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REVIEW ARTICLE

SYNTHESIS OF MAGNETIC NANO CATALYST USING DOPAMINE FUNCTIONALIZED MAGNETIC NANO PARTICLES AND INVESTIGATION OF ITS PROPERTIES IN MIZOROKI–HECK CROSS-COUPLING REACTIONS

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ABSTRACT

A Pd(II) Schiff base complex as an efficient and highly heterogeneous catalyst was developed by immobilization of a palladium complex on the surface of modified Fe3O4 magnetite nanoparticles. These surface-modified nanoparticles were characterized using various techniques such asSEM, TEM, XRD, FT-IR, EDX and VSM. The palladium catalyst exhibited efficient catalytic activity in Suzuki-Miura coupling reactions. This method has notable advantages such as excellent chemoselectivity, mild reaction conditions, short reaction times and excellent yields. The yields of the products were in the range 75–85%. Also, the nanocatalyst can be easily recovered with a permanent magnet and reused at least five times without noticeable leaching or loss of its catalytic activity. The products obtained from the coupling reaction were first examined by TLC techniques and after confirmation were identified by FT-IR& NMR techniques.

KEYWORDS

Pd Catalysis, Heterogeneous Catalyst, Magnetic Nano Catalyst, Mizoroki–Heck, Dopamine

1. INTRODUCTION

Catalysis is becoming a strategic field of technology and science because it represents a new way to meet industry challenges, energy conversion and chemical synthesis. These challenges have always existed throughout history, which with the advancement of man, its scope become wider and the need to address these challenges in the modern world is more considerable (Liu, 2014; Amatore and Jutand, 2000; Hauer, 2020). Magnetic iron oxide and especially magnetite nanoparticles (Fe3O4) (NPs) have been widely used in magnetic recording media, magnetic adsorbents, fluids, targeted drug delivery, data storage and magnetic heterogeneous catalysts (Mizoroki et al., 1971; Mc Cartney and Guiry, 2011; Won et al., 2014; Hyeon, 2003; Xu, 2004; Keypour, 2015; Aghayee, 2016; Keypour, 2016; Keypour, 2017). Most heterogeneous catalysts are recovered from the reaction mixture by filtration or centrifugation. A method for better and easier separation of the magnetic catalysts from the reaction mixture created a successful perspective for the use of this type of catalyst. These catalysts are easily recovered from the reaction vessel by a magnet once the reaction is complete (Mahmoudi-GomYek, 2019; Knowles and Whiting, 2007; Comba, 2010; Gibson and Middleton, 1996; Link, 2004; Firmansjah and Fu, 2007).

In recent years, the prefix nano has more attentions in catalytic studies. Nano catalyst is a combination of two developed fields of catalyst and nano technology. Catalysts were among the first applications of nanotechnology on an industrial scale. The use of fine particles in heterogeneous catalysts reduces the volume of the catalyst and allows the optimal use of the active component. The researchers aim to produce catalysts with high activity and yield, full selectivity, the ability to separate and recover from the reaction mixture, low energy consumption and long life (Ebrahimiasl, 2020; Mahmoudiani, 2021; Ebrahimiasl, 2021; Balali, 2021).

Homogeneous catalysis is generally connected with the problem of separation and wasted inorganics which are too difficult to reuse. In addition, deactivation of soluble palladium complex catalysts by formation of inactive metal particles is often encountered at high reaction temperature. These problems could be principally mini- mized by a heterogeneously catalysed Suzuki reaction. Schiff base transition metal complexes have been extensively studied because of their potential use as catalysts in a wide range of reactions (Ballesteros, 2021; Beletskaya and Cheprakov, 2000; Gross et al., 2017). Dopamine (DA) is used as a stable anchor to provide functional molecules on the surface of iron oxide nanostructures, which due to having a free amine functional group, can be used with various substitutions to generation new catalysts (Shylesh et al., 2010; Polshettiwar and Varma, 2010; Scholefield et al., 1994; Huang, 2020). a cross-coupling reaction is one of the most important reactions in organic chemistry in which two fragments are joined together with the aid of a metal catalyst (Kambe et al., 2011; Bloome et al., 2011; Heck and Nolley, 1972; Nicolaou et al., 2005; Reetz and Westermann, 2000; Martin, 2014; Xiao et al., 2013). The palladium-catalyzed arylation of olefins, universally referred to as the “Heck reaction”, has received increasing attention in the past decade because it is a selective method for the formation of new C-C bonds in a single operational step (da Silva, 2019; Rawal and Iwasa, 1994; Zheng and Newman, 2021; Gil Santiago, 2022).

2. EXPERIMENTS

Synthesis of MNP were prepared by co-precipitation of ferric and ferrous salts under N2 gas. 2.70 g FeCl3 and 1 g of FeCl2 were dissolved into 50 mL of deoxygenated distilled water. After stirring for 60 minutes, chemical precipitation was achieved at 30oC under vigorous stirring by adding of 2 M NaOH solution under N2 gas to adjust pH 8-14. Complete precipitation of Fe3O4 occurred at pH between 8-14 (Hu et al., 2005). The reaction mixture stirs at 70oC for 5 h. the reaction mixture was cooled to room

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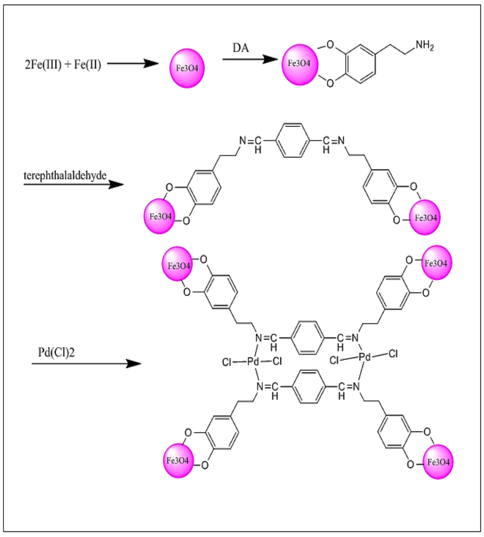
temperature and the precipitates were separated by a magnet and washed with Purified Water until pH neutral. Finally, MNP washed with acetone and dried in oven at 60-700C. The basis of this synthesis and the principles of mass balance of this reaction are as follows:

$Fe^{2+} + 2Fe^{3+} + 8OH^{-} \rightarrow Fe_3O_4 + 4H_2O$

For coating MNP by DA, 1g of MNP First were dispersed by Sonication and then under continuous stirring in 30 mL of 10 mM DA solution (pH=8.5) for 6 h. The polydopamine-modified MNP (Fe3O4 @ DA) were magnetically separated, washed several times with pure water to remove excess DA and then dispersed in 25 ml of water (Balali, 2021). About 1 gr ofFe3O4@DA nanoparticles in 25 ml dry ethanol was sonicated for 30 minutes and then 0.01 mole terephthalaldehyde was added and the mixture was heated at fixed temperature of 70°C for 24 h. The resulting nanoparticles were separated using a magnet and washed with ethanol (Rezaeivala and Keypour, 2014). Resulted Fe3O4@DA@terephthalaldehyde (1 g) was added to a solution of Pd(Cl)2 (0.100g) in Acetonitrile (30 mL) the. The mixture was stirred for 24 h at room temperature. Fe3O4@DA@terephthalaldehyde - Pd(Cl)2 was separated magnetically, washed consecutively by acetone and dried well under ambient temperature. In this study Fe3O4@DA@terephthalaldehyde-Pd(Cl)2 nano magnetic catalyst was used successfully as a recyclable catalyst for heterogeneous Mizoroki–Heck Reactions in aqueous media. The schematic pathways for preparing the Fe3O4@DA@terephthalaldehyde - Pd(Cl)2 nano magnetic catalyst are depicted in Scheme 1.



Scheme 1: Preparation of the Fe3O4@DA@terephthalaldehyde - Pd(Cl)2 nano magnetic catalyst.

SEM study reveals that synthesized nano catalyst is spherical. TEM analysis was performed for size and shape characterization (Figure1).

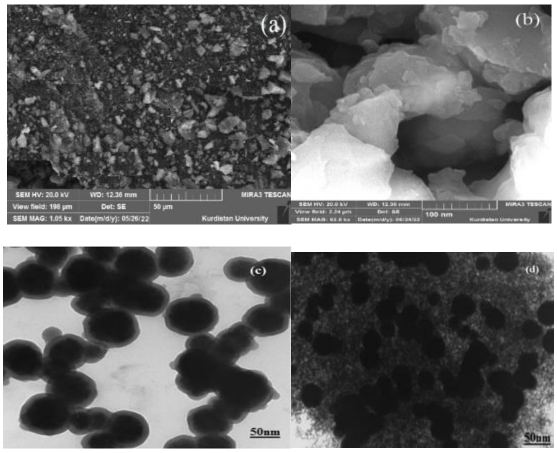


Figure 1: Shows SEM images of Fe3O4@DA (a), Fe3O4@DA@terephthalaldehyde - Pd(Cl)2 nano magnetic catalyst (b) TEM image of Fe3O4@DA (c) and Fe3O4@DA@terephthalaldehyde - Pd(Cl)2 nano magnetic catalyst (d)

The average particle size of sample was estimated according to Scherer's formula, $D= 0.9\lambda/\beta\cos\theta$, where λ is the wavelength of the incident X-ray (0.154 nm), β is the full width of peak at half maxima and θ is the Bragg's angle. The obtained value is 54 nm, consistent with the result measured from the SEM images (Figure 2).

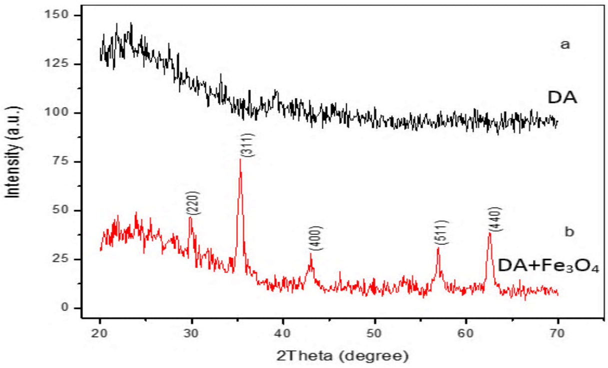


Figure 2: XRD diffractograms for magnetite nanoparticles Fe3O4

Successful synthesis of the Fe3O4@DA@terephthalaldehyde-Pd (Cl)2 nano magnetic catalyst from dopamine functionalization of the Fe3O4 nanoparticles can be inferred from FT-IR techniques (Figure3).

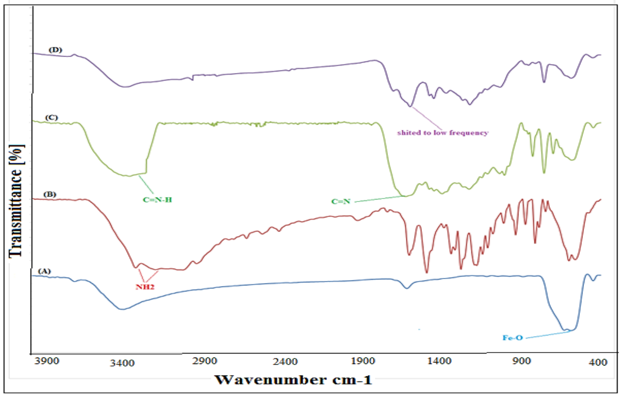


Figure 3: FT-IR of (a) Fe3O4 (b) Fe3O4 @Da (c) Fe3O4@DA@ terephthalaldehyde (d) Fe3O4@DA@terephthalaldehyde – Pd (Cl)2 nano magnetic catalyst.

Figure 3 (curve A) shows the FT-IR spectrum of magnetite nanoparticles Fe3O4. The signal observed at 587 cm−1 is attributed to the Fe-O bond vibration. In the case of Fe3O4@DA nanoparticles (curve B), two bands observed at 3342 and 3219 cm−1 related tofree NH2 on DA, indicate existence of a DA layer around the Fe3O4 nanoparticles. In the next curve (curve C) condensation of all the primary amino group is confirmed by the lack of N–H stretching bands in the IR region (3382 cm-1) and the presence of strong C=N (Schiff base) stretching bands at 1634 cm-1. In the final IR spectra (curve D) of both complexes show a sharp band in the range 1616 cm-1, attributed to (C=N), which is shifted to lower frequency compared to the free ligand (1643 cm-1). Altogether, the aforementioned results confirmed the formation of a DA schiff base with terephthalaldehyde - Pd(Cl)2 layer around the Fe3O4 nanoparticles.

In Figure 4 Energy-dispersive X-ray spectroscopy (EDX), Indicates the presence of elements used in this nano catalyst. The presence of the element gold is due to coating during identification.

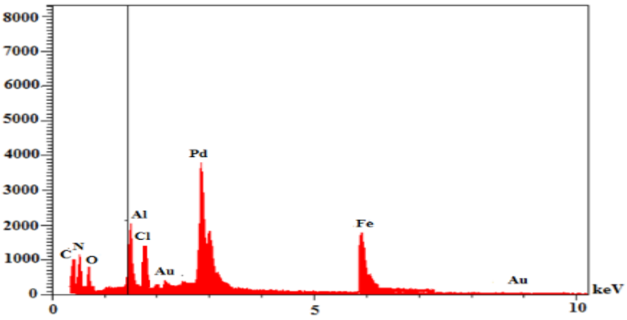


Figure 4: Energy-dispersive X-ray spectroscopy of Fe3O4@DA@terephthalaldehyde – Pd (Cl) 2 nano magnetic catalyst.

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In the case of synthetic nano catalyst, saturation magnetization of the samples was measured using a vibrating sample VSM technique. As it is clear in Figure 5 the magnetization curve is to be without hysteresis, the coercively field and remnant magnetization cannot be found from the curve. It indicates that Fe3O4 nanoparticles have super paramagnetic properties (Figure5). From the magnetization curve, we can also conclude that the saturation magnetization of the pure and modified Fe3O4 nanoparticles decrease from 62.36 to 42.54 emu/g. Thus, we believed that Fe3O4@DA@terephthalaldehyde-Pd (Cl)2 has successfully been synthesized and could be used as catalyst for the highly efficient system for Mizoroki–Heck Reactions proposed in this study.

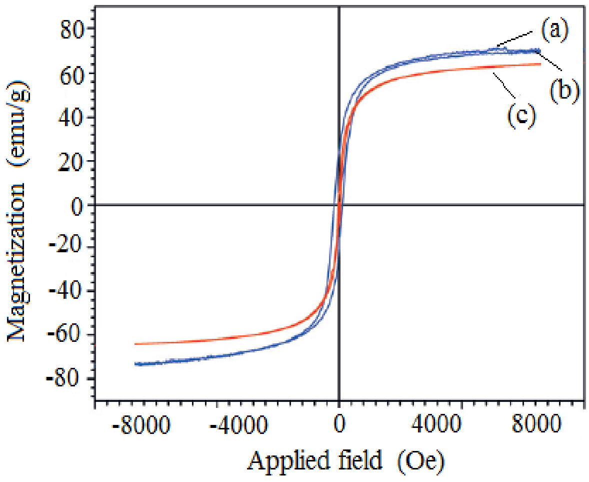


Figure 5: Typical room temperature magnetization curves of (A) Fe3O4, (B) Fe3O4@DA and (C) Fe3O4@DA@terephthalaldehyde – Pd (Cl)2 nanoparticles which characterized by a vibrating sample magnetometer (VSM).

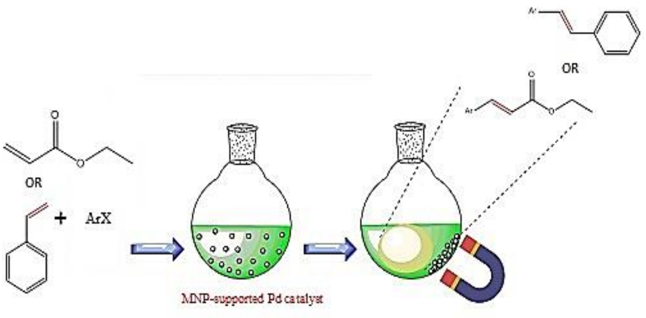
3. RESULTS AND DISCUSSION

3.1 Heck Coupling Reaction

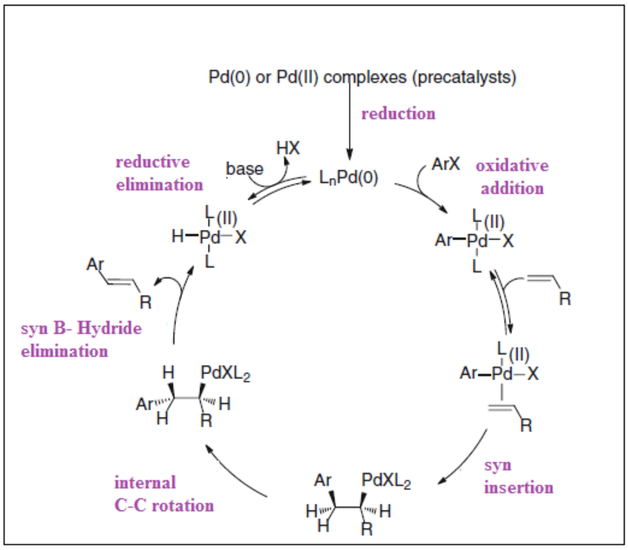
To a conical flask (50 ml) was added a mixture of bromobenzene (1 mmol), styrene (1.5 mmol), triethylamine (2 mmol), dimethylformamide (DMF; 3 ml) and Fe_3O_4@DA@terephthalaldehyde - Pd$(Cl)_2$ (5 mg = 0.0021 mmol Pd) and stirred at 110 °C for 5 h (the reaction was monitored by TLC). After completion of the reaction, the reaction mixture was cooled to room temperature and the catalyst was recovered by centrifugation and washed with ethyl acetate and ethanol. The combined organic layer was dried over anhydrous sodium sulfate and evaporated in a rotary evaporator under reduced pressure. The crude product was purified by column chromatography.

Heck (Mizoroki – Heck) reaction is one the most important reaction in organic chemistry which is used for alkenylation, or arylation of olefinic compounds in the presence of catalytic amounts of Pd (0)(Scheme 2) (Knowles and Whiting, 2007; Bloome et al., 2011; Polshettiwar, 2011; Oestreich, 2009; Phan et al., 2006). Pd (0) is an important and powerful functional catalyst that is used to form a carbon-carbon bonds, which in the absence of this catalyst formation of such bonds is impossible or very difficult (Korpany, 2013; Raganath and Glorius, 2011; Zeni and Larock, 2006). Complex molecular structures including asymmetric stereogenic centers that are very difficult to synthesize can be prepared quickly and efficiently by Heck reaction and in addition the reaction conditions used in this process can be wide range. Toleration of the functional groups and the reproducibility of this reaction is very high (Reetz and Westermann, 2000; Martin, 2014; Madin, 1999).

Scheme 3 shows a simplified sequence of events for the catalytic cycle of the Heck reaction. This cycle begins by the formation of a homogenous palladium (0) complex as the catalytically active species (generated in situ by the reduction of Pd(II) salts (Pd(Cl)2), or by employing a Pd(0) – precatalyst.



Scheme 2: Mizoroki –Heck cross-coupling reaction using a Magnetic Nano Catalyst as the precatalyst



Scheme 3: A general representation of the catalytic cycle for a homogenous Pd(0) species in the Mizoroki –Heck reaction

To optimize the reaction conditions, First we examined the model reactions of 4-bromobenzaldehyde with styrene and with ethyl acrylate (figure 6 curve 1-4).

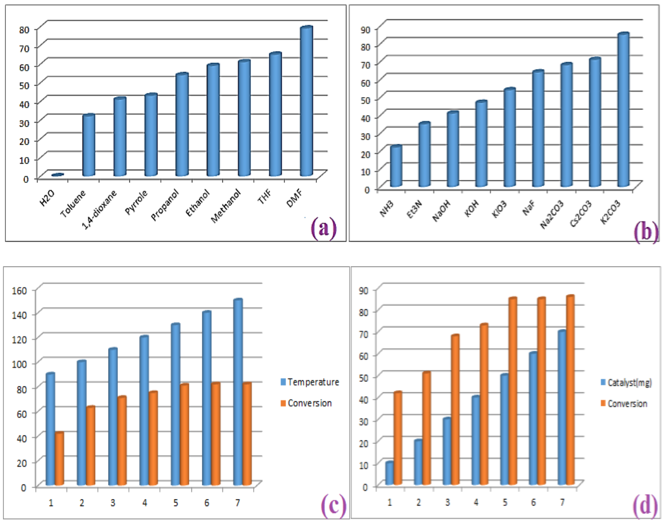
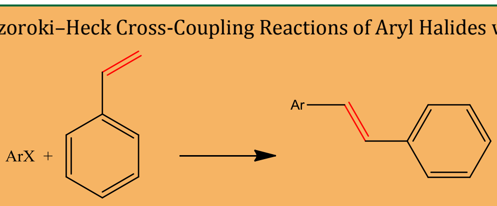
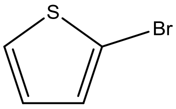
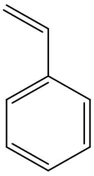
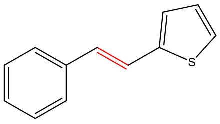
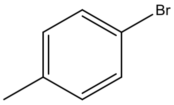
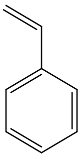
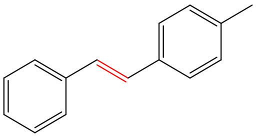
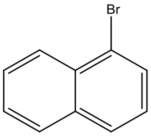
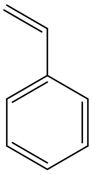
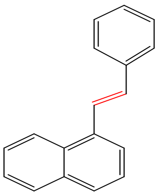
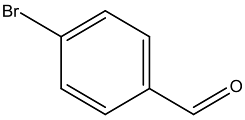
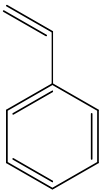
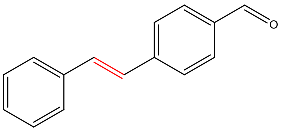
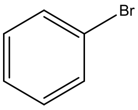
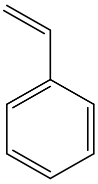
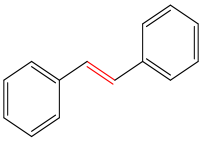
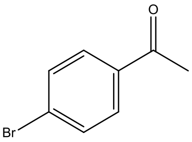
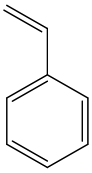
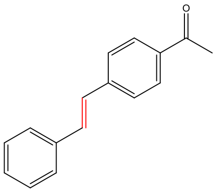
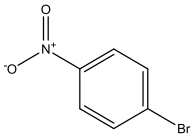
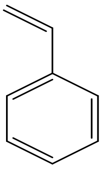
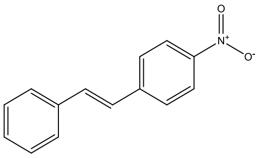


Figure 6: Curves optimize reaction conditions with model reactions of 4-bromobenzaldehyde with styrene to increase efficiency.

Based on the optimization results we selected DMF as solvent, K2CO3 as base, 50 mg of nano catalyst and reaction temperature 130 oC in this report. The catalytic activity of synthesized magnetic nano catalyst was tested in the palladium catalyzed arylation of olefins with different types of aryl halides under two different reaction conditions. In most cases, products were obtained in very good to excellent yields and >97% trans selectivity. Under the optimized reaction conditions, both electron-deficient and electron rich aryl bromides coupled cleanly in good to excellent yields (Table 1).

Table 1: Mizoroki–Heck Cross-Coupling Reactions of Aryl Halides with Styrene



Entry	ArX	R2CH=CH2	Product	Time(h)	Yield1 %
1				20	86
2				22	77
3				24	70
4				20	60
5				17	72
6				16	75
7				20	86

[1] Isolated yield

Employing the optimized reaction conditions, we next examined a variety of substituted Aryl halides having either an electron-releasing or an electron-withdrawing group (Table 2).

As shown in Table 2, all Aryl halides were rapidly converted to the corresponding Heck products with excellent yields, regardless of the electronic nature of the substituents.

[1] Isolated yield

To compare the catalytic properties of our modified magnetic nano catalyst with those of other catalysts reported in the literature, we investigated the results of the Heck-Mizoroki cross-coupling reactions between styrene and aryl halides in the presence of various catalysts and applying different temperatures. Table 3, represents the yields, the using solvents and the catalysts, and the reaction times. All these reactions were carried out in the DMF solution. In comparison to other used catalysts the shorter reaction time (0.5 h) as well the reasonable excellent yield (98%) reveals that the magnetic nano catalyst is a relevant catalyst for the Coupling reactions between styrene and aryl halides. Among all the example reactions in Table 3, the first row represents a reaction that is analogous to ours concerning reactants, product, temperature, and even the yields. However, our reaction is 48 times faster than the other one epitomizes that our new synthesized catalyst is more efficient. Moreover, this new Nano Catalyst is non-toxic, stable, cheap, and easy to separate and due to the large surface area of magnetic nano catalysts, it can be recycled easier and faster than the other reported catalysts.

Table 2: Mizoroki–Heck Cross-Coupling Reactions of Aryl Halides with Ethyl Acrylate

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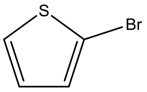
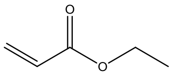
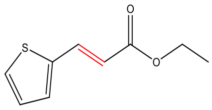
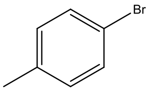
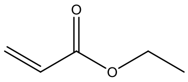
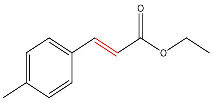
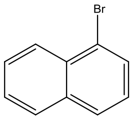
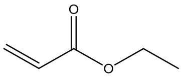
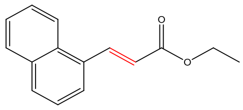
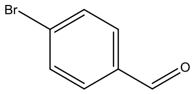
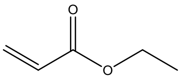
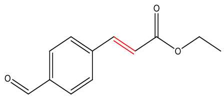
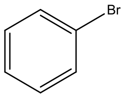
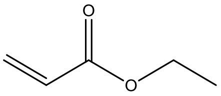
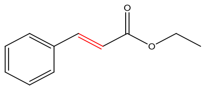
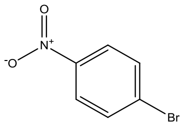
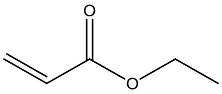
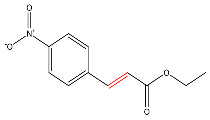
1				14	**89**
2				16	**79**
3				14	**88**
4				10	**92**
5				8	**82**
6				6	**86**

Table 3: Comparison of the Effect of Magnetic Nano Catalyst with Other Catalysts for the Mizoroki–Heck Cross-Coupling Reactions between Styrene and Aryl Halides.

Entry	Ar-Br+Olefines	Catalyst	Conditions	Time	Yield (%)	Ref.
1	Styrene+ 1-Bromo-4-methyl benzene	1,2,3- Triazol-5-ylidene-palladium Complex	NaOAc,DMA,1300C	24h	98	(Inomata, 2011)
2	Styrene+ Bromobenzene	N-Hetrocyclic carbine-Palladium (II) Complex	KOBu, H2O-1200C	8h	90	(Tang, 2011)
3	Styrene+ Bromobenzene	Binuclear Palladium(II) thioamide Complex	K2CO3, DMF,1500C	4h	97	(Raja et al., 2011)
4	Styrene+ 4-Bromobenzaldehyde	Palladacycle Complexes of bidentate phosphine ligands	K2CO3, DMF,1300C	4h	83	(Sabounchei and Ahmadi, 2013)
5	Styrene+ Bromobenzene	[(C ˆC)PdCl2]	NaOAc, DMA, 1750C	1h	100	(Lee, 2004)
6	Styrene+ 4-COMe-Ph-Br	[(N ˆ N)PdCl2]	LDA (TBAB), H2O, 1000C	4.5h	99	(Gil-Molto et al., 2005)
7	Styrene+ 4-Me-Ph-Br	[(P ˆ N)PdCl2]	Cs2CO3, DMF, [nBu4N]Br, 1400C,	4h	66	(Skarzynska and Gniewek, 2011)
8	Styrene+ Bromobenzene	[(C ˆ N)Pd(PPh3)Cl]	NaOAc, NMP, 1400C	24h	60	(Iyer and Jayanthi, 2001)
9	CO2-Me+ Bromobenzene	[(C ˆC)PdI2]	KF (TBAB), DMA, 1400C	30h	76	(Xu, 2005)
10	Styrene+ 1-Bromo-4-methyl benzene	magnetic nano catalyst	K2CO3, DMF, 130o C	0.5h	98	this work

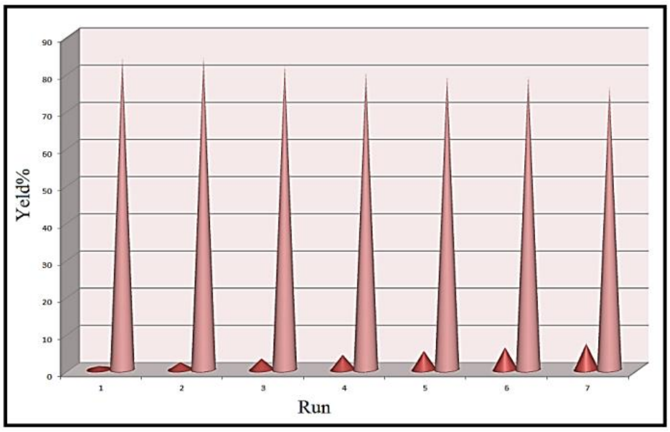


Figure 7: Recycling experiment of the MNP-supported Pd catalyst

Recycling and reuse of catalysts has become a prospect for the synthesis of longer-lasting catalysts due to their high manufacturing costs as well as environmental conditions. Once the reaction is complete, the magnetic nano catalysts can be easily separated from the reaction mixture by a magnet and used in subsequent reactions after washing with water and ethanol and drying in vacuo. More than 97% of catalysts can be recovered each time.

The recovery of magnetic nano catalysts in this study indicates a high-efficiency sequential application.

4. CONCLUSIONS

We have successfully prepared Fe3O4 MNPs and coated them with dopamine as organic shell via a co-precipitation method. A Pd (II) Schiff base complex has been immobilized on the MNPs through a surface modification of Fe3O4 with a Schiff base ligand. The catalyst was found to be easily reusable several times after recovery by separation and drying without significant catalytic deactivation which typically happens due to the leaching of active species or degradation of the structure. The Pd complex is a good heterogeneous catalyst for Heck coupling reaction between aryl halides (I, Br) and styrene. The synthesized nano catalyst was used in the Heck coupling reactions indicating a wide range of functional groups for the carbon-carbon coupling reaction.

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