Research article

Synthesis of nano magnetic supported NHC-palladium and investigation of its applications as a catalyst in the Mizoroki-Heck cross-coupling reaction in H₂O

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ABSTRACT

The unique properties of N-heterocyclic carbenes (NHCs) as an effective ligand for palladium catalytic centers have recently found much attention. In this work, Fe_3O_4 nanoparticle supported palladium(II)–N-heterocyclic carbene catalyst was successfully designed, synthesized and characterized by various methods. The activity of the catalyst was evaluated in the Mizoroki-Heck cross-coupling reaction in which the desired products were obtained in high yield in H_2O as a green solvent. The reaction was carried out in short reaction times using low amounts of the catalyst. Moreover, the catalyst was easily separated from the reaction media and reused for 5 cycles.

1. Introduction

The use of heterogeneous catalysts can be effective in reducing environmental problems [1]. In recent years, various supports such as polymers [2a,b], carbon nanotubes [3], silica [4], and metal oxides [5] have been used as a support to promote the catalytic properties. Therefore, by immobilization of Pd on a suitable support, they could be separated from the product and reused for several times [6]. Among the different supports, magnetic nanoparticles (MNPs) have recently emerged as robust alternatives for immobilization of homogenous catalysts, in which this behavior is due to their high surface area to volume ratio, low porosity, nano scale dimension and high dispersion in the reaction media [7]. Despite the NPs benefits, they can easily be coagulated due to their colloidal nature. As a result, the magnetic form of NPs have been applied to resolve the problem, in which the catalyst can simply be removed from the reaction media by an external magnetic field, with no more filtration, centrifugation or other work up processes. The other important features in the synthesis of heterogeneous catalysts are the size-controlled and dispersion of MNPs [7]. Consequently, in the last few years, a lot of research has been focused on the use of palladium(II)–N-heterocyclic carbene complexes to stabilize the Pd catalytic centers. NHCs are in general defined as singlet carbenes in which the carbene carbon is coupled with two nitrogen atoms within the heterocycle. In comparison with phosphine ligands they are strong σ-donors and have poorer π-acceptor ability, which cause the stronger metal-NHC bond than the metal-phosphorus bond. Also, NHCs have shown high dissociation energies for metal–NHC bonds which resulted in higher thermal stability than phosphine complexes and leads to lower rate of decomposition [8, 9, 10, 11, 12, 13, 14]. Also, NHC complexes were distinguished to be stable toward oxygen and moisture together with lower catalyst loading [15, 16]. Hence, NHCs have recently been used as an interesting class of ligand and have attracted a lot of attention due to their remarkable electronic properties. NHC-metal complexes can be used as supported catalysts mainly for coupling reactions, olefin metathesis, as well as S-arylation coupling [4]. Therefore, in recent years, various supports are employed to heterogenized the catalyst. Moreover, different linkers between the solid support and metal catalytic center were used which could be benzyl, benzyloxy, pyridyl and alkyl (or) long chain alkyl groups. In the case of silica and NPs supported catalysts, usually 3-halopropyltrialkoxy silanes were used as linker [17]. Recently, in order to obtain more stable linker, the 1,2,3-triazole moiety has also been added to it [11]. In 2014, Khosropour's group designed and prepared SPIONs-bis (NHC)-palladium(II) catalyst and used it as an efficient catalyst in C–C coupling reactions under heating or microwave irradiation [18]. In 2016, Hajipour and co-workers also reported the immobilization of a Pd–NHC complex on MNPs by anchoring phenyl-1H-imidazole onto the modified Fe_3O_4 NPs and the recyclable catalyst was used in the Heck and Suzuki–Miyaura cross-coupling reactions [19]. Therefore, as observed, various

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MNP-supported NHC–Pd catalysts have been applied in C–C coupling reactions. Hence, in continuation of our interest in preparing heterogeneous Pd containing catalysts [20], in order to achieve better stability and a minor quantity of palladium leaching we are intending to design and synthesize green supported catalyst Fe_3O_4@Si–NHC–Pd by adding 1, 2,3-triazole moiety to the linker via a click reaction. As a result, for the first time, we have developed a new MNPs-supported catalyst by adding 1,2,3-triazole to linker and NHC as ligand and present its outstanding catalytic efficiency in the Mizoroki-Heck cross-coupling reaction.

2. Experimental

2.1. General

All chemicals were purchased from Merck, Sigma-Aldrich, and Fluka. Melting points were determined using a Büchi B540 melting point apparatus. The IR spectra were recorded on an Fourier Transform Infrared spectroscopy (ABB Bomem model FTLA 2000 spectrophotometer) (KBr).^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded with a commercial Bruker AQS-300 Avance spectrometer using DMSO-d6 or CDCl$_3$ as solvent. Palladium content of the catalyst was determined by inductively coupled plasma (ICP) on a Varian Vista-MPX instrument. X-ray diffraction (XRD) images were provided from 8025-BesTec twin anode XR3E2 X-ray source system. Thermogravimetric analysis was performed using a thermal gravimetric analysis instrument (NETZSCH TG 209 F1 Iris) under nitrogen atmosphere. The surface morphology was applied by scanning electron microscope (SEM) (Vega, TESCAN-Model) equipped with energy dispersive X-ray (EDX) facility.

2.2. Catalyst synthesis

2.2.1. Preparation of Fe_3O_4@SiO_2

Magnetic (Fe_3O_4) nanoparticles were synthesized through coprecipitation method by the reaction of ferric and ferrous ion (2/1 in mol/mol) by using the reported method [11]. In the next step, the obtained Fe_3O_4 (0.5 g, 2.1 mmol), ethanol (50 ml), deionized water (5ml), tetraethoxysilane (TEOS) (0.2 ml), and 5.0 ml of NaOH (10 wt %) were mixed. Then the product, Fe_3O_4@SiO_2 was separated by an external magnetic field, washed repeatedly with ethanol and deionized water and finally dried at 80$^°$ C under vacuum for 10 h. FT-IR (KBr, cm^{-1}): 3445, 2937,1072, 821,653.

2.2.2. Synthesis of compound 2

In a round-bottom flask, 1-methylimidazole (1 g, 12.18 mmol), propargyl bromide (1.9 ml, 25 mmol) and acetone (50 ml) were mixed. The resulting mixture was refluxed for 24 h. Then the solvent was removed and product 2 was obtained as a red liquid [13].

2.2.3. Synthesis of 3-azidopropyltriethoxysilane (3)

In a round bottom flask, a mixture of 3-Chloropropyltriethoxysilane (4.82 g, 20.0 mmol), sodium azide (1.95 g, 30.0 mmol), tetrabutylammonium bromide (TBAB, 1.29 g, 4.0 mmol) and dry acetonitrile (75 ml) was refluxed under nitrogen atmosphere for 24 h. The solvent was then removed under reduced pressure. To the resulting mixture Et$_2$O (30 ml) was added and the suspension was filtered and subsequently washed with Et$_2$O (2 × 10 ml). The combined solvent was evaporated and the colorless liquid as product 3 was formed (4.06 g, 82%) [10, 11].

2.2.4. Synthesis of azide-functionalized MNPs (4)

Fe_3O_4@SiO_2 nanoparticles (1.5 g) were placed in a 100 ml round bottom flask and sonicated in dry toluene (75 ml) for 40 min. Then, 3-azidopropyltriethoxysilane (0.5 g, 2.02 mmol) was added and the mixture was stirred at reflux conditions under nitrogen for 24 h [10, 11]. The completion of the reaction was monitored by TLC (n–hexane-EtOAc: 4/1). Compound 4 was then collected by an external magnet, washed

with acetone, and dried. FT-IR (KBr, cm^{-1}): 3421, 2102, 1650, 1069, 800, 577,461.

2.2.5. Synthesis of compound (5) through click reaction

The mixture of compound 4 (0.5 g), compound 2 (0.8 g), CuI (0.05 g, 0.26 mmol), and K$_2$CO$_3$ (0.5 g, 3.62 mmol) in DMF/THF (100 ml) was placed in a 200 ml round bottom flask and stirred for 24 h at room temperature. The progress of the reaction was monitored by TLC (n–hexane-EtOAc: 4/2). After completion of the reaction the precipitated solids were filtered, washed and dried in air [10, 11, 13].

2.2.6. Preparation of Fe_3O_4@Si–NHC–Pd (6)

Synthesis of Compound 6 was carried out according to the method reported in the literature [16]. In a 25 ml round bottom flask, Pd(OAC)$_2$ (17.0 mg, 0.076 mmol) in 10 ml MeOH was stirred at room temperature for 3 h. Then 0.5 g compound 5 and Na$_2$CO$_3$ (0.5 M, 30 ml) were added to the flask, and the temperature was raised to 60$^°$C for 24 h. To end, the catalyst Fe_3O_4@Si–NHC–Pd was collected by an external magnetic field and washed with acetone, water and acetonitrile. Then it was dried under vacuum overnight. FT-IR (KBr, cm^{-1}): 3494, 3085, 2123, 1656, 1569, 830, 619.

2.3. General procedure for the Heck cross-coupling reaction byFe_3O_4@Si–NHC–Pd

A mixture of the aryl halide (1.0 mmol), alkene (ethyl acrylate or styrene) (1.2 mmol), nanocatalyst (0.272 mol% Pd, 20 mg), base (2 mmol), and solvent (5.0 ml) was placed in 25 ml round bottom flask and was refluxed in an oil bath. The progress of the reaction was followed using TLC. After completion of the reaction, the mixture was cooled and the nanocatalyst separated by a magnet. The mixture was extracted with Et$_2$O (3 × 25 ml) and the solvent evaporated under reduced pressure. The resulting product was purified using thin layer chromatography to obtain pure coupling products in high yield and finally characterized using ^{1}H and ^{13}C-NMR spectroscopies (see supporting information).

3. Results and discussion

The process of preparation of Fe_3O_4@Si–NHC–Pd catalyst has been shown in Scheme 1. At first the silica-coated Fe_3O_4 NPs were synthesized, and chosen as magnetic support (compound 1). In the next step, compound 2 was prepared from the reaction of 1-methylimidazole with propargyl bromide. In order to bring about the triazole moiety in the linker and prepare a more stable catalyst, in this step compound 3 was synthesized from the reaction of 3-Chloropropyltriethoxysilane, sodium azide and tetrabutylammonium bromide under nitrogen atmosphere. Subsequently in order to prepare compound 4, SiO_2-coated Fe_3O_4 nanoparticles (compound 1) were sonicated in dry toluene (75 ml) for 40 min and 3-azidopropyltriethoxysilane (compound 3) was added to it. In this stage, the reaction of (compound 4) with compound 2 through the known click reaction resulted in the formation of triazole moiety to give (compound 5). In the final step compound 5, Pd(OAC)$_2$ and Na$_2$CO$_3$ was heated at 60$^°$C for 24 h to obtain the desired catalyst Fe_3O_4@Si–NHC–Pd.

Modification of Fe_3O_4 NPs was confirmed by FT-IR spectroscopy (Figure 1-a) All samples showed a peak at 653 which is related to (Fe–O). The adsorption bands at 1082 and 821 cm^{-1} are assigned to (Si–O–Si) bands, which are associated with Fe_3O_4 @SiO_2. The broad adsorption at 3300 cm^{-1} is due to –OH stretching of surface hydroxyl groups. Figure 1-b showed a peak at 2104 cm^{-1}, which is attributed to the stretching vibration of organic azide and confirmed incorporation of the azidopropyl group. The sharp peaks at 1569 cm^{-1} and 1659 cm^{-1} are related to C=N and C=C vibrations, respectively. Also a series of bands appeared around 531-619 cm^{-1} are related to Pd–C stretch mode (Figure 1-c). The XRD pattern of the catalyst shows diffraction peaks, which is similar to the standard Fe_3O_4 sample (Figure 2). Also, the broad peak at the range of 20$^°$ to 30$^°$ is in accordance with an amorphous silica layer. Characteristic
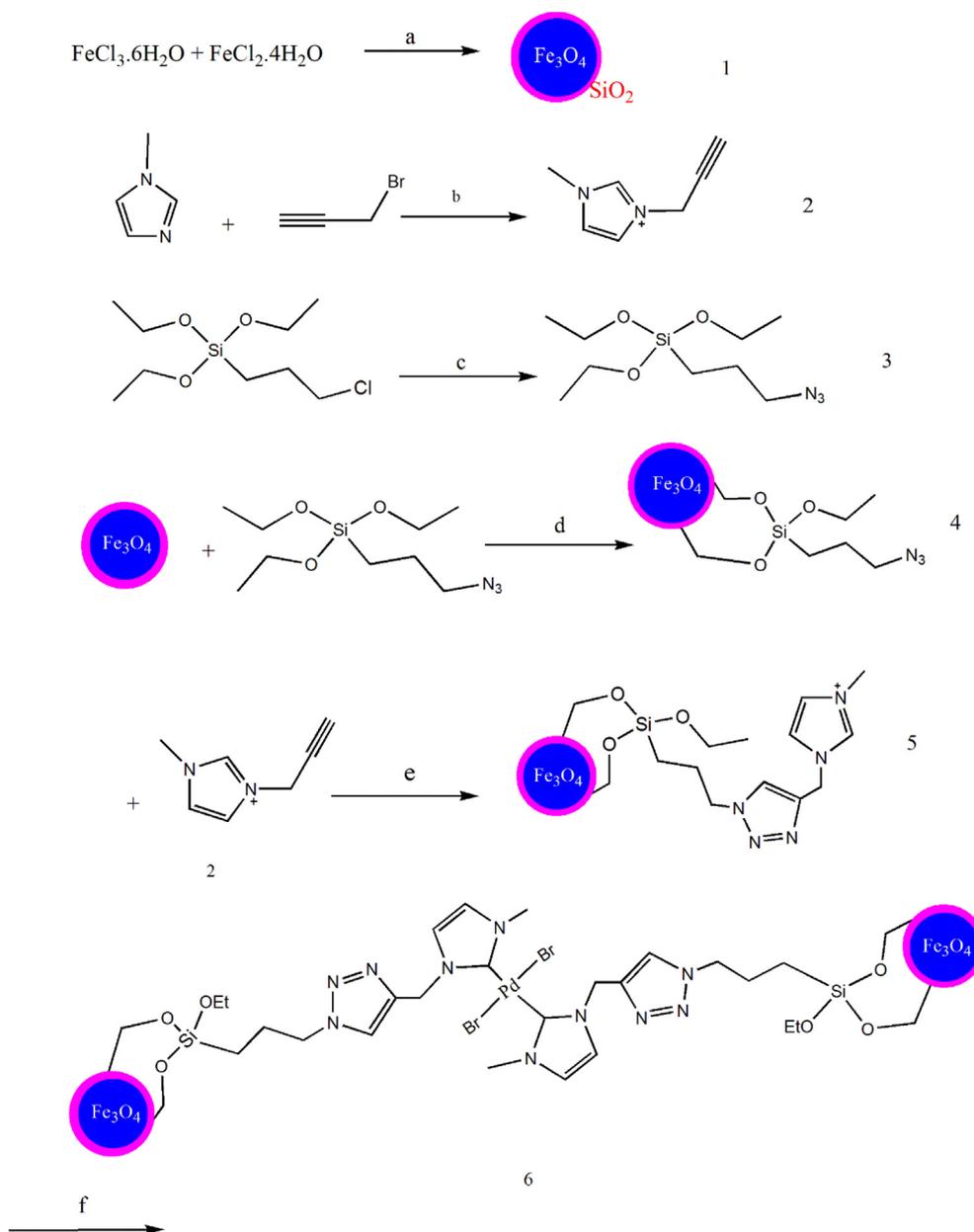
Catalyst: Fe₃O₄ @ Si-NHC-Pd

Scheme 1. Preparation of Fe$_3$O$_4$@Si–NHC–Pd; Reaction conditions: a) synthesis of silica-coated Fe$_3$O$_4$ nanoparticles; b) acetone, refluxed for 24 h; c) NaN$_3$,CH$_3$CN, TBAB, refluxed for 24 h; d) Silica-coated Fe$_3$O$_4$ Nanoparticles, toluene, reflux, 24 h; e) 4, 2, CuI, K$_2$CO$_3$, DMF/THF, 24 h; f) Pd(OAc)$_2$, Na$_2$CO$_3$, MeOH, 24 h.

peaks for Pd nanoparticles were not observed, which confirmed that the Pd nanoparticles were properly dispersed onto the MNPs. Figure 3 illustrated the SEM images of the support Fe$_3$O$_4$@SiO$_2$ and the catalyst Fe$_3$O$_4$@Si–NHC–Pd. As is clear, the size of nano-Fe$_3$O$_4$ core shell was found to be about 43 nm (Figure 3a). Figure 3c and Figure 4 showed the elemental mapping data to confirm the presence of C, N, O, Si, Fe, Br, Pd in the catalyst. The content of palladium was measured by inductively coupled plasma atomic emission spectrometry (ICP-AES) and EDX, which was 1.45 wt%. The thermal stability of the Fe$_3$O$_4$@Si–NHC–Pd was evaluated by thermogravimetric (TG) analysis under nitrogen atmosphere. To estimate the amount of immobilized groups on the surface, elemental analysis and TGA were carried out. The TGA curve in Figure 5 indicated the first weight loss of 1.53% up to 120 °C, which was related to

the removal of adsorbed water on the support. Furthermore, the weight loss below 500 °C which is 13.28% for the catalyst could be assigned to the organic part of the catalyst. Therefore, Fe$_3$O$_4$@Si–NHC–Pd was very stable and could be used at high temperatures. To evaluate the activity of the Fe$_3$O$_4$@Si–NHC–Pd catalyst, it was tested in the Mizoroki-Heck cross-coupling reaction. For optimization of the reaction conditions, the reaction of styrene and 4-iodotoluene was chosen as a model reaction. In order to show the role of solvent on the Mizoroki-Heck reaction, different protic solvent such as EtOH, EtOH/H$_2$O, H$_2$O (Table 1, Entry 4, 5, 6), and aprotic solvents such as DMF, DMSO, and CH$_3$CN (Table 1, Entry 1, 2, 3) was evaluated. The reaction was significantly affected by the nature of the solvent and it was observed that H$_2$O was appeared to be the best reaction medium in comparison to the others (Table 1, entry 6).
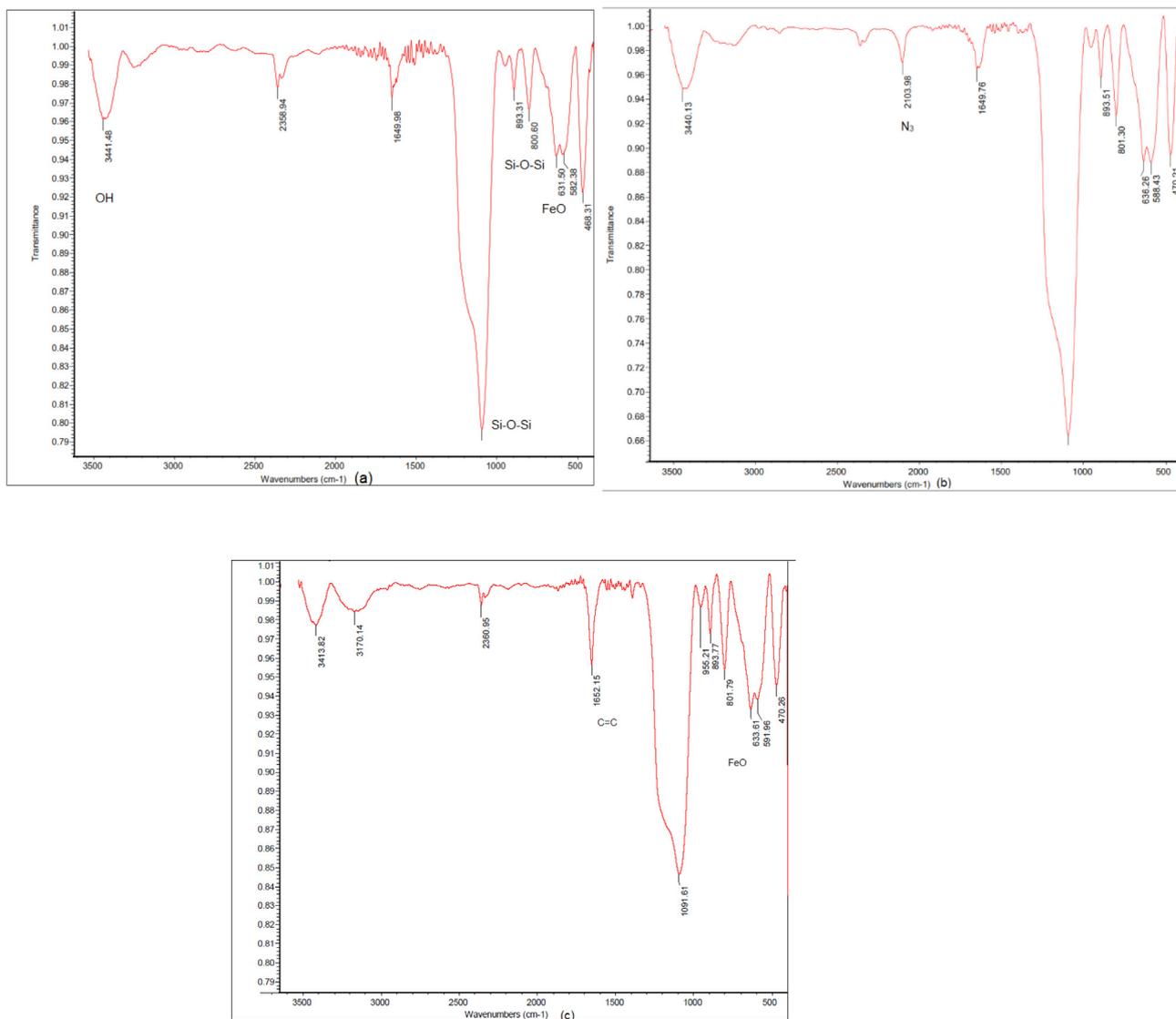
Figure 1. FT-IR spectra of $Fe_3O_4@SiO_2$ (a); azide-functionalized $Fe_3O_4@SiO_2–N_3$ (b); $Fe_3O_4@Si–NHC–Pd$ sample (c).
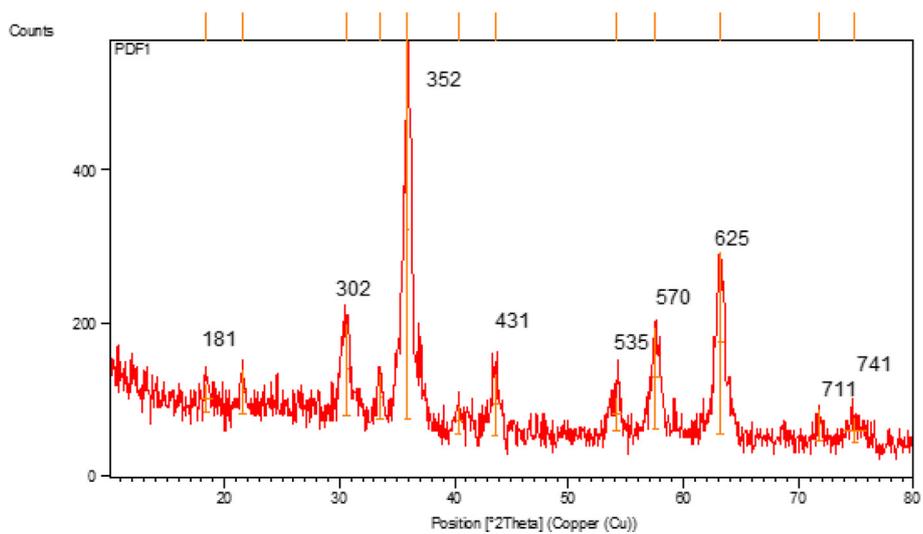
Figure 2. XRD spectrum of $Fe_3O_4@Si–NHC–Pd$
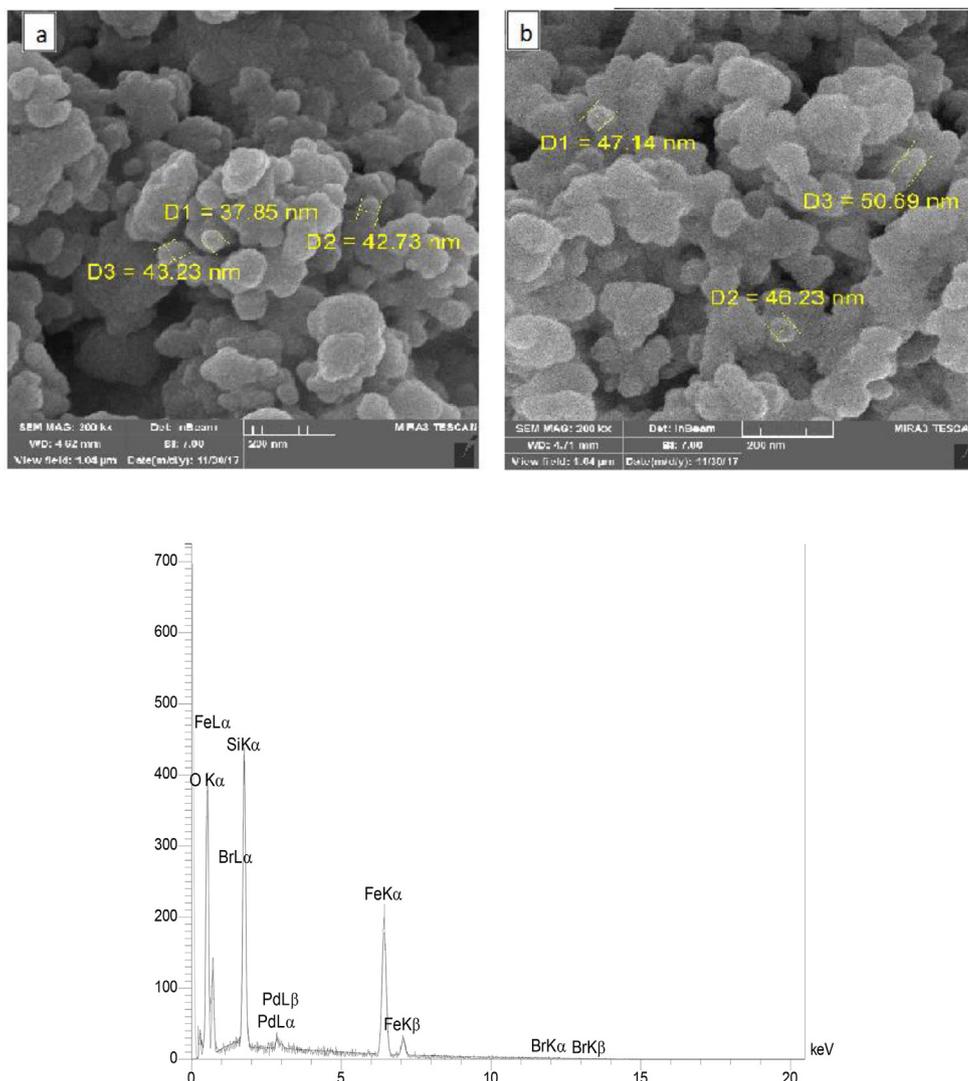
Figure 3. Scanning electron microscopic images of a) Fe3O4@SiO2 b); Fe3O4@Si–NHC–Pd c) EDX spectrum of Fe_3O_4@Si–NHC–Pd include: C: 12.50 %, N: 8.40 %, O: 27.21 %, Si: 13.41 %, Fe: 36.87 %, Br: 0.16 %, Pd: 1.45 %.

Additionally, the influence of inorganic bases such as K_2CO_3, Cs_2CO_3, Na_2CO_3 and organic base Et_3N was explored (entries 8, 9, 10, and 6) and as indicated in Table 1 Et_3N was found to be the best base. To find out the effect of the temperature, the reaction was carried out at 90, 100, 110 °C in which no obvious improvement was observed at higher temperatures thus 90 °C was selected. (Entries 6, 11, 12). Next, we examined different amounts of the catalyst between 10, 15 and 20 mg (0.136, 0.204, 0.272 mol %) of Pd on the Heck reaction (Table 1, Entries 13, 14, 6). As can be seen in Table 1, 20 mg, (0.272 mol %) of the catalyst worked remarkably well with 95% yield of products. When 10 mg, (0.136 mol %) of the catalyst was used the yield dropped.

In Table 2, some electron-rich and electron-poor aryl halides as substrate were studied under the standard reaction conditions. As showed in Table 2, the reaction of aryl iodides and bromides containing electron-rich and electron-poor substituents were achieved with high yields. It is necessary to mention that aryl chloride generated a lower yield. It is worthwhile to note that the reaction is sensitive to the amount of catalyst. Finally, a comparison table between the presented conditions and catalytic activity of the catalyst in this study with other previous Pd catalysts reported in the literature for aryl bromide and styrene is provided (Table 3). Results show that the presented catalyst with minimum weight has high activity in a system.

4. Recyclability test

The easy recovery and reusability of the catalyst is key factor of a heterogeneous catalyst, mainly from the economic and ecological point of view. Therefore, we are intending to study reusability of our catalyst by running the reaction of styrene and 4-iodotoluene under the optimized reaction conditions. After completion of the reaction followed by TLC, the catalyst was separated from the mixture by an external magnet and washed with water and acetone (2×10). It was then dried in an oven at 80 °C for 1 h and was applied for the next run. It is worth noting that the catalyst was reused up to 5 cycles (Figure 6).

In order to confirm the heterogeneity of the Fe_3O_4@Si–NHC–Pd and determine if palladium leaching occurs, the Mizoroki-Heck cross-coupling reaction under optimized conditions (according to Table 1, entry 6) and a hot filtration test were performed. After completion of the reaction, the catalyst was removed using an external magnetic field and the residual solution was then allowed to react for a further 2 h and the amount of the Pd species dissolved into solution was determined using ICP analysis. The results suggested a low amount of palladium is removed from the Fe_3O_4 support and is an evidence of heterogeneous nature of the catalyst. According to the results of ICP, 0.03 % Pd leaching can be found during the reaction, which indicated that the Fe_3O_4@Si–NHC–Pd catalyst is recoverable and stable up to five times (Figure 6).

Atom	Weight %
C	12.50
N	8.40
O	27.21
Si	13.41
Fe	36.87
Br	0.16
Pd	1.45
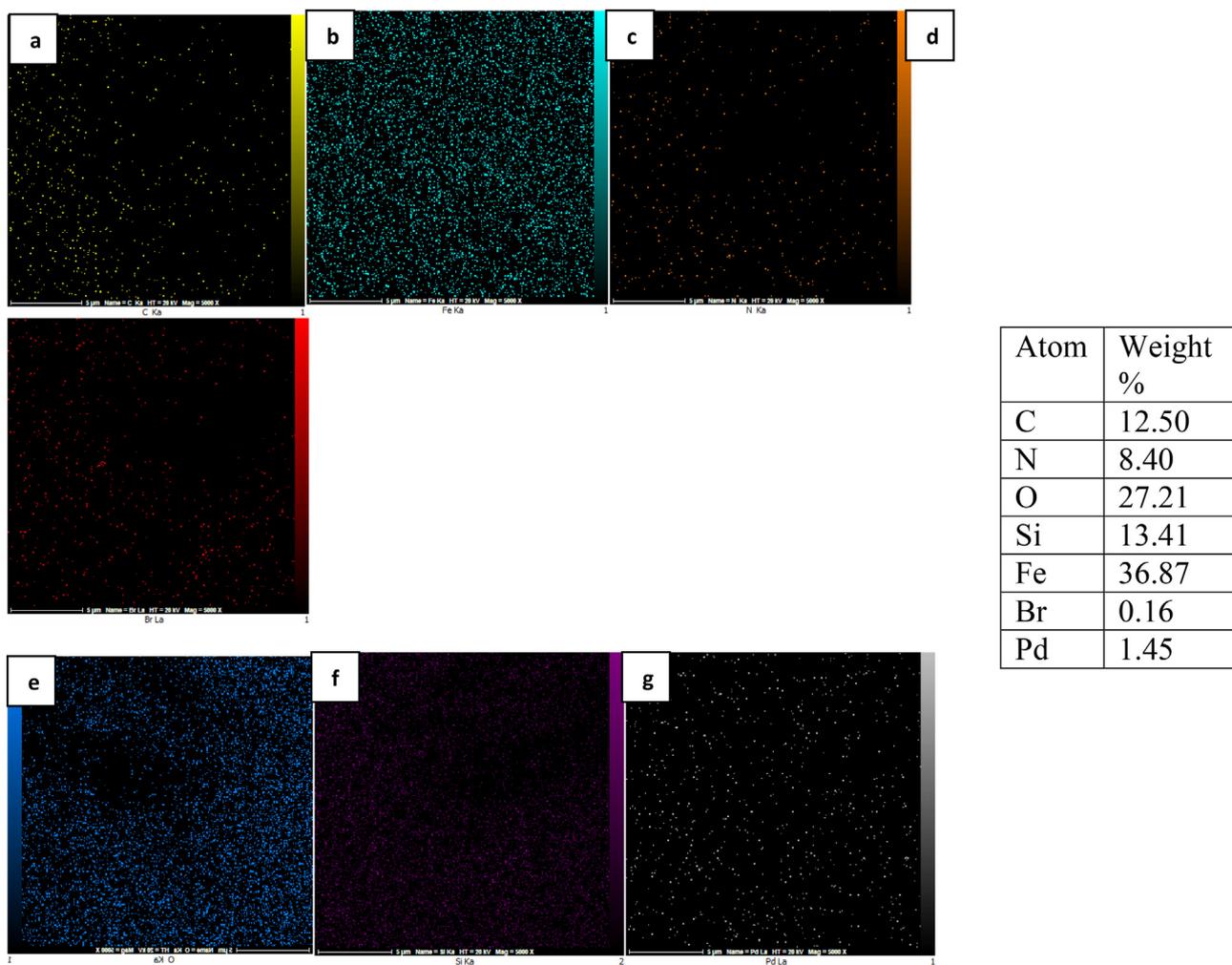
Figure 4. Elemental maps of (a) C, (b) Fe (c) N, (d) Br, (e) O, (f) Si and (g) Pd obtained by EDX.
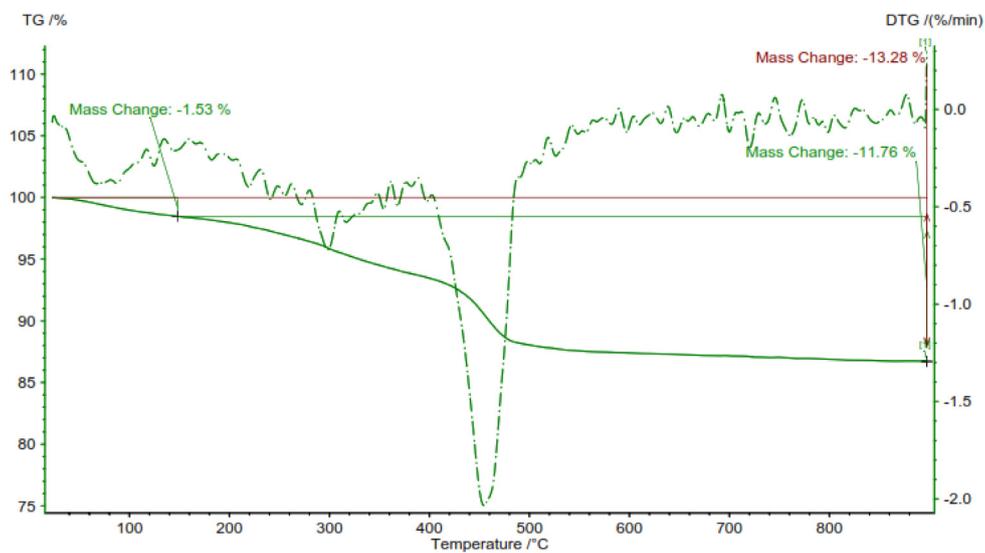
Figure 5. Thermogravimetric curve of the Fe_3O_4@Si–NHC–Pd

Table 1. Optimization of the reaction conditions.[a]

Entry	Solvent	Base	Temp. (°C)	Catalyst (mol%)	Time (h)	Yield[b] (%)
1	DMF	Et$_3$N	90	0.272	7	90%
2	DMSO	Et$_3$N	90	0.272	8	73%
3	CH$_3$CN	Et$_3$N	90	0.272	7	61%
4	EtOH	Et$_3$N	90	0.272	9	80%
5	EtOH/H$_2$O	Et$_3$N	90	0.272	8	85%
6	**H$_2$O**	**Et$_3$N**	**90**	**0.272**	**8**	**95%**
7	DMF/H$_2$O	Et$_3$N	90	0.272	9	95%
8	H$_2$O	K$_2$CO$_3$	90	0.272	9	78%
9	H$_2$O	Cs$_2$CO$_3$	90	0.272	8	85%
10	H$_2$O	Na$_2$CO$_3$	90	0.272	6	61%
11	H$_2$O	Et$_3$N	100	0.272	7	95%
12	H$_2$O	Et$_3$N	110	0.272	7	98%
13	H$_2$O	Et$_3$N	90	0.136	10	80%
14	H$_2$O	Et$_3$N	90	0.204	9	90%

[a] Reaction conditions: styrene, 4-iodotoluene, base (2 mmol), Fe$_3$O$_4$@Si–NHC–Pd and solvent (2 ml).
[b] Yields of isolated product.

Table 2. Heck reaction catalyst by Fe$_3$O$_4$@Si–NHC–Pd[a]
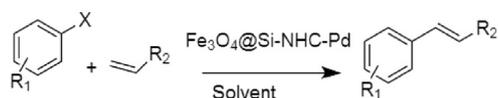
Entry	R$_1$	X	R$_2$	Product	Time (h)	Yield[b] (%)
1	4-Me	I	CO$_2$Me	8a	8	95
2	H	I	CO$_2$Et	8b	8.5	95
3	4-Me	I	Ph	8c	8	95
4	4-OMe	Br	CO$_2$Me	8d	10.5	80
5	4-OMe	Br	CO$_2$Et	8e	11	85
6	4-OMe	Br	Ph	8f	12	85
7	3-OMe	Br	CO$_2$Me	8g	12.25	80
8	3-OMe	Br	CO$_2$Et	8h	12.5	75
9	3-OMe	Br	Ph	8i	15	80
10	4-COMe	Cl	CO$_2$Me	8j	22	75
11	4-COMe	Cl	CO$_2$Et	8k	24	75
12	4-COMe	Cl	Ph	8l	24	75
13	H	Br	CO$_2$Me	8m	10	85
14	4-CN	Br	CO$_2$Et	8n	12	90
15	4-CN	Br	Ph	8°	15	90
16	4-CHO	Br	CO$_2$Me	8p	16	90
17	4-CHO	Br	CO$_2$Et	8q	18	90
18	H	Br	Ph	8r	8	98
19	4-Me	I	CN	8s	8	90
20	4-COMe	Cl	CN	8t	8.5	80

[a] Reaction conditions: styrene, 4-iodotoluene, Et$_3$N, Fe$_3$O$_4$@Si–NHC–Pd catalyst, in H$_2$O at 90 °C.
[b] Yields of isolated product.

Table 3. Comparison of catalytic activity for the Heck cross coupling reaction using Fe$_3$O$_4$@Si–NHC–Pd catalyst with those obtained by reported catalysts.[a]

Entry	Catalyst	Pd (mol %)	Temp. (°C)	Time (h)	Solvent	Yield[b] (%)	Ref.
1	Fe$_3$O$_4$@Si–NHC–Pd	0.272	90	8	H$_2$O	98	This work
2	NO$_2$–NHC–Pd@Fe$_3$O$_4$	1.0	80	6	MeCN	92	[21]
3	Pd NPs@NHC@ZIF-8	0.08	110	2.5	DMF-H$_2$O	90	[22]
4	MnPs–NHC–Pd(II)	0.036	70	0.33	DMF	87	[19]
5	Hydrazon-pd@ZnO	0.26	130	1.5	DMF	85	[23]
6	PdCl$_2$Kryptofix-5	0.9	130	24	DMF	16	[24]

[a] Reaction conditions: Bromobenzene (1 mmol), styrene (1.2 mmol), base, Catalyst and solvent.
[b] Yields of isolated product.
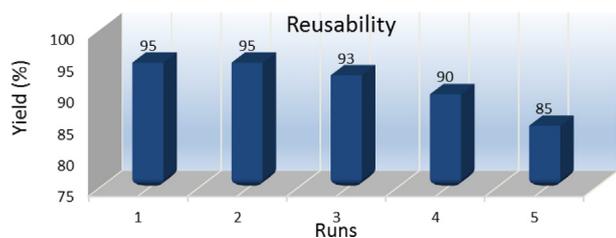
Figure 6. The reusability of the catalyst in Heck reaction; reaction condition: styrene, 4-iodotoluene, Et_3N, Fe_3O_4@Si–NHC–Pd catalyst, in H_2O at 90 °C.

5. Conclusions

In summary, a novel Fe_3O_4@Si–NHC–Pd has been successfully prepared with 1,2,3-triazole moiety using click reaction without any phosphine ligand. Furthermore, the heterogeneous catalyst was applied effectively in the Mizoroki-Heck cross-coupling. The high yield of products, performing the reaction in a green solvent (H_2O), short reaction times, using low amounts of the catalyst are some advantages of this catalyst. Moreover, the recoverability of the catalyst was tested, which showed that it could be reused for 5 runs.

Declarations

Author contribution statement

Razieh Ghavidel Kalishomi:Conceived and designed the experiments; Performed the experiments; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Shahnaz Rostamizadeh: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.

Fatemeh Nouri: Contributed reagents, materials, analysis tools or data; Wrote the paper.

Ali Khazaei: Performed the experiments.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

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