used as the catalyst without any nickel nanoparticles (entries 13–15).

Table 1. Effect of solvent and base in Suzuki Cross Coupling Reactions ^a.



Entry	Cat Loading (mol%)	Solvent	Base	Temp (°C)	Time (Min)	Conversion % ^b
1	3	DMF	K_2CO_3	120	15	10
2	3	DMF	NEt_3	120	15	15
3	3	H_2O	K_2CO_3	120	15	0
4	3	$\text{H}_2\text{O}:\text{EtOH}$	NEt_3	120	15	45
5	3	$\text{H}_2\text{O}:\text{EtOH}$	Cs_2CO_3	120	15	80
6	3	$\text{H}_2\text{O}:\text{EtOH}$	K_2CO_3	100	15	85
7	3	$\text{H}_2\text{O}:\text{EtOH}$	K_2CO_3	120	15	100
8	3	$\text{H}_2\text{O}:\text{EtOH}$	K_2CO_3	120	10	90
9	1	$\text{H}_2\text{O}:\text{EtOH}$	K_2CO_3	120	15	100
10	0.5	$\text{H}_2\text{O}:\text{EtOH}$	K_2CO_3	120	15	100
11	0.05	$\text{H}_2\text{O}:\text{EtOH}$	K_2CO_3	120	15	100
12	0.005	$\text{H}_2\text{O}:\text{EtOH}$	K_2CO_3	120	15	95
13 ^c	-	$\text{H}_2\text{O}:\text{EtOH}$	K_2CO_3	120	15	0
14 ^d	3	$\text{H}_2\text{O}:\text{EtOH}$	K_2CO_3	120	15	0
15 ^e	3	$\text{H}_2\text{O}:\text{EtOH}$	K_2CO_3	120	15	0

^a Iodobenzene (50 mg, 0.25 mmol, 1 eq.) and phenyl boronic acid (35.9 mg, 0.3 mmol, 1.2 eq.), potassium carbonate (101.4 mg, 0.75 mmol, 3 eq.) and $\text{Ni-Fe}_3\text{O}_4/\text{MWCNTs}$ nanoparticles as indicated were heated using Monowave 50 heating reactor. ^b Conversion were determined by Gas Chromatography-Mass Spectroscopy (GC-MS). ^c No catalyst was used. ^d Only MWCNTs was used. ^e $\text{Fe}_3\text{O}_4/\text{MWCNTs}$ was used as the catalyst.

2.2. Recycling of $\text{Ni-Fe}_3\text{O}_4/\text{MWCNTs}$

One of the greatest features of the $\text{Ni-Fe}_3\text{O}_4/\text{MWCNTs}$ nanoparticles is the ease of their removal from the reaction mixture due to the superior magnetic properties. Table 2 demonstrates the remarkable recyclability of $\text{Ni-Fe}_3\text{O}_4/\text{MWCNTs}$ nanoparticles in Suzuki cross coupling reaction of iodobenzene and phenyl boronic acid at 120 °C for 15 min using Monowave 50 heating reactor. As shown, the magnetic $\text{Ni-Fe}_3\text{O}_4/\text{MWCNTs}$ can be successfully recycled in multiple reactions without losing any catalytic activity. This procedure was used for nine consecutive reactions achieving a high yield of the product in each run. The catalyst was effectively removed after each recycling reaction from the reaction mixture by applying an external magnet, washed with a mixture of ethanol and water and reused in the subsequent reaction.

2.3. Diversity of Substrates in Suzuki Cross Coupling Reactions

The scope and diversity of substrates in Suzuki cross coupling reactions were further investigated using a broad range of functionalized aryl halides and phenyl boronic acids as shown in Table 3. These reactions were carried out using 1 mol % of $\text{Ni-Fe}_3\text{O}_4/\text{MWCNTs}$ at 120 °C for 15 min under Monowave 50 heating reactor with $\text{H}_2\text{O}:\text{EtOH}$ as the solvent. The reactions were successfully achieved the relevant biphenyl products in high yields. A diverse array of functionalized substrates in para and meta positions such as aldehyde (1a), ether (1d), nitrile (1e) can be effectively introduced into the Suzuki products by using appropriate aryl substituted iodide. In addition, heterocyclic structures such as iodopyrazine (1c) can be employed as the coupling reagent in these reactions using $\text{Ni-Fe}_3\text{O}_4/\text{MWCNTs}$ nanoparticles. Alternatively, the aryl substituted boronic acids bearing

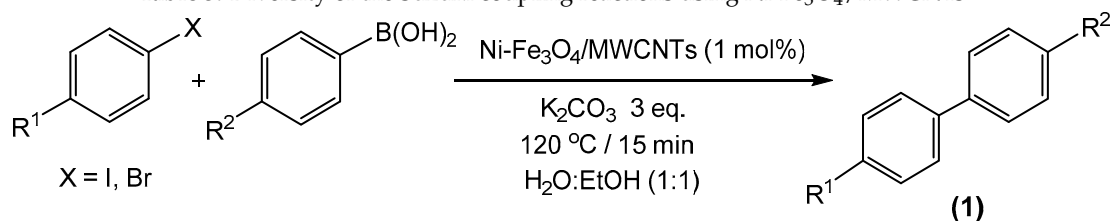
different functionality such as dimethylamino (**1b**), 1,3-benzodioxol (**1d**) and electron donor methoxy group (**1f**) all serve as excellent coupling partners in this process and afford a great yield of corresponding products. Notably, the bromo-substituted arenes can also be applied in these coupling reactions providing a good isolated yield of the Suzuki products (**1g**, **1h**). Interestingly, electron rich aryl bromide, 4-bromoanisole (**1i**) and electron deficient phenyl boronic acid such as 4-formylphenylboronic acid (**1j**) can be successfully employed in these catalytic reactions.

Table 2. Recyclability of Ni-Fe₃O₄/MWCNTs in Suzuki cross coupling reaction ^a.

Run	Conversion % ^b
1	100
2	100
3	100
4	100
5	100
6	100
7	95
8	95
9	95

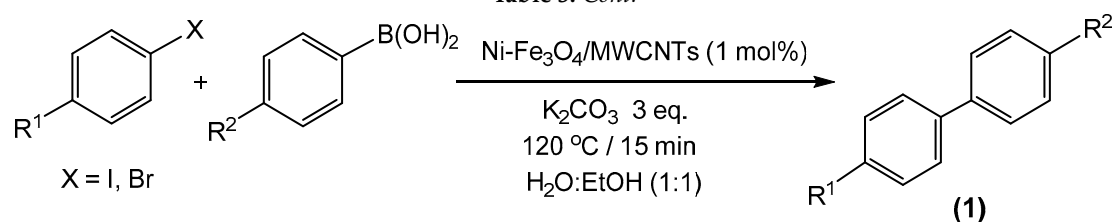
^a Iodobenzene (50 mg, 0.25 mmol, 1 eq.) and phenyl boronic acid (35.9 mg, 0.3 mmol, 1.2 eq.), potassium carbonate (101.4 mg, 0.75 mmol, 3 eq.) and Ni-Fe₃O₄/MWCNTs (3.59 mg, 7.35 μmol, 3 mol%) nanoparticles as indicated were heated using Monowave 50 heating reactor. ^b Conversion were determined by GC-MS.

Table 3. Diversity of the Suzuki coupling reactions using Ni-Fe₃O₄/MWCNTs ^a.



cpd	Aryl-Halide	Boronic Acid	1(%) ^b
a			 95%
b			 92%
c			 98%
d			 95%

Table 3. Cont.



cpd	Aryl-Halide	Boronic Acid	1(%) ^b
e			 90%
f			 88%
g			 82%
h			 80%
i			 85%
j			 82%

^a Aryl halides (0.25 mmol, 1 eq.), phenyl boronic acid (0.3 mmol, 1.2 eq.), potassium carbonate (0.75 mmol, 3 eq.) and Ni-Fe₃O₄/MWCNTs nanoparticles (1.20 mg, 2.45 μmol, 1 mol%) in a mixture of 4 mL H₂O:EtOH (1:1) was heated at 120 °C for 15 min using Monowave 50 heating reactor. ^b Isolated yield.

3. Experimental

3.1. General Methods

MWCNTs 50–85 nm was purchased from Graphene Supermarket. Nickel (II) acetate tetrahydrate and iron (II,III) oxide were obtained from Sigma-Aldrich (St. Louis, MO, USA). Aryl iodides and bromides, phenylboronic acid and other substituted boronic acids were purchased from Sigma-Aldrich (St. Louis, MO, USA), Alfa Aesar (Ward Hill, MA, USA) and ACROS Organics (USA) and used as received. A mixture of ethanol-deionized water

was used as the solvent system for all the reactions. Transmission Electron Microscopy was performed on ThermoFisher Talos F200X G2, a 200 kV FEG (Field Emission Gun, Analytical Scanning Transmission Electron Microscope (S/TEM)). XRD was completed on Rigaku MiniFlex 600 X-ray Diffractometer. Gas Chromatography-Mass Spectroscopy (GC-MS) of organic products was analyzed using a Shimadzu GC-MS QP2010 SE. ^1H and ^{13}C NMR spectra were acquired on a JEOL 400 MHz spectrometer equipped with autosampler. All cross-coupling reactions were performed using Anton-Paar Monowave 50 heating reactor.

3.2. Synthesis of Ni-Fe₃O₄/MWCNTs Nanoparticles

Nickel acetate tetrahydrate 153 mg (12% Ni content), Fe₃O₄ 117 mg (28% Fe content) and MWCNTs (60%, 180 mg) were mixed together in a 20 mL volume zirconium ceramic vial (SPEX CertiPrep). After adding two zirconium balls, the vial was subjected to mechanical shaking using SPEX 8000M ball-mill mixer for 45 min to afford the final product of (Ni-Fe₃O₄/MWCNTs). The mixer provides 1060 cycles per minutes with 5.9 cm back and forth and 2.5 cm side to side mechanical movements.

3.3. Procedure for Recycling the Catalyst

Iodobenzene (50 mg, 0.245 mmol) and phenyl boronic acid (35.9 mg, 0.29 mmol) were dissolved in a mixture of 4 mL H₂O:EtOH (1:1) and placed in a 10 mL vial. Potassium carbonate (101.4 mg, 0.735 mmol) and (Ni-Fe₃O₄/MWCNTs) nanoparticles (3.59 mg, 7.35 μmol , 3 mol%) were added to this mixture and the vial was sealed. The sealed vial was heated at 120 °C for 15 min using Monowave 50 heating reactor. After the reaction was completed, the mixture was diluted with 10 mL of ethanol and centrifuged for 3 min at 3000 RPM. The solvent above the solid catalyst was completely decanted. The ethanol washing was repeated for two additional times to ensure the removal of the organic compounds from the surface of the catalyst. The Ni-Fe₃O₄/MWCNTs nanoparticles were removed by an external magnet, washed with ethanol, and transferred to another Monowave 50 vial where fresh reagents were introduced and heated to the above-mentioned temperature. This procedure was repeated for the duration of the recycling experiments. The formation of the product in each run was determined by GC-MS analysis of the aliquot of the reaction mixture.

3.4. Procedure for Suzuki Cross-Coupling Reactions

The corresponding substituted aryl iodide and bromide (0.25 mmol, 1 eq.) and substituted phenyl boronic acid (0.3 mmol, 1.2 eq.) were dissolved in a mixture of 4 mL H₂O:EtOH (1:1) and placed in a 10 mL Monowave 50 vial. To this was added potassium carbonate (0.75 mmol, 3 eq.) and (Ni-Fe₃O₄/MWCNTs) nanoparticles (3.59 mg, 7.35 μmol , 3 mol%) and the mixture was heated at 120 °C for 15 min using Monowave 50 heating reactor. Upon the completion of the reaction time, the mixture was extracted with dichloromethane (3 \times 10 mL). The organic layers were combined, dried over MgSO₄ and filtered. The solvent was removed in vacuo to afford the solid product which was further purified by flash chromatography using hexane-ethylacetate as eluent.

4. Conclusions

In summary, Ni-Fe₃O₄/MWCNTs was developed using a scalable and efficient method of mechanical shaking in ball-mill. Both nickel and iron transition metals used for making these nanoparticles are inexpensive and highly abundant, and the preparation method is very straightforward and convenient in which no additional chemical reagents or solvent is required. The as-prepared nanoparticles demonstrated remarkable catalytic activity in Suzuki cross coupling reactions of various functionalized substrates with high turnover number (TON) of 19,000 and turnover frequency (TOF) of 76,000 h⁻¹ using Monowave 50 heating reactor at 120 °C within a short reaction time of 15 min. This rapid and uniform heating method has significant impact on the efficiency of the Suzuki reactions in the presence of Ni-Fe₃O₄/MWCNTs by increasing the reaction rates due to providing a clean,

direct and consistent energy for the cross-coupling reactions. In addition, the magnetic properties imparted by Ni-Fe₃O₄ nanoparticles facilitates the catalyst to be easily isolated and recycled for several times without losing its catalytic activity, thus greatly simplifying the ability to purify the reaction product and increasing the economic value of the catalyst. The use of this great catalytic system for other types of cross coupling reactions is currently underway in our laboratory.

Supplementary Materials: General Methods, Characterization Data, ¹H and ¹³C NMR Spectra, and other supporting materials are available online at <https://www.mdpi.com/article/10.3390/catal11040495/s1>.

Author Contributions: A.R.S. supervised the project, analyzed the data and wrote the paper. S.K.F., D.J.I., F.S.M. contributed to the experimental work, analysis and reaction development. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: Data is contained within the article or supplementary material.

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Conflicts of Interest: The authors declare no conflict of interest.

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