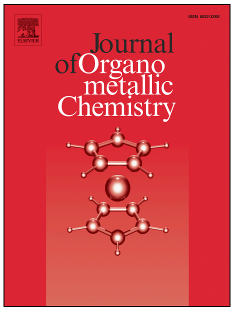

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Palladium anchored on guanidine-terminated magnetic dendrimer (G3-Gu-Pd): An efficient nano-sized catalyst for phosphorous-free Mizoroki-Heck and copper-free Sonogashira couplings in water

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Abstract

In this research, a novel type of Fe_3O_4@silica-supported dendrimer capped by guanidine groups for immobilization of palladium was reported. This novel nano-sized catalyst catalyst was characterized by FTIR, TGA, XRD, FESEM, EDX, VSM, XPS and HRTEM methods. Enhanced catalytic activity of the prepared catalyst in Mizoroki-Heck and copper-free Sonogashira coupling reactions were evaluated in water as a green solvent. The influence of the various reaction parameters such as catalyst dosage, time and temperature on two mentioned C–C coupling reactions were studied. Results showed that the catalyst could be easily recovered by simple separation by an external magnet and reused for five cycles of recovery without considerable losing of its activity.

Keywords: Dendrimer; Magnetic Nanocatalyst; Heterogeneous catalysis; Mizoroki-Heck reaction; Copper-free Sonogashira reaction.

Introduction

Palladium-catalyzed carbon-carbon bond-forming reactions are one of the most useful tools in organic synthesis [1, 2]. Various C-C cross coupling reactions such as Mizoroki-Heck, Suzuki-Miayura, Sonogashira and Stille reactions developed since 1970s [3-11].

Mizoroki-Heck Coupling reaction is the most successful method to synthesis of various substituted stilbene compounds, dienes and conjugated polymers [12]. This reaction has been generally performed in the presence of palladium complexes, some organic or inorganic bases and suitable solvents under mild conditions [7, 13, 14].

Another important catalytic cross-coupling reaction that leading to synthesis of 1,2-biarylethyne or 1,2-alkylarylethyne compounds is sonogashira reaction. Generally, Coupling between terminal alkynes and aryl halides in this reaction, has been catalyzed by palladium Pd^{II}/Pd^{0} complexes and copper (I) salts as a co catalyst [15].

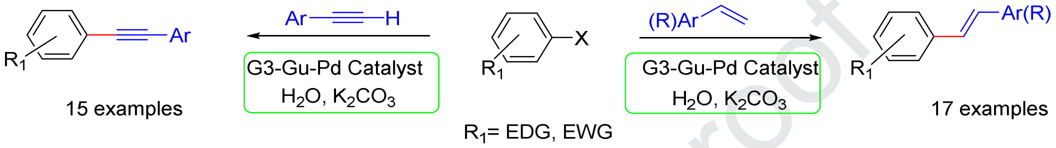
Many Pd catalyst systems used in these above mentioned cross coupling reactions, are homogeneous. Application of these homogenous systems have been confined due to their recycling problems and wastewater pollutions. Therefore, design and application of new heterogeneous catalytic systems have been developed recently [16, 17]. In homogenous system, phosphines or other ligands were added To stabilization of Pd^{II}/Pd^{0} complexes [18]. However, Toxicity of these ligands, led to environment pollutions. In the other hand, purification of the final products, are difficult due to residual Pd contaminations in these systems [19, 20].

Palladium immobilized on nano-sized heterogeneous catalytic systems are introduced as well as the green catalysts, due to their recoverability and independency to ligands requirement. Efficiency and stability of these Pd heterogenic systems are related to support that are often used for the immobilization of Pd nanoparticles [21].

Dendrimers are particularly well-defined branched structure, which are good moiety to stabilization of metals nanoparticles via encapsulation. In the other hand, agglomeration of hosting metal nanoparticles in these dendritic structure can be eliminated [22, 23]. The steric effect between encapsulated nanoparticles is an important factor to high availability of denderimer surface in the reaction media. In addition, controlling the dispersity of dendrimer nanocomposite in common solvents and linking to other surfaces, can be achieved by inducing the various terminal group on the dendrimer templates. All of these unique properties of dendrimers with uniform composition, have been attracted widespread attention in chemical catalysis [24-26].

Despite the more interesting properties of dendritic supports, they often suffer from draw back such as recycling and reuse. Magnetic nanoparticles are considered as a suitable option among the various applicable and valuable support materials for preparation of heterogeneous Pd catalysts systems. The immobilization of Pd on magnetically recoverable supports, can be resolved the problems associated with the filtration of very small particles at the end of reaction. Therefore, magnetic nanoparticles supports have been widely used in many organic transformations, due to their specific properties [23, 27, 28].

In the present work, a novel third generation of a dendrimer terminated to guanidine moiety has been designed and successfully supported on $Fe_3O_4@SiO_2$ nanoparticles as a novel nanostructured organic-inorganic hybrid material for encapsulation of the Pd nanoparticles. After the fully characterization of the prepared nanomaterial (G3-Gu-Pd), we have used G3-Gu-Pd as a novel, reusable and efficient heterogeneous magnetic and dendritic catalyst in the Mizoroki-Heck and copper-free Sonogashira couplings. Variety of aryl halides and alkenes were tested in Mizoroki-Heck reaction in aqueous medium. In addition, copper-free Sonogashira coupling between aryl halides and arylacetylenes also checked in water as the reaction solvent (Scheme 1).



Scheme 1. Green synthesis of alkene and alkyne derivatives

Experimental

General: all of aryl halides, olefins, 1-cyano guanidine, phtalic anhydride, palladium chloride, other reagents and solvents were purchased from Merck Company. Ethynylbenzene, and 1-ethynyl-4-methylbenzene were provided by Sigma-Aldrich Company. ^1H and ^{13}C NMR spectra were recorded on a Brucker Avance DRX (250 MHz) in deutrated solvents. X-ray diffraction patterns were measured on Bruker instrument model D8, Avance. Shimadzu, FT-IR 8300 spectrophotometer was applied to obtain the FT-IR spectra. For ICP analysis an inductively coupled plasma (ICP) analyzer (Varian, Vista-Pro) was employed. The catalyst scanning electron micrograph (SEM) obtained by SEM instrumentation model, XL-30 FEG SEM, Philips, at 20 kV. Transmission electron microscopy (TEM) image was recorded on TEM apparatus model, Zeiss-EM10C at 100 KV. Thermo gravimetric analysis also was performed by SDT Q600 V20.9 Build 20 instrument. Buchi melting point instrument model, B-545 was used to melting points determination of purified products. The reaction improvement was checked by thin layer chromatography on silica gel PolyGram SILG/UV254 plates. All of the products were purified by column chromatography using packed columns by silica gel 60 (70−230 mesh). The known products were characterized by comparison of their spectral and physical data with those reported in the other literatures.

Synthesis of Fe_3O_4 magnetic nanoparticles (MNPs)

MNPs was prepared based on the chemical co-precipitation method [29]. According to this method, first, deionized water (DI-water) together with nitrogen gas was added during 30 min to not only to bring about adequate agitation, but also to hamper the ferrous ions oxidation. Afterwards, $FeCl_3.6H_2O$ (4 g, 14.5 mmol) and $FeCl_2.4H_2O$ (2 g, 10.1 mmol) were dissolved in DI-water (200 mL) under nitrogen atmosphere with severely stirring at 80 °C. After that, the solution was mixed for 30 min, then ammonia solution (25%, 20 mL) was poured drop wise into the solution until the pH raised to about 10 and the stirring continued for 45 min. When ammonium was being added to the solution, it was led to changing of solution color from the brown to dark brown and then became black. After the temperature of the synthesized adsorbent lowered, adsorbent was repeatedly washed using ethanol until reaching pH to the neutral state.

Synthesis of silica coated MNPs (SMNPs)

Based on a modified co-precipitation technique, we synthesized core-shell composite of $Fe_3O_4@SiO_2$ (SMNPs) [29]. Initially MNPs (1.4 gr) was dispersed in absolute ethanol (80 mL) at 40 °C. When the suspension was formed, it was mixed with 25% ammonia (4 mL), DI-water (7.50 mL) and tetraethyl orthosilicate (TEOS, 0.56 mL) for 2 h. The composite was magnetically separated from the suspension using a magnetic field and then dispersed in ethanol (30 mL). For improving the Si–O–Fe bonding, the suspension was kept in a 60 °C water bath for 6 h. $Fe_3O_4@SiO_2$ particles were collected by using an external magnet and then washed with ethanol and water three times until its pH became neutral; and finally, it was gathered using an external magnet, vacuum-dried at 70 °C for 12 h, and ultimately kept in an air tight container.

Synthesis of Bis(phthaloyl)diethylenetriamine

Bis(phthaloyl)diethylenetriamine was prepared based on the procedure described in the literature[30]. A mixture of diethylenetriamine (10.3 g, 0.10 mol) and phtalic anhydride (33.2 g, 0.22 mol) in glacial acetic acid (160 g) was refluxed for 2 h. The solvent was evaporated on a rotary evaporator by boiling water bath and was replaced with 160 g of hot ethanol (95%) with stirring until a solid appeared. The product was filtered and washed with cold ethanol: yield 30.1 g (83%); m.p. 182-183 ºC.

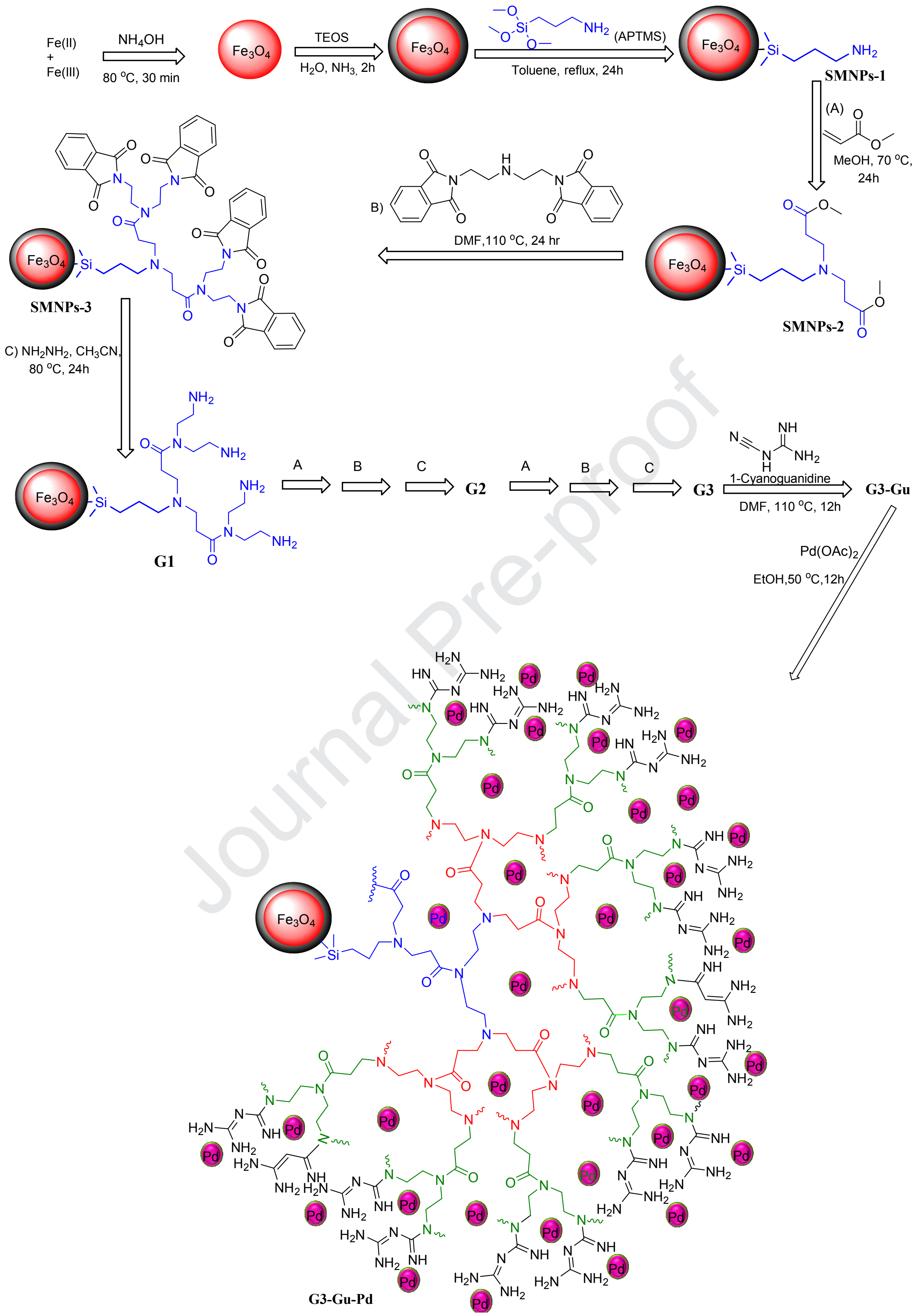
Preparation of magnetic silica-supported dendrimer terminated to guanidine (G3-Gu)

The SMNPs (5.0 g) and (3-aminopropyl) trimethoxysilane (5.0 ml) was refluxed in dry toluene (125 mL) for 24 h. The solids were isolated and washed successively with toluene and ethanol and dried at 80 ºC for 10 h under vacuum. The aminated SMNPs-1 as prepared was then further reacted with methylacrylate (MA) (5.25 g, 50.0 mmol) in methanol (125.0 mL) at 70 ºC for 24 h. The reaction mixture was dispersed subsequently with a large amount of ethanol, then collected using an external magnet and dried under vacuum at 80 ºC for 10 h to afford functionalized SMNPs-2. Subsequently, in a 100 mL flask with a mechanical stirring bar, the obtained functionalized SMNPs-2 (7.0 gr) and DMF (50.0 mL) were heated to 90 ºC. Then bis(phthaloyl)diethylenetriamine (2.69 gr, 68.95 mmol) was dissolved in DMF and then added to the mixture dropwise and the mixture was refluxed at 110 ºC for 24 h. The reaction mixture was magnetically separated and the recovered solid was washed subsequently with a large amount of ethanol and dried under vacuum at 80 ºC for 10 h to afford functionalized SMNPs-3.

In the next step, deprotection of amine groups was performed with hydrazine hydrate. For this, in a round bottom flask equipped with a condenser, functionalized SMNPs-3 (7.5 gr) and hydrazine hydrate (5 mL, aqueous solution 55%) were refluxed in acetonitrile at 80 ºC for 24 h. The resultant solid was separated off with magnetic field, then washed with methanol and denoted as G1. Twice repetition of the above steps (reaction with MA, bis (phthaloyl) diethylenetriamine and deprotonation were performed, respectively, for dendrimer branching) afforded the third-generation dendrimer (G3) product. The obtained dark solid G3 (7.5 gr) was reacted with 1-cyanoguanidine (5.85 gr, 52.15 mmol) in DMF (125 mL) at 110 ºC for 12 h to afford guanidine capped dendrimer grafted on to the surface of SMNPs (G3-Gu) (Scheme 1). The amount of nitrogen content was determined by elemental microanalysis to confirm the formation of dendrimers. The elemental analysis data in Table 1 show the amount of the nitrogen content in G1, G2, G3 and G3-Gu nanomaterials.

Metalation of third generation of guanidine end capped dendritic magnetic support (G3-Gu-Pd)

The mixture of G3-Gu (0.5 gr) and Pd $(OAc)_2$ (0.125 gr) was stirred in absolute ethanol (10 mL) with mechanical stirrer for 12 h at 50-60 ºC. Then crude solid was isolated with external magnet and washed successively with ethanol (2 × 5 mL) and dried at 80 ºC for 12 h under vacuum.



Scheme.2. Synthetic route for the preparation of G3-Gu-Pd catalyst

Table 1. Nitrogen content of the modified nanomaterials.

Sample identifier	Elemental analyses of N (wt%)
G1	0.89
G2	0.94
G3	1.06
G3-Gu	1.59

General procedure for the catalytic Mizoroki-Heck coupling

In a round bottom flask (5 mL) equipped with condenser and mechanical stirrer, aryl halide (1.0 mmol), olefin (1.1 mmol), K_2CO_3 (1 mmol), SDS (0.4 mmol, 0.1 gr), water (3 mL) and G3-Gu-Pd catalyst (10 mg, 0.8 mol% of palladium content) were added. Then, temperature raised to 100 °C in an oil bath and reaction progress was checked by TLC during the reaction mixture stirred and refluxed for the specific time (Table 3). After cooling the reaction mixture, G3-Gu-Pd catalyst was recovered by the external magnet and the resulting product was extracted with ethyl acetate (3 × 5 mL). Then extracted organic layer was dried over Na_2SO_4. After evaporating the solvent by vacuum distillation, and purifying with silica gel column chromatography employing *n*-hexane/ethyl acetate eluent, pure corresponding product was obtained. All of the synthesized products were characterized by melting point, ^{1}H NMR, ^{13}C NMR, IR spectroscopy and elemental analysis (See supporting Information). The data for all compounds were in accordance with to those reported in the other referenced literature.

General procedure for the copper-free Sonogashira coupling

In a round bottom flask (5 ml) equipped with condenser and mechanical stirrer, aryl halide (1.0 mmol), terminal alkyne compound (1.1 mmol), K_2CO_3 (1 mmol), SDS (1 mmol, 0.1 gr), water (3 mL) and G3-Gu-Pd catalyst (12.5 mg, 1 mol% of palladium content) were added. Then the mixture was stirred with mechanical stirrer at 95 °C. Reaction improvement was checked by TLC. Stirring was continued to completion of reaction and time of the reaction was mentioned (Table 5). After cooling the reaction mixture, G3-Gu-Pd catalyst was collected by the external magnet and the resulting product was extracted with ethyl acetate (3 × 5 mL). Then extracted organic layer was dried over Na_2SO_4. After evaporating the solvent by vacuum distillation and purifying the residue with silica gel column chromatography employing *n*-hexane/ethyl acetate eluent, pure corresponding product was obtained.

The products also characterized same as the heck reaction (see Supporting Information).

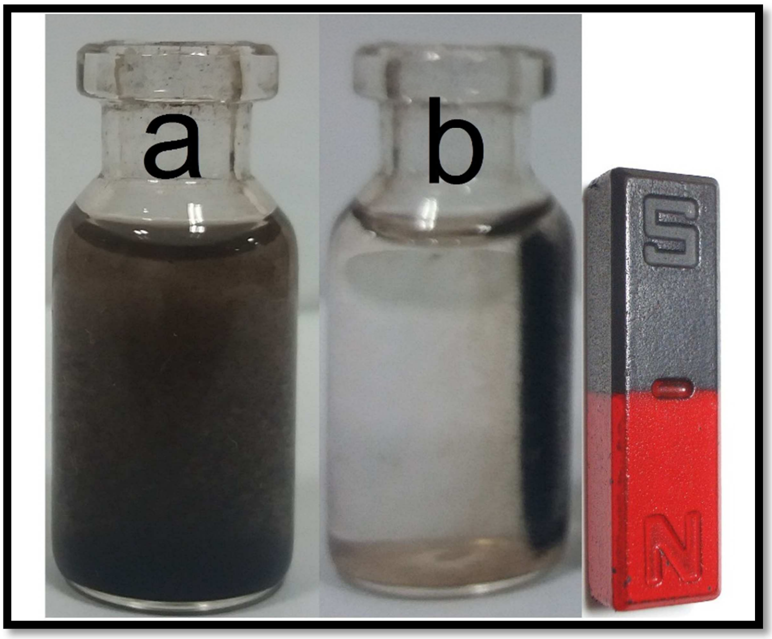


Fig. 1. Schematic representation of G3-Gu-Pd catalyst and its magnetic recycling capability from reaction media. a) G3-Gu-Pd in reaction mixture and b) separated G3-Gu-Pd with external magnet.

Results and Discussion

Characterization of the catalyst

Morphology and particle size of the support (G3-Gu) prepared for immobilization of the |Pd nanoparticles and also the final catalyst (G3-Gu-Pd) were investigated by field emission scanning electron microscopy (FESEM) and results were depicted in Fig. 2a and 2b. The FESEM images of G3-Gu and G3-Gu-Pd show spherical and uniform nanoparticles with size range of <100 nm. The shape of the magnetic nanoparticles was maintained after metalation but a minor enlargement was observed in range of ~10 nm due to the contribution of the Pd nanoparticles around the branches of the magnetic dendrimer.

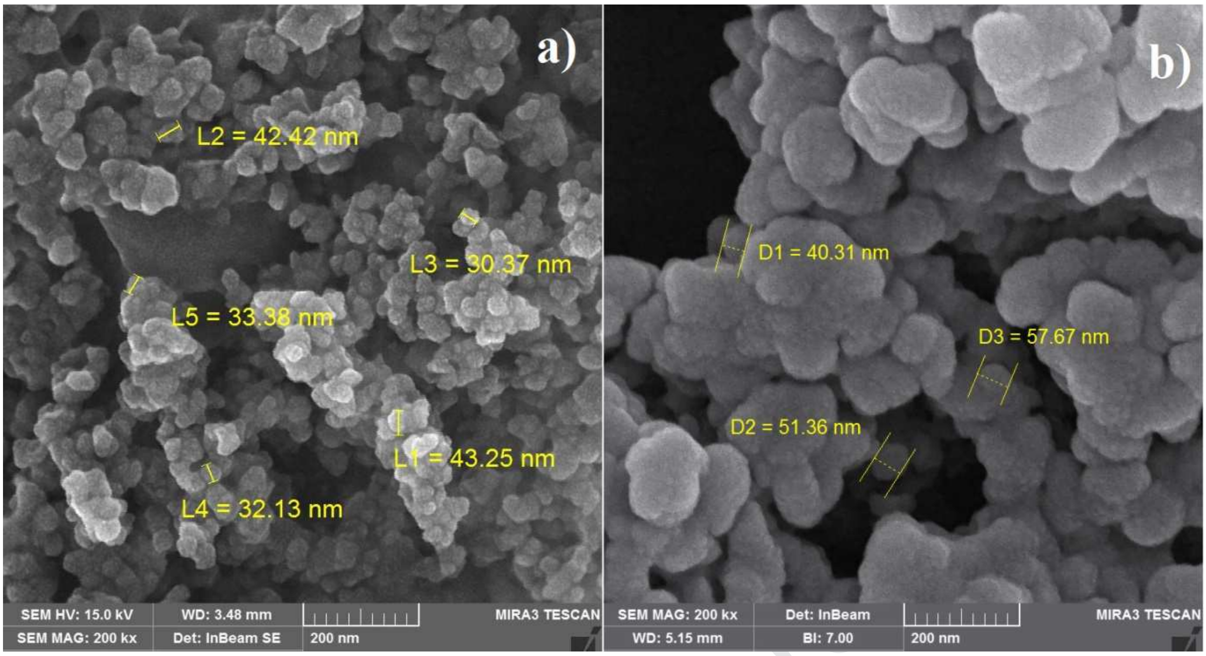
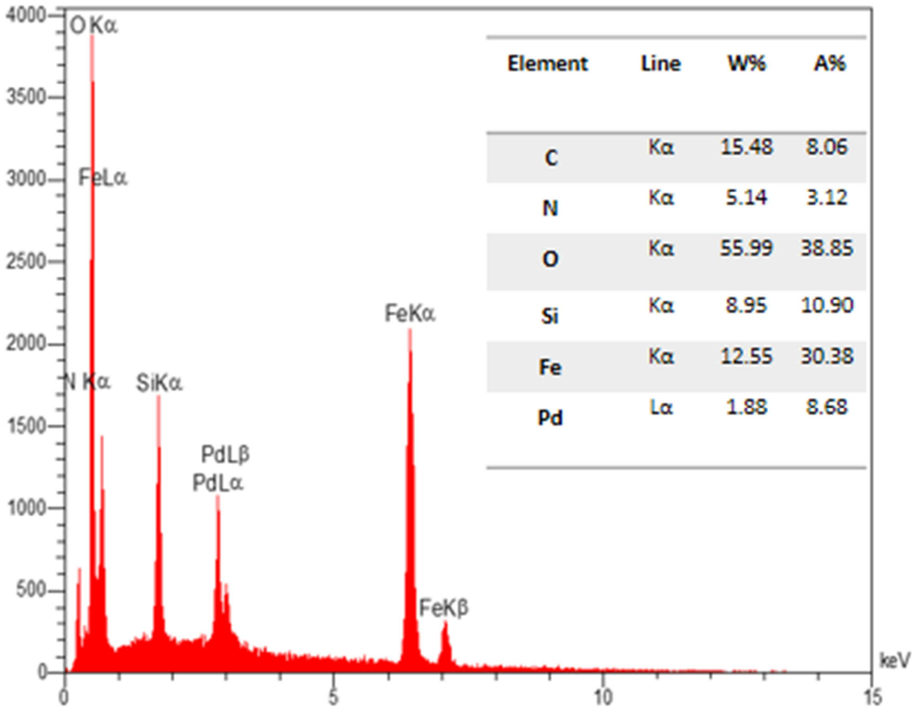


Fig. 2. FESEM image of a) G3-Gu and b) G3-Gu-Pd



Element	Line	W%	A%
C	Kα	15.48	8.06
N	Kα	5.14	3.12
O	Kα	55.99	38.85
Si	Kα	8.95	10.90
Fe	Kα	12.55	30.38
Pd	Lα	1.88	8.68

Fig.3. EDS analysis of G3-Gu-Pd

To investigate the elemental components of the catalyst, energy dispersive X-ray (EDX) analysis was performed and shown in Fig. 3. EDX analysis confirmed the presence of the Fe, O and Si related to the magnetic core (MNPs) and silica shell (SiO_2). In addition, EDX analysis shows carbon and nitrogen corresponding to the organic structure of the dendritic nanocomposite. According to the EDX measurements (Fig. 3), G3-Gu-Pd catalyst prepared in this work contains 1.88 wt% of Pd and the other elements in the catalyst were reported in the table in the corner of Fig. 3. Also the ICP analysis of G3-Gu-Pd catalyst shows that it's containing 0.80 mmol.g^{-1} of the Pd.

Fig. 4. Shows the EDX-SEM elemental mapping of the catalyst. A close examination of the images reveal that the Si, Fe and, specially, the Pd atoms were highly dispersed throughout the catalyst and results confirm no agglomeration of the catalyst species were happened.

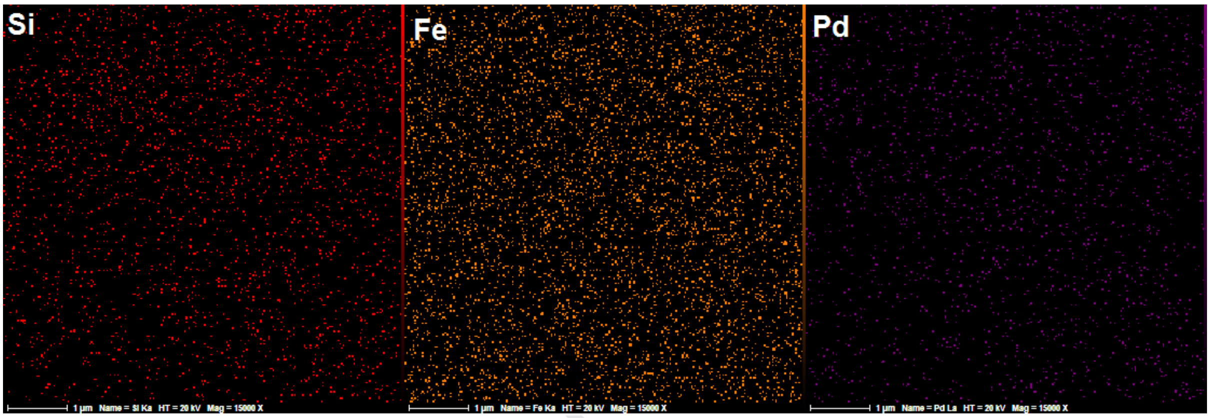


Fig. 4. EDX-SEM elemental mapping of the catalyst.

X-ray diffraction (XRD) analysis is a promising analytical tool for characterization of physical and chemical forms of the magnetic particles incorporated in the silica body. The XRD patterns of the MNPs and final catalyst were prepared in 2θ ranged from 10 to 80° (Fig. 5a). The main peaks at 2θ equated 30.5, 35.9, 43.3, 53.9 57.3, 63.2 and 74.8° for MNPs, which were marked respectively with (220), (311), (400), (422), (511), (440) and (533) indices based on the plane of a cubic spinel structure of the MNPs (JCPDS card no. 19-0629).[31] In addition, similar peaks were seen in the XRD diagrams of synthesized G3-GU-Pd catalyst, confirming that the cubic phase of MNPs is still kept after chemical treatments. No characteristic peaks Of SiO_2 were detected, indicating the SiO_2 was amorphous.[32] In the XRD pattern of G3-Gu-Pd a weak peak at 2θ =40° confirmed the presence of Pd nanoparticles. Nanoparticle size was also determined using Scherrer equation [L = Kl/ (b cos θ)], where l is the wavelength of the Cu-K radiation (0.154178 nm), θ is the Bragg angle, b is the FWHM (full width at half maximum) value of the respective peaks, and K is a constant of value 0.89. The obtained size of G3-Gu-Pd nanoparticles from Scherrer equation was calculated to be ~9.86 nm, which is consistent with the TEM results.

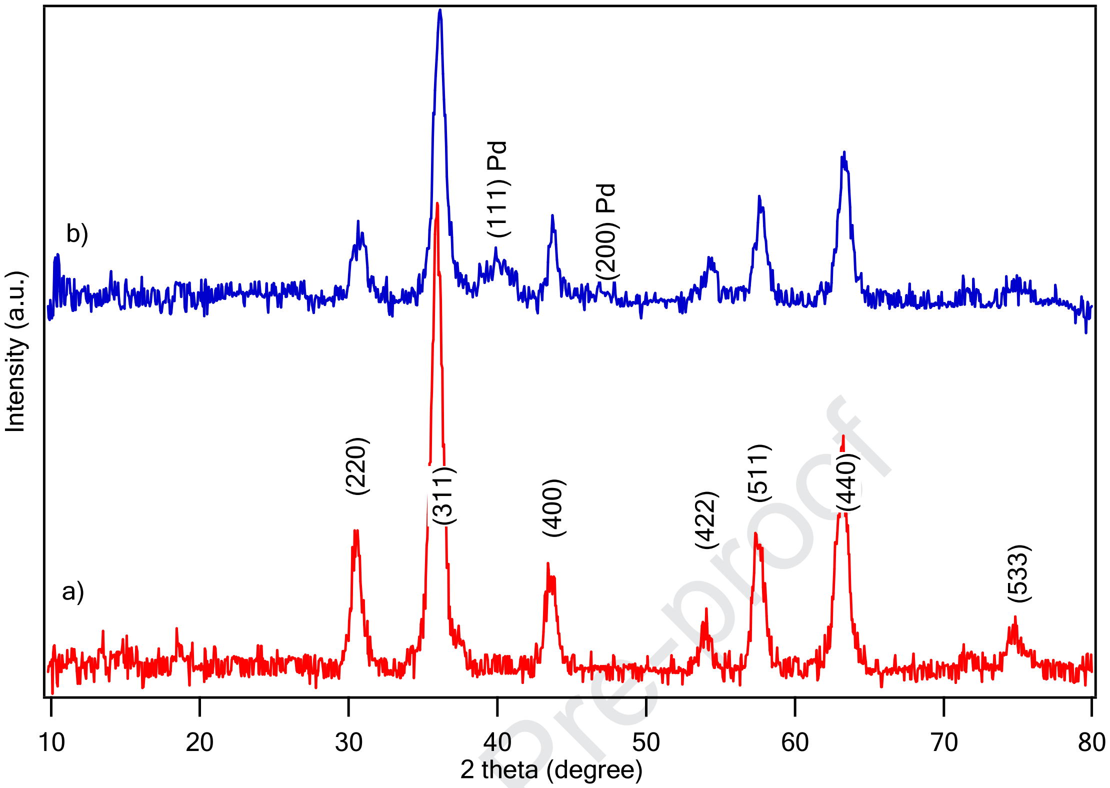


Fig. 5. XRD pattern of a) MNPs and b) G3-Gu-Pd

Catalytic activity and recyclability of the catalyst in copper-free Sonogashira and Mizoroki-Heck reactions are affected from thermal stability of the catalyst because these reactions are usually performed under heating conditions. The TGA of G3-Gu-Pd were performed by heating the sample at the rate of 10 ºC/min under a nitrogen atmosphere (Fig. 6). The TGA/DSC curve shows that the first weight loss occurs before 100 ºC, which was assigned to the release of adsorbed solvents; another at 200 ºC was related to the decomposition of organic ligands grafted on to the silica support. The evaluated temperature for graft removal indicates the high thermal stability for the G3-Gu-Pd catalyst until 200 ºC under a nitrogen atmosphere.

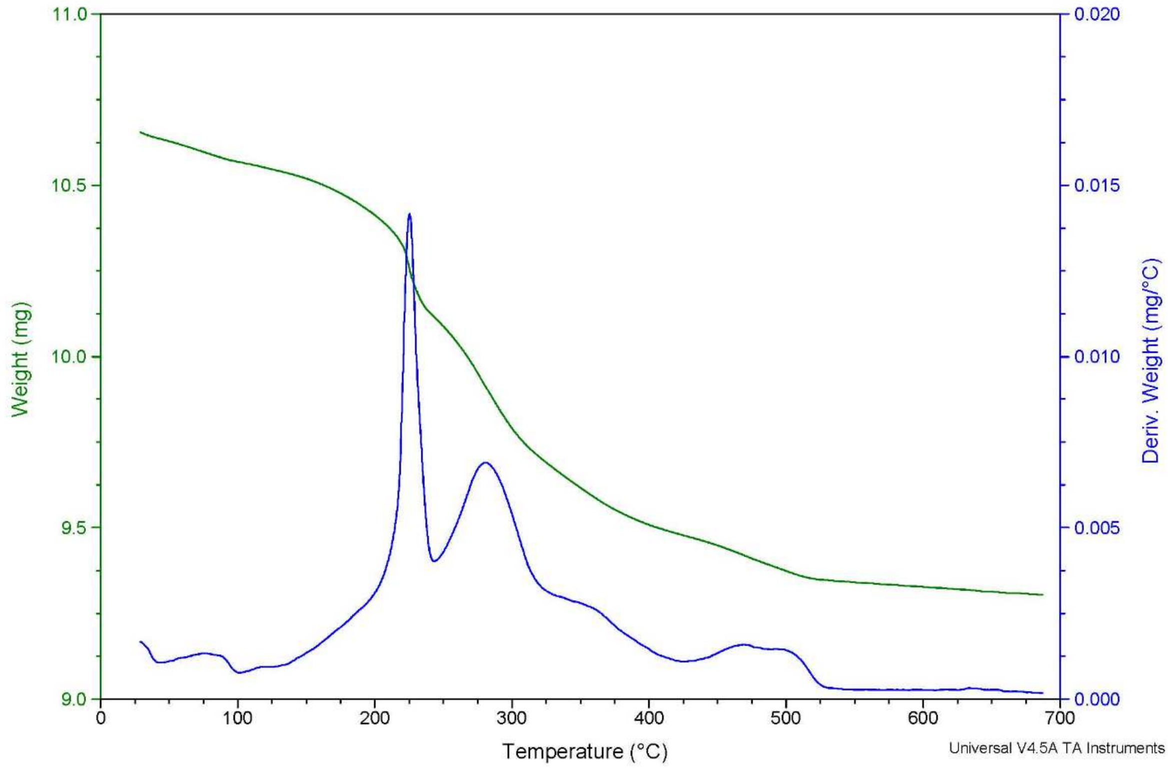


Fig. 6. TGA/DSC analysis of the prepared catalyst

Transmission electron microscopy (TEM) is an effective approach for characterization of nanostructured materials specially core-shell systems such as overall particle size, core size, shell thickness and uniform or nonuniform shell coating. For this, HRTEM image of the catalyst was recorded and depicted in Fig. 7. HRTEM image shows the uniform and spherical shape of G3-Gu and the Pd nanoparticles with the average size of 12 and 4 nm, respectively.

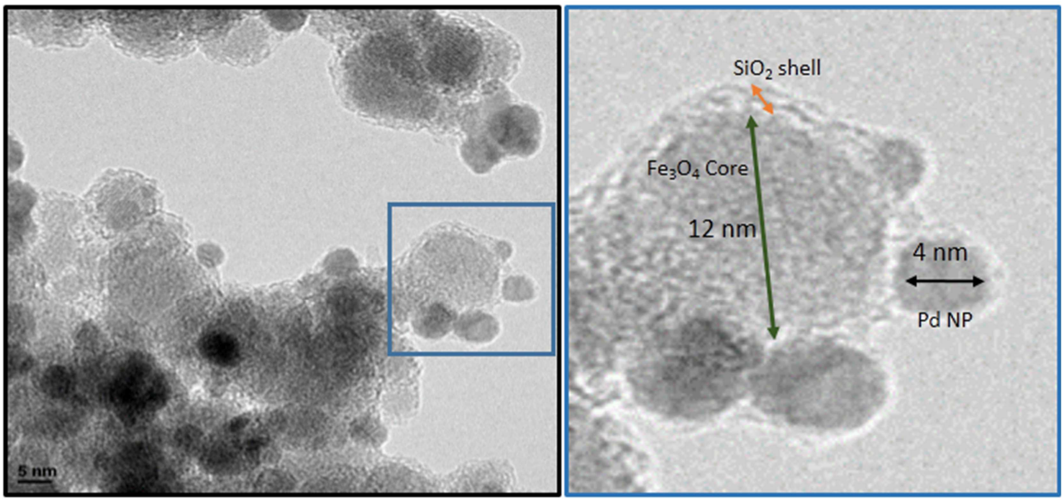


Fig. 7. HRTEM image of the catalyst (G3-Gu-Pd)

FTIR spectra of the first and third generation of the support, G3-Gu and final catalyst were collected in Fig. 8. As can be seen from Fig. 8, the weak peak located at 580 cm^{-1} is assigned to the Fe-O band related to the magnetic core (Fe_3O_4) and this peak was observed in all magnetic samples. The peak at 1083cm^{-1} was attributed to Si-O stretching. The absorption band at 3480 cm^{-}1 was attributed to the OH and amine groups.

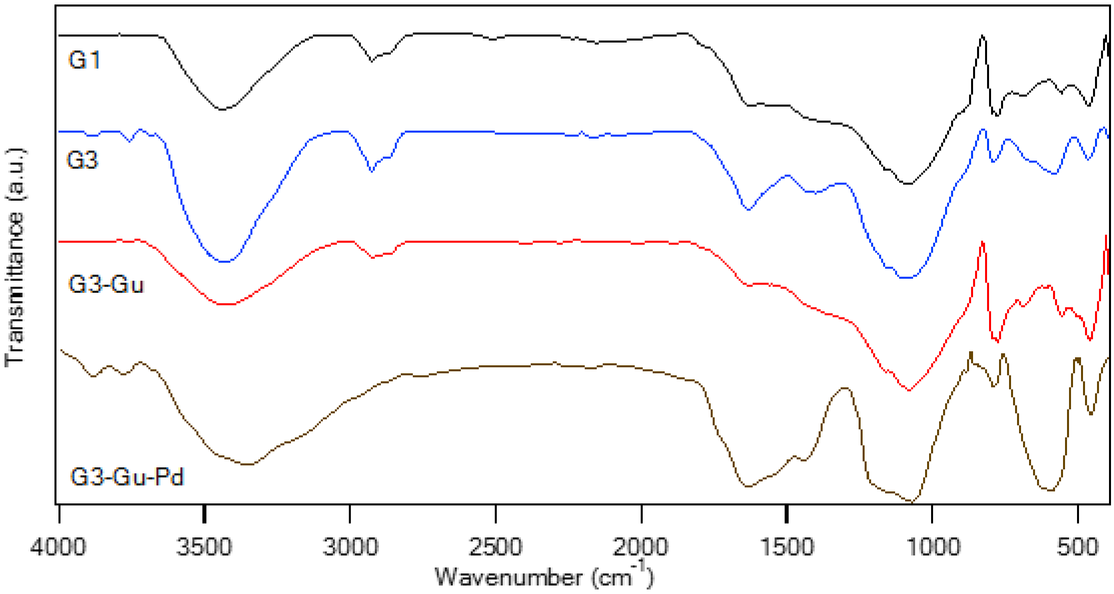


Fig. 8. FTIR spectra of the catalyst and intermediate components.

Magnetic measurements for the bare MNPs and final dendritic catalyst were carried out using a vibrating sample magnetometer (VSM) instrument at 300 K. The magnetization curves are shown for MNPs and G3-Gu-Pd in Fig. 9. No hysteresis is observed in the magnetization curves of exanimated nanoparticles and the saturation magnetization value was found to be equal to 80 and 60 emu g^{-1} for MNPs and G3-Gu-Pd, respectively, and suggesting their superparamagnetic properties. As regards, G3-Gu-Pd nanoparticles have an organic dendritic layer and also Pd nanoparticles around its magnetic core. Besides, a considerable part of the final material is composed from non-magnetic species and magnetization was observed lower than the pure magnetic nanoparticles (MNPs).

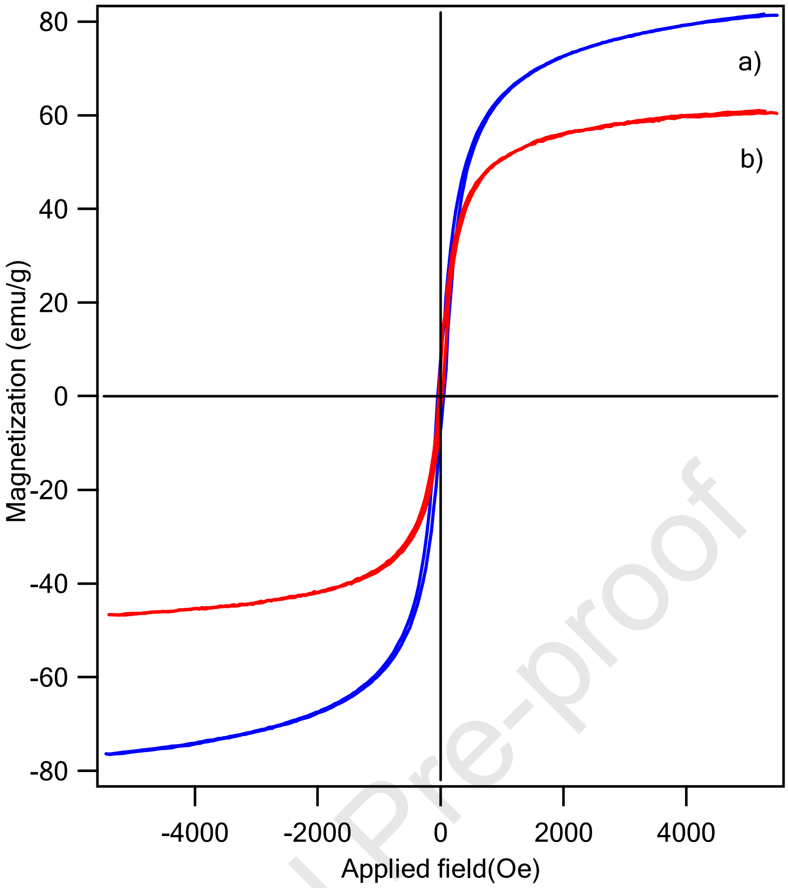


Fig. 9. Magnetization versus applied magnetic field curve for a) MNPs and b) G3-Gu-Pd.

The catalyst was also studied by X-ray photo electron spectroscopy (XPS). Active metal nanoparticles presence in the framework of the dentritic catalyst was re-confirmed using XPS analysis by investigation of binding energy range of 329 to 347 eV (Fig. 10).

The Pd 3d spectra are deconvoluted by two doublets with 5.5 eV splitting distance namely, Pd(0) 3d5/2, Pd(0) 3d3/2 and Pd(II) 3d5/2, Pd(II) 3d3/2, allowing for extracting the binding energy of Pd(0) and Pd(II) to evaluate the electronic property of the catalyst active site. The peak binding energy values of 335.7 eV (Pd 3d5/2) and 341.0 eV (Pd 3d3/2) assign to the Pd(0) nanoparticles and the peaks located at 337.3 eV (Pd 3d5/2) and 342.7 eV (Pd 3d3/2) correspond to the Pd(II) species, which have coordinated to the guanidine end-caped groups of supported dendrimer (Fig. 10). The XPS spectrum declares that Pd(II) ions have been partially reduced to Pd(0) since the area under the peak of Pd(0) nanoparticles is relatively small respect to the coordinated Pd(II).[33] These observations are agreement with the results obtained from the TEM and XRD analysis, confirm the presence of the Pd(0) nanoparticles.

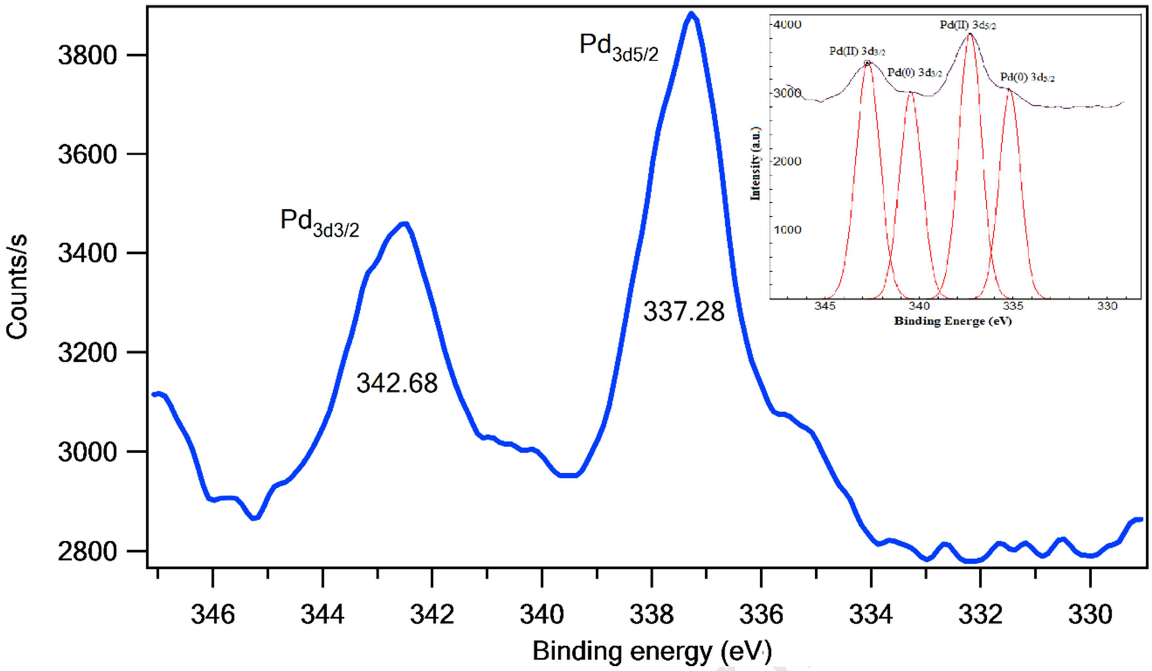


Fig. 10. XPS spectra of the G3-Gu-Pd catalyst in range of the Pd binding energy.

Catalyst activity

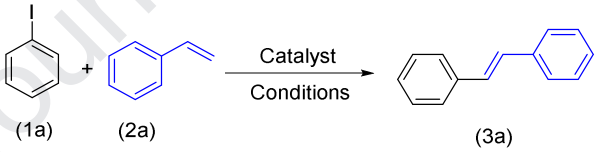
Catalytic efficiency of G3-Gu-Pd was investigated in Mizoroki-Heck and copper-free Sonogashira reactions, as two Pd based catalytic coupling reactions. In each reaction, at first, optimal conditions will be obtained and then optimal conditions were applied to synthesize other derivatives. In addition recoverability and reusability of the catalyst was checked precisely.

Mizoroki-Heck Reaction

The catalytic activity of the G3-Gu-Pd catalyst, was evaluated in Mizoroki-Heck coupling reaction between iodobenzene and vinyl benzene as a model reaction. The effects of type of solvent, base, temperature and amount of the catalyst were evaluated by this reaction and the results are shown in Table 2.

At first, the model reaction was performed in dimethylformamide (DMF) using K_2CO_3 as base in the presence of G3-Gu-Pd catalyst (10 mg, 0.8 mol % Pd) at 120 ^{o}C. In this conditions trans-1.2-diphenylethylene was obtained in 87% isolated yield after 6 h (Table 2, entry 1). During our optimization studies, we tried to use water as a green solvent. First, the mixture of (1:1) water: DMF used as solvent and the product was obtained about 84% yield (Table 2, entry 2). Examination of other solvents such as acetonitrile and toluene show the reaction yield decrease below to 74% (Table 2, entries 3 and 4). When the water used as the sole solvent, the reaction yield was obtained 78%, however with addition of SDS (0.5 mmol) as surfactant, the reaction yield reached to 87% which is comparable with DMF solvent (Table 2, entries 5 and 6). Thus we continued our optimization studies with water solvent and the various surfactant tested and results show SDS is the best one with loading of 0.4 mmol (entries 6-11). For evaluating the effect of temperature, the model reaction was performed at 85 °C, and the decreasing in yield of reaction was observed obviously (entry 12). We also tested different bases in the Heck coupling reaction with G3-Gu-Pd catalyst and no superiority related to K_2CO_3 was observed, so it was selected as base in this reaction (Table 2, entries 10, 12-16). Also good yield of 1, 2- diphenylethylene was obtained in the presence of 1 mmol K_2CO_3 (Table 2, entry17). At the end of optimization, catalyst loading was checked out and various amount of the catalyst was loaded in to the model reaction. When 1 mol % (12.5 mg) of the G3-Gu-Pd catalyst was used, the result doesn’t change, but when the amount of the catalyst was decreased to 0.6 mol %, decreasing in the yield of reaction was observed (Table 2, entries 19 and 20). Consequently the optimum conditions for this coupling reaction catalyzed by G3-Gu-Pd catalyst explained as below: aryl halide (1 mmol), alkene (1.1 mmol), K_2CO_3 (1 mmol), H_2O (3 mL), SDS (0.4 mmol), G3-Gu-Pd catalyst (0.8 mol %) at 100 °C under reflux condition.

Table 2. Optimization of solvent, temperature, base, surfactant and catalyst quantity in the Mizoroki-Heck reaction between iodobenzene and styrene in the presence of catalyst.[a]

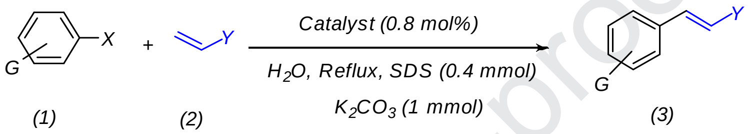


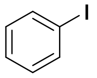
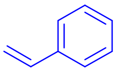
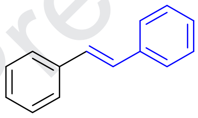
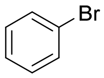
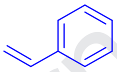
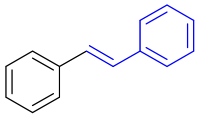
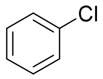
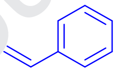
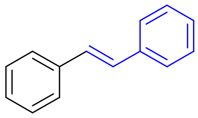
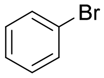
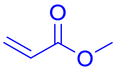
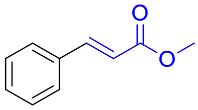
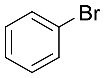
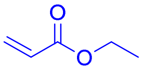
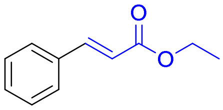
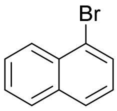
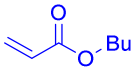
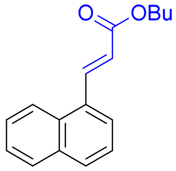
Entry	Temp. (°C)	Solvent	Catalyst amount (mg) (Pd (mol %))	Base (mmol)	Surfactant (mmol)	Time (h)	Yield (%)[b]
1	120	DMF	10 (0.8)	K_2CO_3 (2)	-	6	87
2	110	DMF:H_2O 1:1	10 (0.8)	K_2CO_3 (2)	-	6	84
3	100	CH_3CN	10 (0.8)	K_2CO_3 (2)	-	10	68
4	110	Toluene	10 (0.8)	K_2CO_3 (2)	-	6	74
5	80	H_2O	10 (0.8)	K_2CO_3 (2)	-	6	78
6	100	H_2O	10 (0.8)	K_2CO_3 (2)	SDS (0.5)	6	87
7	100	H_2O	10 (0.8)	K_2CO_3 (2)	TBAB (0.5)	6	86
8	100	H_2O	10 (0.8)	K_2CO_3 (2)	PEG-200 (0.5)	6	82
9	100	H_2O	10 (0.8)	K_2CO_3 (2)	Dodecylamine (0.5)	6	80
10	100	H_2O	10 (0.8)	K_2CO_3 (2)	SDS (0.4)	6	87
11	100	H_2O	10 (0.8)	K_2CO_3 (2)	SDS (0.3)	6	86
12	85	H_2O	10 (0.8)	K_2CO_3(2)	SDS(0.4)	10	76

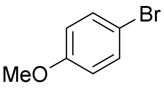
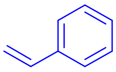
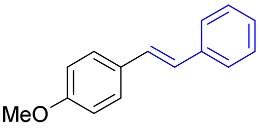
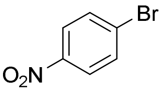
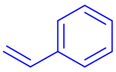
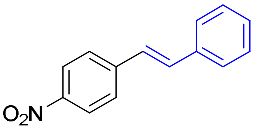
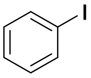
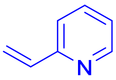
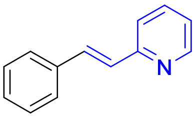
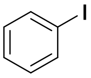
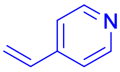
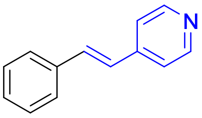
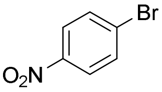
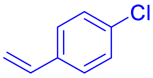
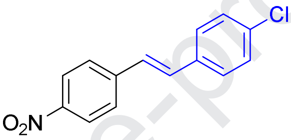
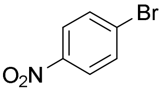
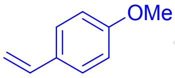
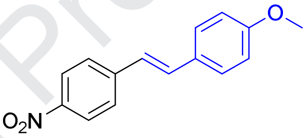
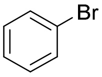
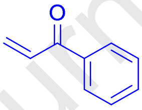
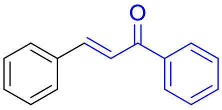
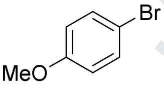
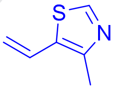
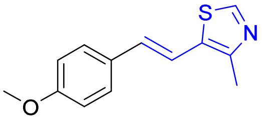
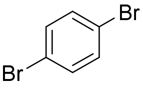
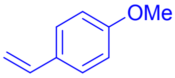
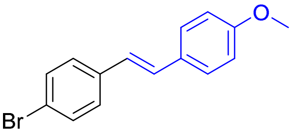
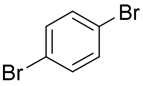
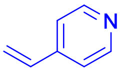
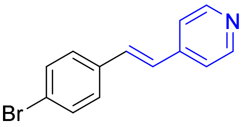
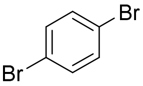
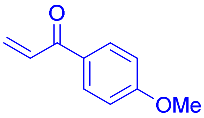
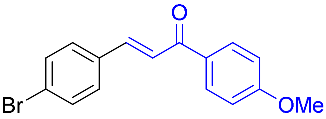
13	100	H_2O	10 (0.8)	Et_3N (2)	SDS (0.4)	8	83
14	100	H_2O	10 (0.8)	Na_2CO_3 (2)	SDS (0.4)	6	80
15	100	H_2O	10 (0.8)	K_3PO_4 (2)	SDS (0.4)	8	78
16	100	H_2O	10 (0.8)	NaOH (2)	SDS (0.4)	8	45
17	**100**	**H_2O**	**10 (0.8)**	**K_2CO_3 (1)**	**SDS (0.4)**	**6**	**87**
18	100	H_2O	10 (0.8)	K_2CO_3 (0.5)	SDS (0.4)	8	86
19	100	H_2O	12.5 (1)	K_2CO_3 (1)	SDS (0.4)	6	87
20	100	H_2O	7.5 (0.6)	K_2CO_3 (1)	SDS (0.4)	10	84

[a] Reaction conditions: iodobenzene (1 mmol), styrene (1.1 mmol), base (2 mmol), solvent (3 mL) and surfactant in the presence of G3-Gu-Pd as the catalyst. [b] Isolated yield.

Table 3. Mizoroki-Heck reaction between different aryl halides and various alkene in the presence of G3-Gu-Pd catalyst[a]



Entry	Substrate (1)	Substrate (2)	Product (3)	Time (h)	Yield[b](%)
1			 3a	6	87
2			 3a	12	84
3			 3a	24	62
4			 3b	8	88
5			 3c	8	87
6			 3d	10	84

7			 3e	14	82
8			 3f	12	90
9			 3g	6	88
10			 3h	6	90
11			 3i	12	91
12			 3j	12	84
13			 3k	12	86
14			 3l	12	83
15			 3m	18	78
16			 3n	12	86
17			 3o	12	80

[a]Reaction conditions: aryl halide (1 mmol), alkene (1.1 mmol), K_2CO_3 (1 mmol), H_2O (3 mL), SDS (0.4 mmol), Reflux, G3-Gu-Pd catalyst (0.8 mol %). [b]Isolated yield.

To developing the activity of the G3-Gu-Pd catalyst, we tested various aryl halides with various alkene in Mizoroki-Heck reaction (Table 3).

Under optimized conditions, it is possible to synthesize different alkene compounds using various aryl halides and alkenes. In this protocol iodobenzene reacted faster in term of time and higher in yield than bromobenzene and chlorobenzene (Table 3, entries 1-3). Acrylates were also reacted with aryl and naphtylbromide with moderate yields (Table 3, entries 4- 6). The reaction was sensitive to the nature of group on the aryl halides and vinylic compounds. Reaction yields of 4-bromoanisole and 1-bromo-4-nitrobenzene shows this effect (Table 3, entries 7, 8). Also, 2-vinylpyridine and 4-vinylpyridine reacted under normal condition and corresponding styrylpyridines were produced in excellent yields (Table 3, entries 9, 10). 4-bromonitrobenzene coupled with 4-chlorostyrene and 4-methoxystyrene with 91% and 84% yields, respectively (Table 3, entries 11, 12). Also bromobenzene reacted with acrylophenone and corresponding chalcone was obtained in 86% yields (Table 3, entry 13). Compounds 3l was produced using 4-methyl-5-vinylthiazole as a heterocyclic vinylic substrate under normal conditions (entry 14). Also 1, 4-diboromobenzene worked moderately in this protocol (Table 3, entries 15-17).

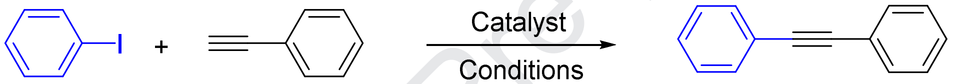
Copper-free Sonogashira reaction

Now in this part, another important application of G3-Gu-Pd catalyst was investigated as a magnetic nanocatalyst for the efficient copper-free Sonogashira reaction between various terminal alkynes and aryl halides in green solvent. Efficiency of the G3-Gu-Pd catalyst in the coupling reaction between iodobenzene and ethynylbenzene as a simple model reaction was evaluated.

Initially, the copper-free Sonogashira reaction performed in toluene at 110 °C in the presence of G3-Gu-Pd (10 mg) catalyst and K_2CO_3 (2 mmol) as the base and the corresponding product was obtained with 65% yield after 12 h (Table 4, entry 1). The yield of this coupling reaction in DMF after 8 h was increased to 81% (Table 4, entry 2). When the model reaction performed in the mixture of DMF: H_2O (1:1) and pure water, the yield of product reached to 80% and 74%, respectively (Table 2, entries 3, 4). However, by addition of SDS surfactant in water, yield was reached to 83% (Table 2, entry 5). Different surfactant were also tested in this coupling reaction and the best results obtained with SDS surfactant (Table 4, entries 5-8).

In this way, the 0.4 mmol amount of SDS surfactant sufficient for this coupling reaction (Table 4, entries 9-10). Reaction temperature was investigated on the model reaction and the best results obtained at 110 °C under the reflux condition (Table 4, entries 9, 11). Some bases, including KOt-Bu, Et_3N, K_2CO_3, and Na_2CO_3 were tested in the model reaction and the best result was observed when K_2CO_3 used as base (Table 4, entry 12-14). Also amount of base was optimized and 1.0 mmol was sufficient for this reaction (Table 4, entries 15-17). Then, the catalyst loading was optimized and 1 mol% of Pd (equal to 12.5 mg catalyst) was selected as optimum amount for completion of the reaction (Table 4, entries 18-19). Consequently, the optimum conditions explained as follows: G3-Gu-Pd catalyst (12.5 mg), phenylacetylene (1.1 mmol), of aryl halide (1.0 mmol), K_2CO_3 (1 mmol), SDS (0.4 mmol) and H_2O (3 mL) at 100 ºC under reflux conditions.

Table 4. Optimization study of copper-free Sonogashira reaction of iodobenzene and phenylacetylene catalyzed by G3-Gu-Pd catalyst.[a]



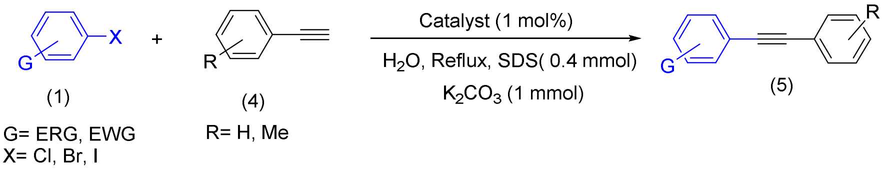
(1a) (4a) (5a)

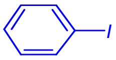
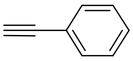
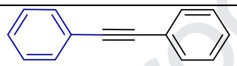
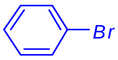
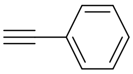
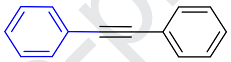
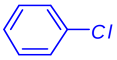
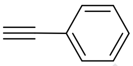
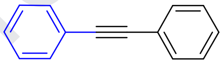
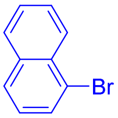
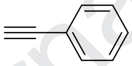
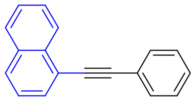
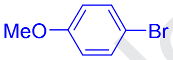
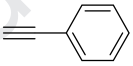
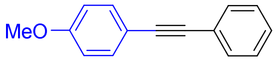
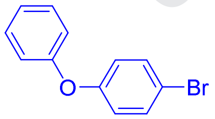
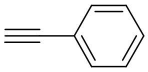
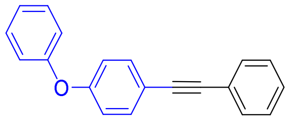
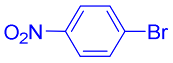
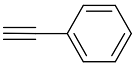
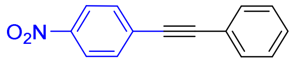
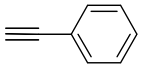
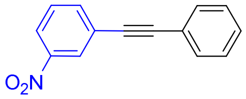
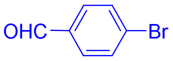
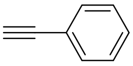
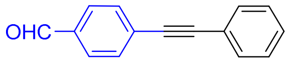
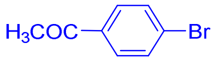
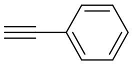
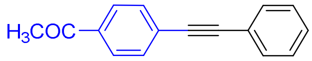
Entry	Temp. (°C)	Solvent	Catalyst amount (mg): (Pd (mol %))	Base (mmol)	Surfactant (mmol)	Time (h)	Yield (%)[b]
1	110	Toluene	10 (0.8)	K_2CO_3 (2)	-	12	65
2	110	DMF	10 (0.8)	K_2CO_3 (2)	-	8	81
3	110	DMF:H_2O 1:1	10 (0.8)	K_2CO_3 (2)	-	8	80
4	100	H_2O	10 (0.8)	K_2CO_3 (2)	-	10	74
5	100	H_2O	10 (0.8)	K_2CO_3 (2)	SDS (0.5)	8	83
6	100	H_2O	10 (0.8)	K_2CO_3 (2)	TBAB (0.5)	8	81
7	100	H_2O	10 (0.8)	K_2CO_3 (2)	PEG-200 (0.5)	8	76
8	100	H_2O	10 (0.8)	K_2CO_3 (2)	Dodecylamine (0.5)	8	72
9	100	H_2O	10 (0.8)	K_2CO_3 (2)	SDS (0.4)	8	83
10	100	H_2O	10 (0.8)	K_2CO_3 (2)	SDS (0.3)	8	80
11	85	H_2O	10 (0.8)	K_2CO_3 (2)	SDS (0.4)	12	65
12	100	H_2O	10 (0.8)	Na_2CO_3 (2)	SDS (0.4)	8	82
13	100	H_2O	10 (0.8)	*t*-BuOK (2)	SDS (0.4)	10	64
14	100	H_2O	10 (0.8)	Et_3N (2)	SDS (0.4)	10	80
15	100	H_2O	10 (0.8)	K_2CO_3 (1.5)	SDS (0.4)	8	83
16	100	H_2O	10 (0.8)	K_2CO_3 (1)	SDS (0.4)	8	84
17	100	H_2O	10 (0.8)	K_2CO_3(0.5)	SDS (0.4)	8	80
18	**100**	**H_2O**	**12.5 (1)**	**K_2CO_3 (1)**	**SDS (0.4)**	**8**	**85**

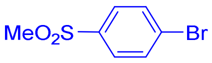
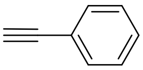
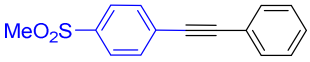
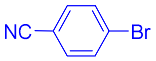
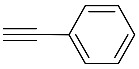
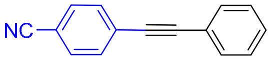
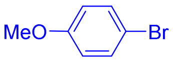
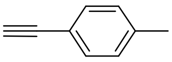
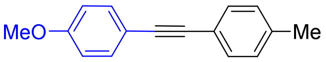
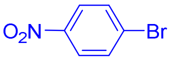
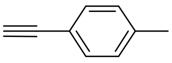
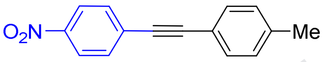
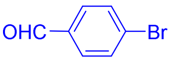
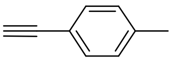
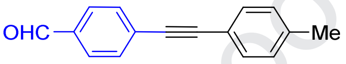
19	100	H_2O	15.6 (1.2)	K_2CO_3 (1)	SDS (0.4)	8	84

[a]Reaction conditions: iodobenzene (1 mmol), phenylacetylene (1.1 mmol), base (mmol), surfactant, solvent (3 mL) and G3-Gu-Pd catalyst (12.5 mg, 1 mol %). [b]Isolated yield

Table 5. Copper-free sonogashira reaction between various aryl halides and acetylene compound in the presence of G3-Gu-Pd catalyst.[a]



Entry	Substrate (1)	Substrate (4)	Product (5)	Time (h)	Yield[b] (%)
1			 6a	8	85
2			 6a	12	84
3			 6a	24	60
4			 6b	12	81
5			 6c	14	83
6			 6d	18	81
7			 6e	12	90
8			 6f	12	86
9			 6g	12	89
10				12	88

			6h		
11			 6i	12	88
12			 6j	12	86
13			 6k	18	81
14			 6l	14	89
15			 6m	14	87

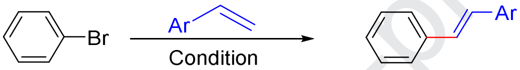
[a]Reaction conditions: aryl halide (1 mmol), arylacetylene (1.1 mmol), K_2CO_3 (1 mmol), catalyst (1 mol %), SDS (0.4 mmol), H_2O (3 mL) at 100 °C. [b]Isolated yields.

The optimized condition was used for the evaluation of catalyst efficiency of G3-Gu-Pd catalyst for copper-free Sonogashira reaction in water. A series of aryl halides have coupled with acetylene compounds and the results are shown in Table 5. Aryl halides with electron-rich and electron-poor group were tested under the optimized conditions and the corresponding products were obtained with satisfactory yields. Iodobenzene was reacted with phenylacetylene to produce 1, 2-diphenylethyne after 8 h with 85% yield in water (Table 5, entry 1). Satisfactory yield was also obtained with bromobenzene (Table 5, entry 2). The yield of chlrobenzene after 24 h was 60% (Table 5, entry 3). Naphthalene bromide also participated in this reaction and produce related ethyne with 81% yield (Table 5, entry 4). Time and yield of the reaction are sensitive to the nature of substituent on the aryl halide. Electron-donating group needed more reaction time and the corresponding yield is lower respect to the electron-withdrawing groups. For example the reaction of phenylacetylene with 4-bromoanisole and 4-bromo phenyl ether give 83% and 81% isolated yield of desired products after 14 h, respectively (Table 5, entries 5 and 6), while electron withdrawing groups such as nitro gave higher yields of coupled products (Table 5, entries 7 and 8). Other electron-withdrawing groups on 4-position, on the aromatic ring such as -CHO, -$COCH_3$, -SO_2Me and -CN follow this rule (Table5, entries 8-12).

4-Ethynyl toluene also gave good yields with aryl bromide but in case of 4-bromo anisole the reaction time is longer than 4-bromobenzaldehyde and 1-bromo 4-nitrobenzene (Table 5, entries 13-15).

In order to show the efficiency of heterogeneous denderitic G3-Gu-Pd catalyst in the Mizoroki-Heck reaction, this protocol was compared to the other catalytic systems (Table 6). Comparison was performed in terms of the solvent, reaction temperature, amounts of the Pd-catalyst, product yields and reaction time. As shown in Table 6, G3-Gu-Pd catalytic system shows a high efficiency in this coupling reaction in green solvent under the optimized reaction. Also amount of the used catalyst (base on the Pd mol %) is the same or lower than the other reported systems.

Table 6. Comparison of the efficiency of the G3-Gu-Pd catalyst with the other recently reported Pd-catalyst in the Mizoroki-Heck reaction.

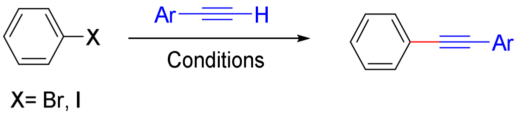


Entry	Catalyst (Pd mol %)	Solvent	Temp. (°C)	Additional conditions	Time (h)	Yield (%) [a]	Ref.
1	Pd@Fe_3O_4NPs (1)	DMF	110	NaOAc	24	76	[34]
2	Pd-PPh_2-G2-PAMAM-SiO_2 [b]	DMF	110	NaOAc	48	69	[26]
3	nanostructured silica I-Pd [c](10)	CH_3CN	80	Et_3N	24	70	[35]
4	G2-Pd [d] (1)	DMF	140	N_2,[Bu_4N]Br, ,Cs_2CO_3	4	84	[36]
5	γ-Fe_2O_3(Pd-DABCO) (3)	DMF	100	Et_3N	1	87	[37]
6	G3-Gu-Pd (0.8)	H_2O	100	SDS, K_2CO_3	12	84	This work

[a] Isolated yield. [b] Palladium complexed on to phosphonated polyamine dendrimers based on silica [c] Pd nanoparticles on modified silica with pyridine. [d] Palladium(0) complexed on PAMAM dendrimers.

Also, efficiency of the heterogeneous denderitic G3-Gu-Pd catalyst in the copper-free Sonogashira reaction in water was compared to the other catalytic systems (Table 7). As shown below, G3-Gu-Pd catalytic system also shows a high efficiency in copper-free Sonogashira reaction in green solvent under the optimized reaction. Also time of the reaction is short and amount of catalyst (based on the Pd mol %) is the same or lower than the other reported catalytic systems.

Table 7. Comparison of the efficiency of the G3-Gu-Pd catalyst with the other recent reported Pd-based catalysts in the Sonogashira reaction.



Entry	Catalyst (Pd mol %)	Solvent	Temp. (°C)	Additional conditions	Time (h)	Yield (%) [a]	Ref.
1	NS-MCM-41-Pd-Cu-I [a]	Toluene	100	But_3N, X= Br	24	56	[34]
2	SiO_2@Fe_3O_4–Pd (1)	DMF	100	K_2CO_3, X= Br	6	79	[26]
3	MNPs–PdNPs(1.5) [b]	THF	65	N_2, Et_3N, X=I	24	85	[35]
4	I-Pd (10) [c]	CH_3CN	80	Et_3N, X= I	24	80[d]	[36]
5	Pd@Fe_3O_4 NPs (1)	DMF	110	Pipiridine, X= I	24	83	[37]
6	G3-Gu-Pd (1)	H_2O	100	SDS, K_2CO_3, X= Br	12	84	This work

[a] palladium nanoparticle on MCM-41 bipyridyl complex. [b] PEGylated γ-Fe2O3–Pd nanoparticle catalysts with positive dendritic effects. [c] Nanostructured silica functionalized with pyridine sites. [d] Yield based on GC analysis.

Recycling of the G3-Gu-Pd catalyst in Mizoroki-Heck reaction

Economic benefit and environment considerations of the heterogeneous catalysts were affected by the recoverability and reusability in a catalytic process. The recycling of the G3-Gu-Pd catalyst in Mizoroki-Heck reaction was investigated by the reaction of iodobenzene and vinyl benzene as a model reaction under optimized reaction conditions. At the end of the reaction, the catalyst was collected by magnetic field, then dispersed and washed with ethylacetate (3 mL). Recovered catalyst, repeatedly dispersed in water (3 mL) and stirred mechanically for an hour. Then isolated by magnet and dried at 80°C for 6 h. The catalyst could be recycled for at least five runs without obvious loss of its efficiency (Fig. 11).

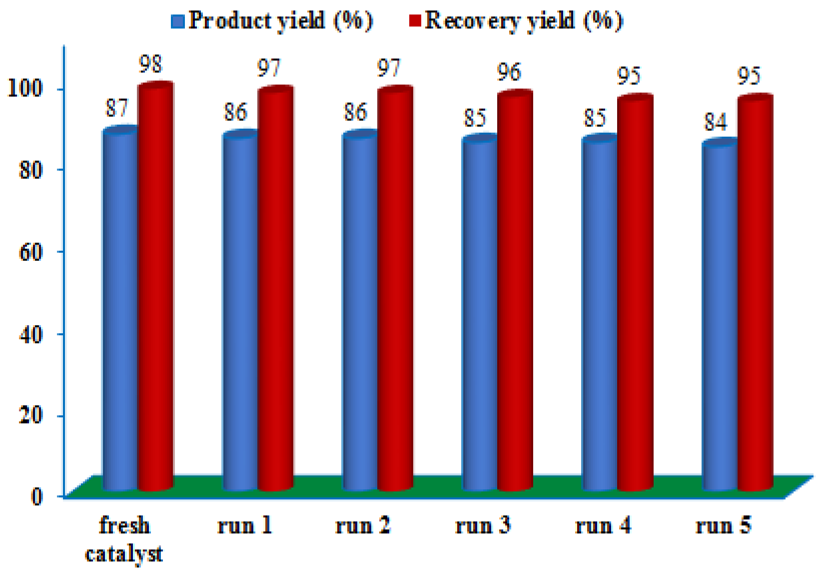


Fig 11. Recycling of catalyst in Mizoroki-Heck reactions[a, b]

[a]Reaction conditions: iodobenzene (1.0 mmol), styrene (1.1 mmol), K_2CO_3 (1 mmol), recovered G3-Gu-Pd catalyst (10 mg), SDS(0.4 mmol), H_2O (3.0 mL) at 100 °C, [b]Isolated yield.

The ICP analysis of the reused catalyst after each cycle of reusing for the investigation of the Pd leaching was performed and results were summarized in Table 8. According to results were illustrated in this table, only very small amount of the Pd (less than 3.5%) was leached from the magnetic G3-Gu support after 5 cycles of reuse.

Table 8. ICP analysis results of the fresh and reused catalyst after five cycles of reuse.

Entry	Catalyst	Pd (mol %)
1	Fresh catalyst	0.80
2	Cycle 1	0.79
3	Cycle 2	0.79
4	Cycle 3	0.78
5	Cycle 4	0.77
6	Cycle 5	0.77

The hot filtration test is another way to checking the heterogeneity of the catalyst. According to this test, if the catalyst is not heterogeneous in practice, the catalytically active particles are leached from the support during hot filtration and release in reaction and they catalyze the reaction. For this test, we performed the reaction of iodobenzene and styrene with aqueous solution obtained from filtrate of the model reaction. Under optimized condition the amount of product obtained in this way was about less than 2.5%, confirming that reaction catalyzed heterogeneously and no significant amount of the Pd leached from the catalyst.

Recycling of the G3-Gu-Pd catalyst in the copper-free Sonogashira reaction

Recycling experiments in the copper-free Sonogashira coupling were performed by using the reaction of iodobenzene and phenylacetylene under the optimized conditions. After stopping the reaction, the G3-Gu-Pd catalyst collected from the reaction mixture by magnetic field. The collected catalyst, isolated from the magnet and dispersed in ethyl acetate (3mL). The catalyst repeatedly collected by magnet and then dispersed in water and washed with water (3mL), then dried at 80 ^{o}C for 6 h. The results show that the catalyst can be reused at least for five cycles, and no decreasing in its activity was observed (Fig.12).

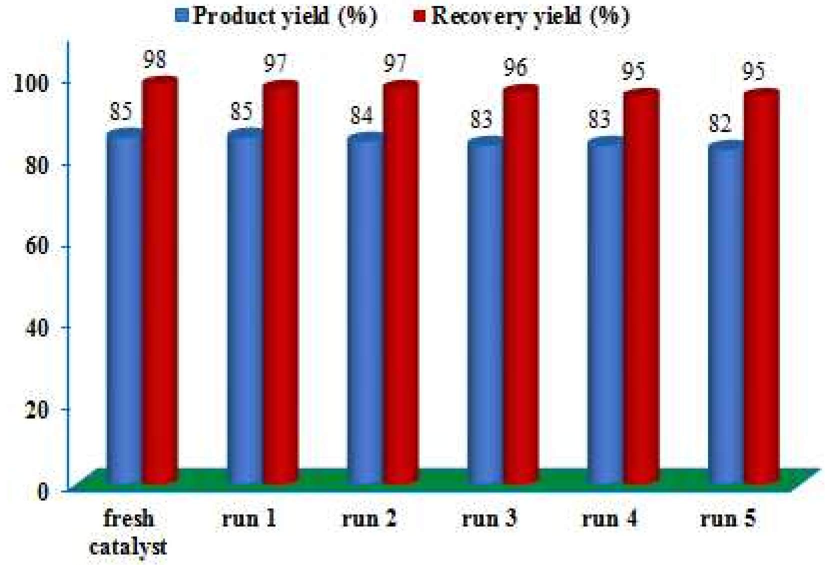


Fig 12. Recycling of the catalyst in copper-free Sonogashira reaction[a,b]

[a]Reaction conditions: iodobenzene (1.0 mmol), phenylacetylene (1.1 mmol), K_2CO_3 (1 mmol), recovered G3-Gu-Pd catalyst (12.5 mg), SDS(0.4 mmol), H_2O (3.0 mL) at 100 °C. [b]Isolated yield.

Also the results obtained from ICP analysis show that the amount of leached Pd after 5 times of reusability was about 4.5 % in Sonogashira coupling reaction, and this test confirmed that the magnetic silica-dendrimer-guanidine (G3-Gu) is a very effective support for the Pd nanoparticles (Table 9).

Table 9. The ICP analysis results of fresh and reused catalyst after five time of reusability in Sonogashira coupling.

Entry	Catalyst condition	Pd (mol %)
1	Fresh catalyst	1
2	Run1	0.99
3	Run2	0.97
4	Run3	0.97

5	Run4	0.96
6	Run5	0.95

When the copper-free Sonogashira coupling reaction between iodobenzene and phenylacetylene was performed with aqueous filtrate of model reaction only 4% of diphenylethyne was obtained. All of these results according to the heterogenic activity of G3-Gu-Pd-catalyst and demonstrated that this catalyst is an effective heterogeneous catalyst system.

Conclusion

In summary, novel silica magnetic-supported third-generation dendrimer capped by guanidine Pd catalyst have been developed and used in the Mizoroki-Heck and copper-free Sonogashira reactions, in which the immobilized dendrimer acted as a stabilizer for preventing the nanoparticles from agglomeration, as a recycling vehicle, as well as a ligand in catalysis. This novel catalyst has been characterized by various techniques such as FESEM, EDS, FTIR, TGA/DSC, XRD, VSM, and HRTEM. Catalytic activity of the prepared catalyst was evaluated in two important cross coupling reactions: Mizoroki-Heck and copper-free Sonogashira. Trace amount of the catalyst was used for the mentioned coupling reactions, and also amount of the Pd leached from the catalyst was very low. The products were obtained with good to excellent yields by simple procedure in water as green and lovely environment solvent. Due to these advantages that mentioned above, this novel Pd based catalytic system can be easily recovered and reused for several times without loss of activity.

Supporting Information

^{1}HNMR and ^{13}CNMR spectra of the synthesized compounds were collected in the supplementary information file.

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Conflict of Interests

The authors declare that there are no conflicts of interest regarding the publication of this paper