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Cite this: DOI: 10.1039/d0nj04133e

## Ligand and additive free aerobic synthesis of diynes using Pd–CuFe<sub>2</sub>O<sub>4</sub> magnetic nanoparticles as an efficient reusable catalyst<sup>+</sup>

Herein, we present the synthesis of Pd-CuFe<sub>2</sub>O<sub>4</sub> magnetic nanoparticles as an efficient and recyclable

catalyst for the oxidative homocoupling of various terminal alkynes to form symmetric 1,3-diynes. The catalyst was found to be effective with very low palladium loading. The protocol has the advantages of

easy synthesis of the catalyst, mild reaction conditions, short reaction times, excellent product yields and

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enhanced recyclability of the catalyst.

Received 16th August 2020, Accepted 26th September 2020

DOI: 10.1039/d0nj04133e

rsc.li/njc

### 1. Introduction

Diynes are useful building blocks in the synthesis of organic conductors,<sup>1</sup> macrocyclic annulenes,<sup>2–4</sup> carbon-rich materials,<sup>5</sup> supramolecular switches,<sup>6</sup> conducting polymermaterials,<sup>7</sup> *etc.* These compounds possess prominent biological activities such as antimicrobial, antitumor, antibacterial, and anti-HIV,<sup>8</sup> to name a few; thus, significant attention has been devoted to the synthesis of diynes by many chemists.

The earliest and most remarkable methods for the synthesis of diynes include Glaser-Hay coupling<sup>9,10</sup> and Cadiot-Chodkiewicz coupling.<sup>11</sup> But these processes require an excess of alkynes and toxic organic amine bases. Although the homocoupling of terminal alkynes has been investigated for more than 140 years, from the economic and environmental viewpoints, the development of new approaches continues to be of great importance and interest. Among all the methods for the synthesis of diynes, the palladium-catalyzed homocoupling reactions of terminal alkynes<sup>12-14</sup> and Sonogashira cross coupling reactions of aryl-halides with terminal alkynes<sup>15,16</sup> have achieved much significance. Several mild and efficient methods have been reported for the synthesis of diynes using different Pd catalysts, e.g., Pd(dba)<sub>2n</sub>-Bu<sub>4</sub>NBr;<sup>17</sup> PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>;<sup>18</sup> PdCl<sub>2</sub> CuI;<sup>19</sup> Pd(OAc)<sub>2</sub> CuI;<sup>20</sup> (PPh<sub>3</sub>)<sub>2</sub> PdCl<sub>2</sub>, CuI, PPh<sub>3</sub>;<sup>21</sup> and Pd<sub>2</sub>Au.<sup>22</sup> However, these reactions require high loadings of palladium, which often cannot be recovered. Scientists therefore tried to perform these reactions using different catalysts in the absence of palladium using less expensive metals like nickel,<sup>23,24</sup> cobalt,<sup>25</sup> titanium,<sup>26</sup> gold<sup>27,28</sup> and

copper<sup>29–36</sup> along with some high molecular weight ligands. But these processes involve multiple steps in the synthesis of the catalyst and this increases the overall cost, making the process tedious and expensive; the reactions also normally required longer reaction times with sufficiently high temperatures.

In accordance with the principles of Green chemistry,<sup>37</sup> scientists have always tried to find an alternative to toxic chemicals using recyclable, low cost catalyst systems. Thus, nowadays, nanoparticles serve as an excellent heterogeneous catalyst in various organic transformations, because of their high surface area to volume ratio, enhanced stability, selectivity, chemical inertness *etc.* But, because of their nanosize, the recovery and isolation of these tiny nanoparticles after the completion of the reaction is a difficult task. This difficulty has been overcome by the use of Magnetic Nanoparticles (MNPs) in present day catalysis reactions. In addition, they show high chemical reactivity and thermal stability.

Among the magnetic compounds, the nano magnetic ferrites are very good catalyst systems and serve as excellent catalytic supports.<sup>38</sup> They have shown remarkable catalytic applications such as the synthesis of thiazolidin-4-ones;<sup>39</sup> benzoimidazo[1,2-*a*] pyrimidines and tetrahydrobenzo[4,5]imidazo-[1,2-*d*]quinazolin-1(2*H*)-one;<sup>40</sup> and 2,4,5-trisubstituted imidazoles.<sup>41</sup>

Therefore, a more economical approach using magnetic nanoparticles on Pd has nowadays served as an alternative method for various C–C bond formation reactions due to their easy recovery and recyclability.

Recently, many researchers have combined  $\text{CuFe}_2\text{O}_4$  magnetic nanoparticles and palladium, which was shown to exhibit high activity in various transformations such as the selective hydrogenation of arylacetylenes<sup>42</sup> and the cyanation of aryl halides.<sup>43</sup> This catalyst has shown efficient catalytic activity compared to other nanoparticles because of the synergistic effect between palladium and copper nanoparticles.



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In this context, we attempt to synthesize Pd–CuFe<sub>2</sub>O<sub>4</sub> magnetic nanoparticles (MNPs) with a very low amount of Pd loading and use them as a catalyst for the synthesis of various symmetric 1,3-diynes. The CuFe<sub>2</sub>O<sub>4</sub> MNPs were synthesized using the biogenic route according to our previous report,<sup>44</sup> without using any harsh reaction conditions or any reducing agent, using *Camellia sinensis* var. Assamica (Tea) leaves. Tea leaves contain various polyphenolic compounds that might be mainly responsible for the synthesis of biogenic nanoparticles. The catalyst proved to be highly efficient, yielding almost all the substrates in excellent to good yields even after five recycles. To the best of our knowledge, no such usage of MNPs for the synthesis of diynes has been reported so far (Scheme 1).

### 2. Experimental

#### 2.1 Synthesis of Pd-CuFe<sub>2</sub>O<sub>4</sub> MNPs

For the synthesis of Pd–CuFe<sub>2</sub>O<sub>4</sub> we adopted a two-step process. Firstly, we prepared magnetic nanoparticles according to our previously reported method using *Camellia sinensis* var. Assamica (Tea) leaf extract.<sup>44</sup> In the second step, we coated Pd with the prepared MNPs in which 100 mg of the MNPs was dispersed in ethanol and then 100 mg of Pd(OAc)<sub>2</sub> was quickly added under ultrasonication for 1 h to obtain a fine mix. Finally 1 ml of 80% NH<sub>2</sub>·NH<sub>2</sub>·H<sub>2</sub>O was added dropwise into the mixture. After 30 min, the solid products were collected using a magnet and washed thoroughly with distilled water and ethanol several times (Scheme 2).

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#### 2.2 General procedure for homocoupling reactions

The prepared Pd-CuFe<sub>2</sub>O<sub>4</sub> MNPs were used as the catalyst for the homocoupling of various terminal alkynes. The reactions were performed in a 50 ml round bottom flask at a temperature of 60 °C. 1 mmol of terminal alkyne, 2 mol% Pd-CuFe<sub>2</sub>O<sub>4</sub>, 4 mmol of triethyl amine (TEA) and 3 ml of n-butyl alcohol (*n*-BuOH) were subjected to magnetic stirring for an appropriate time period (Scheme 3). The progress of the reaction was monitored using TLC. After the completion of the reaction, the products were diluted with 30 ml of distilled water and extracted with ethyl acetate, and the combined organic layer was washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated in a rotary evaporator under reduced pressure. The products were purified using column chromatography on silica gel with hexane as the eluent to afford the corresponding 1,3-divnes. The products were confirmed using GC-MS, <sup>1</sup>H-NMR, and <sup>13</sup>C-NMR analyses.

## 3. Results and discussion

#### 3.1 Catalyst characterization

The crystallite phase and purity of the synthesized Pd-CuFe<sub>2</sub>O<sub>4</sub> MNPs were characterized using powder X-ray diffraction (XRD) analysis (Fig. 1). The Bragg reflections and crystallographic faces of magnetite Pd-CuFe<sub>2</sub>O<sub>4</sub> appeared at 20: 23.8, 27.2, 29.92, 32.72, 35.3, 40.1 (Pd), 43, 46.06 (Pd), 49.06, 53.64, 56.96, 58.48, 62.28, 63.7, 68.34 (Pd), and 82.26 (Pd), which are consistent with the (111), (202), (220), (113), (311), (111), (400), (200), (331), (422), (333), (511), (404), (440), (220), and (311) planes, respectively. These values are comparable with the XRD information of JCPDS card numbers 034-0425 (t-CuFe2O4) and 89-4897 (Pd).<sup>48</sup> Thus, it was confirmed that Pd was doped in the lattice of tetragonal CuFe<sub>2</sub>O<sub>4</sub> and formed solid Pd-CuFe<sub>2</sub>O<sub>4</sub> MNPs. By using the Scherrer equation,<sup>49</sup> the average crystallite size of Pd-CuFe<sub>2</sub>O<sub>4</sub> MNPs was found to be 5.228 nm. Moreover, by considering the FWHM of the Pd peaks from the XRD analysis and by using the Scherrer equation, the average crystallite size of Pd in the nanoparticle was found to be 2.618 nm.

The SEM images exhibited the agglomerated nature of Pd– $CuFe_2O_4$  [Fig. 2(a)]. This might be because of its magnetic nature. Fig. 2(b) shows that the precious Pd metal homogeneously covered the surface of  $CuFe_2O_4$  which was revealed by

$$R \xrightarrow{\qquad Pd-CuFe_2O_4 MNPs} R \xrightarrow{\qquad Factor R} R$$

#### R= Aliphatic/ Aromatic

Scheme 3 General scheme for the homocoupling of various terminal alkynes.



the presence of smaller particles on the surface of the Pd-doped sample. The energy dispersive X-ray (EDX) analysis [Fig. 2(c)] shows the presence of Pd, Cu, Fe and O with an elemental distribution of Cu = 19.42%, Fe = 26.02%, O = 52.58%, and Pd = 1.98%. Thus, it was confirmed that no impurity was present in the nanoparticle.

From the low resolution TEM image, the nanoparticle was found to be spherical in shape [Fig. 3(a)]. Bright fringes were observed in the SAED pattern, which also confirmed the highly crystalline nature of the MNPs as revealed by the XRD analysis [Fig. 3(b)]. The crystallographic (111), (202), (220), (113), and (311) planes corresponding to tetragonal CuFe<sub>2</sub>O<sub>4</sub> along with the (111) plane of palladium were clearly indexed in the SAED pattern. The fringe separations of 0.202 nm and 0.193 nm were present in the HR-TEM image [Fig. 3(c)], which were in good agreement with the (400) plane of CuFe<sub>2</sub>O<sub>4</sub> and the (200) plane of Pd. The observance of the fringes in different directions



Fig. 2 (a) SEM image; (b) SEM image showing Pd particles on the surface of  $CuFe_2O_4$ ; and (c) EDX analysis showing the presence of O, Cu, Fe and Pd in the synthesized Pd-CuFe<sub>2</sub>O<sub>4</sub> MNPs (inset shows the compositional analysis of the elements present).



Fig. 3 (a) Low resolution TEM image; (b) SAED pattern showing different crystallographic planes; (c) HRTEM image; and (d) particle size histogram of the TEM image.

indicated that the nanoparticles were polycrystalline in nature. From the size distribution histogram, determined using a large number of particles in the TEM image, the average particle size of the nanoparticle was found to be 6.02 nm [Fig. 3(d)].

The ICP-AES analysis showed that the amounts of Pd, Fe and Cu loading in 57 mg of the compound are 0.000324 mmol, 0.03629 mmol, and 0.02265 mmol, respectively.

XPS analysis was performed to determine the oxidation state of Pd in the sample along with the proper stoichiometry of Cu and Fe [Fig. 4]. In the survey scan [Fig. 4(a)], the peaks corresponding to Cu, Fe, O and Pd were found. The Cu 2p scan [Fig. 4(b)] shows two distinct peaks with binding energies of 934.19 eV and 954.26 eV, which can be attributed to Cu  $2p_{3/2}$ and Cu  $2p_{1/2}$ , respectively. The presence of two strong satellite peaks at 941.97 and 962.69 eV is characteristic of Cu in the +2 oxidation state.<sup>50</sup> The Fe 2p scan [Fig. 4(c)] depicts the  $2p_{3/2}$ peak at 711.60 eV and  $2p_{1/2}$  peak at 724.56 eV with its satellite peak at 719.68 eV, which is characteristic of Fe in the +3 oxidation state.<sup>51</sup> Fig. 4(d) clearly shows the presence of a peak for Pd  $3d_{5/2}$  at 335.90 eV and  $3d_{3/2}$  at 341.14 eV, which shows the 0 (zero) oxidation state of Pd.<sup>52</sup> Thus, all the above results confirmed the formation of Pd–CuFe<sub>2</sub>O<sub>4</sub> MNPs.

The magnetic study of the catalyst was performed using VSM analysis at room temperature [Fig. 5]. The *M*–*H* curve showed an S-type plot. The sample showed a coercivity ( $H_{ci}$ ) of 37.66 Oe, a magnetization ( $M_s$ ) of 26.82 emu g<sup>-1</sup> and a retentivity ( $M_r$ ) of 0.72004 emu g<sup>-1</sup>. The magnetization value of 26.82 emu g<sup>-1</sup> proved that the sample was ferromagnetic in nature. Thus, it could be established that a magnetically retrievable sample formed that could be used for catalytic applications.

By using the Brunauer–Emmett–Teller (BET) method, the nitrogen adsorption–desorption isotherms of both  $Pd-CuFe_2O_4$ 



Fig. 4 XPS spectra: (a) survey scan of Pd–CuFe $_2O_4$ ; (b) Cu 2p; (c) Fe 2p; and (d) Pd 3d.



Fig. 5 (a) VSM spectra of Pd–CuFe<sub>2</sub>O<sub>4</sub> MNPs; (b) enlarged M-H curve showing coercivity and retentivity.

and  $CuFe_2O_4$  were studied at a temperature of 77.3 K, see Fig. 6. The BET analysis showed that when Pd is incorporated on  $CuFe_2O_4$ , the surface area of  $CuFe_2O_4$  increases from 20.309 m<sup>2</sup> g<sup>-1</sup> to 39.748 m<sup>2</sup> g<sup>-1</sup> and the total pore volume also



Fig. 6  $\,$  N\_2 adsorption–desorption isotherm of CuFe\_2O\_4 and Pd–CuFe\_2O\_4 samples obtained at 77.3 K.

increases. However, pore diameter decreases in  $Pd-CuFe_2O_4$ . The results are tabulated in Table S1 (ESI<sup>†</sup>). This also indicates directly that  $CuFe_2O_4$  is wrapped by Pd, as shown in the SEM image in Fig. 2(b).

Furthermore, we compared the  $Pd-CuFe_2O_4$  MNPs with previously reported catalyst systems in terms of the amount of Pd metal contained (Table 1).

## 3.2 Homocoupling of different substrates using Pd-CuFe<sub>2</sub>O<sub>4</sub> MNPs

**3.2.1 Optimization of the reaction conditions.** We synthesized various diynes using the prepared  $Pd-CuFe_2O_4$  as the catalyst. Our prime goal was to screen different solvents for the reaction (Table 2) and, thus, we took phenylacetylene as the model substrate. It was found that *n*-BuOH was the best solvent for the reaction (Table 2, entry 10). The reaction temperature was set at around 60 °C, and the reaction worked well for most of the substrates, making the process highly efficient and comparatively quicker compared to previously reported Pd-catalyst systems.

We then optimized the amount of catalyst for the model reaction of phenylacetylene and found that only 2 mol% (6.89 mg) catalyst was sufficient for the smooth progress of the reaction (Table 3, entry 8).

We further optimized our reaction using different alcohols as solvents and varying the temperature (Table 4). From our investigations, it was found that both EtOH and *n*-butyl alcohol provided good results for the reaction, but compared to *n*-BuOH, EtOH required more time and the product yield was

Table 1 A comparison study of  $\mathsf{Pd}{-}\mathsf{CuFe}_2\mathsf{O}_4$  MNPs with previous reported catalysts

S. no.	Catalyst	Metal (mol%)	Ref.
1	Fe <sub>3</sub> O <sub>4</sub> /SiO <sub>2</sub> -NH <sub>2</sub> /SA/Pd	Pd (0.05)	53
2	Fe <sub>3</sub> O <sub>4</sub> @PUVS-Pd	Pd (0.09)	54
3	Fe <sub>3</sub> O <sub>4</sub> @PUNP-Pd	Pd (0.1)	55
4	$Fe_3O_4/P(GMA-AAMMA-Pd)$	Pd (0.2)	56
5	Pd-CuFe <sub>2</sub> O <sub>4</sub>	Pd (0.0324)	This work

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 Table 2
 Optimization of the solvent<sup>a</sup>

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Entry	Solvent	Base	(mmol) Catalyst (m	g) Time (h)	Isolated yield (%)	
1	<i>n</i> -BuOH	1	—	48	_	
2	n-BuOH	_	1	48	_	
3	n-BuOH	1	1	7	50	
4	n-BuOH	1	1	24	93	
5	n-BuOH	1	2	6	60	
6	n-BuOH	1	3	6	72	
7	n-BuOH	2	6	6	80	
8	n-BuOH	3	6	4	95 <sup>b</sup>	
9	n-BuOH	4	6	3	95 <sup>b</sup>	
10	n-BuOH	4	6	45 min	95 <sup>c</sup>	
11	CH <sub>3</sub> CN	4	6	24	78	
12	Toluene	4	6	24	60	
13	DMF	4	6	24	73	
14	DMSO	4	6	24	80	
15	$H_2O$	4	6	24	60	

<sup>*a*</sup> Phenylacetylene (1 mmol), solvent (3 ml), base (TEA = triethylamine), catalyst (Pd–CuFe<sub>2</sub>O<sub>4</sub>, 0.000324 mmol of Pd per 57 mg), r.t. = 23 °C unless otherwise noted. <sup>*b*</sup> 40 °C. <sup>*c*</sup> 60 °C.

Table 3 Optimization of the amount of catalyst for the homocoupling of phenylacetylene  $^{\rm a}$ 

$\frown$	Pd-CuFe₂O₄ MNPs (catalyst) TEA (4 mmol), n-BuOH, 60°C, air		<b>_</b>
Entry	Amount of catalyst (mol%)	Time (h)	$\operatorname{Yield}^{b}(\%)$
1	0	24	_
2	0.05	5	70
3	0.1	4	75
4	0.5	3.5	75
5	1	2.5	80
6	1.5	2.5	80
7	1.74	45 min	95
8	2	30 min	95
9	2.5	30 min	95

<sup>*a*</sup> Phenylacetylene (1 mmol), 60 °C in air, *n*-BuOH (3 ml), catalyst (Pd–CuFe<sub>2</sub>O<sub>4</sub> MNPs, 0.000324 mmol of Pd per 57 mg), TEA (4 mmol). <sup>*b*</sup> Isolated yield after column chromatography.

also low (Table 4, entry 2). Moreover, as can be found in the literature, both EtOH and *n*-BuOH are considered as green solvents.<sup>57</sup> Thus, we chose *n*-BuOH as the best solvent for the reaction at a temperature of 60  $^{\circ}$ C (Table 4, entry 3).

As it was observed that the presence of a base is essential for the formation of diynes, we optimized the reaction conditions with various bases in air (Table 5). Compared to the inorganic bases, the organic bases including primary amines, secondary amines and tertiary amines were more effective, with triethylamine being the best (Table 5, entry 2) at the temperature of 60 °C.

We also tested the homocoupling reaction of phenylacetylene under the optimized conditions using  $CuFe_2O_4$  MNPs as the catalyst, but it failed to show a positive homocoupling reaction. It was witnessed that when Pd was supported on  $CuFe_2O_4$  MNPs, the coupling reaction afforded the best result

Table 4 Optimization using different alcohols<sup>a</sup>

$\langle \rangle$	Pd-CuFe <sub>2</sub> O <sub>4</sub> MNPs (2 m TEA, Solvent (3 mL) Time (h), air	nol%) , 60°C,	
Entry	Solvent	Time (h)	Isolated yield (%)
1	МеОН	5	No product
2	EtOH	2	80
3	n-BuOH	0.5	95
4	Polyethylene glycol	5	75
5	Isopropanol	3	80
6	Triethylene glycol	3.5	70
7	Ethylene glycol	5	No product

 $^a$  Phenylacetylene (1 mmol), Pd–CuFe<sub>2</sub>O<sub>4</sub> MNPs (2 mol%, 6.89 mg, 0.000324 mmol of Pd per 57 mg), 60  $^\circ$ C, solvent (3 ml), TEA (4 mmol).

Table 5 Optimization of bases for the homocoupling of phenylacetylene catalyzed by Pd–CuFe $_2O_4~\text{MNPs}^a$ 



<sup>*a*</sup> Phenylacetylene (1 mmol), Pd–CuFe<sub>2</sub>O<sub>4</sub> MNPs (2 mol%, 6.89 mg, 0.000324 mmol of Pd per 57 mg), 60  $^{\circ}$ C, air, solvent (3 ml), base (4 mmol). <sup>*b*</sup> Isolated yield after column chromatography.

(Table 6). The exact reason for this is not known and further studies on this are under progress. But it clearly indicated that Cu only synergistically supports<sup>58</sup> the activity of Pd and is not active by itself for the reaction alone.

**3.2.2** Substrates scope. After optimization of the reaction conditions, we used the catalyst for the homocoupling of different substituted terminal alkynes (Table 7). Within the stipulated time, the catalytic oxidative homocoupling of all the phenylacetylenes (Table 7, entries 1–8), which contain electron-withdrawing as well as electron-donating substituents, proceeded readily to afford the corresponding diyne derivatives

 Table 6
 Optimization using different catalyst systems<sup>a</sup>

	Pd-CuFe <sub>2</sub> O <sub>4</sub> MNPs TEA, BuOH (3 mL), min. air	(2 mol%) 60°C, 30 →	
Entry	Catalyst	Time (h)	Yield <sup><math>b</math></sup> (%)
1	Blank	24	_
2	CuFe <sub>2</sub> O <sub>4</sub>	18	—
5	Pd/CuFe <sub>2</sub> O <sub>4</sub>	0.5	95

 $^a$  Phenylacetylene (1 mmol), 60 °C in air, *n*-BuOH (3 ml), catalyst (2 mol%), TEA (4 mmol).  $^b$  Isolated yield after column chromatography.

	, ,		
R	Pd-CuFe <sub>2</sub> O <sub>4</sub> MNPs (2 mol%) 60°C in air TEA(4 mmol), n-BuOH (3mL)	$\rightarrow$	
Entry	R	Time (min)	$\operatorname{Yield}^{b}(\%)$
1	Н	30	95
2	<i>p</i> -OMe	25	98
3	<i>m</i> -OMe	25	95
4	<i>p</i> -Me	30	97
5	<i>m</i> -Me	30	96
6	<i>p</i> -Br	30	88
7	p-NO <sub>2</sub>	30	85
8	3-NH <sub>2</sub>	30	80
9	1-Heptyne	60	70
10	(2-Propynyl)cyclohexane	60	63
<sup>a</sup> Alkynes	(1 mmol), Pd–CuFe <sub>2</sub> O <sub>4</sub>	MNPs (2 r	nol%, 6.89 mg

Alkynes (1 mmol), Pd–CuFe<sub>2</sub>O<sub>4</sub> MNPs (2 mol%, 6.89 mg, 0.000324 mmol of Pd per 57 mg), 60 °C, air, *n*-BuOH (3 ml), TEA (4 mmol). <sup>*b*</sup> Isolated yield after column chromatography, 60 °C.

in 80–98% yields, thus indicating the fact that the electronic nature of the substituents had little influence on the yield. Moreover, steric hindrance also did not obviously affect the reaction yields and catalytic activity (Table 7, entries 2 vs. 3 and entries 4 vs. 5). However, alkyl substrates required longer reaction times compared to the aryl substrates and the yields were also low (Table 7, entries 9 and 10).

#### 3.3 Catalyst leaching and recyclability test

3.3.1 Hot filtration test. Considering the economic and green potential, recyclability is an important factor where heterogeneous catalysis is concerned.<sup>59</sup> Thus, it was necessary to know the working principle of the active catalyst, *i.e.* whether it is operating heterogeneously or homogeneously. To observe this, a hot filtration test was performed using phenylacetylene (1 mmol), TEA (4 mmol), n-BuOH (3 ml), and Pd-CuFe<sub>2</sub>O<sub>4</sub> (2 mol%, 6.89 mg) at a temperature of 80 °C in a 50 ml round bottom flask. The reaction was stopped after 10 min, the catalyst was separated by using an external magnet (40% yield was determined using GC-MS analysis), and the reaction was allowed to continue under the same reaction conditions for 3 h without the solid catalyst. It was observed that this reaction did not proceed and the reagents remained intact up till 3 h of reaction time (using GC-MS analysis), which ruled out the possibility of homogeneous/semi-heterogeneous catalysis. Thus, it was proved that the working mode of our catalyst was heterogeneous.

**3.3.2 Recyclability test.** Moreover, the recyclability of the catalyst was tested using the model substrate of phenylacety-lene under the optimized conditions. After the completion of the reaction, the catalyst was easily removed from the reaction mixture using an external magnet and dried at 40 °C and reused for a fresh batch of reaction [Fig. S1 (ESI†)]. The catalyst was easily recyclable up to the 5th cycle without any significant loss in the catalytic activity [Fig. S2 (ESI†)]. However, after the 5th cycle, there was a slight loss in the catalytic activity, as we weighed out the catalyst was observed during catalysis. XPS



Fig. 7 XPS spectra: (a) survey scan of recycled  $Pd-CuFe_2O_4$ ; (b) Cu 2p; (c) Fe 2p; and (d) Pd 3d of the recycled catalyst after the 4th cycle.

analysis of the recycled catalyst was performed after the 4th cycle to check if there was any change in the oxidation state of the catalyst (Fig. 7). The amount of catalyst found in the 4th cycle was 4.27 mg (0.000324 mmol of Pd per 57 mg). It was observed that the oxidation state of all three metals remained intact with slight changes in the binding energy. Thus, the oxidation states of the metal in the recycled catalyst were  $Cu^{2+}$ ,  $Fe^{3+}$  and Pd<sup>0</sup>. Therefore, with a very low amount of Pd loading, our catalyst proved to be very efficient for the synthesis of various diynes.

#### 3.4 Mechanism

The exact mechanism of alkyne homocoupling reaction is not clearly known. Thus, based on the above results and according to a literature survey,<sup>60</sup> we would like to propose a brief mechanistic pathway for the Pd–CuFe<sub>2</sub>O<sub>4</sub> catalyzed homocoupling of terminal alkynes (Fig. 8). For our convenience, to provide the reaction mechanism, we would like to take phenylacetylene as the model substrate.



Fig. 8 Proposed mechanism for the  $Pd-CuFe_2O_4$  catalyzed oxidative homocoupling reaction.

Table 8 Comparison of the efficiency of the Pd-CuFe<sub>2</sub>O<sub>4</sub> MNPs with those of some reported catalyst systems for the homocoupling reaction of phenylacetylene

Catalyst	Reaction conditions	Temp. (°C)	Time (h)	Yield (%)	Ref.
$CuCl_2 \cdot 2H_2O$ (0.1 mmol)	NaOAc, PEG	120	1.5	99	62
$Cu_2ophen_2$ (5 mol%)	TBAB (5 mol%), $H_2O$	rt	10	95	63
Ni(dppe)Cl <sub>2</sub> (5 mol%)	$Ag_2O$ (1 equiv.), 1,2-dichloroethane	rt	4	97	64
$Pd(OAc)_2$ (2 mol%), CuI (2 mol%)	DABCO, MeCN	rt	2	90	65
Сu(п)-SBA-15 (50 mg)	DMSO, air	100	4	97	66
CuCl (5 mol%)	CH <sub>3</sub> CN, O <sub>2</sub> , blue LED light	rt	7	98	67
$Cu(OTf)_2$ (5 mol%)	DBU, acetone	rt	5	92	68
Pd–CuFe <sub>2</sub> O <sub>4</sub> MNPs (2 mol% <i>i.e.</i> 6.89 mg)	<i>n</i> -Butanol, air, TEA	60	0.5	95	This work

For heterogeneous catalysed reactions, it is widely accepted that Pd in solution as a colloid or complex is the true catalytically active species.<sup>61</sup> We believe that Pd is activated by  $CuFe_2O_4$ , which helps in better desorption and leads to faster formation of complexes or colloids in the solution, and on completion of the reaction, the palladium is redeposited onto the support or Pd clusters. Thus,  $CuFe_2O_4$  acts as a reservoir for the Pd species.

Initially, oxygen from air dissolved in the reaction solution, oxidizing the Pd(0) nanoparticles on the surface of  $CuFe_2O_4$  MNPs to Pd( $\pi$ ). The *n*-BuOH solvent quenches the resulting oxygen anion, but the quantities of this one-time reaction are too small to be determined. The deprotonation of the terminal alkyne by the base (Et<sub>3</sub>N) leads to the acetylide, which reacts with Pd-CuFe<sub>2</sub>O<sub>4</sub> to form the Pd( $\pi$ ) acetylide complex. Then, through transmetalation, another acetylide adds to Pd( $\pi$ ). Pd( $\pi$ ) is then reduced to Pd(0) by reductive elimination, which results in the formation of a homocoupling product.

#### 3.5 Comparison efficiency with other reported catalysts

We compared the efficiency of our synthesized MNPs with other reported catalysts for the synthesis of various 1,3-diynes. The efficiency was checked with the homocoupling of phenylacetylene, and it revealed that our reaction and catalyst were superior compared to those mentioned in other works with respect to reaction time, amount of catalyst and reaction conditions. The results are tabulated in Table 8.

## 4. Conclusion

Here, we have demonstrated a cost efficient pathway for the synthesis of various diynes using Pd–CuFe<sub>2</sub>O<sub>4</sub> MNPs as the catalyst with a very small amount of Pd loading (0.000324 mmol in 57 mg of the catalyst) without using any harsh reaction conditions. The support of MNPs in Pd enhances the recyclability of the catalyst up to the 5th cycle, reduces the amount of Pd loading and results in no loss in the activity of the catalyst. Thus, this protocol serves as an economic and green procedure for the synthesis of symmetrical 1,3-diynes with a reduction in the amount of expensive Pd metal in the catalyst. In addition, this procedure has the advantages of excellent to good yields of the products and short reaction times.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

The authors acknowledge SAIF NEHU Shillong, CIF IIT Guwahati, CSIC Dibrugarh University, SAIF IIT Bombay, IIT Kanpur, and IIT Bombay for providing the analytical services.

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