Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Pd supported on clicked cellulose-modified magnetite-graphene oxide nanocomposite for C-C coupling reactions in deep eutectic solvent

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ARTICLE INFO

Magnetite-graphene oxide nanocomposite

Keywords:

Pd catalyst

Coupling reaction

Deep eutectic solvent

Cellulose

ABSTRACT

Cellulose-modified magnetite-graphene oxide nanocomposite was prepared via click reaction and utilized for immobilization of palladium (Pd) nanoparticles without using additional reducing agent. The abundant OH groups of cellulose provided the uniform dispersion and high stability of Pd nanoparticles, while magnetite-graphene oxide as a supporting material offered high specific surface area and easy magnetic separation. The as-prepared nanocomposite served as a heterogeneous catalyst for the Heck and Sonogashira coupling reactions in various hydrophilic and hydrophobic deep eutectic solvents (DESs) as sustainable and environmentally benign reaction media. Among the fifteen DESs evaluated for coupling reactions, the hydrophilic DES composed of dimethyl ammonium chloride and glycerol exhibited the best results. Due to the low miscibility of catalyst and DES in organic solvents, the separated aqueous phase containing both of the catalyst and DES can be readily recovered by evaporating water and retrieved eight times with negligible loss of catalytic performance.

1. Introduction

Palladium-catalyzed C-C cross-coupling transformations have attracted considerable research attention as a mean toward industrially beneficial chemicals (Biffis, Centomo, Zotto, & Zecca, 2018; Zhang, Mao, Wang, Phan, & Zhang, 2020; Zhu & Lindsay, 2019). The most explored examples of C--C coupling processes catalyzed by Pd compounds are Heck and Sonogashira, which involve coupling of aryl or alkyl halides with terminal alkenes and alkynes, respectively (Cao et al., 2020; Li, Feng, & Li, 2019; Sardarian, Eslahi, & Esmaeilpour, 2019). The resulting products of both reactions are of substantial importance as major building blocks and key intermediates in material science, natural products, pharmaceuticals, and conducting polymers (Cheng et al., 2020; Zheng, Zhao, Xu, & Zeng, 2020). During the last decades, heterogeneously Pd-catalyzed C-C coupling reactions have received much interest owing to their several advantages over homogeneous catalytic systems, such as easy work up procedures and facile catalyst recycling (Nuri et al., 2020; Tashrifi et al., 2019).

Nowadays, biopolymers such as chitosan, cellulose, and cyclodextrins are being utilized as supports for manufacturing heterogeneous Pd catalysts (Tukhani, Panahi, & Khalafi-Nezhad, 2018; Wang et al., 2019). Among the various biopolymers, cellulose, one of the most abundant organic polymers in nature, has been widely utilized as catalyst support. Cellulose is inexpensive, non-toxic, renewable, biodegradable, and environmental friendly, all of which make it an excellent candidate for being used as support in catalytic systems (Dong, Wu, Chen, & Wei, 2017; Kandathil, Kempasiddaiah, Sasidhar, & Patil, 2019). Moreover, cellulose with its large surface area and free hydroxyl groups can act both as ligand and reducing agent for the formation and stabilization of metal nanoparticles and provides straightforward diffusion of the reagents to nanoparticles. It also helps in the well dispersion of metal nanoparticles and prevents them from aggregation (Goswami & Das, 2018). Compared with other biopolymers, cellulose can easily be functionalized with a multitude of functions owing to the presence of abundant hydroxyl groups on its backbone and form either soluble or insoluble catalyst supports via chemical modification (Wang, Hu, Xue, & Wei, 2014). Different noble metal nanoparticles supported on cellulose have been demonstrated to be effective catalysts for various reactions (Jebali et al., 2018).

One of the challenges of using cellulose as support is that its stable dispersion hinders facile separation for recycling purposes. Conjugation of cellulose with solid supports which can facilitate its separation and recycling, provides a very promising solution to this challenge (Sabaqian, Nemati, Heravi, & Nahzomi, 2017). To date, various covalent and

https://doi.org/10.1016/j.carbpol.2020.117109

Received 29 June 2020; Received in revised form 11 September 2020; Accepted 12 September 2020 Available online 20 September 2020 0144-8617/© 2020 Elsevier Ltd. All rights reserved.







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Scheme 1. Schematic preparation method of GO-Fe₃O₄-Cellulose-Pd.

non-covalent strategies have been successfully developed for conjugation of cellulose with solid supports (Freudenberg et al., 2005; Kabiri & Namazi, 2014; Sabaqian et al., 2017; Wang et al., 2018; Yin, Chen, Zhang, Zhang, & Zhang, 2019). Among them, the copper-catalyzed azide-alkyne cycloaddition (CuAAC) may be preferable due to its simple and mild reaction procedure, high efficiency and selectivity, and lack of side reactions (Sharma, Rathod, Singh, Kumar, & Sasson, 2018; Zhang, Li, Li, Wang, & Wang, 2019).

In addition to recyclability of catalyst, the solvents have a key effect on the environmental impact of organic transformations. Thus, many attempts have been directed toward the replacement of hazardous volatile organic solvents by greener media. In this regard, deep eutectic solvents (DESs) as a new family of green reaction media have become the focus of several researches due to their outstanding physicochemical properties (Marset et al., 2017; Quirós-Montes, Carriedo, García-Álvarez, & Soto, 2019). DESs possess favorable characteristics such as non-toxicity, facile synthesis methods, biodegradability, easy recyclability, low vapor pressure, and low melting point, which fully correspond with green chemistry principles (Liu et al., 2020; Saavedra, González-Gallardo, Meli, & Ramón, 2019). Consequently, they are promising alternatives to volatile organic solvents for utilization in organic transformations. Despite these interesting properties of DESs, there are only a few reports on the utilization of DESs as media in the Heck and Sonogashira coupling reactions (Grabner, Schweiger, Gavric, Kourist, & Gruber-Woelfler, 2020; Ilgen & Konig, 2009; Marset et al., 2017, 2019; Messa et al., 2020; Saavedra et al., 2019).

Conjugation of high surface area graphene oxide (GO) with magnetic nanoparticles, specifically Fe_3O_4 nanoparticles, produces the useful magnetic graphene oxide nanocomposite with facile separation efficiency which is a promising candidate for use as catalyst support combining the advantages of both GO and magnetic nanoparticles (Sharma, Sharma, Sharma, Paul, & Clark, 2019; Xing et al., 2020). Accordingly, we decided to employ cellulose-modified magnetite-graphene oxide nanocomposite for immobilization of Pd nanoparticles for designing a heterogeneous Pd catalyst. As far as we know, modification of magnetite-graphene oxide nanocomposite using cellulose containing abundant OH groups, which have strong ability to stabilize metal nanoparticles, has never been applied for stabilization of Pd nanoparticles. The catalytic performance of the prepared catalyst in the Heck and Sonogashira coupling reactions in different DESs as green and recyclable reaction media is reported.

2. Experimental

2.1. Catalyst preparation

The preparation method of GO-Fe₃O₄-Cellulose-Pd was illustrated in Scheme 1. Briefly, GO was modified with magnetite nanoparticles to obtain GO-Fe₃O₄. Then, the hydroxyl groups on the surface of GO-Fe₃O₄ were reacted with 3-CPTES, followed by the substitution reaction of chloro groups with azide ions to achieve GO-Fe₃O₄-N₃. Subsequently, the click reaction of azide groups in GO-Fe₃O₄-N₃ with pre-synthesized alkyne-functionalized cellulose afforded GO-Fe₃O₄-Cellulose. Finally, GO-Fe₃O₄-Cellulose-Pd heterogeneous catalyst was synthesized by treatment of GO-Fe₃O₄-Cellulose with palladium acetate in absolute ethanol. According to the inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis, the total loading of Pd in the prepared catalyst was found to be 0.41 mmol.g⁻¹. Full details about the preparation method of GO-Fe₃O₄-Cellulose-Pd are provided below.

2.1.1. Preparation of magnetite-graphene oxide nanocomposite (GO-Fe₃O₄)

GO was synthesized according to modified Hummers procedure as described elsewhere (Marcano et al., 2010). Magnetite-graphene oxide nanocomposite (GO-Fe₃O₄) was obtained according to literature procedure (See supporting information) (Amiri, Shabani, Dadfarnia, & Sadjadi, 2019).

2.1.2. Preparation of azide-functionalized GO-Fe₃O₄ (GO-Fe₃O₄-N₃)

GO-Fe₃O₄ (1 g) was suspended in 40 mL of dry toluene under sonication for 30 min. After addition of 3-chloropropyltriethoxysilane (3-CPTES, 3 mL), the mixture was refluxed for 24 h under nitrogen atmosphere. The obtained solid (GO-Fe₃O₄-Cl) was magnetically collected, washed with ethanol to remove the unreacted silylating agent, and dried at 80 °C under vacuum. The GO-Fe₃O₄-Cl (1 g) was sonicated in dimethylformamide (DMF, 50 mL) for 30 min and after addition of NaN₃ (2 mmol, 0.13 g), the suspension was stirred at 80 °C for 10 h. Final product was isolated with a permanent magnet, washed with DMF several times, and dried at 80 °C under vacuum to afford GO-Fe₃O₄-N₃.

2.1.3. Preparation of clicked cellulose-modified GO-Fe₃O₄ (GO-Fe₃O₄-Cellulose)

Alkyne-functionalized cellulose was prepared according to the earlier report (Mangiante et al., 2013) and characterized by FT-IR spectroscopy (Figure S1). On the other hand, $GO-Fe_3O_4-N_3$ (1 g) was uniformly dispersed in 60 mL of dry DMF under ultrasonic condition. After that, alkyne-functionalized cellulose (2 g), copper (II) sulfate (0.1 g), and sodium ascorbate (2 g) were added to the above mixture and stirred at 50 °C for 24 h. The mixture was cooled down to room temperature and the product was isolated by magnetic separation, washed with DMF and water repeatedly, and dried at 80 °C under vacuum.

2.1.4. Immobilization of Pd nanoparticles on GO-Fe₃O₄-Cellulose

GO-Fe₃O₄-Cellulose (1 g) was ultrasonically dispersed in absolute ethanol (50 mL). After addition of palladium acetate (0.5 mmol, 0.11 g), the mixture was stirred for 24 h at room temperature. The resultant black solid (GO-Fe₃O₄-Cellulose-Pd) was collected with utilizing a magnet, washed thoroughly with large volume of hot ethanol until washing were colorless, and dried at 80 °C under vacuum.

2.2. Preparation of DESs

DESs were synthesized according to previous works (Jiang et al., 2019; Makoś, Słupek, & Gębicki, 2020; Shekaari, Ahadzadeh, & Karimi, 2019; Zhang, Vigier, Royer, & Jérôme, 2012). They were prepared by mixing choline chloride (ChCl), dimethyl ammonium chloride (DMAC),

Table 1

The effect of various reaction conditions on the Heck reaction in the presence of
GO-Fe ₃ O ₄ -Cellulose-Pd. ^a

Entry	Catalyst (mol%)	DES (molar ratio)	Base	T (°C)	Time (h)	Yield (%) ^b
1	1	ChCl:Urea	K ₂ CO ₃	100	5	73
2	1	(1.2) ChCl:CA (1:1)	K ₂ CO ₃	100	5	45
3	1	ChCl:MA	K ₂ CO ₃	100	5	78
4	1	ChCl:Gly (1:2)	K ₂ CO ₃	100	5	91
5	1	ChCl:EG (1:2)	K ₂ CO ₃	100	5	86
6	1	ChCl:OX (1:1)	K ₂ CO ₃	100	5	58
7	1	ChCl:BA (1:1.5)	K ₂ CO ₃	100	5	85
8	1	DMAC:Urea (1:2)	K ₂ CO ₃	100	5	81
9	1	DMAC:CA	K ₂ CO ₃	100	5	43
10	1	DMAC:MA	K ₂ CO ₃	100	5	89
11	1	DMAC:Gly (1:2)	K ₂ CO ₃	100	5	98
12	1	TBAB:OA	K ₂ CO ₃	100	5	26
13	1	TBAB:DA (1:2)	K ₂ CO ₃	100	5	37
14	1	TOMAC:OA (1:2)	K ₂ CO ₃	100	5	28
15	1	TOMAC:DA (1:2)	K ₂ CO ₃	100	5	41
16	1.25	DMAC:Gly (1:2)	K ₂ CO ₃	100	5	98
17	0.75	DMAC:Gly (1:2)	K ₂ CO ₃	100	5	98
18	0.5	DMAC:Gly (1:2)	K ₂ CO ₃	100	6.5	92
19	none	DMAC:Gly (1:2)	K ₂ CO ₃	100	24	0
20	0.75	DMAC:Gly (1:2)	K ₂ CO ₃	80	5	61
21	0.75	DMAC:Gly (1:2)	K ₂ CO ₃	120	5	98
22	0.75	DMAC:Gly (1:2)	Et ₃ N	100	8	34
23	0.75	DMAC:Gly (1:2)	NaOH	100	10	23
24	0.75	DMAC:Gly (1:2)	Na ₂ CO ₃	100	7	74
25	0.75	DMAC:Gly (1:2)	КОН	100	6	57
26	0.75	DMAC:Gly (1:2)	K ₃ PO ₄	100	5	82

^a Reaction conditions: iodobenzene (1 mmol), n-butyl acrylate (1.2 mmol), base (2 mmol), and DES (3 mL).

^b Isolated yields.

tetrabutylammonium bromide (TBAB), or trioctylmethylammonium chloride (TOMAC) as hydrogen bond acceptor and urea, citric acid (CA), malonic acid (MA), glycerol (Gly), ethylene glycol (EG), oxalic acid (OX), boric acid (BA), octanoic acid (OA), or decanoic acid (DA) as hydrogen bond donor with the molar ratio given in Table 1. The mixtures were stirred vigorously in an oil bath in a temperature range between 70 and 90 °C for 2-3 h until clear and homogeneous liquids were obtained.

2.3. Typical method for the Heck coupling reaction

To a mixture of aryl halide (1 mmol), alkene (1.2 mmol), and K_2CO_3 (2 mmol) in DES (DMAC:Gly, 3 mL), 0.018 g of GO-Fe₃O₄-Cellulose-Pd



Fig. 1. (a) FT-IR spectra of GO, GO-Fe₃O₄, GO-Fe₃O₄-N₃, GO-Fe₃O₄-Cellulose, and GO-Fe₃O₄-Cellulose-Pd, (b) XRD patterns of GO, GO-Fe₃O₄, and GO-Fe₃O₄-Cellulose-Pd, (c) XPS survey spectrum of GO-Fe₃O₄-Cellulose-Pd, and (d) high-resolution XPS spectrum of Pd 3d.

(0.75 mol%) was added. The mixture was stirred at 100 °C and the progress of reaction was checked by thin layer chromatography (TLC). The mixture was quenched with water (15 mL) after completing the reaction, and extracted with ethyl acetate (3 × 10 mL). The organic extract was dried over Na₂SO₄ and concentrated under vacuum. Purification of the obtained crude product was performed by column chromatography on silica gel. The aqueous phase, which contained both of the catalyst and DES, was used for another run after evaporation of water.

2.4. Typical method for the Sonogashira coupling reaction

A mixture of phenylacetylene (1.2 mmol), aryl halide (1 mmol), K_2CO_3 (2 mmol), and GO-Fe₃O₄-Cellulose-Pd (1 mol%, 0.024 g) in 3 mL of DES (DMAC:Gly) was left under stirring at 120 °C. After completing the reaction (monitored by TLC), the mixture was quenched with water (10 mL) and extracted with ethyl acetate (3 \times 10 mL). The work-up procedure was performed similar to the Heck coupling reaction.

3. Results and discussion

3.1. Characterization of GO-Fe₃O₄-Cellulose-Pd

In order to approve the successful modification in each step, the FT-IR spectra of the resulted samples were obtained and depicted in Fig. 1a. In the spectrum of primary GO, the peaks at 1000–1300 cm⁻¹ were assigned to the C—OH vibrations of phenolic groups and C—O—C vibrations of epoxy groups. Also, the peaks located at 1607 and 1715 cm⁻¹ were due to the C—C stretching vibrations of aromatic skeletal network and the C=O stretching vibrations, respectively (Masteri-Farahani, Hosseini, & Forouzeshfar, 2020). After introducing magnetite nanoparticles, two peaks emerged at 510 and 630 cm⁻¹ corresponding to the Fe-O stretching vibrations in Fe₃O₄ nanoparticles (Aliyari, Alvand, & Shemirani, 2016). For GO-Fe₃O₄-N₃, a sharp peak at 2175 cm⁻¹ was appeared due to the stretching vibration of azide (-N₃) groups, which revealed their attachment on the surface of GO-Fe₃O₄. Moreover, the bands corresponding to the C–H stretching vibrations of the propyl chain in silylating agent were observed at about 2800–3000 cm⁻¹ (Sharma et al., 2018). After click reaction of GO-Fe₃O₄-N₃ with alkyne-functionalized cellulose, the characteristic peak of azide group at 2000–2200 cm⁻¹ was vanished indicating the conversion of azide groups to triazole rings and the successful attachment of cellulose to GO-Fe₃O₄ (Sharma et al., 2018). Furthermore, the intensity of O–H stretching vibrations at 3420 cm⁻¹ increased dramatically owing to the existence of abundant O–H groups on the surface of supported cellulose. The spectrum of GO-Fe₃O₄-Cellulose-Pd showed almost no change after loading of Pd nanoparticles on the surface of GO-Fe₃O₄-Cellulose.

The phase composition of the samples were explored by X-ray diffraction (XRD) analysis (Fig. 1b). The XRD pattern of GO revealed an intense peak at $2\theta = 11.3^{\circ}$, corresponding to (001) plane (Masteri-Farahani et al., 2020). For GO-Fe₃O₄, the observed diffraction peaks can be attributed to crystal planes of Fe₃O₄ with face centered cubic structure (JCPDS Card no. 19-0629). Meanwhile, the (001) reflection peak of GO was not appeared in GO-Fe₃O₄ due to the incorporation of magnetite nanoparticles between the nanosheets of GO (Moztahida et al., 2019). The characteristic diffraction peaks of Fe₃O₄ crystal structure were detected in the XRD pattern of GO-Fe₃O₄-Cellulose-Pd, implying that the structure of GO-Fe₃O₄ was not destroyed during the catalyst preparation. Moreover, the XRD pattern of catalyst also demonstrated three new weak peaks at 40° , 46° , and 67° which can be indexed to (111), (200), and (220) crystal planes of Pd (0), respectively (Tukhani et al., 2018). The weakness of the peaks is due to small size of Pd nanoparticles and their well-dispersion on the surface of GO-Fe₃O₄-Cellulose.

X-ray photoelectron spectroscopy (XPS) was utilized to clarify the surface chemical composition of the catalyst. Fig. 1c depicts the XPS



Fig. 2. SEM image, EDX spectrum, and elemental mapping images of GO-Fe₃O₄-Cellulose-Pd.

survey spectrum of GO-Fe₃O₄-Cellulose-Pd demonstrating the signals of C 1s, N 1s, O 1s, Si 2s, Si 2p, Fe 2p, and Pd 3d, confirming the overall chemical composition of the catalyst. In the high-resolution XPS spectrum of Pd (Fig. 1d), the Pd $3d_{5/2}$ and Pd $3d_{3/2}$ peaks were clearly observed at 335.67 and 341.18 eV, respectively, consistent with the existence of Pd in the oxidation state of zero i.e. Pd° (Stadler et al., 2019). Meanwhile, no peaks assignable to the Pd²⁺ oxidation state were detected, implying that all of the Pd²⁺ ions in the catalyst structure were completely reduced to Pd°. The results further inferred that cellulose component acted as reducing agent as well as stabilizer for Pd nanoparticles and prevented from their oxidation.

The chemical composition of prepared catalyst was further examined by energy dispersive X-ray (EDX) spectroscopy. As shown in Fig. 2, significant peaks corresponding to C, N, O, Si, Fe, and Pd elements can be seen in the EDX spectrum of GO-Fe₃O₄-Cellulose-Pd. Moreover, EDX elemental mapping images of GO-Fe₃O₄-Cellulose-Pd revealed that all of the elements were uniformly distributed on the surface of catalyst.

The microstructure and morphology of GO, GO-Fe₃O₄, and GO-Fe₃O₄-Cellulose-Pd were monitored by scanning electron microscopy (SEM) and transition electron microscopy (TEM) techniques. Fig. 3a demonstrates the SEM image of GO with the lamellar morphology. In comparison with the bare GO, GO-Fe₃O₄ (Fig. 3b) revealed the existence of Fe₃O₄ nanoparticles on the surface of GO nanosheets. Also, as

observed in the SEM image of GO-Fe₃O₄-Cellulose-Pd (Fig. 3c), the morphology of the catalyst was the same as GO-Fe₃O₄.

The TEM image of GO in Fig. 3d shows a layered and sheet-like structure characteristic of GO structure. After incorporation of magnetite, well-dispersed spherical Fe_3O_4 nanoparticles with diameters of about 10 nm can be seen on the surface of GO nanosheets without any aggregation (Fig. 3e). From the TEM image of GO-Fe₃O₄-Cellulose-Pd (Fig. 3f), it can be found that the preparation process of the catalyst had no influence on the microstructure of GO-Fe₃O₄ nanocomposite and Fe₃O₄ nanoparticles remained well-dispersed on the GO surface.

The magnetic behavior of GO-Fe₃O₄ and GO-Fe₃O₄-Cellulose-Pd were explored with vibrating sample magnetometry (VSM) and the magnetization curves were presented in Fig. 4a. Both samples exhibited almost zero coercivity and remanence in their magnetization curves, demonstrating their superparamagnetic features. The saturation magnetization value of GO-Fe₃O₄-Cellulose-Pd was decreased to 19.8 emu g⁻¹ compared with GO-Fe₃O₄ (37.1 emu g⁻¹) due to the presence of cellulose and Pd nanoparticles within the GO-Fe₃O₄ nanocomposite. Despite the reduction in saturation magnetization, the catalyst was easily isolated magnetically by setting an external magnet near the wall of the vial as shown in the inset of Fig. 4a.

To examine the thermal stability of the synthesized catalyst, thermogravimetric analysis (TGA) was carried out. The TGA curve of GO-



Fig. 3. SEM images of (a) GO, (b) GO-Fe₃O₄, and (c) GO-Fe₃O₄-Cellulose-Pd, and TEM images of (d) GO, (e) GO-Fe₃O₄, and (f) GO-Fe₃O₄-Cellulose-Pd.



Fig. 4. (a) Magnetization curves of GO-Fe₃O₄ and GO-Fe₃O₄-Cellulose-Pd, and (b) TGA curve of GO-Fe₃O₄-Cellulose-Pd.

Fe₃O₄-Cellulose-Pd in Fig. 4b exhibited two weight losses. The first negligible weight loss (2%) occurred below 150 °C owing to desorption of moisture and volatile species. The next weight loss after 150 °C was attributed to the decomposition of organic parts and cellulose in the catalyst structure.

3.2. Catalytic activity of GO-Fe₃O₄-Cellulose-Pd

After characterizing the catalyst structure, its catalytic performance was firstly evaluated in the Heck coupling reaction. The coupling of nbutyl acrylate with iodobenzene was chosen as model reaction to determine the optimum reaction conditions. The effect of reaction parameters was investigated in this reaction and the details were provided in Table 1. As seen in Table 1, the use of hydrophilic DESs resulted in higher product yields (Table 1, entries 1–11) compared to hydrophobic DESs (Table 1, entries 12–15). The plausible reason might be the hydrophilic nature of the catalyst that provides more dispersion in hydrophilic DESs and thus enhances its catalytic activity. Among the various hydrophilic DESs investigated, DMAC:Gly was the most effective solvent for this reaction. Therefore, DMAC:Gly was identified as the solvent of choice for further investigations.

Next, the catalyst amount was varied from 0.5 mol% to 1.25 mol% (Table 1, entries 16–18). It was found that employing 0.75 mol% of catalyst was appropriate for this reaction. On the other hand, to clarify the effect of catalyst, a blank reaction was conducted without catalyst, in which no product was obtained even after 24 h (Table 1, entry 19). The temperature effect on the reaction was also explored and it was found that with decreasing the temperature to 80 °C, a significant decrease in the product yield was observed (Table 1, entry 20). However, the increase of reaction temperature to 120 °C did not show any substantial increment in the product formation (Table 1, entry 21). Finally, different bases were screened (Table 1, entries 22–26), among which K₂CO₃ was found to be most suitable. According to the data acquired, entry 17 in Table 1 was chosen as the optimized reaction conditions for the Heck reaction.

To demonstrate the scope and generality of the methodology, the



Scheme 2. Heck reaction of various aryl halides and alkenes in the presence of GO-Fe₃O₄-Cellulose-Pd. Reaction conditions: aryl halide (1 mmol), alkene (1.2 mmol), K₂CO₃ (2 mmol), and DMAC:Gly (3 mL). Yields were isolated.

Heck coupling reaction of different aryl halides and alkenes was explored under the optimized reaction conditions (Scheme 2). Different alkyl acrylates as well as styrene were reacted with iodo-, bromo-, and chlorobenzene and desired coupling products were formed with excellent yields. Moreover, the reaction of n-butyl acrylate and styrene with a wide range of aryl halides achieved remarkable yields irrespective of the existence of any electron-donating or electron-withdrawing substituents in the aryl halides. As expected, aryl iodides reacted at a faster rate than aryl bromides and chlorides. Overallw, styrene exhibited higher reactivity than n-butyl acrylate towards the Heck reaction under the optimized conditions. It can be concluded that GO-Fe₃O₄-Cellulose-Pd has excellent catalytic activity in the Heck coupling reaction.

The impressive results of the Heck reaction encouraged us to examine the catalytic activity of the prepared catalyst in the Sonogashira reaction. The optimized reaction conditions were determined using iodobenzene and phenylacetylene as model coupling reaction under diverse conditions and the results were summarized in Table S2. Among the different experimental conditions investigated, the optimum reaction conditions for the Sonogashira reaction were 1 mol% of catalyst, K_2CO_3 as base, and DMAC:Gly as solvent at 120 °C (Table S2, entry 20).

After optimizing the reaction conditions, the scope of methodology was explored with diverse aryl halides (Scheme 3). As can be seen in Scheme 3, aryl iodides, bromides, and chlorides with both electron-donating and electron-withdrawing substituents were coupled with phenylacetylene to form the desired products with high yields. It is noteworthy that no product associated with the homo-coupling reaction of phenylacetylene was detected in all of the examined reactions. The results indicated the high efficiency of GO-Fe₃O₄-Cellulose-Pd in catalyzing the Sonogashira coupling reaction.

In order to show the superiority of the present work, the catalytic



Scheme 3. Sonogashira reaction of various aryl halides and phenylacetylene in the presence of GO-Fe₃O₄-Cellulose-Pd. Reaction conditions: aryl halide (1 mmol), phenylacetylene (1.2 mmol), K₂CO₃ (2 mmol), and DMAC:Gly (3 mL). Yields were isolated.

Table 2

Comparison of the catalytic activity of GO-Fe₃O₄-Cellulose-Pd with other reported Pd-catalysts in the Heck and Sonogashira reactions.

Entry	Catalyst (mol%)	Reaction	Reaction conditions	Time (h)	Yield (%)	Ref
1	Fe ₃ O ₄ /GO-Cellulose-Pd (0.75)	Heck	DMAC:Gly, K ₂ CO ₃ , 100 °C	3.5	95	(This work)
2	PTFE-PdNPs (1.0)	Heck	H ₂ O, KOH, 90 °C	15	91	(Ohtaka et al., 2018)
3	Pd-MPMO (1.9)	Heck	DMF, Et ₃ N, 100 °C	4	58	(Elavarasan, Kala, Muhammad, Bhaumik, & Sasidharan, 2019)
4	Pd/CuFe ₂ O ₄ (4.0)	Heck	DMSO, K ₂ CO ₃ , 120 °C	12	90	(Lakshminarayana et al., 2018)
5	Pd@CS/PAAS (5.0)	Heck	DMA, Et ₃ N, 110 °C	5	95	(Du et al., 2020)
6	PdNPs/Wood (2.6)	Heck	DMF, K ₂ CO ₃ , 100 °C	6	86	(Chao et al., 2019)
7	KjPdC (1.0)	Heck	DMF, NaOAc, 110 °C	24	100	(Santos et al., 2014)
8	$Pd(N,O-L^{Me})_2$ (0.3)	Heck	DMF, K ₂ CO ₃ , 100 °C	15	95	(Ardizzoia, Ghiotti, Therrien, & Brenna, 2018)
9	Fe ₃ O ₄ /GO-Cellulose-Pd (1.0)	Sonogashira	DMAC:Gly, K ₂ CO ₃ , 120 °C	8	91	(This work)
10	Bipyridine-Palladium (3.0)	Sonogashira	Ph ₃ PMeBr:Gly, ⁱ Pr ₂ NH, 60 °C	16	84	(Saavedra et al., 2019)
11	PdNPs/DNA (0.5)	Sonogashira	MeOH, Cs ₂ CO ₃ , 65 °C	24	85	(Camacho, Martín-Garcí, Contreras-Celedón, Chacón-García, & Alonso, 2017)
12	MNP-PdNPs (1.5)	Sonogashira	THF, Et ₃ N, 65 °C	24	85	(Wang et al., 2015)
13	MMT@Pd/Cu (1.0)	Sonogashira	EtOH, K ₂ CO ₃ , 65 °C	16	97	(Xu et al., 2014)
14	Pd@HNTs-T-CD (6.0)	Sonogashira	EtOH/ H ₂ O, K ₂ CO ₃ , 60 °C	1.5	90	(Sadjadi, 2018)
15	palladium salen complex	Sonogashira	i-PrOH, K ₂ CO ₃ , RT	7	98	(Gogoi, Dewan, Borah, & Bora, 2015)
	(2.0)					
16	NHC-palladium complex (1.0)	Sonogashira	DMSO, K ₂ CO ₃ , 100 °C	1	61	(Yang et al., 2012)

activity of GO-Fe₃O₄-Cellulose-Pd was compared with earlier reported Pd-based catalysts in the Heck reaction of iodobenzene and styrene and Sonogashira reaction of iodobenzene and phenylacetylene. From Table 2, it is visible that the current catalyst reveals a comparable catalytic efficiency in coupling reactions. More importantly, the use of natural cellulose as both reducing and stabilizing agents for Pd, the utilization of DES as solvent, and the recovery of the catalyst and DES in fast and easy manner make this system greener than most of the listed

systems.

3.3. Recyclability and stability of GO-Fe₃O₄-Cellulose-Pd and DES

The recycling experiments of GO-Fe₃O₄-Cellulose-Pd and DES were performed in the mentioned Heck and Sonogashira model coupling reactions under the optimized reaction conditions. The hydrophilic character of the catalyst and DES provided an easy strategy for their



Fig. 5. Recyclability of the catalyst and DES for the Heck (red diagram) and Sonogashira (green diagram) model reactions under the optimized reaction conditions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

recycling. After completing the reactions, the mixture was quenched with addition of water and ethyl acetate to form a biphasic system. The organic phase was separated for further product purification and analysis and the aqueous phase which contained both of the catalyst and DES was recovered by evaporating water under vacuum and charged again with fresh reagents and K_2CO_3 for the next run. As presented in Fig. 5, both of the catalyst and DES could be efficiently reused eight times without noticeable decrease in activity. After eight runs, the catalyst was separated easily from the aqueous phase with an external magnet.

FT-IR spectrum and SEM image (Figure S2a-b) of the recycled catalyst revealed that the structure and morphology of the catalyst remained unchanged even after eight successive recyclings. Furthermore, the VSM analysis proved that the magnetic property of the catalyst remained nearly identical after eight recyclings (Figure S2c). The amount of Pd in the catalyst after 8th runs was 0.37 mmol g⁻¹ which in comparison with the fresh one (0.41 mmol.g⁻¹) showed negligible leaching. This could be attributed to the abundant OH groups of the cellulose in the catalyst structure, which prevented the leaching of Pd during catalytic cycles and made the active sites more stable.

4. Conclusion

In summary, cellulose-modified magnetite-graphene oxide nanocomposite was successfully synthesized through click reaction, followed by immobilization of Pd nanoparticles on its surface to form a hydrophilic/magnetically recoverable heterogeneous Pd catalyst. Cellulose acted as both reducing and stabilizing agent for Pd nanoparticles and eliminated the requirement of a reducing agent. The catalytic activity of the obtained catalyst was investigated in the Heck and Sonogashira coupling reactions in various hydrophilic and hydrophobic deep eutectic solvents (DESs). Remarkable yields were achieved in the coupling reactions of various aryl bromides and iodides with alkenes or alkynes in the hydrophilic DES composed of dimethyl ammonium chloride and glycerol. Owing to the very low solubility of the prepared catalyst and DES in organic solvents, the separated aqueous phase containing both of the catalyst and DES can be conveniently recovered by evaporating water and reused eight times with sustained activity. Interestingly, abundant OH groups of cellulose on the surface of the catalyst prevented the leaching and agglomeration of Pd nanoparticles during the catalytic reactions and improved the recyclability of the catalyst. Overall, the preparation of this catalyst using natural cellulose, the use of DES as reaction medium, facile recovery of catalyst and DES, and the simple separation of the catalyst by a magnet make this catalytic system a good candidate towards the aim of green chemistry and catalysis.

CRediT authorship contribution statement

Mahsa Niakan: Investigation, Data curation, Writing - original draft. Majid Masteri-Farahani: Project administration, Supervision, Writing review & editing. Hemayat Shekaari: Investigation, Data curation. Sabah Karimi: Investigation, Writing - original draft.

Acknowledgements

The authors gratefully acknowledge financial support (Grant Number H/4/361) from Kharazmi University.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.carbpol.2020.117109.

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