

## **Low-amount Palladium supported on Fe-Cu MOF: Synergetic Effect between Pd, Cu and Fe in Sonogashira-Hagihara coupling reaction and Reduction of Organic Dyes**

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## **Abstract:**

FeCu MOF has been prepared via solvothermal method and the resulting bimetallic MOF was employed in the stabilization of Pd species. Obtained Pd(II)@NH<sub>2</sub>BDC-FeCu MOF could act as an effective environmental catalyst in Sonogashira-Hagihara coupling reaction and the reduction of organic dyes. This recyclable catalyst demonstrated high catalytic activity for Sonogashira-Hagihara reaction of aryl iodides and aryl bromides with alkynes. Rhodamine B and methyl red as organic dyes were instantly reduced (1 second). Pd(II)@NH<sub>2</sub>BDC-FeCu/MOF was characterized by TEM, XPS, FT-IR, BET, XRD, SEM, and <sup>13</sup>C, <sup>1</sup>H NMR spectrum. In addition, the synthesized catalyst was recyclable and reusable for 6 sequential times without deteriorating remarkable in catalytic performance for reaction of iodobenzene with phenylacetylene.

## **1. Introduction**

Stable catalytic processes by using transition metals [1] are necessary in environmental remediation at the large scale as well as in the formation of products such as pharmaceuticals, chemical and agrochemicals. Homogeneous palladium catalysts play a significant role in catalysis process, organic synthesis and transformations although less in environmental remediation [2]. However, the use of homogeneous palladium catalyst for large scale application is difficult due to having several disadvantages such as low thermal and chemical stability, high price, difficult separation and hard recovery from the reaction media [3]. Deficiencies of homogeneous catalysts can be eliminated by using their heterogeneous counterpart samples. To reach this target, various solid supports such as metal oxides [4], clay [5] and molecular sieves [6] and porous materials such as zeolites, CeO<sub>2</sub> [7-9], ZrO<sub>2</sub> [10], SiO<sub>2</sub> [11-15], activated carbon (AC) [16-20], metal-

organic frameworks (MOFs) have been employed as promising supports for palladium incorporation and resulting material considered as suitable platforms for producing catalytic heterogeneous systems in which Pd species act as the active species [21].

Metal organic frameworks (MOFs) as new class of nanoporous compounds have been widely examined due to their unique properties such as tunable pore sizes, high surface areas and thermal stability. Owing to these prominent properties, MOFs presented broadly application in environmental remediation including gas storage [22], adsorption [23], molecules separation [24-25], catalysis [26-30] and drug delivery [31]. MOFs supported Pd catalysts have been reported in different C-C coupling reaction such Suzuki-Miyaura, Sonogashira-Hagihara, Mizoroki-Heck reactions, hydrogenation reaction, *N*-alkylation of amines with alcohols [32-37].

Azo dyes are compounds widely found in wastewaters, constituting a serious threat for the environment. The dyes utilized in different industries are toxic for aquatic organisms due to chemical and biological stability and usually it is hard to eliminate them by natural degradation methods [38-42]. Recently, several suitable techniques for remove of these pollutants have been developed by researchers [43-47]. Reduction process of these dangerous pollutants in the presence of metal ions or nanoparticles as the catalyst and hydrogen sources is one of the commonly used approaches [48-49]. Along this line, noble metal nanoparticles or ions such as gold, silver, platinum and palladium have received remarkable attention for application in diverse fields such as organic dyes reduction [50-53].

Sonogashira-Hagihara coupling reaction have received much attention as an important synthetic technique for constructing of C (sp<sup>2</sup>)-C (sp) bond via the coupling between of aryl halides with terminal alkynes. The achieved derivatives of their products are broadly utilized in the preparation of natural and pharmaceutical products [54-55], polymer compounds [56] and material science

[57-59]. Traditional procedure for Sonogashira-Hagihara coupling reaction performed by using palladium catalysis as well as copper salts as co-catalyst [60–70] which mostly in presence of various ligands or additives under homogeneous conditions occurred to obtain higher yield of the desired products [71]. In spite of various reported copper-free Sonogashira-Hagihara reaction catalyzed by Pd, it is proved that existence of Cu can promote reactions to proceed under efficient and mild conditions. Due to new electronic and chemical properties of bimetallic catalysts resulting from synergistic effect between various metal ions, recently, increasing attentions have been paid to design and synthesis of different bimetallic or multimetallic catalysts in different organic transformations [72-75]. MOFs having active metal species are excellent candidate for stabilization of other active metals to produce active bimetallic or trimetallic catalysts in different organic transformation. The resulting bimetallic or trimetallic MOFs often exhibited superior activity, surface area and stability in comparison with single-metal MOFs. Hence, researchers employed BMOF as promising support for the stabilization of palladium active species [76-79].

Herein, preparation of Pd(II)@NH<sub>2</sub>BDC-FeCu MOF via the immobilization of Pd on the surface of NH<sub>2</sub>BDC-FeCu MOF and its application as an active and efficient environmental heterogeneous catalyst in Sonogashira-Hagihara couplings and the reduction of organic dyes.

## **2. Experimental**

### **2.1. Materials**

Copper (II) chloride hexahydrate (CuCl<sub>2</sub>.6H<sub>2</sub>O, 99%), Palladium chloride (PdCl<sub>2</sub>), Iron (III) chloride hexahydrate (FeCl<sub>3</sub>.6H<sub>2</sub>O, 99%), 2-Aminotherephthalic acid (NH<sub>2</sub>-BDC,99%), aryl halides, phenylacetylene , Rhodamine B (RhB), Methyl red (MR), sodium borohydride (NaBH<sub>4</sub>)

and *N,N*-dimethylformamide (DMF, 99.9%) prepared from Merck Millipore-Sigma, Sigma-Aldrich, and Acros .

## 2.2. Preparation of NH<sub>2</sub>BDC-FeCu MOF

FeCl<sub>3</sub>.6H<sub>2</sub>O (1 mmol, 270.3 mg) and CuCl<sub>2</sub>.6H<sub>2</sub>O (1 mmol, 170.5 mg) were dissolved in 7 mL DMF and in another flask, 2-aminoterephthalic acid (1 mmol, 181.1 mg) was dissolved in 7 mL DMF. Two solutions were mixed together and then, 1 mL EtOH was added. The resulting solution was stirred for 20 min at room temperature and then sonicated for 15 min. Afterward the solution was transferred into a 50 mL Teflon-lined autoclave and heated at 150°C for 24 h. The brown product was separated by using centrifugation, washed with DMF and absolute ethanol for three times. In the next stage, pure product was achieved via a dissolving in 50 mL DMF and refluxed in 153 °C to remove the excess of ligands. At the end, final product was filtered and washed with DMF and ethanol for 3 times and then dried in vacuum oven at 70 °C in 24 h.

## 2.3. Preparation of Pd@NH<sub>2</sub>BDC-FeCu/MOF

0.3 g of the prepared NH<sub>2</sub>BDC-FeCu MOF was dissolved in 20 mL of DMF and sonicated for 5 min. In another flask, 6 mg PdCl<sub>2</sub> dissolve in 2 mL DMF by sonicate assistance. Then, palladium solution was added dropwise to the MOF solution during 20 min. Next, mixture was stirred at 80 °C for 20 h. In last step, mixture was centrifuged and resulting solid was washed with DMF and absolute ethanol and dried in vacuum oven at 70 °C for 10 h.

## 2.4. General method for Sonogashira-Hagihara coupling reaction

ArX (0.5 mmol), Pd@NH<sub>2</sub>BDC-FeCu MOF catalyst (17.5 mg, for ArI and 25 mg for ArBr), DABCO (0.75 mmol, 168 mg) and DMF (2 mL) were added to a flask under argon

atmosphere. The alkyne (0.8 mmol) was then added and the reaction mixture was stirred at 60°C for aryl iodides and 80 °C for aryl bromides. Progress of reactions was monitored by GC. After completion of the reaction, the reaction mixture was cooled down to room temperature and the organic phase was washed with H<sub>2</sub>O (6 mL) and crude product extracted with ethyl acetate (3×5 mL). The pure product was achieved by column or plate chromatography using hexane and ethyl acetate.

### **2.5. General method for the reduction of RhB and MR**

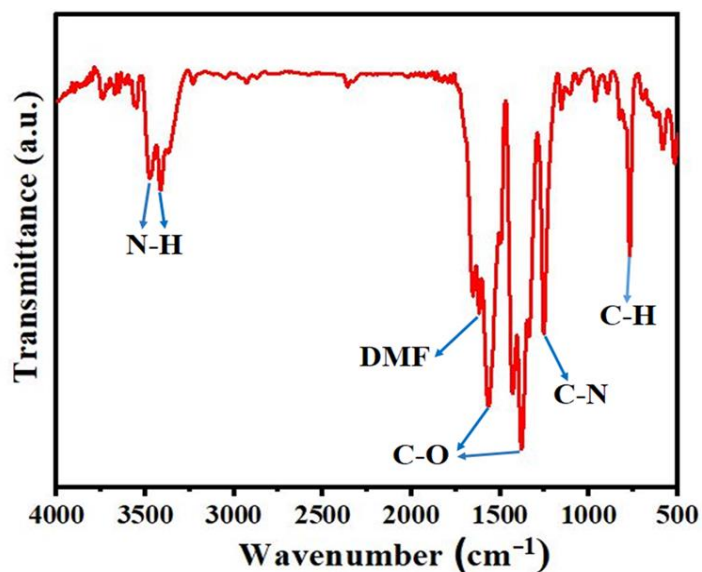
3 ml of RhB or MR aqueous solution (0.05 mM), 0.5 ml of NaBH<sub>4</sub> aqueous solution (0.05 mM) and catalyst (1 mg) were added to a quartz cuvette and desired mixture stirred at room temperature. The progress of the reaction was recorded by UV–Visible spectroscopy.

## **3. Result and Discussion**

### **3.1. Characterization of Pd@NH<sub>2</sub>-BDC-FeCu MOF**

FT-IR analysis is conducted to identify the chemical structure of the prepared Pd@NH<sub>2</sub>BDC-FeCu MOF in the range of 500 to 4000 cm<sup>-1</sup> (Fig. 1). The appeared peaks at 3460 and 3334 cm<sup>-1</sup> related to asymmetric and symmetric vibration of the amino groups [80]. Generally, 2-aminoterephthalic acid ligand exhibits a broad peak at 2970 cm<sup>-1</sup>, due to the existence of –OH group [81]. Hence, after synthesis of desired MOF, the stretching vibration peak of –OH disappeared, confirming the coordination between desired metals and –COOH group of 2-aminoterephthalic acid. The absence of a peak ca. 1677 cm<sup>-1</sup> also indicated the absence of any unreacted 2-aminoterephthalic acid ligand. The vibration peak of C–H assigned to the benzene ring

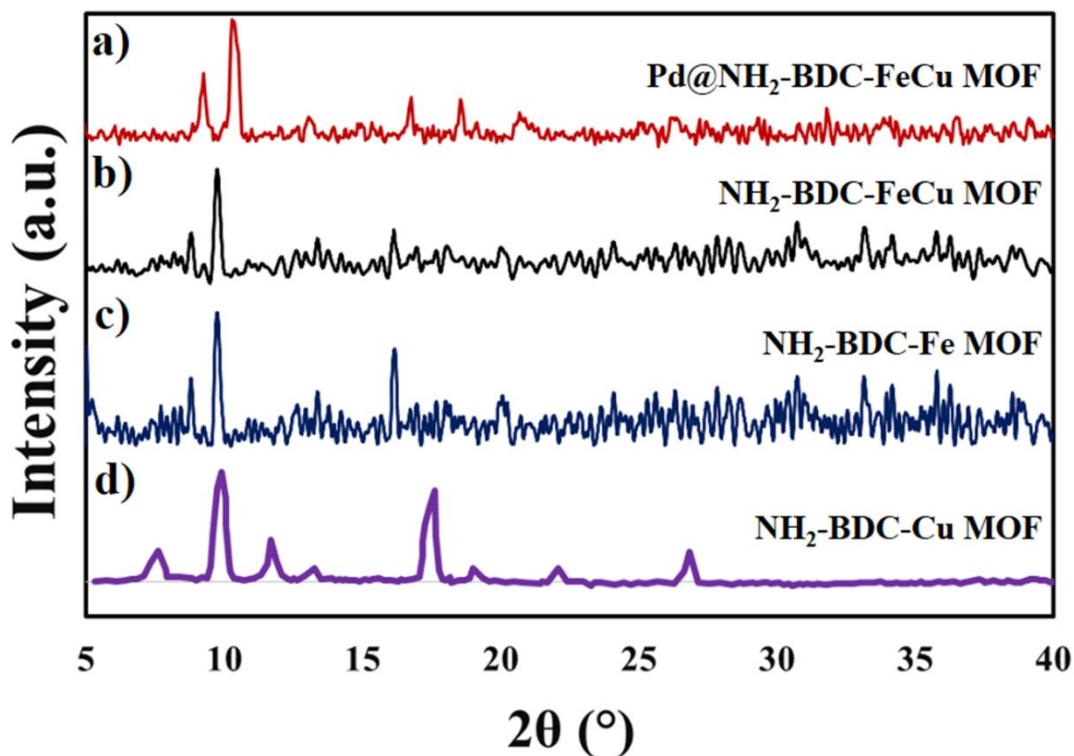
appeared at  $768\text{ cm}^{-1}$  [82]. Two peaks centered at  $1578$  and  $1381\text{ cm}^{-1}$  were corresponded to symmetric and asymmetric stretching of C–O of carboxylate group [83] while the band at  $1255\text{ cm}^{-1}$  could be assigned to stretching vibrations of C–N group, respectively.[84-85] Coordinated DMF observed at  $\sim 1651\text{ cm}^{-1}$  is related to CONH bands [86].



**Fig 1.** IR spectrum of Pd@NH<sub>2</sub>-BDC-FeCu MOF

XRD pattern data of Pd@NH<sub>2</sub>-BDC-FeCu MOF, NH<sub>2</sub>-BDC-FeCu MOF, NH<sub>2</sub>-BDC-Fe MOF and NH<sub>2</sub>-BDC-Cu MOF are presented in Figure 1. XRD Patterns of Pd@NH<sub>2</sub>-BDC-FeCu MOF were similar to those of synthesized FeCu/MOF that confirmed the crystal structure of Pd@NH<sub>2</sub>-BDC-FeCu MOF is maintained after Pd incorporation, while, no special diffractions were observed for Pd metal in its XRD pattern. XRD patterns of Pd@NH<sub>2</sub>-BDC-FeCu MOF were also compared to XRD patterns of NH<sub>2</sub>-BDC-Fe MOF and NH<sub>2</sub>-BDC-Cu MOF. These results showed the sharp reflections of (002) and (101) in  $2\theta = 9.2^\circ$  and  $10.2$  and also poor reflections associated to NH<sub>2</sub>-BDC-Fe MOF appeared in XRD pattern of Pd@NH<sub>2</sub>-BDC-FeCu MOF. This observation revealed the integrity of Fe-

MOF structure upon copper incorporation within the prepared framework (Fig. 2). In addition, XPS results proved the prepared MOF coordination with Pd(II) by showing the two peaks at 338 and 343.1 eV, respectively related to Pd<sup>(II)</sup>3d<sub>5/2</sub> and Pd<sup>(II)</sup>3d<sub>3/2</sub>. (Fig. 3c) [87].



**Fig 2.** XRD pattern dates of a) Pd@NH<sub>2</sub>-BDC-FeCu MOF in comparison with b) NH<sub>2</sub>-BDC-FeCu MOF; c) NH<sub>2</sub>-BDC-Fe MOF; d) NH<sub>2</sub>-BDC-Cu MOF

Generally, XPS analysis illustrated the existence of six elements including oxygen, carbon, nitrogen, copper, iron and palladium in synthesized Pd@NH<sub>2</sub>-BDC-FeCu MOF (Fig. 3a). This result demonstrated that there was a feeble signal for palladium because of low amount of Pd in Pd@NH<sub>2</sub>-BDC-FeCu MOF. The observation of peaks at 711.3 and 725.5 eV associated to



Fe<sup>3+</sup> 2p<sub>3/2</sub> and Fe<sup>3+</sup> 2p<sub>1/2</sub> and peaks at 710.7 and 723.4 eV assigned to Fe<sup>2+</sup> 2p<sub>3/2</sub> and Fe<sup>2+</sup> 2p<sub>1/2</sub> (Fig. 3b) [88]. Also, two main peaks located at 932.1 eV and 952.4 are matched with Cu 2p and the attendance of satellite peak in the range of 938-946 eV, associated to of Cu<sup>2+</sup> (Fig 3d) [89].

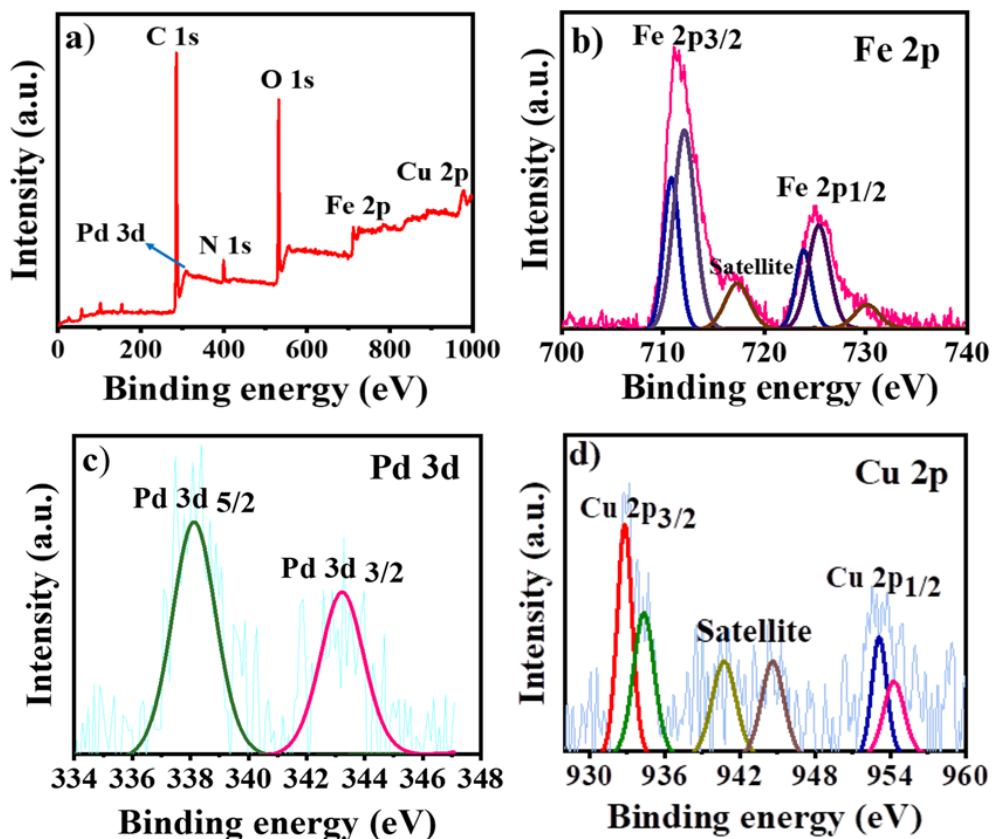
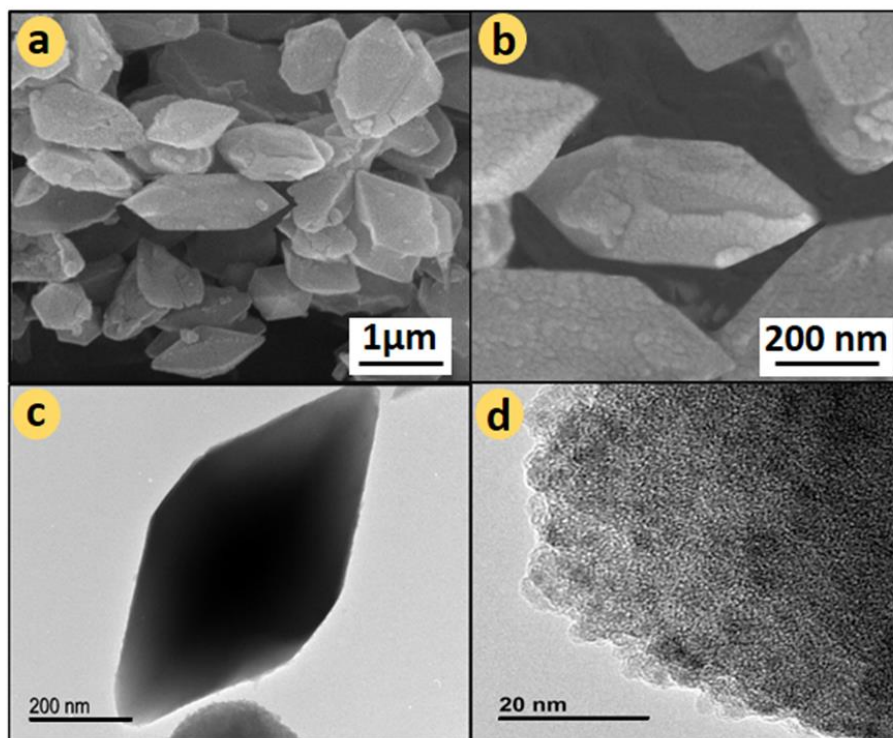


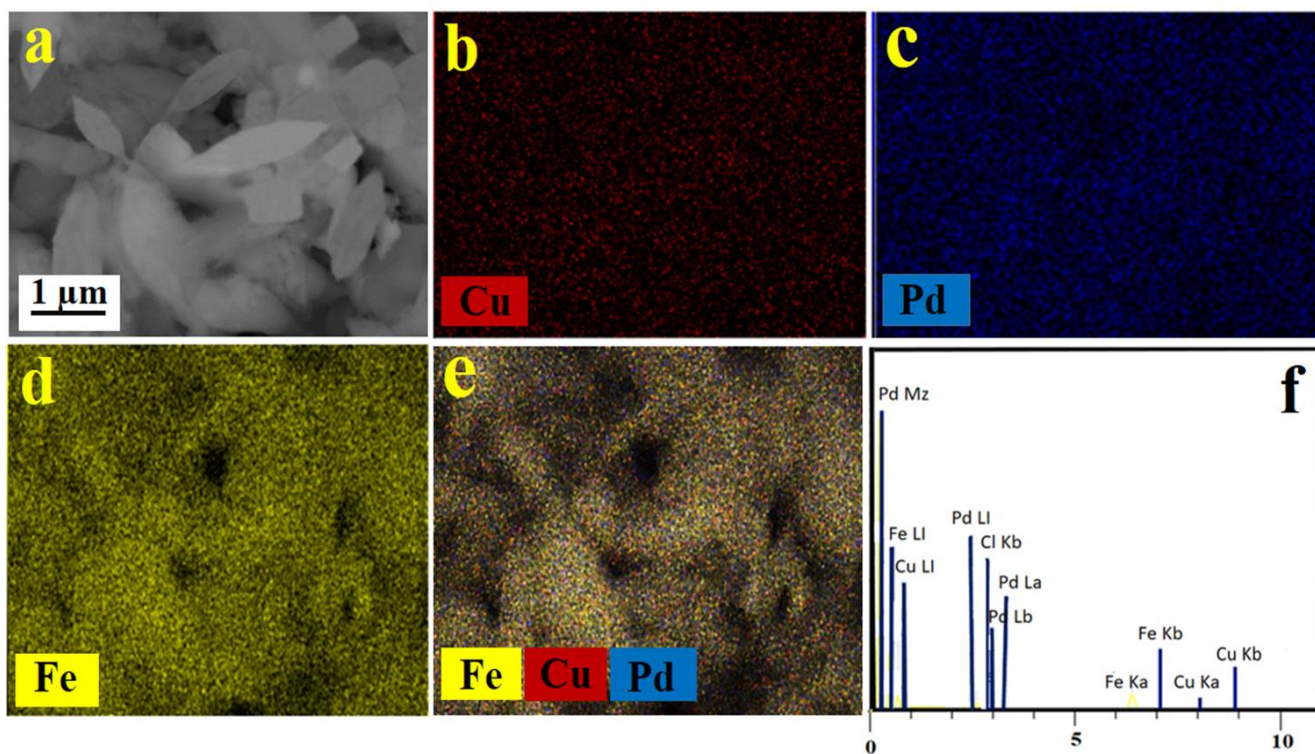
Fig 3. XPS analysis of Pd@NH<sub>2</sub>-BDC-FeCu MOF from a) survey scan b) Fe c) Pd d) Cu

Pd@NH<sub>2</sub>-BDC-FeCu MOF morphology was further examined by TEM and SEM images. SEM images demonstrated that desired catalyst has spindle morphology. TEM images were also recorded from Pd@NH<sub>2</sub>-BDC-FeCu MOF to evaluate the degree of possible Pd (II) aggregation loaded on NH<sub>2</sub>-BDC-FeCu MOF during MOF preparation. These images revealed that there were no aggregated Pd particles on the synthesized MOF (Fig. 4).

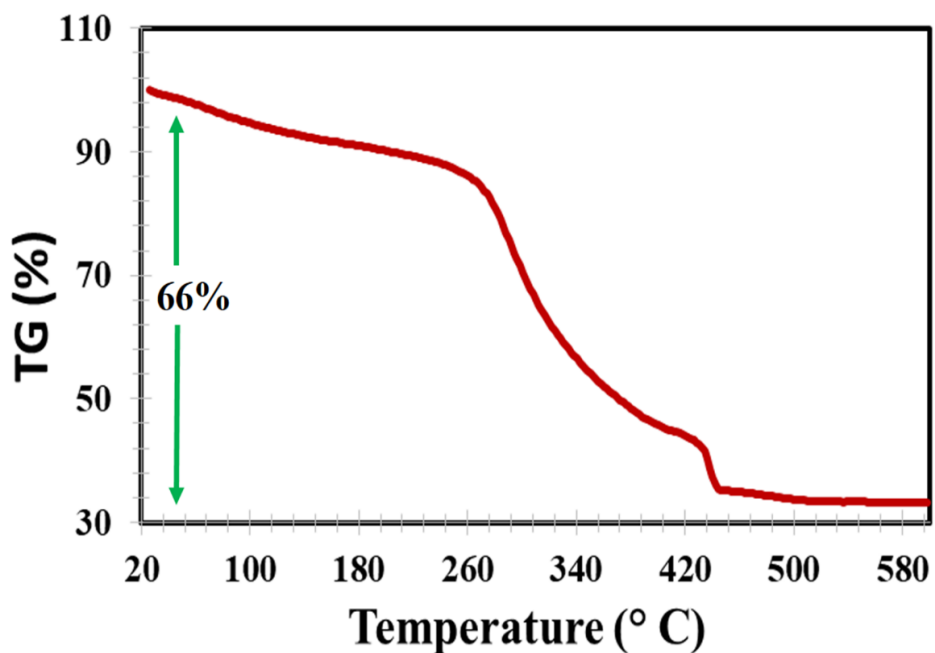


**Fig 4.** a,b) SEM and c,d) TEM images of Pd@NH<sub>2</sub>-BDC-FeCu MOF in different magnification

Elemental mapping and EDX analyses of Pd@NH<sub>2</sub>-BDC-FeCu MOF catalyst, confirmed the presence of Fe, Cu and Pd in this catalyst. TGA analysis was carried out for determination of structural and stability of the catalysts (Fig. 5). TGA of Pd@NH<sub>2</sub>-BDC-FeCu MOF showed that weight decrease took place in three regions. First weight loss ca. 8 wt% was at 70-95°C in diagram, related to the loss of the solvent molecules from Pd@NH<sub>2</sub>-BDC-FeCu/MOF pores. A second weight loss at 200-230°C was corresponded to the loss of coordinated DMF. The most mass loss was at 280°C ca ~44% corresponded to loss organic linkers. The completely decomposition occurred at 440°C with 66% mass loss (Fig. 6).



**Fig 5.** (a) SEM image Pd@NH<sub>2</sub>-BDC-FeCu MOF (b) corresponding elemental mapping images of (b) Cu, (c) Pd, (d) Fe and (e) Fe, Pd, Cu (f) EDX analysis of Pd@NH<sub>2</sub>-BDC-FeCu MOF

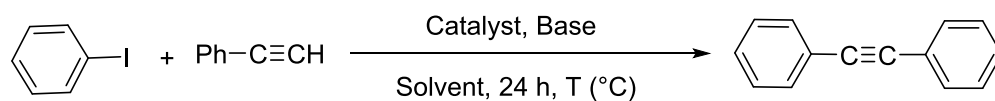


**Fig 6.** TGA analysis of Pd@NH<sub>2</sub>-BDC-FeCu MOF

### 3.2. Catalytic performance

The catalytic efficiency of prepared Pd@NH<sub>2</sub>BDC-FeCu MOF was firstly investigated in the Sonogashira-Hagihara alkynylation coupling reaction of aryl halides with terminal alkynes. The reaction of iodobenzene with phenylacetylene was chosen as test reaction and the influence of various parameters including catalyst loading, type of base, solvent and reaction temperature were examined (Table 1). Initial results showed that excellent yields could be obtained by using of 0.1 mol% Pd, 0.2 mol% Cu, 1.9 mol% Fe loading in DMF solvent and DABCO base at 80 °C (Table 1, entry 1). When the reaction temperature decreased to 70 °C, 60 °C and 50 °C, excellent yields were also achieved at 70 °C, 60 °C (only reduced yields obtained at 50 °C; Table 1, entries 2-4). Hence, 60 °C selected as optimum temperature for performing the reaction. The catalytic activity of Pd @NH<sub>2</sub>BDC-FeCu/MOF catalyst with trace Pd loading (0.07 mol% Pd, 0.17 mol% Cu, 1.4 mol% Fe) was also examined affording lower yields (Table 1, entry 5). Therefore, the system containing 0.1 mol% Pd, 0.2 mol% Cu, 1.9 mol% Fe loading was selected as optimum. Higher yields were also obtained in DMF as compared to any other solvents in the presence of DABCO as optimum base (Table 1, entries 6-10 and 11-15). In this regard, 0.1 mol% Pd, 0.2 mol% Cu, 1.9 mol% Fe loading amount, DMF as a solvent, DABCO base and 60 °C were chosen as the most appropriate and optimized reaction conditions. (Table 1, entry 3). It is noteworthy that palladium loading on MOF Fe-Cu plays a main role in conducting the reaction and significantly influences the catalytic activity. Indeed, blank runs (in the absence of Pd) only provided the desired product in 15% yield (Table 1, entry 16).

**Table 1.** Optimization of reaction condition for the Sonogashira-Hagihara reaction of iodobenzene with phenylacetylene catalyzed by Pd@NH<sub>2</sub>BDC-FeCu MOF.<sup>a</sup>

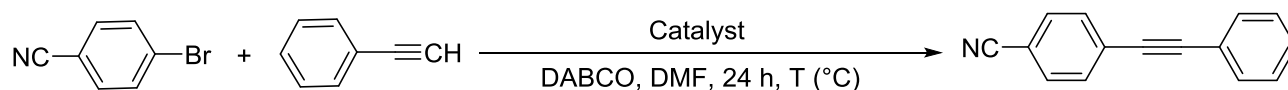


Entry	Cat. Fe (mol %)	Cat. Cu (mol %)	Cat. Pd (mol %)	Base	Solvent	T (°C)	Yield (%) <sup>b</sup>
1	1.9	0.2	0.1	DABCO	DMF	80	>99
2	1.9	0.2	0.1	DABCO	DMF	70	>99
3	1.9	0.2	0.1	DABCO	DMF	60	>99
4	1.9	0.2	0.1	DABCO	DMF	50	82
5	1.4	0.17	0.07	DABCO	DMF	60	76
6	1.9	0.2	0.1	DABCO	PEG-200	60	80
7	1.9	0.2	0.1	DABCO	H <sub>2</sub> O:EtOH	60	10
8	1.9	0.2	0.1	DABCO	1,4-dioxane	60	33
9	1.9	0.2	0.1	DABCO	Xylene	60	45
10	1.9	0.2	0.1	DABCO	Toluene	60	20
11	1.9	0.2	0.1	K <sub>2</sub> CO <sub>3</sub>	DMF	60	72
12	1.9	0.2	0.1	NaOH	DMF	60	25
13	1.9	0.2	0.1	<i>t</i> -BuOK	DMF	60	65
14	1.9	0.2	0.1	KOH	DMF	60	21
15	1.9	0.2	0.1	Et <sub>3</sub> N	DMF	60	5
16	1.9	0.2	-	DABCO	DMF	60	15

<sup>a</sup>Reaction conditions: iodobenzene (0.5 mmol), phenylacetylene (1 mmol), base (0.75 mmol), solvent (2 mL), catalyst (see column).<sup>b</sup>GC yields.

Reaction conditions were further optimized for the coupling reaction of aryl bromides with phenylacetylene. Coupling reactions of aryl bromides with alkyne were slow in comparison with iodides and our initial investigation for the reaction of 4-bromobenzonitrile with phenylacetylene under optimum conditions afforded the desired alkyne only in 17% yield (Table 2, entry 1). Hence, for increasing the yield of aryl bromides, the reaction temperature was increased to 70 °C and 80 °C. Under these conditions, the yield of 4-(phenylethynyl)benzonitrile obtained was 61% and 80%, respectively (Table 2, entries 2-3). Next, the coupling reaction of 4-bromobenzonitrile with phenylacetylene was tested with enhancement of the Fe, Cu and Pd loading to 2.8, 0.3 and 0.15 mol%, respectively at 80 °C. Results showed that excellent yield achieved (Table 2, entry 4). Hence, 2.8 mol% Fe, 0.3 mol% Cu and 0.15 mol% Pd at 80 °C selected as the optimum conditions for the coupling reaction of aryl bromides with phenylacetylene. In order to prove important role of Pd, Cu and Fe in catalytic activity of the Pd@NH<sub>2</sub>BDC-FeCu MOF, we prepared NH<sub>2</sub>BDC-FeCu MOF, NH<sub>2</sub>BDC-Fe MOF, NH<sub>2</sub>BDC-Cu MOF, Pd@NH<sub>2</sub>BDC-Fe MOF and Pd@NH<sub>2</sub>BDC-Cu MOF [90-91] and after their initial characterizations (supporting information) their catalytic activity were investigated in same Sonogashira-Hagihara reaction (Table 2, entries 6-9). Results showed that poor yields were obtained (Table 2, entries 6-7) using NH<sub>2</sub>BDC-Fe MOF, NH<sub>2</sub>BDC-Cu MOF and NH<sub>2</sub>BDC-FeCu MOF as catalyst. Furthermore, Pd supported on Cu or Fe MOFs (Pd@NH<sub>2</sub>BDC-Fe MOF and Pd@NH<sub>2</sub>BDC-Cu MOF) gave lower yields than Pd@NH<sub>2</sub>BDC-FeCu MOF (Table 2, entries 8-9) confirming the important roles of all three metals in catalytic activity.

**Table 2.** Optimization of reaction condition for the **Sonogashira-Hagihara** reaction of 4-bromobenzonitrile with phenylacetylene by using different catalyst.<sup>a</sup>



Entry	Catalyst	Cat. Fe (mol %)	Cat. Cu (mol %)	Cat. Pd (mol %)	T (°C)	Yield (%) <sup>b</sup>
1	Pd@NH <sub>2</sub> BDC-FeCu MOF	1.9	0.2	0.1	60	17
2	Pd@NH <sub>2</sub> BDC-FeCu MOF	1.9	0.2	0.1	70	61
3	Pd@NH <sub>2</sub> BDC-FeCu MOF	1.9	0.2	0.1	80	80
4	<b>Pd@NH<sub>2</sub>BDC-FeCu MOF</b>	<b>2.8</b>	<b>0.3</b>	<b>0.15</b>	<b>80</b>	<b>92</b>
6	NH <sub>2</sub> BDC-Fe MOF	2.8	–	–	80	1
7	NH <sub>2</sub> BDC-Cu MOF	–	0.3	–	80	20
5	NH <sub>2</sub> BDC-FeCu MOF	2.8	0.3	–	80	5
8	Pd@NH <sub>2</sub> BDC-Fe MOF	2.8	–	0.15	80	65
9	Pd@NH <sub>2</sub> BDC-Cu MOF	–	0.3	0.15	80	47

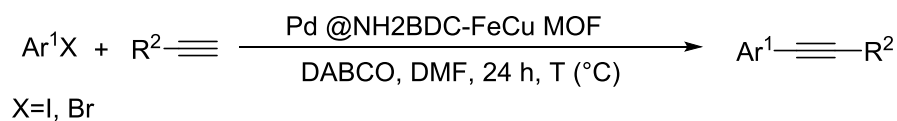
<sup>a</sup> Reaction conditions for coupling reaction of aryl iodides: ArBr (0.5 mmol), alkyne (1 mmol), DABCO (0.75 mmol), catalyst (see column) and DMF (2 mL). <sup>b</sup>GC yields

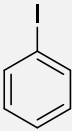
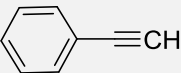
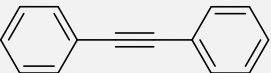
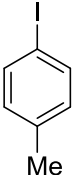
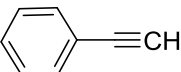
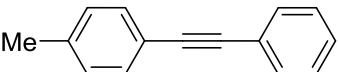
Under optimized reaction conditions for aryl iodides, the Sonogashira-**Hagihara** coupling reaction of extensive range of structurally aryl halides with alkynes were investigated. Firstly, Sonogashira-**Hagihara** reaction of aryl iodides including electron-donating groups such as methyl and methoxy groups and electron-withdrawing groups such as CN, NO<sub>2</sub>, CHO, Cl, and F rapidly progressed and the desired products were obtained in excellent yields (Table 3 entries 1–10). Also, excellent yield were obtained in the coupling



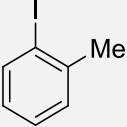
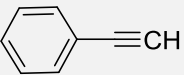
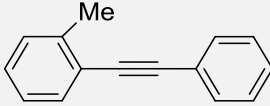
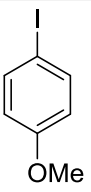
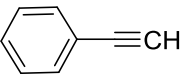
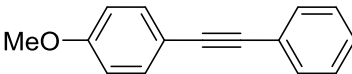
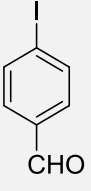
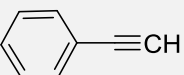
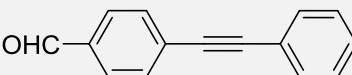
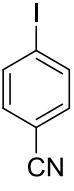
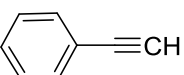
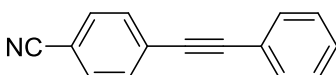
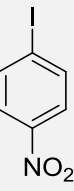
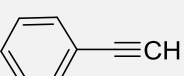
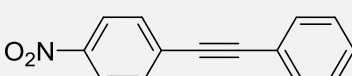
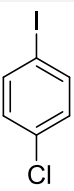
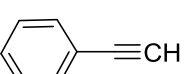
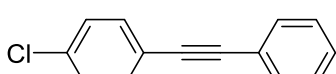
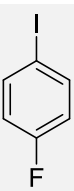
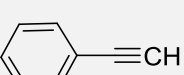
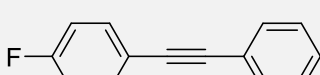
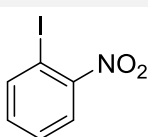
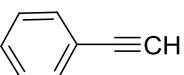
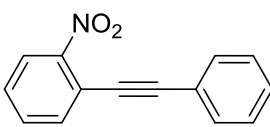
reaction of heteroaromatic including 2-iodothiophene with and 2,5-diiodothiophene with alkynes (Table 3, entry 11-13). Coupling reactions of iodobenzene, 2-iodothiophene and 1-iodo-4-nitrobenzene with other alkynes such as propargyl alcohol gave the desired alkynes in excellent yields (Table 3, entries 14–16). Moreover, the effect of Pd@NH<sub>2</sub>BDC-FeCu MOF catalyst was studied in the alkylation coupling reaction of various aryl bromides with terminal alkyne under optimized condition for aryl bromides. Results indicated that aryl bromides bearing electron-withdrawing groups such as NO<sub>2</sub>, CN and CHO with phenylacetylene occurred efficiently and corresponding products were achieved in excellent yields (Table 3, entries 17–20). At the end, arylations of phenylacetylene took place with heterocyclic bromides such as 5-bromopyrimidine and 2-bromopyridine affording corresponding products in 82% and 87% yield, respectively (Table 3, entries 21-22).

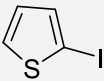
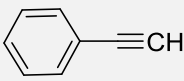
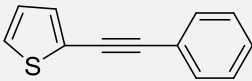
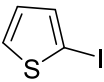
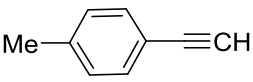
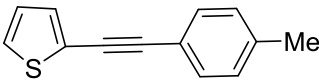
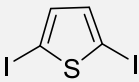
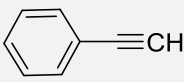
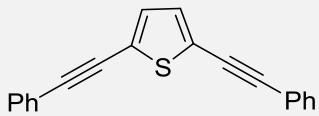
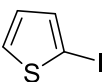
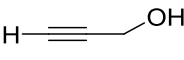
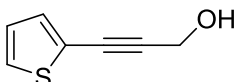
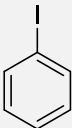
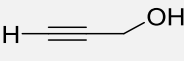
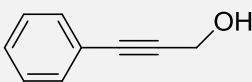
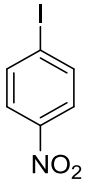
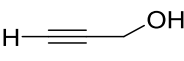
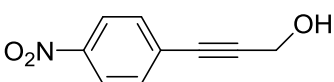
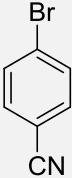
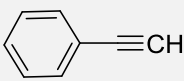
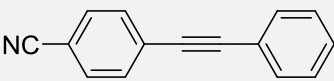
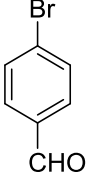
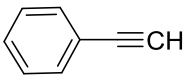
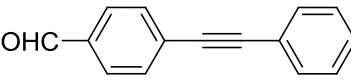
**Table 3.** Sonogashira-Hagihara reaction of aryl iodides<sup>a</sup> and aryl bromides<sup>b</sup> with phenylacetylene catalyzed by Pd @NH<sub>2</sub>BDC-FeCu MOF.



Entry	Ar <sup>1</sup>	R <sup>2</sup>	Product	Yield (%)
1				>99
2				96



3				93
4				90
5				>99
6				>99
7				>99
8				95
9				97
10				92

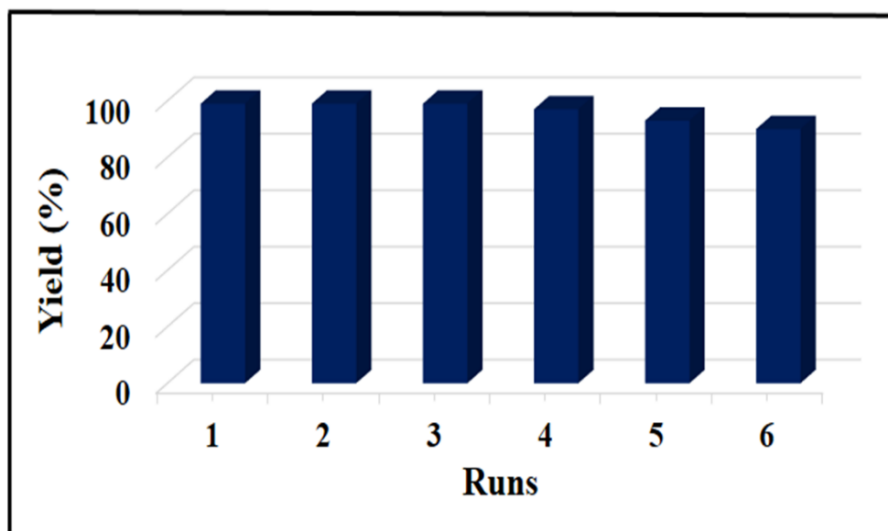
11				>99
12				94
13				80
14				98
15				96
16				>99
17				92
18				90

19				93
20				85
21				82
22				87

<sup>a</sup> Reaction conditions for coupling reaction of aryl iodides: ArI (0.5 mmol), alkyne (1 mmol), DABCO (0.75 mmol), catalyst (1.9 mol% Fe, 0.2 mol% Cu and 0.1 mol% Pd, 17.5 mg) and DMF (2 mL) at 60 °C.

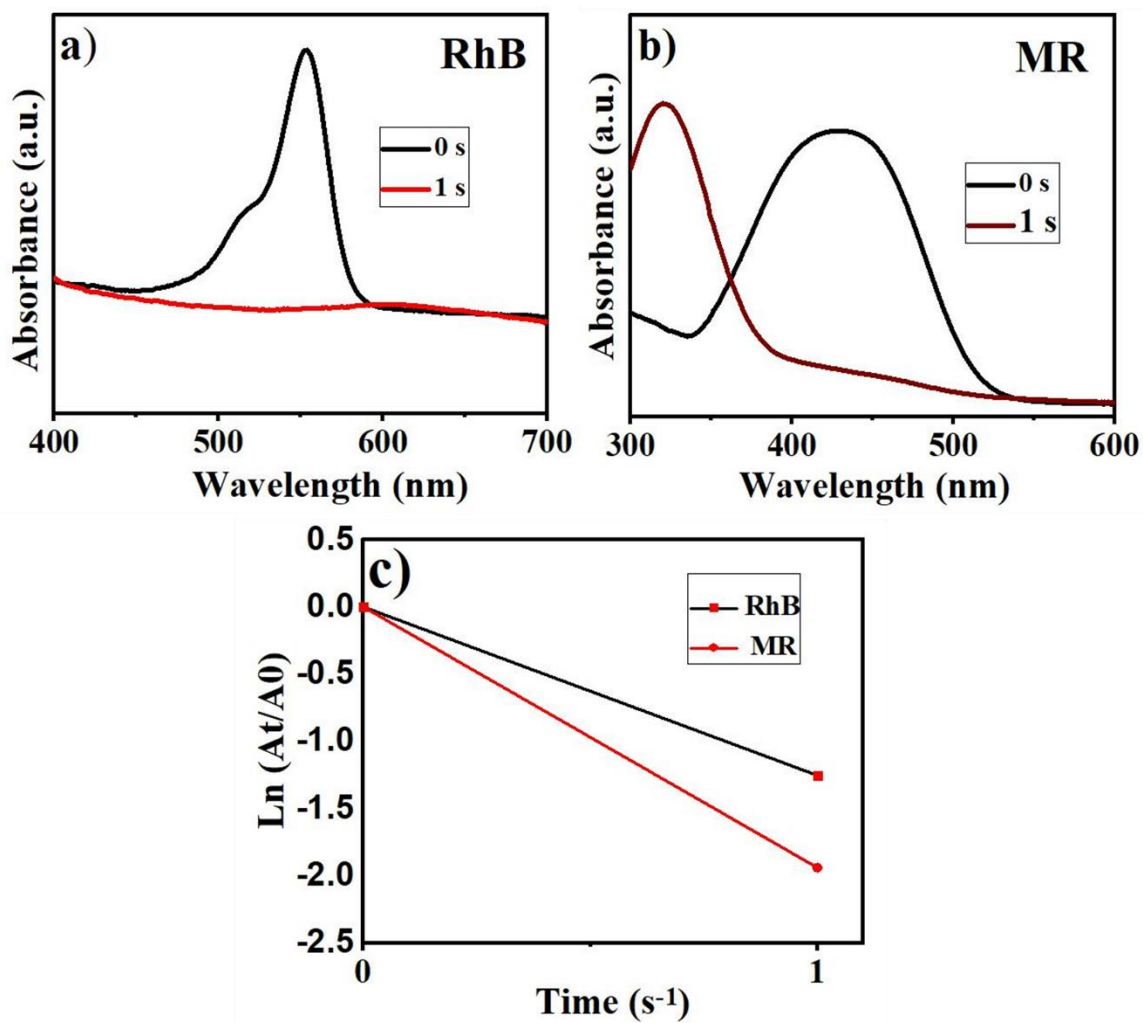
<sup>b</sup> Reaction conditions for coupling reaction of arylbromides: ArBr (0.5 mmol), alkyne (1 mmol), DABCO (0.75 mmol), catalyst (2.8 mol% Fe, 0.3 mol% Cu and 0.15 mol% Pd, 25 mg) and DMF (2 mL) at 80 °C.

Recycling and reuse of the heterogeneous palladium catalysts are necessary factors from economically, sustainable chemistry and environmental points of view. For this aim, we have investigated the recycling of this catalyst for the coupling reaction of iodobenzene with phenylacetylene under optimized conditions. In order to recycle this catalyst, after reaction completion ca. 24 h, the desired catalyst separated by using centrifugation and next was washed with ethyl acetate and EtOH for three times. After drying of catalyst, the catalyst was used in other cycles of reaction. Results displayed that Pd@NH<sub>2</sub>BDC-FeCu MOF catalyst recycled and reused for 6 consecutive times with small declining in catalytic activity (Fig. 7).



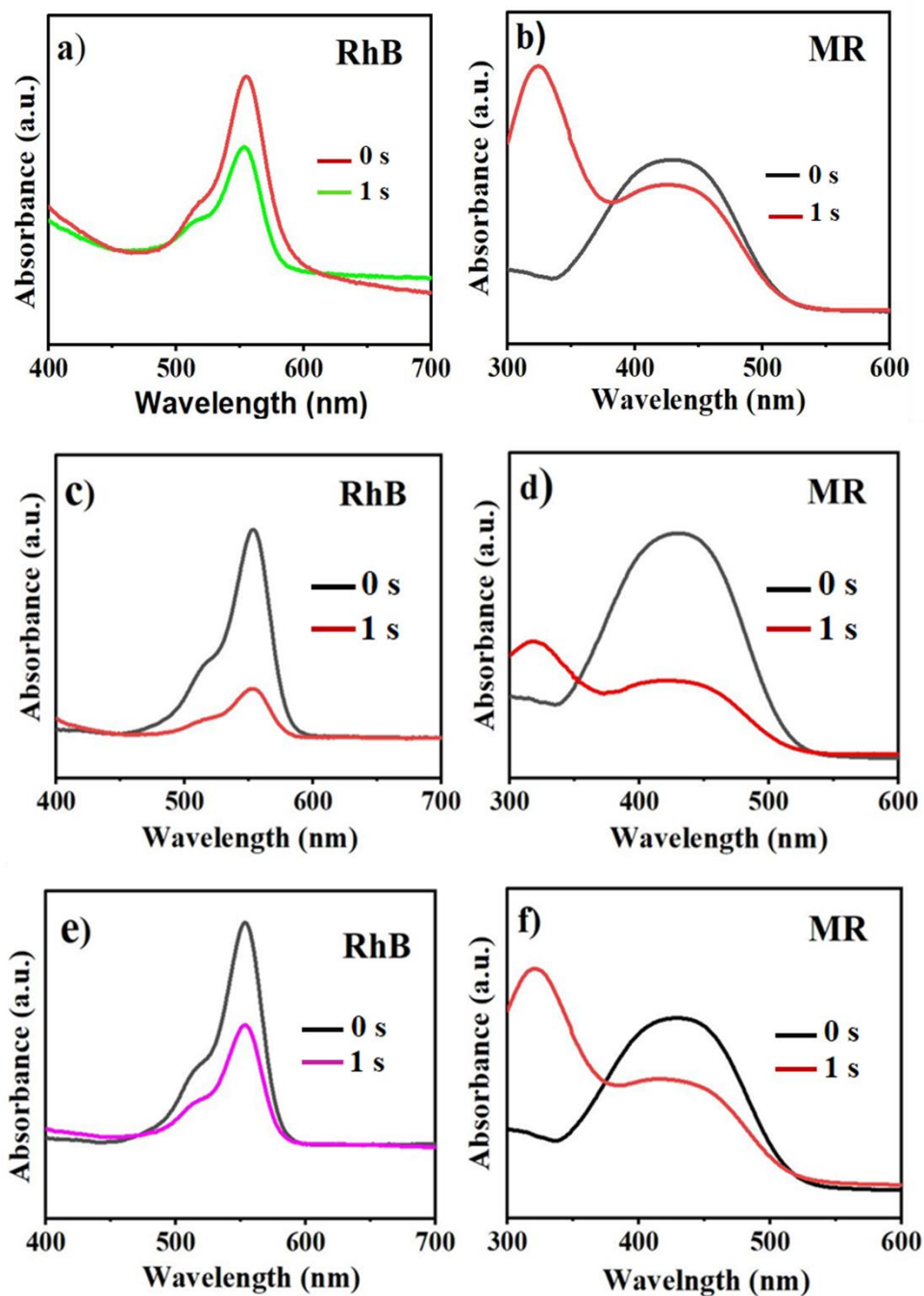
**Fig 7.** Recycling of Pd@ NH<sub>2</sub>BDC FeCu MOF for 6 runs

The catalytic activity of Pd@NH<sub>2</sub>BDC-FeCu MOF was further expanded in the reduction of dyes e.g. methyl red (MR) and rhodamine B (RhB). The reaction was conducted at room temperature and progress of the reaction was checked by using UV-visible spectrum. Rhodamine B (RhB) is a hazardous cationic dye that is broadly utilized in various industries. The absorption peak of RhB detected at  $\lambda=554$  nm was chosen for monitoring the catalytic reduction. In the presence of both Pd@NH<sub>2</sub>BDC-FeCu MOF catalyst and NaBH<sub>4</sub> as the reducing agent, the absorption peak of RhB was quickly declined in 1s (Fig. 8a). Also, methyl red (MR) was another usual water contaminant, which extensively found in wastewaters. MR exhibited strong absorption peaks at  $\lambda=435$  nm in the aqueous medium. Figure 8b demonstrates that in the presence of Pd@NH<sub>2</sub>BDC-FeCu MOF catalyst and NaBH<sub>4</sub> solution, rapid disappearing of MR occurred in 1s with reduced MR achieved ca. 100%. Moreover, Fig. 8c indicates a linear correlation between time and  $\ln(A_t/A_0)$  corresponding to the pseudo-first-order kinetics for RhB and MR. Rate constant (k) calculated through it were  $1.2 \text{ s}^{-1}$  and  $1.9 \text{ s}^{-1}$  for RhB and MR, respectively.



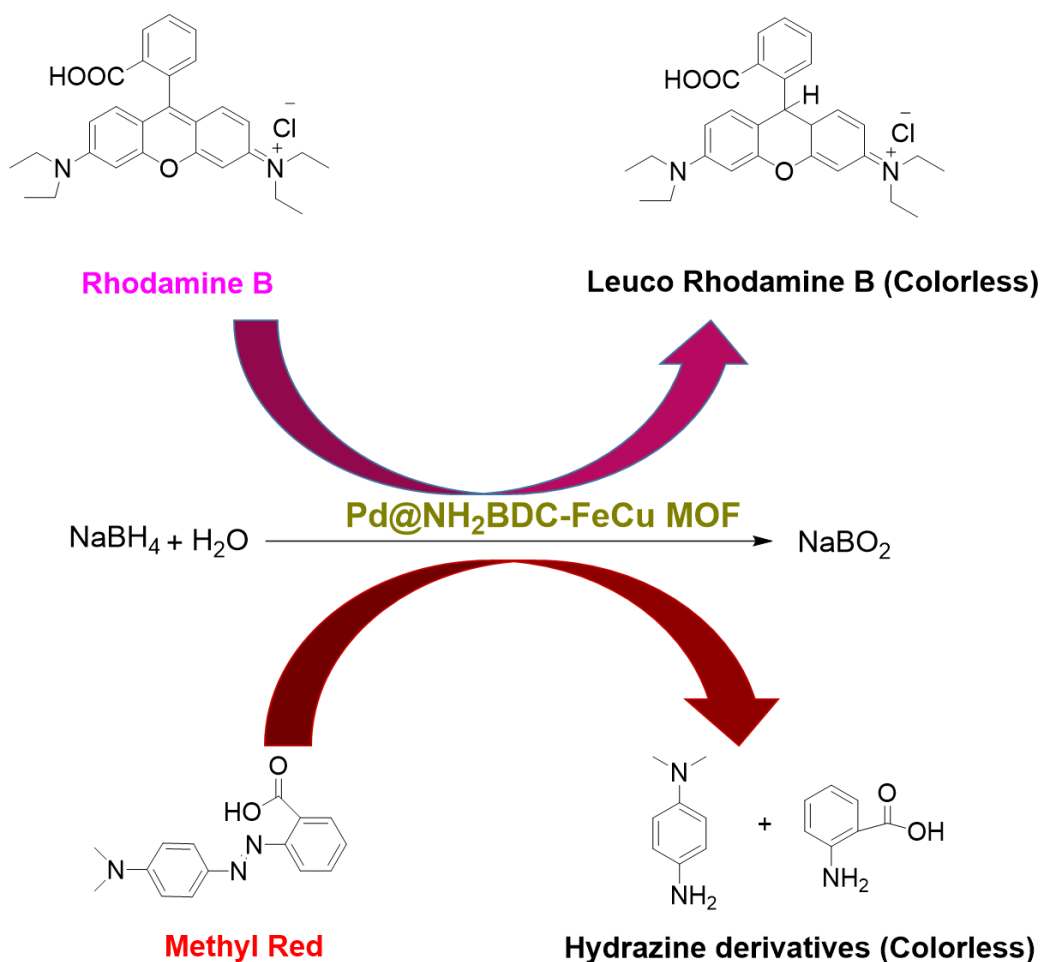
**Fig. 8** UV-visible spectra for the reduction of a) RhB, b) MR in the presence of Pd@NH<sub>2</sub>BDC-FeCu MOF catalyst and NaBH<sub>4</sub> and c) Plots of  $\ln(A_t/A_0)$  versus reaction time for the reduction of RhB and MR in 1s.

In order to compare the catalytic activity of prepared trimetallic catalyst (Pd@NH<sub>2</sub>BDC-FeCu MOF) with bimetallic catalysts, we also investigated the catalytic reduction of RhB and MR with NH<sub>2</sub>BDC-FeCu MOF, Pd@NH<sub>2</sub>BDC-Fe MOF and Pd@NH<sub>2</sub>BDC-Cu MOF catalysts in 1s (Figure 9). Results showed that only 31% reduced RhB and 19% reduced MR by using NH<sub>2</sub>BDC-FeCu MOF and as well as 66% reduced RhB and 60% reduced MR by using Pd@NH<sub>2</sub>BDC-Fe MOF obtained in 1s. At the end, reduction of RhB and MR using Pd@NH<sub>2</sub>BDC-Cu MOF occurred with 45% and 34% conversion in 1s, respectively. Hence, Pd@NH<sub>2</sub>BDC-FeCu MOF catalyst have the highest catalytic activity than the other compared bimetallic catalyst.



**Fig 9.** UV–visible spectra for the catalytic reduction of RhB and MR by using a,b)  $\text{NH}_2\text{BDC-FeCu}$  MOF catalyst; c,d) Pd@ $\text{NH}_2\text{BDC-Fe}$  MOF; e,f) Pd@ $\text{NH}_2\text{BDC-Cu}$  MOF

The proposed mechanism for the reduction of MR and RhB by using Pd@NH<sub>2</sub>BDC-FeCu MOF is the same well-known mechanism for the metal catalyzed reduction reactions of MR and RhB. For explanation of this mechanism, firstly produced H<sub>2</sub> from the reaction of NaBH<sub>4</sub> and H<sub>2</sub>O in the presence of Pd@NH<sub>2</sub>BDC-FeCu MOF catalyst that can reduce Rhodamine B to leuco rhodamine B and Methyl Red to Hydrazine derivatives (Figure 10) [92–93].



**Fig 10.** Possible mechanism for the reduction of methyl Red (MR) and Rhodamine B (RhB) in the presence of Pd@NH<sub>2</sub>BDC-FeCu MOF catalyst and NaBH<sub>4</sub> reductant



## Conclusions

A recyclable and effective palladium supported on NH<sub>2</sub>BDC-FeCu MOF catalyst was synthesized and characterized. The activity of the Pd@NH<sub>2</sub>BDC-FeCu MOF catalyst was investigated in the Sonogashira-Hagihara coupling reaction and reduction of organic dyes such as rhodamine B and methyl red. Results pointed to a high activity in the Sonogashira-Hagihara reaction of aryl iodides and aryl bromides with alkynes as well as almost instantaneous reduction of RhB and MR. Generally, Pd@NH<sub>2</sub>BDC-FeCu MOF catalyst showed the highest activity in comparison with NH<sub>2</sub>BDC-FeCu MOF, NH<sub>2</sub>BDC-Fe MOF, NH<sub>2</sub>BDC-Cu MOF, Pd@NH<sub>2</sub>BDC-Fe MOF and Pd@NH<sub>2</sub>BDC-Cu MOF in Sonogashira-Hagihara coupling reaction of 4-bromobenzonitrile with phenylacetylene as well as in the reduction of RhB and MR. Indeed, synergic effect between metals of Fe, Cu and Pd led to enhance the catalytic performance in these reactions. Pd@NH<sub>2</sub>BDC-FeCu MOF could be recycled for six sequential runs without considerable diminution in activity for reaction of iodobenzene with phenylacetylene. TEM and SEM analyses showed that the morphology of the Pd@NH<sub>2</sub>BDC-FeCu MOF maintained and did not change after six runs.

## Acknowledgments

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CTQ2016-80375-P, CTQ2017-82935-P and PID2019-107268GB-I00), Generalitat Valenciana (IDIFEDER/2021/013) and the University of Alicante.

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