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FULL PAPER

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Synthesis and characterization of 4-AMTT-Pd(II) complex over $Fe_3O_4@SiO_2$ as supported nanocatalyst for Suzuki-Miyaura and Mizoroki-heck cross-coupling reactions in water

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Immobilization of Pd(II) nanoparticles on silica-coated modified magnetite particles has been readily achieved via a surface modification of Fe_3O_4 particles with 4-amino-5-methyl-4-H-1,2,4-triazole-3-thiol (4-AMTT) as a ligand. This magnetite nanocatalyst was characterized by various analyses such as FT-IR, SEM/EDX, ICP-AES, VSM, TEM, XRD, XPS and TGA. This nanocatalyst showed admirable catalytic activity for Suzuki-Miyaura and Mizoroki-Heck cross-coupling reactions under mild conditions in water, and could be simply separated by an outer magnet and reused for several times.

KEYWORDS
Heck, magnetite nanocatalyst, palladium, Suzuki, water

1 | INTRODUCTION

Palladium-catalyzed coupling reactions are adaptable and impressive methods for C-C bond creations.[1,2] Among them, the Mizoroki-Heck and Suzuki-Miyaura coupling reactions play significant roles in new synthetic chemistry.[3,4]

The original Suzuki and Heck reactions commonly progress in the presence of a homogeneous palladium catalyst, which makes its separation boring, if not inconceivable, and might cause unbearable palladium pollution of the products.[5–7] A way to conquer this obstacle would be the employ of a heterogeneous palladium catalyst.[8–14]

Expansion of recyclable and recoverable catalysts for industrial purposes has become essential from both the economic and environmental points of view. To attain this purpose, numerous catalysts have been immobilized or anchored on supports such as polystyrene,[15–20] chitosan,[8,21–24] silica,[22,25–27] clays,[28–30] molecular sieves,[31,32] carbon nanotubes[33,34] and activated carbon[34–36] could be simply separated from corresponding products and recovered without any waste of metal.

In modern organic synthesis, chemists have concentrated on the magnetic-based nanocatalysts[37–40] that are heterogeneous catalysts and have a higher surface area to volume ratio, which raises their selectivity and activity. In addition, these magnetic nanocatalysts permit too easy separation from the reaction admixture through an outer magnet that not only removes the requirement to onerous centrifugation and filtration routes but also decreases energy spending, catalyst waste and preserves time in attaining catalyst reusability.[41,42]

Fe_3O_4 (magnetite) has numerous uses in catalysis[41–47] but, its applications are finite by its propensity to collect around each other, capability to oxidation and low resistance in acidic media. Several policies have been discovered to protect these particles again oxidation and collection of Fe_3O_4 particles as masses, one of the most encouraging being the utilization of silica[48,49] as shielding material due to its bio adaptability and inertness, tremendous thermal and mechanical stability and convenient surface area with plenty Si-OH bonds.

Some kinds of magnetic nanomaterials have developed for the utilization of catalysis covering the procurement of nanocomposite materials including of magnetic core which have been covered by the shell of silica anchored catalytically active nanomaterials. For example this shell can cover by metal nanoparticles such as palladium nanoparticles. These nanoparticles have shown enormous options as catalysts for Heck and Suzuki coupling reactions.[50,51]

Despite all the progresses on catalyst context, organic solvents still stay the favored medium for performing Heck and Suzuki reactions. These solvents carry environmental concerns, lately, many endeavors have been directed towards employing water as solvent for these reaction. The employment of water as solvent in organic synthesis is a significant objective for the progress of environmentally sound chemical procedures. These distinctive features include non-toxic, low price, non-flammable, high availability, high dielectric constant and compatibility with environment.[52]

Nevertheless, among a lot of palladium catalyzed Suzuki and Heck reactions, there are a handful of cases have been reported that deal with these reactions in neat water.[16,17,20]

In this work, we report the synthesis of $Fe_3O_4@SiO_2$-4-AMTT-Pd(II) and its catalytic properties in Heck and Suzuki coupling reactions and its catalytic features under mild conditions in neat water as a solvent. The simple preparation of this nanocatalyst, its high stability toward air and adaptability with a broad range of aryl halides make it perfect catalytic option for Suzuki and Heck reactions in water (Scheme 1).

2 | RESULTS AND DISCUSSION

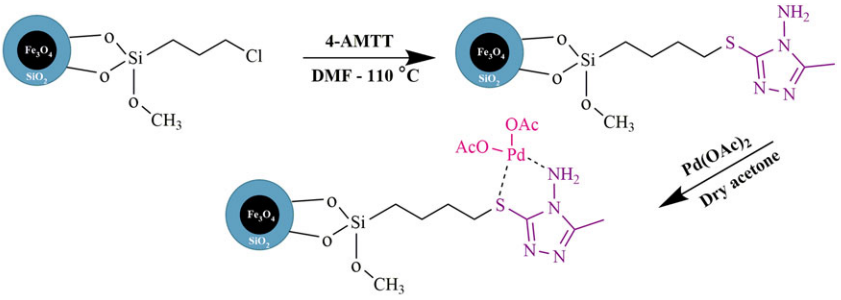
The $Fe_3O_4@SiO_2$-4-AMTT-Pd(II) nanocatalyst was prepared according the procedure shown in Scheme 1. The prepared catalyst was well characterized by FT-IR spectroscopy, XRD, VSM, TGA, SEM-EDX, TEM, XPS and ICP techniques.

The fourier transforms infrared (FT-IR) spectra of (a) Fe_3O_4, (b) $Fe_3O_4@SiO_2$ and (c) $Fe_3O_4@SiO_2$ modified by chloropropyltrimethoxysilane was shown in Figure S1 (in supplementary data). In Figure S1a, the band at 567 cm^{-1} is related to Fe-O bending vibration. The silica coating of magnetite particles was confirmed by observation of high-intensity band about 1100 cm^{-1} assigned to asymmetric stretching bonds of Si-O-Si and Si–OH stretching vibrations. The broad peak in range 3433 cm^{-1} is assigned to the O–H stretching vibration. In Figure 1c, a band at 680 cm^{-1} can be assigned to the C–Cl band. In FT-IR spectrum depicted in Figure S2a, the characteristic peaks of C = N stretching (1635 cm^{-1}), C-N stretching (1424 cm^{-1}), C-S stretching (619 cm^{-1}) vibrations are assignable to the $Fe_3O_4@SiO_2$-4-AMTT-Pd(II).[53,54] Finally signal characteristic of Pd–N vibrations detected in spectrum (Figure 2b) (471 cm^{-1}) confirm the structure of the catalyst. Because of the importance recover catalysts in chemical reactions, the ability to recover the catalyst was studied. As is clear from the infrared spectrum, catalyst before and after the five times recovery has not changed much and is relatively stable (Figure S3).

The X-ray diffraction patterns of $Fe_3O_4@SiO_2$-4-AMTT-Pd(II) is shown in Figure S4. XRD diffraction peaks at 2θ = 30.1°, 43.1°, 53.4°, 56.9° and 62.5° indicating that the Fe_3O_4 particles in the catalyst structure. The broad peak from 2θ = 15° to 27° ascribed to SiO_2. The XRD pattern confirms that Pd(II) is successfully loaded on the catalyst.[55]

The magnetic property of the synthesized nanocomposite was characterized by a vibrating sample magnetometer (VSM) and Figure S5 shows its typical magnetization curve. Ms (saturation magnetization) of Fe_3O_4 is 69.4 emu/g and the Ms of the nanocatalyst prepared in this study is ~18 emu/g. Because of the coating of MNPs with silica, the magnetization value of the catalyst is significantly lower than that of bare Fe_3O_4 particles.

Thermal analysis of the catalyst gives information about the stability of $Fe_3O_4@SiO_2$-4-AMTT-Pd(II) catalyst. In the TGA curve of catalyst (Figure S6b), the weight



SCHEME 1 Synthesis of $Fe_3O_4@SiO_2$-4-AMTT-Pd(II) nanocatalyst

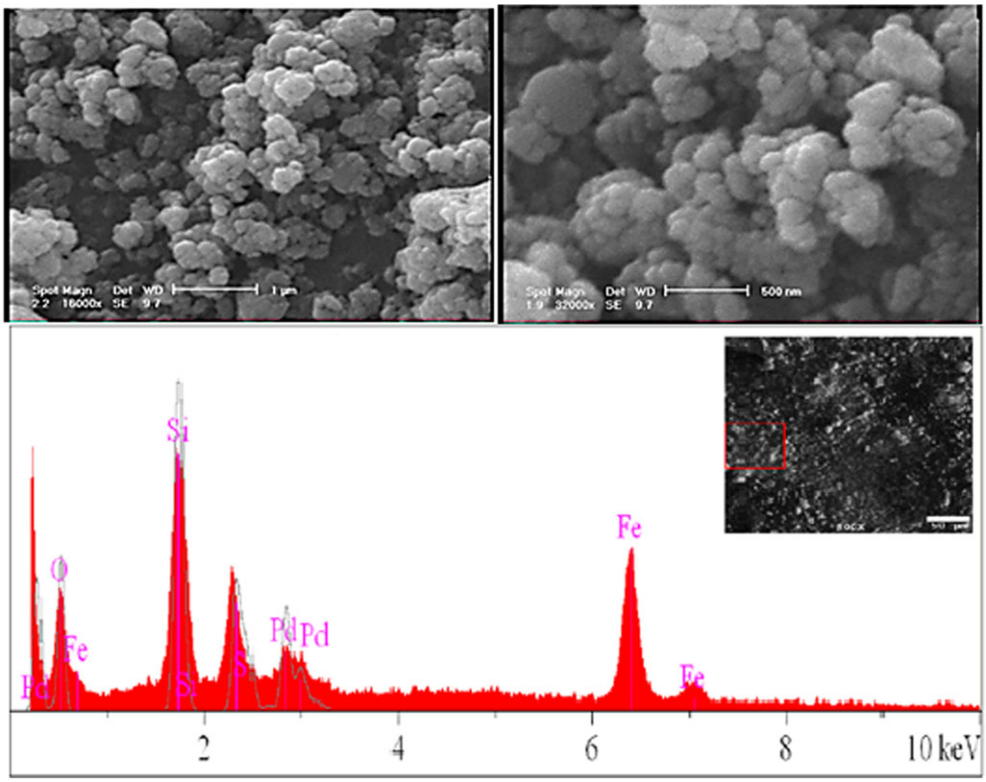


FIGURE 1 FE-SEM and SEM/EDX of $Fe_3O_4@SiO_2$-4-AMTT-Pd(II) nanocatalyst

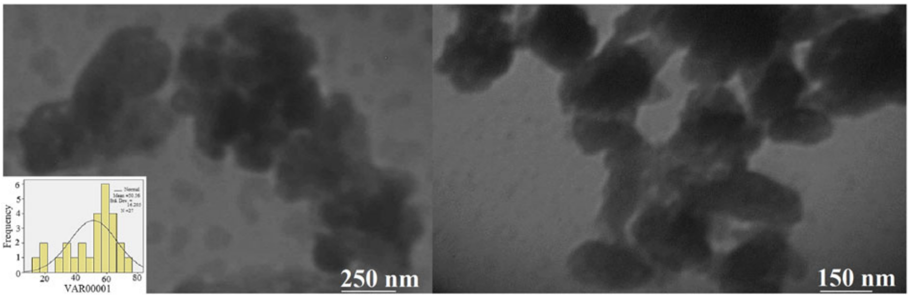


FIGURE 2 TEM images and histogram of $Fe_3O_4@SiO_2$-4-AMTT-Pd(II) nanocatalyst

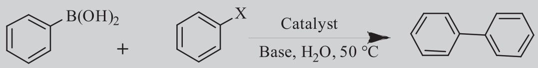
loss at temperatures below 200 °C is due to the removal of physically adsorbed solvent and surface hydroxyl groups. In the second step, at about 280 °C to nearly 555 °C is attributed to the decomposition of the coating organic layer in the nanocatalyst. Therefore, the weight loss between 280–555 °C gives the organic grafting ratios to the magnetic catalyst. Palladium XPS spectra of $Fe_3O_4@SiO_2$-4-AMTT-Pd(II) only shows the peaks of Pd(II) binding energy at 337.8 eV (Pd 3d5/2) and 343.0 eV (Pd 3d3/2) (Figure S7).

The FE-SEM images in Figure 1, show spherical external morphologies of the catalyst. The content of palladium was measured by inductively coupled plasma (ICP) analysis, it being 0.22 mmol g^{-1}. As clearly observed, according to the EDX spectrum (Figure 1), the presence of palladium is demonstrated in the $Fe_3O_4@SiO_2$-4-AMTT-Pd(II) catalyst. The EDX spectrum also indicates other elements, including Si, O and Fe, which are present in the catalyst substrate.

TEM images of $Fe_3O_4@SiO_2$-4-AMTT-Pd(II) catalyst showing the morphology of Pd nanoparticles on the magnetic silica support. The histogram indicating of the particle size distribution. The nanoparticle size is about 14–74 nm (Figure 2).

After characterizing the $Fe_3O_4@SiO_2$-4-AMTT-Pd(II) catalyst, its catalytic activity was examined in Mizoroki–Heck and Suzuki–Miyaura cross-coupling reactions. In initial study, the reaction between iodobenzene and bromobenzene as model substrates and phenylboronic acid in water at 50 °C for 2.5 h, was tested, and the effects of various conditions such as base, temperature, time and amount of the catalyst were compared (Table 1).

TABLE 1 Optimization of the conditions for Suzuki–Miyaura coupling reactions of iodobenzene and bromobenzene with phenylboronic acid[a]



Entry	X	Base	Catalyst (mol %)	Time (h)	Yield (%)[b]
1	I	Et_3N	0.1	2.5	95
2	I	Piperidine	0.1	2.5	94
3	I	Pyrrolidine	0.1	2.5	90
4	I	Pyridine	0.1	2.5	86
5	I	KOH	0.1	2.5	93
6	I	Na_2CO_3	0.1	2.5	95
7	I	K_2CO_3	0.1	2.5	99
8	I	K_2CO_3	0.05	2.5	79
9	I	K_2CO_3	0.07	2.5	85
10[c]	I	K_2CO_3	0.1	2.5	60
11	I	K_2CO_3	0.1	2.0	87
12	Br	K_2CO_3	0.1	2.5	50
13	Br	K_2CO_3	0.1	3.5	68
14	Br	K_2CO_3	0.1	4.5	68

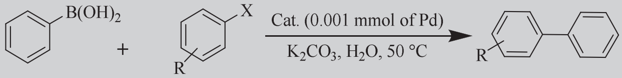
[a] Conditions: halobenzene (1.0 mmol), phenylboronic acide (1.2 mmol), base (2.0 mmol), H_2O (3.0 ml), 50 °C.

[b] GC yield.

[c] Reaction at 35 °C.

Optimization of the base was first performed using organic and inorganic bases under identical reaction conditions (Table 1, entries 1-7). It was found that among the tested bases best yield was obtained with K_2CO_3 (Table 1, entry 7). Then, the effect of different amounts of catalyst were studied (Table 1, entries 7-9), and it was found that the best value was 0.1 mol% of Pd (Table 1, entry 7). In continuation, the effects of

TABLE 2 Suzuki–Miyaura cross-coupling of aryl halides and phenylboronic acid in the presence of Fe_3O_4@SiO_2-4-AMTT-Pd(II) catalyst[a]

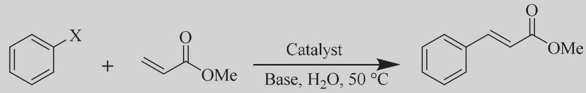


Entry	X	R	Time (h)	Yield (%)[b]
1	I	H	2.5	99
2	I	4-Br	2.5	98
3	I	4-OMe	2.5	98
4	Br	H	3.5	68
5	Br	4-NO_2	3.5	80
6	Br	3-NO_2	3.5	90
7	Br	4-OMe	3.5	60
8	Br	4-CN	3.5	90
9	Cl	H	4.5	52
10	Cl	4-NO_2	4.5	58
11	Cl	4-OMe	4.5	49

[a] Reaction conditions: aryl halide (1.0 mmol), phenyl boronic acid (1.2 mmol), K_2CO_3 (2.0 mmol), nanocatalyst (0.1 mol% Pd), H_2O (3.0 ml), 50 °C.

[b] GC yield.

TABLE 3 Optimization of reaction conditions for Mizoroki–heck reactions of iodobenzene and bromobenzene with methyl acrylate[a]



Entry	X	Base	Catalyst (mol%)	Time (h)	Yield (%)[b]
1	I	Pyridine	0.1	4.0	64
2	I	Et_3N	0.1	4.0	85
3	I	Piperidine	0.1	4.0	90
4	I	Pyrrolidine	0.1	4.0	74
5	I	Na_2CO_3	0.1	4.0	97
6	I	K_2CO_3	0.1	4.0	99
7	I	K_2CO_3	0.05	4.0	75
8	I	K_2CO_3	0.07	4.0	84
9[c]	I	K_2CO_3	0.1	4.0	70
10	I	K_2CO_3	0.1	3.0	82
11	Br	K_2CO_3	0.1	4.0	83
12	Br	K_2CO_3	0.1	5.0	95
13	Br	K_2CO_3	0.1	6.0	95

[a] Conditions: halobenzene (1.0 mmol), methyl acrylate (1.2 mmol), base (2.0 mmol), H_2O (3.0 ml), 50 °C.

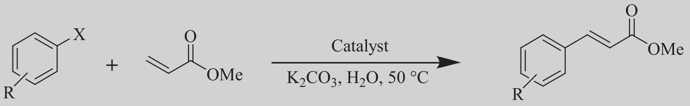
[b] GC yield.

[c] Reaction at 35 °C.

reaction temperature and time, were also investigated. When the reaction temperature was decreased, lower yield was achieved (Table 1, entry 10). As it can be seen, for bromobenzene a little more time under the optimized conditions was needed to obtain substantial yield (Table 1, entry 13).

After successful development of the optimal catalytic system, the nanocatalyst for the reaction of various aryl iodides, aryl bromides and aryl chlorides with phenylboronic acid under optimized conditions was applied. The results are summarized in Table 2. As clearly evident from Table 2, the coupling reactions of

TABLE 4 Scope of Mizoroki-heck cross-coupling reaction[a]



Entry	X	R	Time (h)	Yield (%)[b]
1	I	H	4	99
2	I	4-Br	4	97
3	I	4-OMe	4	92
4	I	4-CO_2Me	4	100
5	I	4-NO_2	4	100
6	Br	H	5	95
7	Br	4-NO_2	5	98
8	Br	4-OMe	5	90
9	Cl	H	6	83
10	Cl	4-NO_2	6	88
11	Cl	4-OMe	6	79

[a] Reaction conditions: aryl halide (1.0 mmol), methyl acrylate (1.2 mmol), K_2CO_3 (2.0 mmol), nanocatalyst (0.1 mol%), H_2O (3.0 ml), 50 °C.

[b] GC yield.

phenylboronic acid with electron withdrawing aryl halides in comparison to electron-donating groups was achieved better conversions. In addition, the aryl iodides and aryl bromides gave better yields of the aryl chlorides.

The activity of this catalytic system for the Mizoroki–Heck reaction was also investigated. In order to optimize reaction conditions, a reaction was studied by using methyl acrylate and aryl halides in the presence of various bases in water at 50 °C (Table 3). As it seems, the reaction in the presence of K_2CO_3 as base, the amount of catalyst 0.1 mol% of Pd, at 50 °C and 4 h, the best product formation results has indicated (Table 3, entry 6).

Under the optimized reaction conditions, the general applicability of the Fe_3O_4@SiO_2-4-AMTT-Pd(II) complex as a catalyst for Mizoroki–Heck reaction of methyl acrylate with different aryl halides containing electron withdrawing or donating substituents was explored. The results are shown in Table 4.

A comparison of the Suzuki-Miyaura and Mizoroki-Heck cross coupling reactions yields between homogeneous and heterogeneous Pd nanoparticles is shown homogeneous catalytic systems give higher yields of products but they have harsh conditions such as organic solvents or bases, high temperatures and high consumption of palladium salts.[56–58]

The recyclability of the solid catalyst was checked in the coupling of iodobenzene and 4-chloroanisole with phenylboronic acid under optimized conditions. After completion of each run, the catalyst was separated by external magnet, washed with water and acetone and reused. As shown in Table 5 the Fe_3O_4@SiO_2-4-AMTT-Pd(II) catalyst can be reused five times without significant loss of activity. Also, the catalyst reusability in Mizoroki–Heck reaction is shown in Table 6.

In order to explore whether the catalyst was behaving in a truly heterogeneous manner or palladium species dissolved in solution caused by leaching, mercury poisoning test were conducted with the model reactions in the optimum conditions (Table 1, entry 13 and Table 2, entry 12) by Fe_3O_4@SiO_2-4-AMTT-Pd(II). This model reactions was done for 1.75 h (for Suzuki reaction) and 2.5 h (for Heck reaction) without any mercury and yields for catalyst were 39% (for Suzuki reaction) and 52% (for Heck reaction). Then, 100 molar equivalents of mercury, relative to the Pd catalyst, was added separately in to the reactions and continued for another 1.75 h and 2.5 h. After the allowed time the expected products were obtained with 68% and 95% yields. This test showed that the mechanisms for both of reactions fallow a heterogeneous pathway.

TABLE 5 Reuse of catalyst system for Suzuki–Miyaura cross-coupling of iodobenzene with phenylboronic acid[a]

Run	1	2	3	4	5
Yield (%)[b, c]	99	99	95	93	92
Yield (%)[b, d]	49	48	45	43	40

[a] Reactions were carried out using 1.0 mmol of aryl halide, 1.2 mmol phenylboronic acid, 2.0 mmol K_2CO_3, nanocatalyst (0.1 mol%(, 3.0 ml water and 2.5 h for iodobenzene and 4.5 h for 4-chloroanisole at 50 °C.

[b] GC yield.

[c] Reaction was done with iodobenzene.

[d] Reaction was done with 4-chloroanisole.

TABLE 6 Recyclability of catalyst in Mizoroki-heck reaction[a]

Run	1	2	3	4	5
Yield (%)[b, c]	99	99	95	93	92
Yield (%)[b, d]	79	79	77	75	72

[a] Reaction carried out with Iodoobenzene (1.0 mmol), methyl acrylate (1.2 mmol), K_2CO_3 (2.0 mmol), nanocatalyst (0.1 mol%), H_2O (3.0 ml) and 4.0 h for iodobenzene and 6.0 h for 4-chloroanisole at 50 °C.

[b] GC yield.

[c] Reaction was done with iodobenzene.

[d] Reaction was done with 4-chloroanisole.

3 | CONCLUSIONS

In this work we have described synthesis and characterization of efficient, and air stable Fe_3O_4@SiO_2-4-AMTT-Pd(II) nanocatalyst and application of catalyst system for the Suzuki–Miyaura and Mizoroki–Heck cross-coupling reactions in mild and green conditions)water solvent and low temperature) were investigated. The desired products were obtained in good yields within short times. Also, the Fe_3O_4@SiO_2-4-AMTT-Pd(II) catalyst could be recovered easily by an external magnet without a significant loss of its catalytic activity. Moreover, almost low amount of palladium were used in reactions.

4 | EXPERIMENTAL

4.1 | Synthesis of Fe_3O_4@SiO_2-4-AMTT-Pd(II) catalyst

First, Fe_3O_4 nanoparticles were prepared by conventional co-precipitation of iron(II) sulphate and iron(III) chloride according to a reported procedure.[59] In the second step, to a mixture containing 1 g of Fe_3O_4, 20 ml water, 80 ml ethanol, 3 ml ammonia and 3 ml tetraethyl orthosilicate (TEOS) were added under reflux for 24 h to obtain MAGNPs-Silica core–shell materials.[60] Next, A mixture of SiO_2@Fe_3O_4 (1.0 g) in dry toluene (30 ml) was sonicated for 45 min. 3-chloropropyl trimethoxysilane

(0.9 ml) was added to the dispersed SiO_2@ Fe_3O_4 to in toluene and slowly heated to 105 °C. The reaction mixture was stirred at this temperature for 20 h. The resulting chloro-functionalized Fe_3O_4@SiO_2 was separated by an external magnet and washed several times with diethyl ether and CH_2Cl_2, and dried under vacuum.[61] For the preparation of supported 4-AMTT ligand, in a round-bottom flask equipped with mechanical stirrer and condenser, chloro-functionalized Fe_3O_4@SiO_2 (1.0 g) and 4-amino-5-methyl-4H-1,2,4-triazole-3-thiol (4-AMTT, 1.0 g, 7.68 mmol) was refluxed in DMF (40 ml) at 110 °C for 24 h. The residue was separated from the mixture using an external permanent magnet, washed several times with DMF and finally dried under vacuum. Finally, palladium acetate (0.5 g) dissolved in dry acetone was added a drop to the magnetic support and the mixture stirred for 10 hours at room temperature. Then, the resulting powder as the final catalyst was collected using an external permanent magnet and washed with dry acetone multiple times. Palladium content was determined 4.9% by ICP.

4.2 | General procedure for Suzuki cross-coupling reaction by Fe_3O_4@SiO_2-4-AMTT-Pd(II) nanocatalyst

A mixture of the aryl halide (1.0 mmol), phenyl boronic acid (1.2 mmol), K_2CO_3 (2.0 mmol) and catalyst (0.001 mmol of Pd) was added to water (3 ml) in a round-bottom flask equipped with condenser and was heated at 50 °C in an oil bath. The mixture was stirred continuously during the reaction and monitored by both TLC (n-hexan:ethyl acetate, 5:1) and gas chromatography (GC). After the reaction was complete, the mixture was cooled to room temperature and diluted with ethyl acetate and water. Then, the catalyst was separated using an external magnetic. The organic phase dried over $CaCl_2$, and the solvent was evaporated by rotary. The product was isolated by column chromatography (n-hexane:ethyl acetate, 5:1) to afford the corresponding products in yields of 49–99%.

4.3 | General procedure for Mizoroki–heck reaction by Fe_3O_4@SiO_2-4-AMTT-Pd(II) nanocatalyst

An aryl halide (1.0 mmol) and methyl acrylate (1.2 mmol) were added to a mixture of Fe_3O_4@SiO_2-4-AMTT-Pd(II) nanocatalyst (0.001 mmol of Pd), K_2CO_3 (2.0 mmol) and water (3 mL) in a glass flask equipped with a condenser and refluxed under conventional heating conditions while stirring vigorously and monitoring by both TLC (n-hexan: ethyl acetate, 3:1) and GC. After the reaction was complete, the mixture was cooled to room temperature and diluted with ethyl acetate and water. Then, the catalyst was separated using an external magnetic. The organic phase dried over $CaCl_2$, and the solvent was evaporated by rotary. The yields of products was measured by GC (conversion% of product*selectivity% of product) to afford the corresponding products in yields of 79–99%.

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