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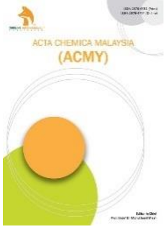

RESEARCH ARTICLE

ANCHORAGE OF PD INTO MODIFIED ISORETICULAR METAL–ORGANIC FRAMEWORK-3 AS A HETEROGENEOUS CATALYST FOR MIZOROKI–HECK CROSS-COUPLING REACTIONS

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ABSTRACT

In recent days, nanohybrid metal organic frameworks (MOF) have been considered as next generation catalysts due to their unique features like large surface to volume ratio, tailorable geometry, uniform pore sizes and homogeneous distribution of active sites. In this report, we address the thiophene-2-aldehyde modified 3D Zn-centred MOF IRMOF-3 following a post synthetic modification approach (schiff base IRMOF-3). Utilizing the excellent chelating ability of thiophene-2-aldehyd, Pd ions are immobilized over the host matrix MOF. The as-synthesized material was physicochemically characterized using a broad range of analytical techniques like FT-IR, electron microscopy, EDS, elemental mapping, and XRD. Subsequently the material has been catalytically employed in the classical Suzuki–Miyaura coupling towards the synthesis of diverse biphenyl derivatives at sustainable conditions. There are very few reports on the covalently modified MOFs towards the organic coupling reactions. The catalyst has been isolated by centrifugation and recycled in 10 consecutive runs with almost insignificant leaching and minute decrease in reactivity.

KEYWORDS

Metal–Organic Framework-3, Mizoroki–Heck cross-coupling, Postsynthetic

1. INTRODUCTION

Metal-organic frameworks (MOFs) have received considered attention and found a broad range of applications in various fields including catalysis in organic transformations, drug delivery, and hydrogen storage. These wide ranges of applications come from their unique architectures high specific surface area, large porosity, flexible pore structure, remarkable variety of functional groups selection, and easy structural functionalization (Huang, 2017). The design and synthesis of innovative molecular scaffolds with unique structural and biological properties to use in catalytic processes is an exciting subject (Konnerth, 2020). It is shown that MOFs could be possible candidates to plug the gap between homogeneous and heterogeneous catalysis (Wang, 2020). Schiff bases can incorporate a variety of metal ions so that they can be used in new catalysts synthesis (Ali, 2021).

Besides many applications of Palladium (Pd) such as in electronics, dentistry, medicine, hydrogen purification, chemical applications, groundwater treatment, and jewelry it is a well-known catalyst. It is a key component of fuel cells in which hydrogen reacts with oxygen to produce electricity, heat, and water (Wieser, 2013). One of the reaction mechanisms in which Pd compounds play the main role as a catalyst is the Heck reaction (also called the Mizoroki–Heck reaction). It is the chemical reaction of an unsaturated halide (or triflate) with an alkene in the presence of a base and a palladium catalyst (or palladium nanomaterial-based catalyst) to form a substituted alkene (Rezaeivala and Keypour, 2014). Reaction Mechanism involves organopalladium intermediates (Eddaoudi, 2002).

In recent years Heck cross-coupling reactions have been used in the pharmaceutical industry. Mizoroki-Heck cross-coupling reactions have emerged among the most direct and atom economical routes to internal alkenes that are important intermediates in the pharmaceutical, agrochemical, and polymer industries. The reactions are efficiently catalyzed by palladium complexes (Heck and Nolley, 1972; Yin and Liebs2007; Lyons and Sanford, 2010; Malgas-Enus, 2011; Xu et al., 2011; Jagtap, 2017; Christoffel and Ward, 2018; Mpungose, 2018). The reported catalytic systems involve various nitrogen and phosphorus-based ligands with a large scope of substrates under different experimental conditions (Blaser, 2001; Mansour, 2021). Palladium nanoparticles were also used efficiently to catalyze the coupling of aryl iodides with styrene derivatives (Muimhneachain and McGlacken, 2015; Jin, 2018; Ortiz, 2018; Li, 2019; Datta, 2019). The activity of the palladium catalysts, in these reactions, is connected to the feasible interchange between Pd(0) and Pd(II) or Pd(II) and Pd(IV) species (Muimhneachain and McGlacken, 2015). However, deactivation of the catalyst, lack of tolerance to some functional groups, and high sensitivity to air and moisture are some of the drawbacks.

Likewise, harsh conditions and high catalyst loading are common in these systems. Table 1 shows some examples of Heck cross-coupling utilizing in manufacturing valuable drugs. Palladium is the base element in all the used catalysts in the production of these materials. There have been a lot of efforts to prepare new organometallics based on Pallidum to achieve more effective catalysts. Chemical vapor deposition effectively was used to include Pd in the organometallic compounds. Sabo et al. deposited Pd into a highly porous MOF-5 by palladium acetoacetate in the $CHCl_3$ solution (Sabo, 2007). Park et al. prepared a highly dispersed Pd(II) in a MOF for C-H activation and functionalization of naphthalene (Hossain,

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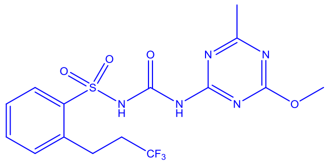
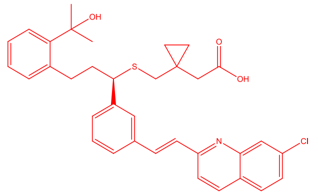
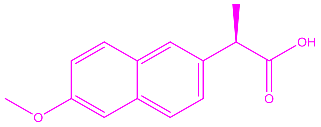
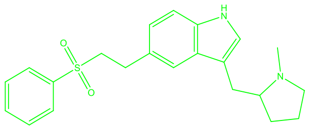
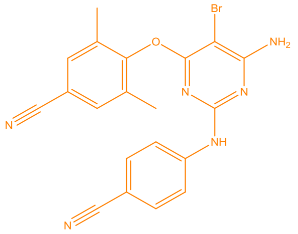
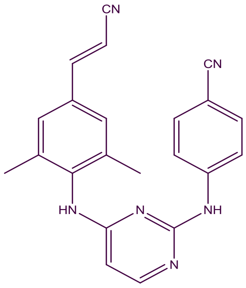
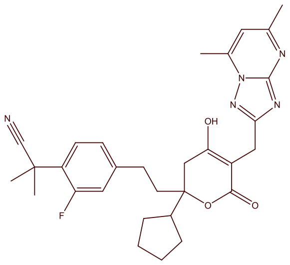
2013). Nuri et. al. deposited palladium acetate on the surface of IRMOF-3 to produce IRMOF-3 /Pd (II) and used it as a heterogeneous catalyst for the Heck coupling reaction (Nuri, 2019). In this study, new modified MOFs were synthesized and characterized. The synthesized MOFs were used for the post-synthetic Mizoroki–Heck reaction.

Table 1: Mizoroki–Heck Cross-Coupling Reactions in Pharmaceutical Industry

Structure & Name	Company	Use	Scale	Catalyst/Reaction Conditions	Reference
	Novartis	Herbicide	Multi – ton	Pd(dba)$_2$ 25 °C ton 200; TOF ca. 50 h^{-1}	(Blaser, 2001; Mansour, 2021; Muimhneachain and McGlacken, 2015; Jin, 2018; Ortiz, 2018; Li, 2019; Datta, 2019; Sabo, 2007; Hossain, 2013; Nuri, 2019; Budarin, 2010)
	Merck	Asthma Drug	-	Pd (OAC)$_2$ Et$_2$N, MeCN 85 °C	(King, 2001)
	Albermarle, Hoechst AG	Non-steroidal antiinflammatory drug	Multi – ton	PdCl$_2$, CuCl$_2$	(Blaser, 2001; Kiss, 2001; Siskin and Katritzky, 2000; Harrington and Lodewijk, 1997)
	Pfizer	Migraines	multi-kg	Pd (OAC)$_2$/ P(o-tolyl)$_3$ Et$_3$N, DMF, reflux 80% yield	(Li, 2004)
	Johnson & Johnson	HIV	6k L	Pd(OAc)$_2$/ Tri-*o*-toly-phoshine	(Camp, 2006; Budarin, 2010)
	Johnson & Johnson	HIV	6k L	Pd (OAc)$_2$, P(*o* tol)$_3$, Et$_3$N, CH$_3$CN, 150 °C	(Camp, 2006; King, 1993)
	Pfizer	Hepatitis C polymerase inhibitor	40 kg scale	Pd (OAC)$_2$ LiCl LiOAc Et$_3$N	(Guillemont, 2005)

2. EXPERIMENTAL

2.1 Catalyst Preparation

In this study, the traditional method was used for the Isoreticular metal-organic framework (IRMOF-3) preparation. In this case, 1.795 g $Zn(NO_3)_2{\cdot}6H_2O$ (6 mmol) and 0.370 g 2-Aminoterephthalic acid (2 mmol) was dissolved in 50 mL *N,N*-dimethylformamide (DMF), and sonicate for 30 min at room temperature (Keypour, 2000;Inomata, 2011; Tang, 2011). This solution was sealed and heated in the oven at 100 °C for 24 h. The obtained crystals were separated, washed three times with DMF and chloroform, then immersed into chloroform for 24 h to remove DMF guest molecules from the prepared IRMOF-3 and finally dried at 50 °C under reduced pressure (Scheme 1) (Eddaoudi, 2002).

The schiff base IRMOF-3 was synthesized according to the reported procedure (Keypour, 2000). A solution of 500 mg IRMOF-3 in 30 ml ethanol was added to a solution of 0.56 g (5.0 mmol) thiophene-2-aldehyde (T2A) in 20 ml dry ethanol allowing it to react at 70 °C for 24 h. Then the solvent was evaporated under reduced pressure by rotary. The resulting modified IRMOF-3 was filtered and washed three times frequently with ethanol. The modified IRMOF-3 was dried at room temperature for several hours. 400 mg of this product was dispersed in 30 ml acetonitrile using an ultrasonic bath for 30 min. In the next step, a yellow solution of $PdCl_2$ (40 mg) in 30 ml of acetonitrile was added to the dispersed modified IRMOF-3 and the mixture was stirred 24 h at room temperature. Finally, modified IRMOF-3 /Pd(II) was separated by decantation and washed successively with acetonitrile, ethanol, and acetone to remove the unattached substrates (Scheme 2).

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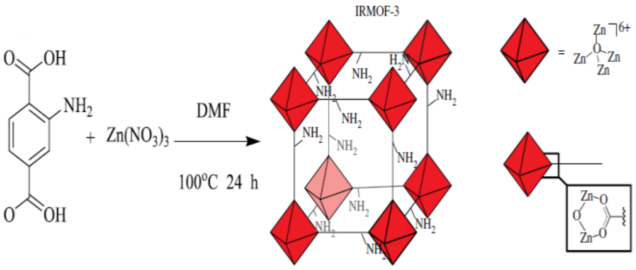
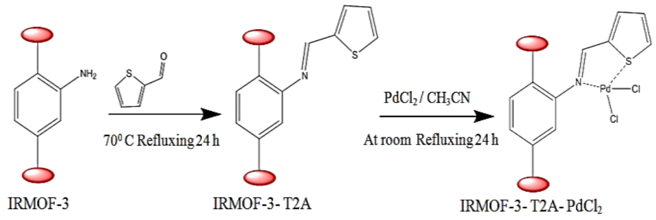


Scheme 1: The Reparation of IRMOF-3 Catalyst



Scheme 2: The Preparation of Modified IRMOF-3 /Pd (II) Catalyst

The prepared modified IRMOF-3/Pd (II) catalyst was characterized using Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), thermogravimetric analysis (TGA), scanning electron microscope (SEM), and energy-dispersive X-ray spectroscopy (EDX).

3. RESULTS AND DISCUSSION

3.1 Catalyst Characterization

3.1.1 FTIR Spectrum

The functional groups on the synthesized IRMOF-3/Pd(II) solid were investigated by FTIR spectroscopy which is shown in Figure 1. The FTIR spectrum of IRMOF-3 represented major stretching vibrations at 3400-3600 cm^{-1} (OH stretching) 1717 cm^{-1} (C=O stretching), 1690cm^{-1} (C=N). All these peaks show blueshifts as Pd comes in the complex in IRMOF-3-T2A- $PdCl_2$ reveals that the Pd complex is formed successfully.

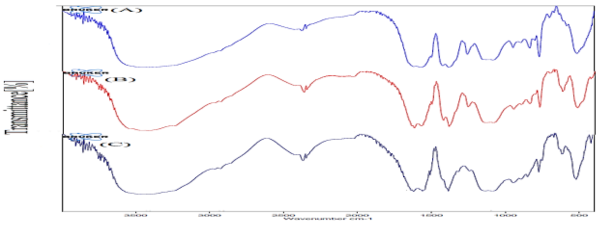


Figure 1: FTIR spectroscopy for IRMOF-3(A), IRMOF-3-T2A(B), IRMOF-3-T2A- $PdCl_2$(C)

3.1.2 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) spectrum was used to investigate the thermal stability of the prepared IRMOF-3 which is depicted in Figure 2. TGA shows a weight depletion up to 100 °C which can be related to the evaporation of water molecules from pores of MOF and aromatic groups. After this weight loss, the weight does not change up to 400 °C which shows high thermal stability for the synthesized IRMOF-3.

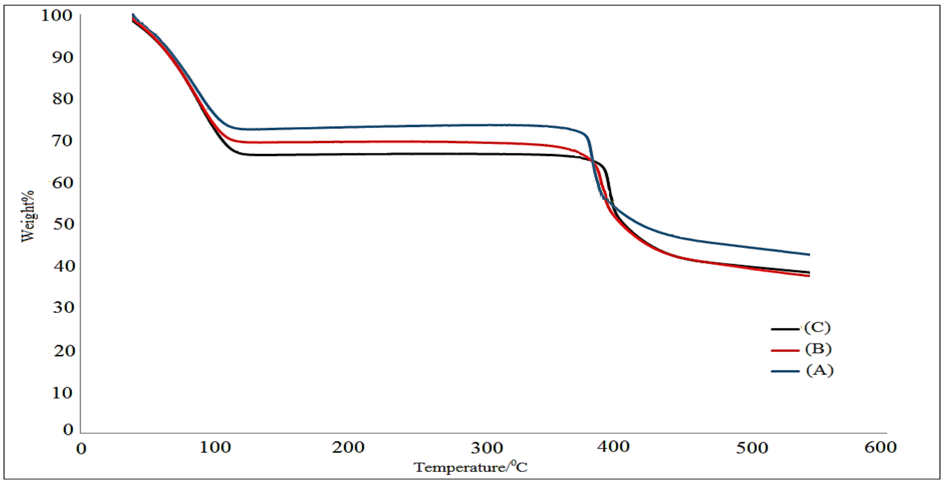


Figure 2: TGA for IRMOF-3(A), IRMOF-3-T2A(B), IRMOF-3-T2A- $PdCl_2$(C)

3.1.3 Scanning Electron Microscopy Analysis

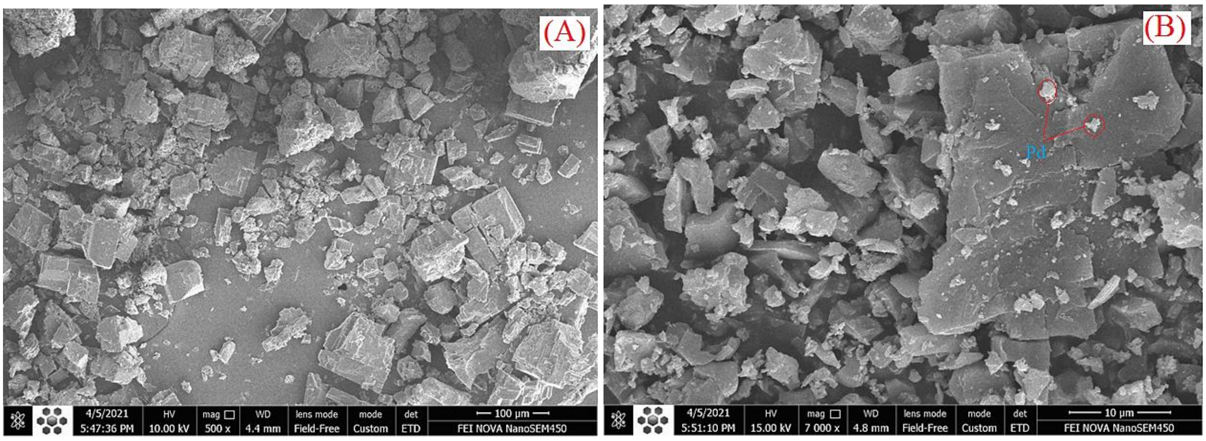


Figure 3: SEM of IRMOF-3(A), IRMOF-3-T2A- $PdCl_2$(B)

The morphology, shape, and size of the prepared modified IRMOF-3/Pd(II) catalyst were identified by field emission scanning electron microscopy (SEM) (Figure3). The structure of the IRMOF-3 catalyst shows uniform rough cubic crystals (Figure 3 A). These cubic structures have been partially destroyed after PdCl2 loading in IRMOF-3/Pd (II)

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3.1.4 Energy-Dispersive X-Ray Spectroscopy

To identify the elemental composition of IRMOF-3-T2A- $PdCl_2$ energy-dispersive X-ray spectroscopy (EDX) at random points on the surface of the MOF was performed (Figure 4). The EDX spectra of untreated IRMOF-3-T2A- $PdCl_2$ show the major peak of Carbon (C), Oxygen, (O), Nitrogen (N), Zinc (Zn) Chlorine (Cl), and Sulfur (S) elements. The intense peak of Pd is another proof of the successful formation of secondary palladium complex within cavities of IRMOF-3

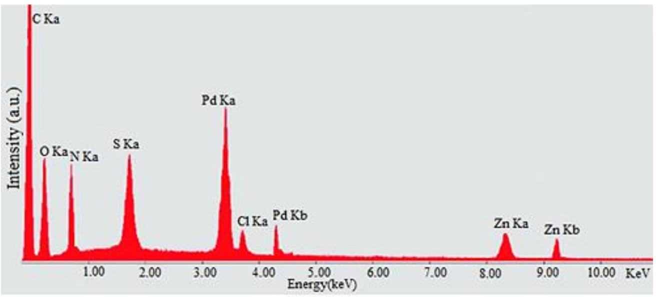


Figure 4: EDX spectra of IRMOF-3-T2A- $PdCl_2$

3.1.5 Powder X-Ray Diffraction

The Powder X-ray diffraction (PXRD) patterns of IRMOF-3 and modified IRMOF-3/Pd(II) are shown in (Figure 5). By increasing the lateral peaks and the stability of the main peaks during the synthesis steps, it is possible to realize the successful synthesis of the desired Nanocatalyst on the MOF. The large broad peaks located around 5° to 20° in XRD patterns of both compounds can be assigned to the IRMOF-3 diffraction peak. The diffraction angles appearing at 2θ= 44° indicating the $PdCl_2$ have been successfully loaded on the IRMOF-3. The mean size of Pd particles is around 40 nm and was calculated using the Debye-Scherrer formula.

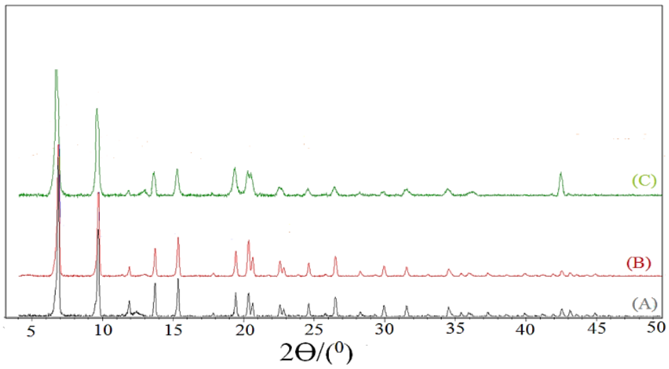
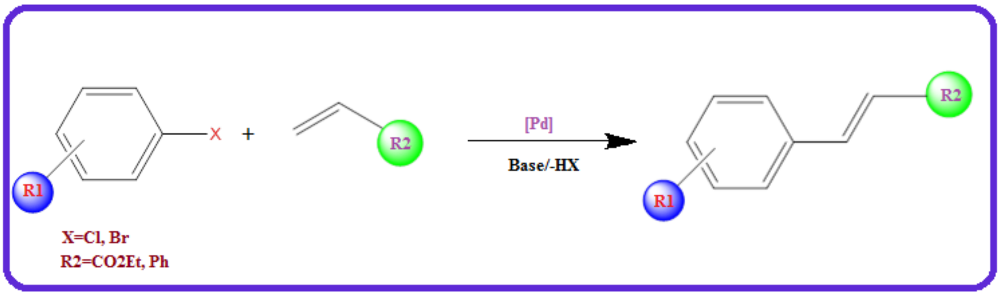


Figure 5: PXRD data for IRMOF-3(A), IRMOF-3-T2A(B), IRMOF-3-T2A-$PdCl_2$(C)

3.2 Optimization of the Conditions for Mizoroki –Heck Cross-Coupling Reaction

To optimize the reaction conditions for Mizoroki –Heck cross-coupling reaction, First, the model reactions of 4-bromobenzaldehyde with styrene and with ethyl acrylate (Scheme 3). was stated. The parameters that were investigated for this reaction include the base type, the solvent, the catalyst amount, and the reaction temperature. The higher yield in the desired time reveals better results. Based on Figures 6 A-D DMF was selected as the solvent, K_2CO_3 as the base, 50 mg of Nano catalyst, and the reaction temperature 130 ^oC as the optimized parameters for the further reactions.



Scheme 3: Mizoroki –Heck cross-coupling reaction using a modified IRMOF-3 /Pd(II) as the precatalyst

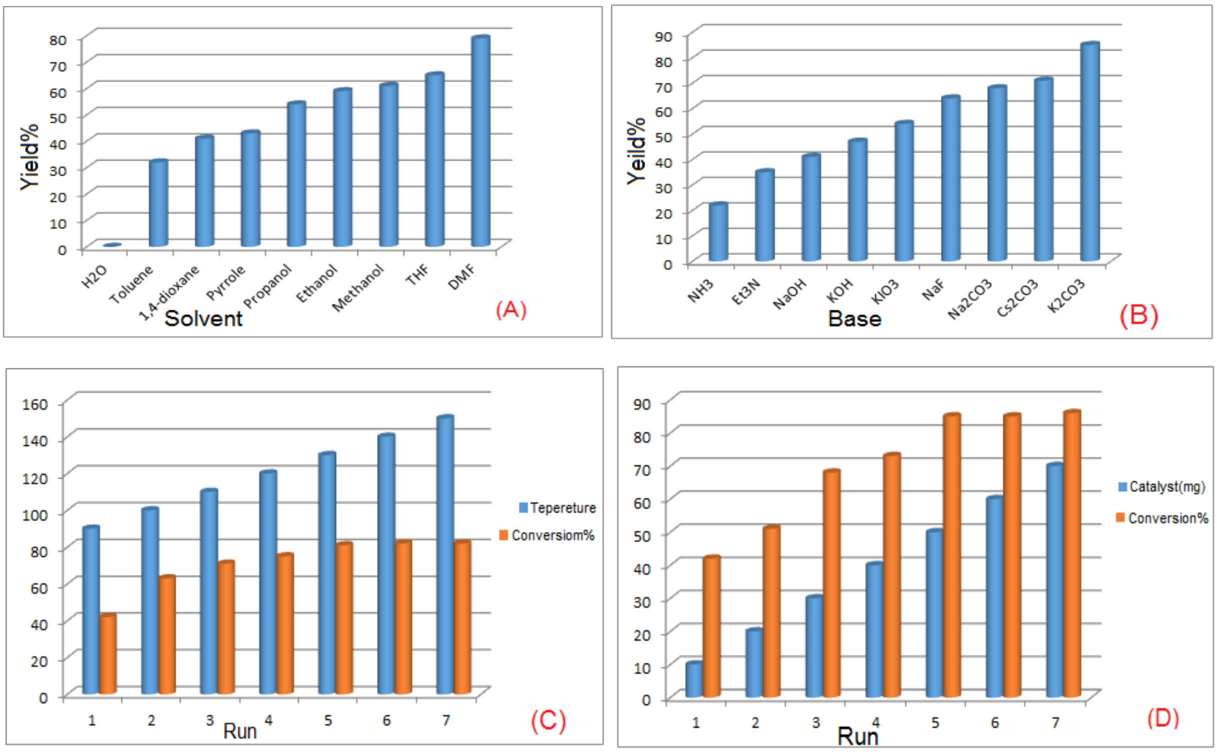


Figure 6: Curves optimize reaction conditions with model reactions of 4-bromobenzaldehyde with styrene to increase efficiency

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3.3 Study the Catalytic Activity of IRMOF-3/Pd(II)

The catalytic activity of synthesized modified IRMOF-3/Pd(II) catalyst was tested in the palladium-catalyzed arylation of olefins with different types of aryl halides under two different reaction conditions. Thus, the reaction of different aryl compounds (ArX) and two kinds of olefines i.e., styrene and ethyl acrylate have been studied and results are summarized in Tables 1 and 2 respectively. Moreover, the time needed for the reactions as well as the yields of each reaction is shown in these tables. The obtained reaction yields (higher than 95%) in the reasonably small times reveal that our synthesized MOF catalyst is fully optimized for these types of Heck reactions.

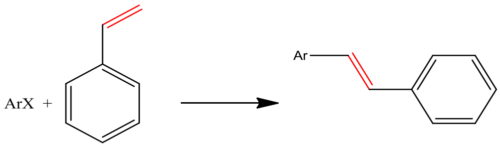
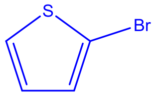
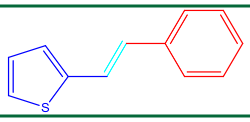
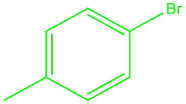
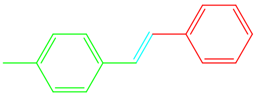
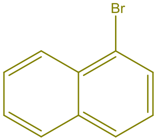
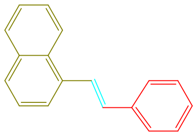
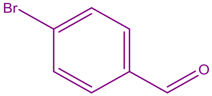
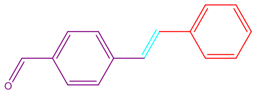
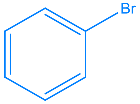
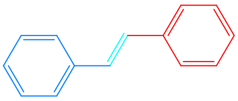
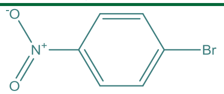
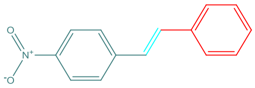


Table 2: Heck Cross-Coupling Reactions Between Aryl Halides and Styrene and Derivatives

ArX	Product	Time	Yield[1] %
		35min	98%
		30 min	98%
		30min	95%
		40min	95%
		35min	99%
		35min	95%

We also investigated a variety of substituted Aryl halides having either electron-releasing or electron-withdrawing groups (Table 3). All aryl halides were rapidly converted to the corresponding Heck products with excellent yields regardless of the electronic nature of the substituents.

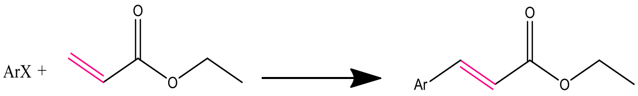
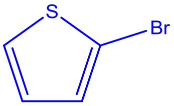
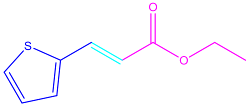
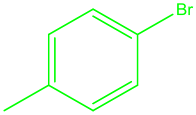
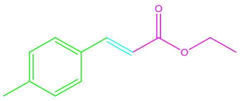
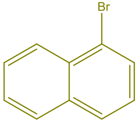
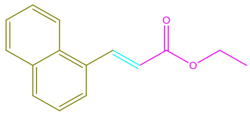
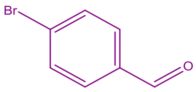
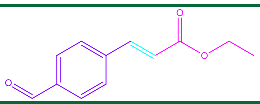
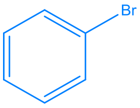
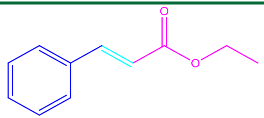
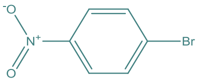
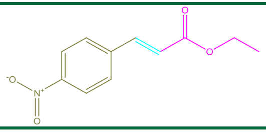


Table 3: Mizoroki–Heck Cross-Coupling Reactions of Aryl Halides with Ethyl Acrylate

ArX	Product	Time (min)	Yield[1] %
		30	95
		35	99
		35	97
		40	96
		30	95
		40	97

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3.4 Comparison of our IRMOF-3 /Pd(II) Catalyst with Other Catalysts in Heck Reactions.

To compare the catalytic properties of our modified IRMOF-3 /Pd (II) 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 4 represents the yields, the using solvents and the catalysts, and the reaction times. All these reactions were carried out in the DMF solution. In the comparison to other used catalysts the shorter reaction time (0.5 h) as well the reasonable excellent yield (98%) reveals that the IRMOF-3 /Pd(II) is a relevant catalyst for the Coupling reactions between styrene and aryl halides (Raja et al., 2011; Sabounchei and Ahmadi, 2013; Lee, 2004; Gil-Molto et al., 2005). Among all the example reactions in Table 4, 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 MOFs, it can be recycled easier and faster than the other reported catalysts (Skarzynska and Gniewek, 2011; Iyer and Jayanthi, 2001).

Table 4: Comparison of The Effect of IRMOF-3 /Pd(II) Catalyst with Other Catalysts for The Mizoroki–Heck Cross-Coupling Reactions Between Styrene and Aryl Halides.

Entry	Ar-Br+Olefines	Catalyst	Conditions	Time (h)	Yield (%)	Ref.
1	Styrene+ 1-Bromo-4-methyl benzene	1,2,3- Triazol-5-ylidene-palladium Complex	NaOAc,DMA,130^{0}C	24	98	[35]
2	Styrene+ Bromobenzene	N-Hetrocyclic carbine-Palladium (II) Complex	KOBu, H_2O-120^{0}C	8	90	[36]
3	Styrene+ Bromobenzene	Binuclear Palladium(II) thioamide Complex	K_2CO_3, DMF,150^{0}C	4	97	[37]
4	Styrene+ 4-Bromobenzaldehyde	Palladacycle Complexes of bidentate phosphine ligands	K_2CO_3, DMF,130^{0}C	4	83	[38]
5	Styrene+ Bromobenzene	$[(C\,\hat{}\,C)PdCl_2]$	NaOAc, DMA, 175^{0}C	1	100	[39]
6	Styrene+ 4-COMe-Ph-Br	$[(N\,\hat{}\,N)PdCl_2]$	LDA (TBAB), H_2O, 100^{0}C	4.5	99	[40]
7	Styrene+ 4-Me-Ph-Br	$[(P\,\hat{}\,N)PdCl_2]$	Cs_2CO_3, DMF, $[nBu_4N]Br$, 140^{0}C,	4	66	[41]
8	Styrene+ Bromobenzene	$[(C\,\hat{}\,N)Pd(PPh_3)Cl]$	NaOAc, NMP, 140^{0}C	24	60	[42]
9	CO_2-Me+ Bromobenzene	$[(C\,\hat{}\,C)PdI_2]$	KF (TBAB), DMA, 140^{0}C	30	76	[43]
10	Styrene+ 1-Bromo-4-methyl benzene	IRMOF-3/Pd(II) catalyst	K_2CO_3, DMF, 130^{o} C	0.5	98	this work

3.5 Recoverability and Recyclability

As the recycling and reusing of the catalysts have become a prospect for the synthesis of longer-lasting catalysts due to their high manufacturing costs as well as the environmental conditions, the modified IRMOF-3 /Pd(II) catalyst was easily separated from the reaction mixture by filtration, washed, and reused in subsequent reactions (Xu, 2005). The recycling and reusing of the catalyst were repeated 10 times and the results are summarized in Figure 7. Using a recycled catalyst smoothly reduces the catalyst efficiency however, achieving 88% production yield after 10 times usage, represents a high order of reproducibility of IRMOF-3 /Pd(II) catalyst.

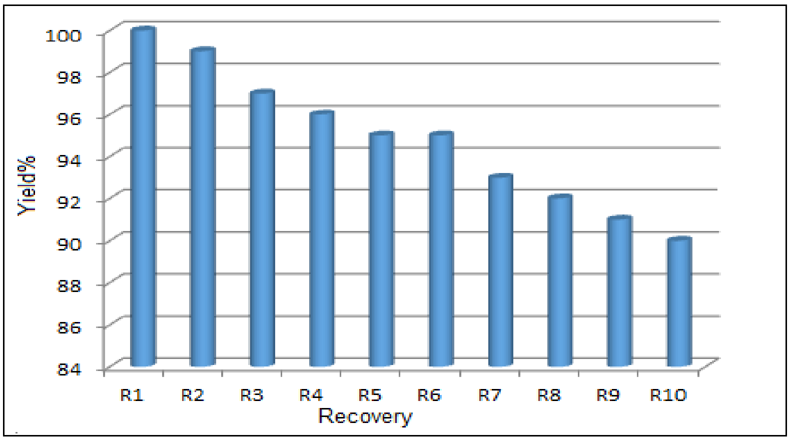

Figure 7: Recycling experiment of the modified IRMOF-3 /Pd(II) catalyst

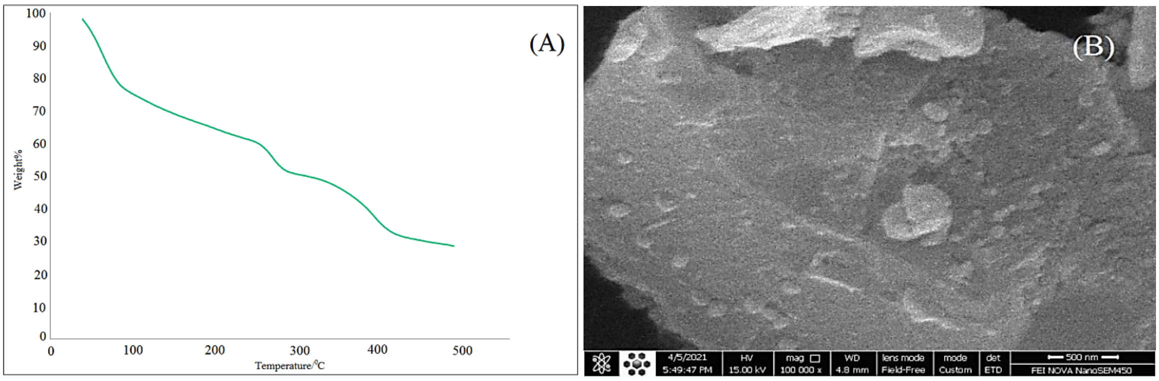

Figure 8: Thermo Gravimetric Analysis (TGA) for IRMOF-3 /Pd(II) catalyst after recovery (A) Scanning Electron Microscope (SEM) for IRMOF-3 /Pd(II) catalyst after recovery (B)

TGA and SEM analysis of the recycled IRMOF-3 /Pd(II) are shown in figure 8. The TGA curve of recycled IRMOF-3 /Pd(II) catalyst (Figure 8 A) is not analogous to the originally synthesized catalyst (Figure 2). The continuous weight loss of catalyst in the recovered catalyst is due to the impurities which were absorbed during the reactions and now release by increasing the temperature. The SEM (figure 8 B) shows only one crystalline grain of the recovered catalyst which is very analogous to the crystalline grains of the original crystal (Figure 3 B). Thus, we can conclude that despite impurity absorbed into the used catalyst the original crystalline structure does not change during its uses in the reaction.

After theoretical and experimental studies on these modified Nano polymers and proving their stability in reactions, it is necessary to use this class of compounds more than before.

4. CONCLUSION

In the present study, IRMOF-3 was prepared using the hydrothermal method. The post-modified IRMOF-3 /Pd(II) was synthesized by adding $PbCl_2$ to the suspension of IRMOF-3. The successful preparation of IRMOF-3 /Pd(II) was characterized by FT-IR, TGA, SEM, EDX, and XRD analysis. The synthetic IRMOF-3 /Pd(II) catalyst was used as the catalyst for a specific class of Mizoroki–Heck cross-coupling reactions. High efficiency and good quality recovery make this Nano catalyst popular.

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