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FULL PAPER

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Synthesis of palladated magnetic nanoparticle ($Pd@Fe_3O_4$/AMOCAA) as an efficient and heterogeneous catalyst for promoting Suzuki and Sonogashira cross-coupling reactions

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Palladium supported magnetic nanoparticle ($Pd@Fe_3O_4$/AMOCAA) was easily prepared in the presence of Scrophularia striata extract and fully characterized by FT-IR, SEM, VSM, TEM, TGA, XRD and EDAX. It was successfully employed as an easily separable and reusable effective heterogeneous catalyst classical Suzuki and Sonogashira cross-coupling reaction. Sustainability of the methodology was reserved by easy recovery of the catalyst using an external magnet and reusing it for 7 times without appreciable loss of its catalytic activity.

KEYWORDS

magnetic support, Pd catalyst, Sonogashira reaction, sustainable chemistry, Suzuki reaction

1 | INTRODUCTION

In recent years, the reactions involving cross-coupling carbon–carbon bond formation have drawn widespread interest due to their versatile implications in organic transformation, especially in the total synthesis of natural products, long-chain organic molecules for organo-electronic applications and the development of bioactive molecules.[1–6]

Due to a plethora of application and unique features of C-C cross-coupling reactions, a great deal of research has been devoted to the development of easily isolable and renewable novel heterogeneous catalysts.[7–12] Palladium is the most applicable metal being used as catalyst in cross-coupling reactions, especially in Suzuki reaction that is one of the most commonly used coupling reactions especially in the synthesis of hetrococyles[13] and total synthesis of natural products. The growing tendency to Suzuk reaction is mostly due to the use of available, easy to handle and safe starting materials.[14] Formation of C-C bonds from this reaction is frequently the key-step of most total syntheses of natural products[15,16] which led to awarding the Chemistry Nobel Prize to its discoverer, Prof. Akira Suzuki, in 2010, of course shared with Richard Heck and Ichi Negishi.[17]

Suzuki reaction results in the formation of the bi-aryl compounds which are often employed as appropriate ligands and also are the key intermediates for the manufacture of various drugs such as antiplatelet, antidiuretic, anti-inflammatory, antiviral (Figure 1.).[18–21]

Another type of Pd-based cross-coupling reaction is called Sonogashira reaction is.[22] In this reaction, a Pd (II) salt promotes the cross-coupling between a sp-hybridized carbon atom of an alkyne and a sp^2 carbon atom of an aryl or vinyl halide (or triflate). Substituted alkynes,[23] are the products of Sonogashira coupling and may be useful in the synthesis of heterocycles[24] pharmaceutical complex molecules,[25] natural products[26] and polymeric and optical materials (Figure 2).[27,28]

The original Suzuki and Sonogashira reactions were performed in the presence of,active homogeneous catalysts which later extensively developed converted also via Pd- heterogenized catalyst by being immobilized over various supports such carbon nanotubes, magnetic nanoparticles, molecular sieves (SBA-15 and MCM-41), metal oxides, ionic liquids and various polymers.[29–34] Among these supports, magnetic nanoparticles have

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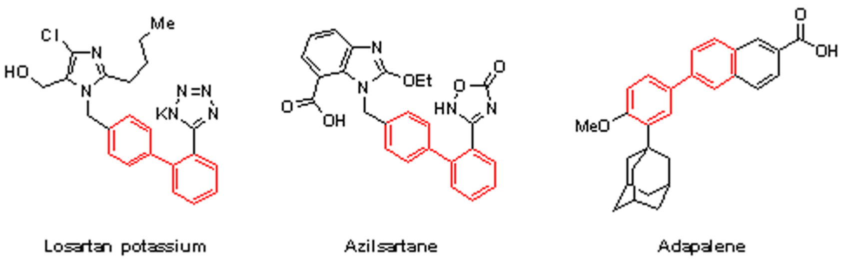


FIGURE 1 Some biologically important bi-aryls

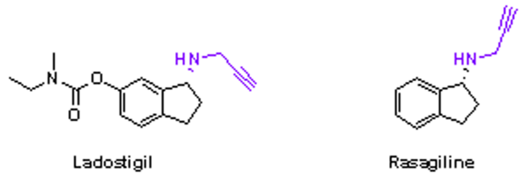
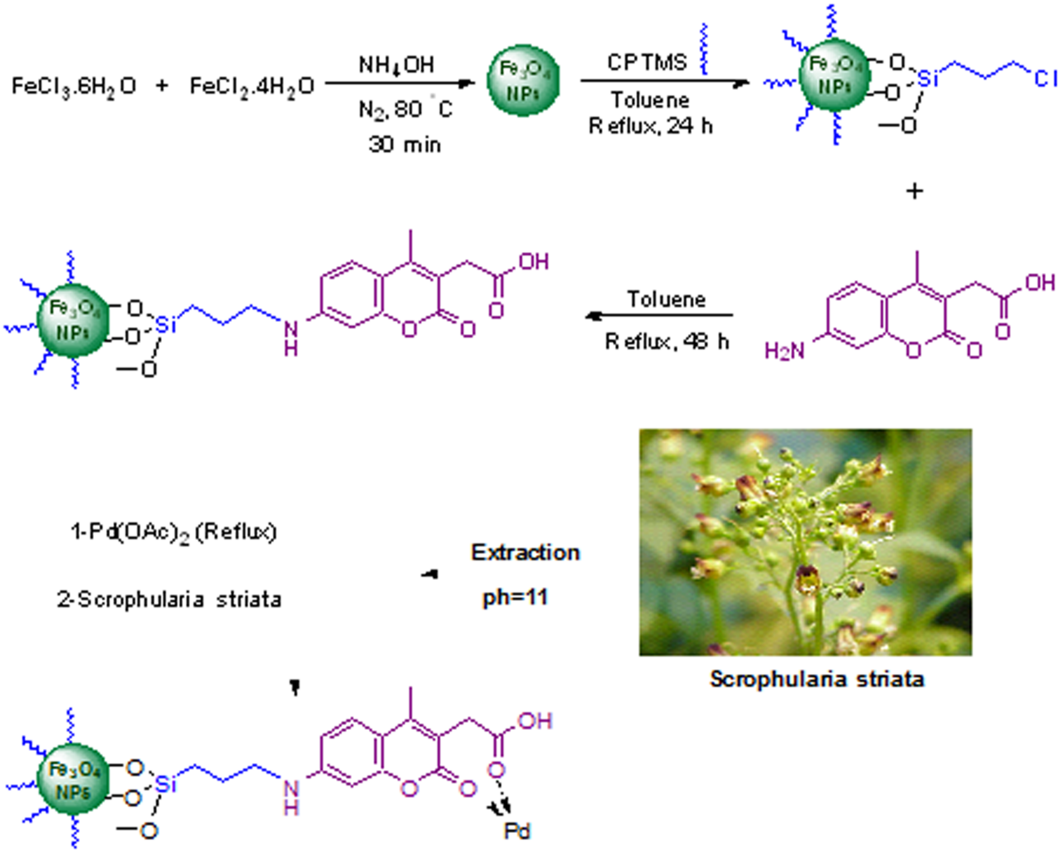


FIGURE 2 Two substituted alkynes prepared via Sonogashira reaction, under clinical trials for Alzheimer's disease

drawn sheer attention in last decade due to their versatile properties like high thermal and mechanical stability, large internal surface area, ease of separation using a magnet bar and high concentration of surface OH groups for secondary functionalization.[35–44]

Two main drawbacks of Pd- nanoparticles (Pd-NPs) catalysts are their considerable leaching of the Pd species to the reaction mixture causing the less catalytic activity in the next cycles; and aggregation of the MNPs leading to the increase of MNPs' size and decrease of their surface area, thus resulting in their decrease in their catalytic activity. Hence, using an appropriate support circumvent the above- mentioned problems to provide the suitable size of Pd–NPs and to avoid their leaching and thus to increase the catalyst activity and recyclability.

In this regard, herein, we wish report the classical Suzuki and Sonogashira cross-coupling reactions catalyzed by palladium complexed with 2-(7-amino-4-methyl-2-oxo-2H-chromen-3-yl)acetic acid modified in magnetic nanoparticles. High yield, short time reaction, easy



SCHEME 1 Synthesis of Pd@Fe_3O_4/AMOCAA

separation of catalyst and reusability are the most important features of our protocol.

2 | EXPERIMENTAL

2.1 | Materials and measurements

The chemicals used for the preparation of (Pd@Fe_3O_4/AMOCAA) and studying its catalytic activity included Iron (III) Chloride Hexahydrate ($FeCl_3.6H_2O$), Iron (II) Chloride Tetrahydrate ($FeCl_2.4H_2O$), 3-(trimethoxysilyl)propyl methacrylate (MAPTMS), 2-(7-amino-4-methyl-2-oxo-2H-chromen-3-yl)acetic acid, triethylamine, ammonia solution, toluene, Methanol, ethanol, Pd $(OAc)_2$, scrophularia striata extract, aryl halide, arylboronic acid, halobenzenes, phenylacetylene, propargyl alcohol, K_2CO_3, Cs_2CO_3, KOH, NaOH, distilled water and EtOH, were all purchased from Sigma-Aldrich

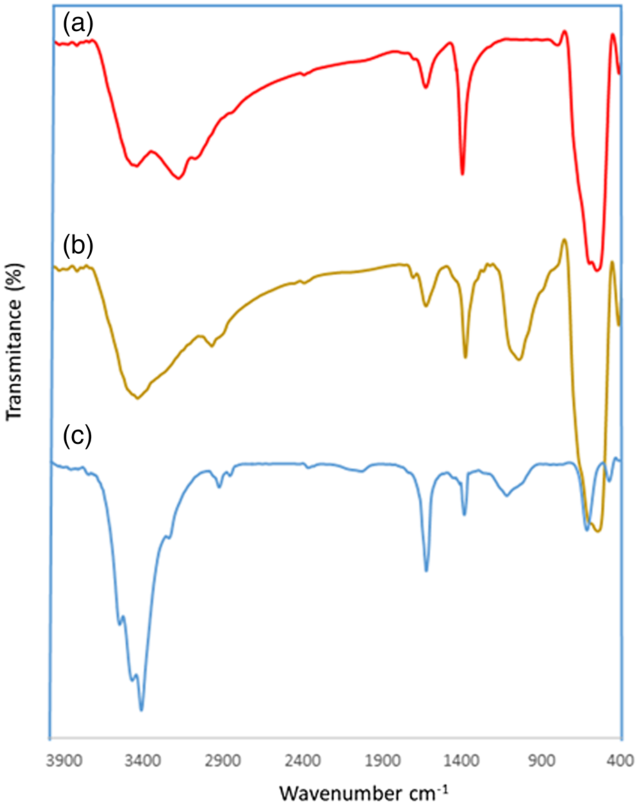


FIGURE 3 FTIR spectrum of bare Fe_3O_4 nanoparticles (a), chloro-functionalized Fe_3O_4 (b) and Pd@Fe_3O_4/AMOCAA (c)

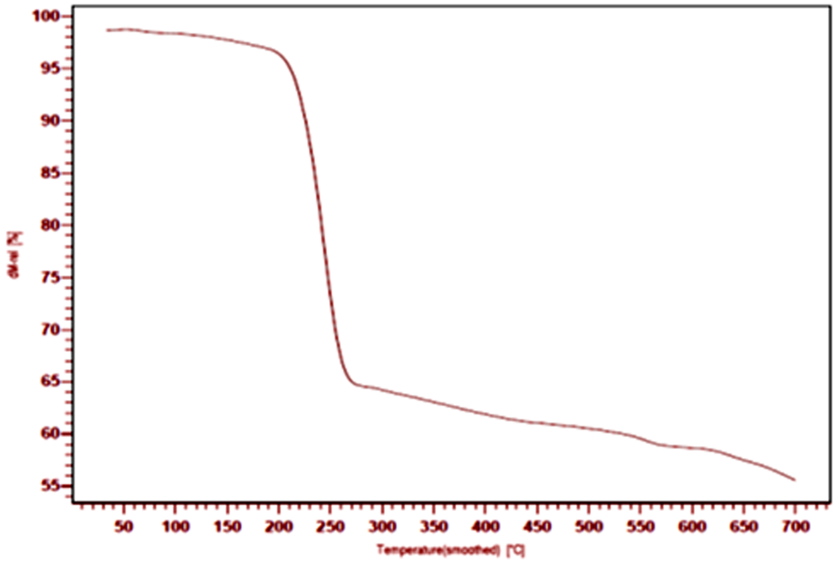


FIGURE 4 The TGA diagram of Pd@Fe_3O_4/AMOCAA

and used as received with no further purification. All other materials used in this study were analytical grade.

The formation of $Pd@Fe_3O_4$/AMOCAA was confirmed by using various characterization techniques

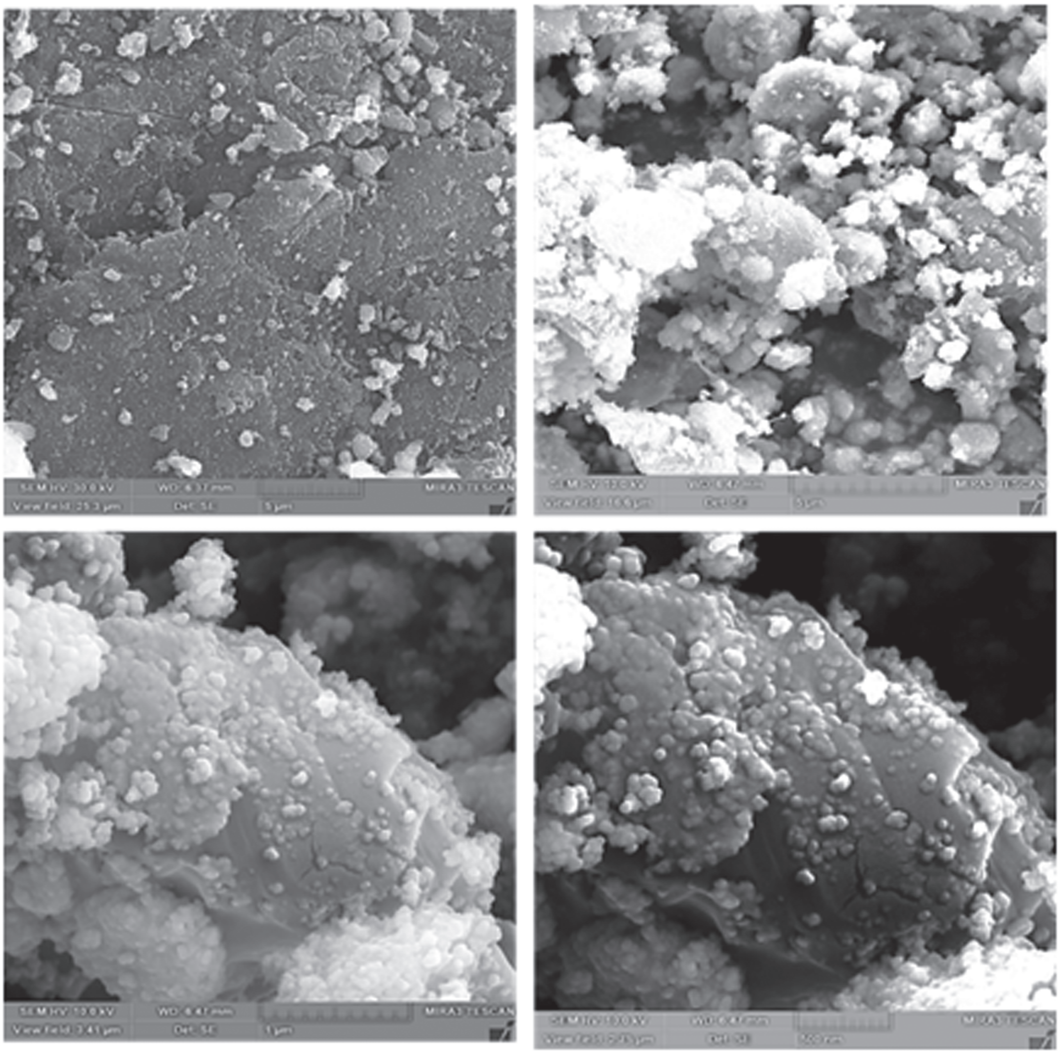


FIGURE 5 SEM images of $Pd@Fe_3O_4$/AMOCAA catalyst at different magnifications

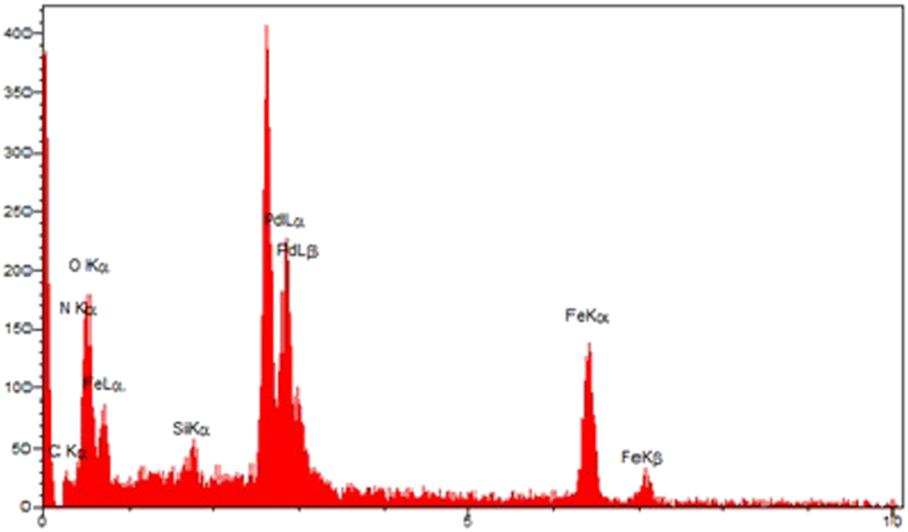


FIGURE 6 EDX spectrum of $Pd@Fe_3O_4$/AMOCAA

including SEM (FESEM-TESCAN MIRA3), TGA (Shimadzu DTG-60), FT-IR (Bruker VERTEX 80 v model using the KBr pellets), XRD (Co radiation source with a wave length = 1.78897 Å, 40 Kv) and EDAX (TSCAN).

2.2 | Preparation of (Pd@Fe_3O_4/AMOCAA): General procedure

After the synthesis of Fe_3O_4 nanoparticles according to the recently reported method,[31] 1 g of the prepared magnetic nanoparticles was dispersed in solution contain 1.5 ml of 3-chloropropyltrimethoxysilane (CPTMS) in 20 ml dry toluene under reflux condition. After 24 hr, the final product was separated with assistance of a magnetic device, washed with hexane and dried at 50 °C to give the Fe_3O_4 coated with CPTMS. Then, 2 mmol of 2-(7-amino-4-methyl-2-oxo-2H-chromen-3-yl) acetic acid and 1.5 mmol triethylamine were added to dry toluene under reflux conditions for 48 hr. The final product (anchored Fe_3O_4 with 2-(7-amino-4-methyl-2-oxo-2H-chromen-3-yl)acetic acid) was separated by a magnetic bar, washed with deionized water/ethanol and dried at

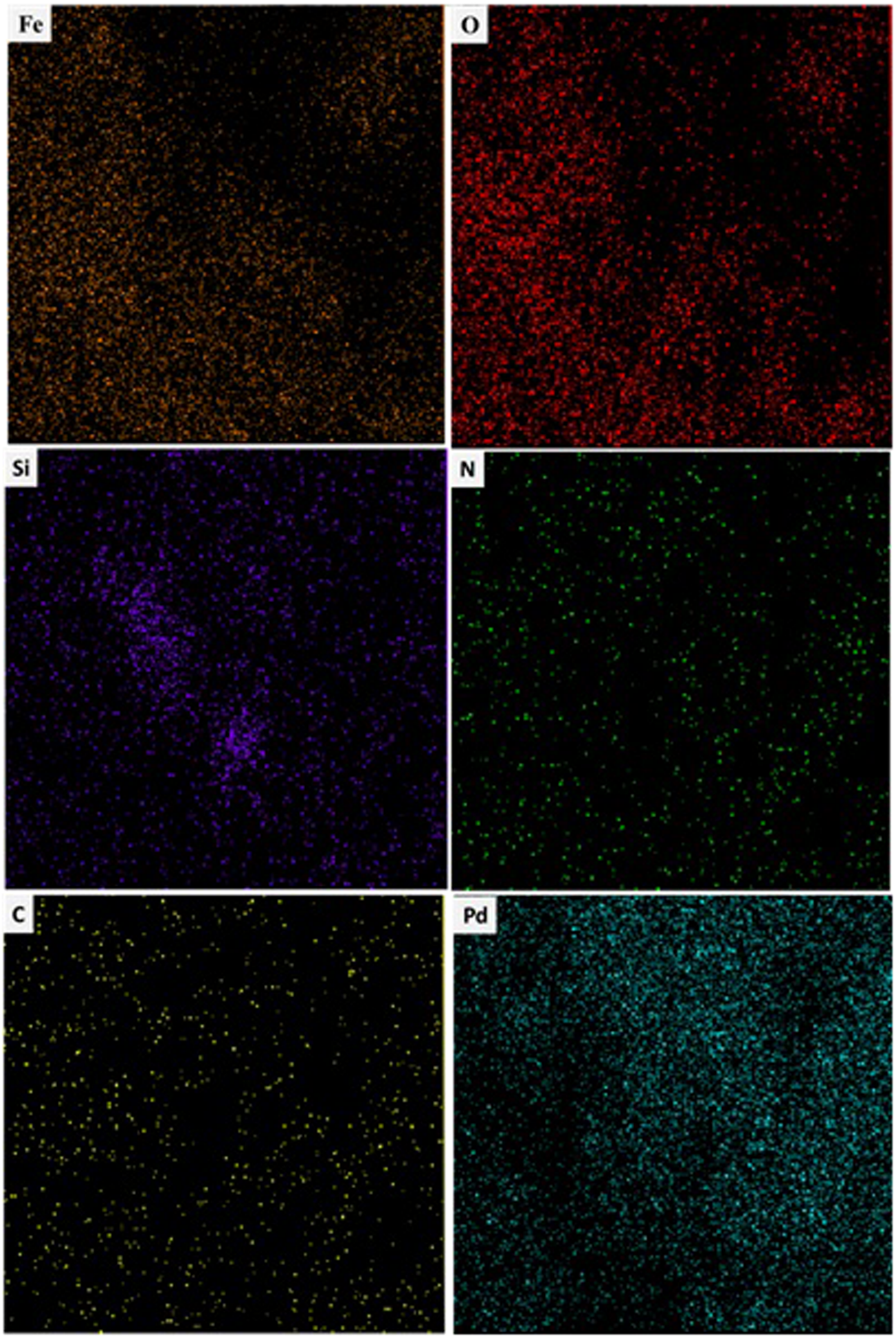


FIGURE 7 The X-ray map analysis of Pd@Fe_3O_4/AMOCAA catalyst

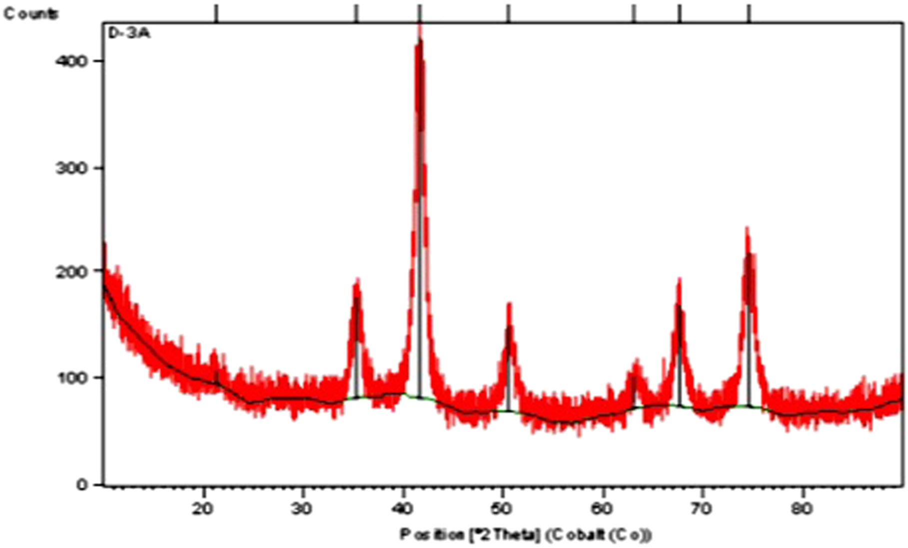


FIGURE 8 XRD pattern of $Pd@Fe_3O_4$/AMOCAA

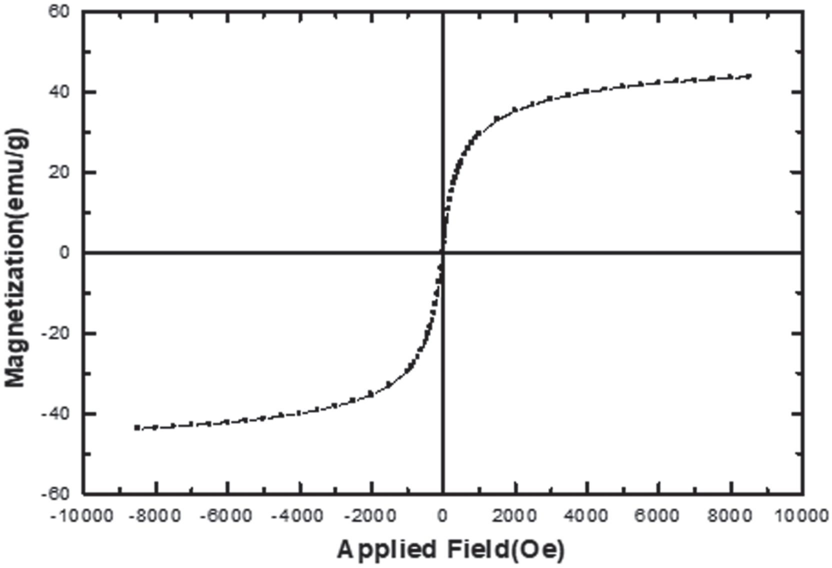


FIGURE 9 Magnetization curves for $Pd@Fe_3O_4$/AMOCAA catalyst at room temperature

50 °C. In the final step, 0.5 g Pd $(OAc)_2$ was added to solution of anchored Fe_3O_4 with 2-(7-amino-4-methyl-2-oxo-2H-chromen-3-yl)acetic acid (AMOCAA) (1 g) in absolute ethanol (30 ml) and refluxed for 16 hr. Then Pd (II) ions reduced with scrophularia striata and then final powder separated by magnetic field and washed with ethanol to afford the planned heterogeneous catalyst (Scheme 1).

3 | RESULTS AND DISCUSSION

3.1 | Catalyst characterization

After successful synthesis of $Pd@Fe_3O_4$/AMOCAA, SEM, FT-IR, EDX, VSM, TEM, XRD, TGA and ICP techniques were used to determine the structure of nanocomposite.

FT-IR spectra of bare Fe_3O_4 nanoparticles (a), chloro-functionalized Fe_3O_4 (b) and $Pd@Fe_3O_4$/AMOCAA (c) recorded in the range of 400–4000 cm^{-1}. Figure 3 shows the O-H and Fe-O stretching vibration at approximately 3400–3500 and 580 cm^{-1}, respectively, in all samples. In the FT-IR spectra of chloro-functionalized Fe_3O_4, the presence of the characteristic absorption bands around 2850–2950 were confirmed the presence aliphatic C-H stretching vibration. The C=O stretching vibration at approximately 1620, in FT-IR spectra of $Pd@Fe_3O_4$/AMOCAA (c) was also confirmed the successful grafting of ligand on the surface of Fe_3O_4.

The quantitative determination of the organic groups on the surface of Fe_3O_4 nanostructure determined by using TGA analysis that obtained about 35% for prepared catalyst between 200 and 270 °C. The data of TGA analysis was shown the decomposition of functional groups chemisorbed onto the surface of Fe_3O_4 nanoparticle (Figure 4).

The spherical shape of $Pd@Fe_3O_4$/AMOCAA nanoparticles was confirmed by using SEM images in Figure 5.

The presence of Fe, O, N, C and Pd specie in the $Pd@Fe_3O_4$/AMOCAA nanocatalyst was confirmed by the energy-dispersive X-ray spectroscopy (EDX) analysis (Figure 6). Amount of Pd loaded on modified magnetic nanoparticles was obtained 1.32 mmol g^{-1} by ICP analysis.

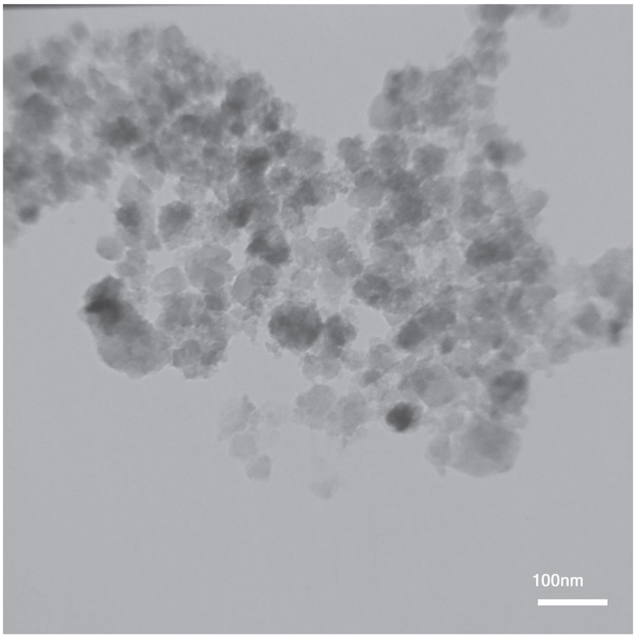


FIGURE 10 TEM images of $Pd@Fe_3O_4$/AMOCAA catalyst

The X-ray mapping of $Pd@Fe_3O_4$/AMOCAA was recorded in order to evaluate the dispersion of Pd active sites in the catalyst in which indicated a good dispersion of Pd on surface of catalyst (Figure 7).

The structural and textural properties of catalyst recorded by powder X-ray diffraction (Figure 8) which in that the presence of a six peaks assigned to (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), and (4 4 0) reflections verified the magnetite phase (JCPDS#01–075-0449) of Fe_3O_4.

The magnetic property of $Pd@Fe_3O_4$/AMOCAA was investigated using vibrating sample magnetometer (VSM) technique (Figure 9). More importantly, VSM measurements for Fe_3O_4 nanoparticles (77 emu g^{-1})[31] is higher than $Pd@Fe_3O_4$/AMOCAA (43.41 emu g^{-1}). Decrease in magnetic property of $Pd@Fe_3O_4$/AMOCAA is due to the immobilization of Pd complex on the surface of Fe_3O_4 nanoparticles.

As shown in TEM images, $Pd@Fe_3O_4$/AMOCAA nanocatalyst was made up of uniform quasi-spherical particles with a diameter range of about 30–40 nm (Figure 10).

3.2 | Catalytic activity

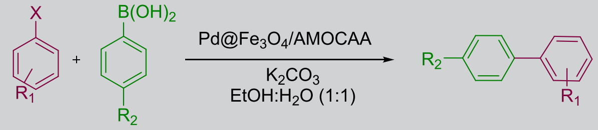
In the next step, the catalytic activity of $Pd@Fe_3O_4$/AMOCAA was studied. Considering the importance of the coupling reaction and the utility of biaryls for the synthesis of more biologically active compounds, the Suzuki reaction was targeted. Initially, a model reaction

TABLE 1 Optimization of the reaction conditions for Suzuki and Sonagashira coupling reaction catalyzed by $Pd@Fe_3O_4$/AMOCAA

Entry	Reactin Condition	Catalyst (g)	Suzuki/Sonagashira Time (h)		Suzuki/Sonagashira Yield (%)	
1	H_2O/r.t	0.02	4	3	73	70
2	EtOH/r.t	0.02	4	3	70	67
3	H_2O-EtOH/r.t	0.02	3.5	2.5	86	85
4	uloene/r.t	0.02	4	3.5	74	70
5	CH_3CN/r.t	0.02	3.5	3.5	71	69
6	H_2O-EtOH/50	0.02	3.2	2.5	95	93
7	H_2O-EtOH/80	0.02	2	1.8	100	97
8	H_2O/50 °C	0.02	3.5	3	85	80
9	H_2O/80 °C	0.02	3	2.5	95	92
10	EtOH/50 °C	0.02	4	3	83	80
11	EtOH/80 °C	0.02	3	2.5	92	90
12	Tuloene/80 °C	0.02	3.5	3.5	89	88
13	H_2O-EtOH/80 °C	0.01	3	3	97	94
14	H_2O-EtOH/80 °C	0.03	2	1.8	100	98

Reaction conditions: K_2CO_3 (3 mmol), $Pd@Fe_3O_4$/AMOCAA as catalyst, Solvent (5 ml).

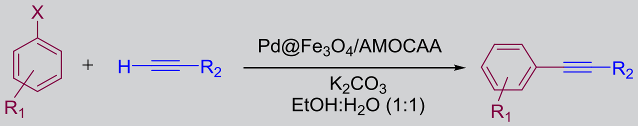
TABLE 2 Suzuki reaction of various aryl halides with aryl boronic acids catalyzed by Pd@Fe_3O_4/AMOCAA



Entry	R_1	R_2	X	Time (h)	Yield (%)[b]
1	H	H	I	1.5	100
2	H	H	Br	1.5	95
3	H	H	Cl	2.5	75
4	H	Me	I	1.5	90
5	H	Me	Br	3	79
6	H	Me	Cl	4	75
7	4-Me	H	I	1.5	99
8	4-Me	H	Br	1.5	96
9	4-Me	H	Cl	3	79
10	4-NO_2	H	I	1.5	98
11	4-NO_2	H	Br	2	96
12	4-NO_2	H	Cl	3	78
13	4-Me	Me	I	2	95
14	4-Me	Me	Br	3	60

Reaction conditions: Aryl boronic acid (1.2 mmol), Aryl halide (1 mmol), K_2CO_3 (3 mmol), Pd@Fe_3O_4/AMOCAA as catalyst, EtOH: H2O (5 ml), 80 °C.

TABLE 3 Pd@Fe_3O_4/AMOCAA catalyzed Sonogashira reaction of various halides with terminal alkynes



Entry	R_1	R_2	X	Time (h)	Yield (%)[b]
1	H	Ph	I	1	96
2	4-Me	Ph	I	1.2	91
3	4-MeO	Ph	I	1.2	90
4	4-NO_2	Ph	I	1	92
5	1-naphtalene	Ph	I	2	79
6	H	CH_2OH	I	1.5	89
7	4-Me	CH_2OH	I	1.8	93
8	4-MeO	CH_2OH	I	1.8	91
9	4-NO_2	CH_2OH	I	1.5	92
10	1-naphtalene	CH_2OH	I	2	85
11	H	Ph	Br	2	84
12	H	Ph	Cl	3	82

Reaction conditions: alkynes (1.2 mmol), Aryl halide (1 mmol), K_2CO_3 (3 mmol), Pd@Fe_3O_4/AMOCAA as catalyst, EtOH: H_2O (5 ml), 80 °C.

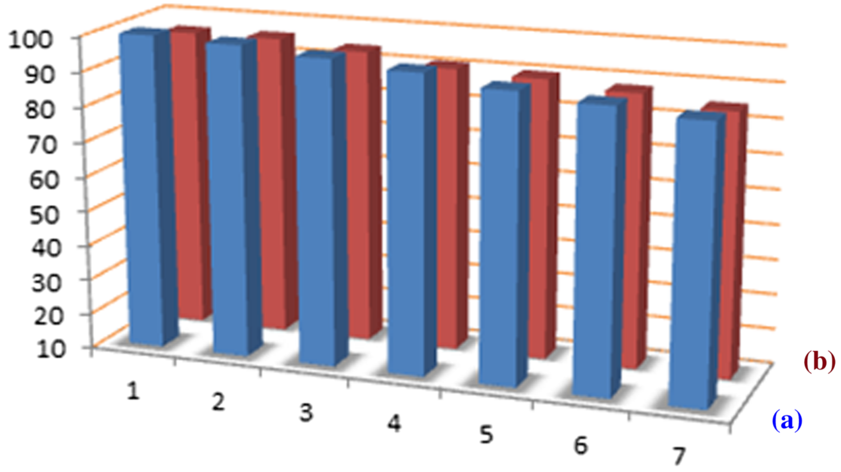


FIGURE 11 Recyclability of the $Pd@Fe_3O_4$/AMOCAA catalyst in the (a) Suzuki-Miyaura and (b) Sonogashira coupling reactions

of 4-bromotoluene and phenyl boronic acid was selected to optimize the catalyst amount, solvent, and the reaction condition. H_2O-EtOH (1:1) as the solvent showed the most favorable results among other tested solvents, EtOH, H_2O, Toluene, $CHCl_3$ and CH_3CN (Table 1). Besides, the best results were found in the presence of 0.02 g of the catalyst.

In the following, the catalytic activity of $Pd@Fe_3O_4$/AMOCAA was investigated for Sonogashira coupling reaction in the absence of copper co-catalyst. The reaction of iodobenzene and phenylacetylene was selected as a model reaction and performed in the presence of various solvents temperature, bases and the catalyst amount. In this reaction, the use of H_2O-EtOH (1:1) as the solvent, K_2CO_3 as the base, and 0.02 g of the catalyst resulted the high yield of the product.

Next, the generality of the presented protocol was investigated. For this purpose in Suzuki reaction, various substituted aryl halides and aryl boronic acids with different electronic properties, were applied as substrates. The results are summarized in Table 2.

With the optimized reaction conditions in hand, the generality of this methodology was confirmed in Sonogashira reaction by applying different alkynes and aryl halides. The results are summarized in Table 3.

3.3 | Catalyst recyclability

Finally, the recyclability of $Pd@Fe_3O_4$/AMOCAA aforementioned model Suzuki and Sonogashira cross-coupling reactions were studied. For the purpose, in both model reactions upon the completion of reactions the magnetic catalyst was easily separated using a simple magnet bar, washed with methanol and dried (at 60 °C, overnight) and then used in the next run of the reactions. The results of recycling of $Pd@Fe_3O_4$/AMOCAA after seven reaction runs is depicted in Figure 11. As can be realized after 7 runs no appreciated in loss of catalyst activity were observed. It was be found that the leaching of palladium from catalyst surface is very negligible in the Suzuki reaction. According to ICP-OES analysis, the exact amount of loaded palladium at least for six consecutive cycles was found to be 1.27 mmol g^{-1}.

4 | CONCLUSION

In conclusion, herein, we presented a new and recoverable catalyst, prepared by complexing Pd with coumarin-3-acetic acid derivative tailored magnetic nanoparticles and investigated its catalytic activity in the C-C bond formation reaction via two classical reactions, namely Suzuki and Sonogashira cross-coupling reactions. More importantly, the use of non-toxic and commercially available or easily accessible stating materials, easy recovery and potential recyclability, high yields in short reaction times, the operational simplicity, high activity and high stability have made this protocol suitable for industrial and pharmaceutical applications.in addition for executing in bench.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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