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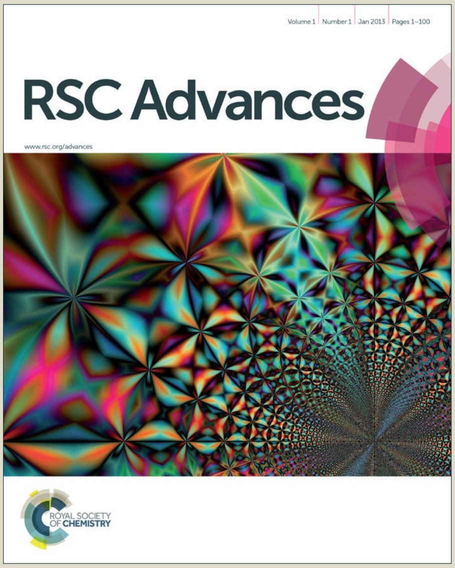

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ARTICLE

A Click Strategy for the Immobilization of Palladium nanoparticles onto Silica: Efficient and recyclable catalysts for carbon–carbon bond formation under mild reaction conditions

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An interesting silica-supported nano-palladium catalyst was successfully prepared through ‘‘click’’ reaction of azide-functionalized silica with methylpropargylimidazolium bromide followed by immobilization of palladium nanoparticles (NPs), in which the click-triazole as an important functional entity acts as both a stable linker and a good chelator. The palladium-NPs are stabilized by synergistic effect of coordination and electrostatic interactions. The as-prepared nanocatalyst was well characterized and found to be highly efficient in Heck and Suzuki–Miyaura coupling in terms of activity and recyclability in aqueous ethanol under phosphine-free and low Pd loading (0.1 mol%) conditions.

Introduction

Heterogeneous catalysis is noteworthy for both academic and industrial synthesis owing to its advantages over homogeneous catalysis.[1-3] These solid-supported catalysts improve catalyst stability and facilitate the separation of the catalyst from reaction media. In fact, one of the challenging areas of research in heterogeneous catalysis is stabilization of nano-catalysts on a solid surface.[4, 5] Supported nano-catalysts are manufactured by reacting a functionalized surface with available functional groups on the catalyst atoms.

The palladium-catalyzed coupling reactions are classified nowadays among the most general transformations in organic synthesis, which have great applications in both laboratory and large-scale synthesis.[6, 7] In view of advanced synthesis, the non-renewable use of expensive palladium catalysts is less valuable, in particular, for industrial scale synthesis. Over the past few years, considerable interest has been focused on metallic nanoparticles (NPs) because of their potential applications in various fields. Metal-NPs usually display unique properties in comparison with their bulk materials and the isolated atoms in catalytic reactions.[8] In recent years, Pd-NPs have been widely used as efficient catalysts for the important reactions involving low catalyst loadings mild and environment-friendly conditions. The metal-NPs stabilized on the solid surface have been widely used as efficient catalysts in organic synthesis. The stabilizers are generally Ligands,[9] polymers,[10] ionic liquids (ILs),[11] and dendrimers[12] have developed as common metal-stabilizers in the literatures.The novel supported palladium nano-catalysts can be applied in a diversity of reactions, including Heck and Suzuki carbon-carbon coupling reactions.[13, 17] The copper(I)-catalyzed azide–alkyne cycloaddition[18] (CuAAC), known as the ‘‘click reaction’’,[19] has shown wide applications in bioconjugation,[20] drug discovery,[21] and polymerscience[22] during the past decade. Additionally, the 1,2,3-triazoles produced in the CuAAC reaction have also drawn much attention for metal-catalyst immobilization as a highly stable linker or/and a chelator to graft catalysts onto the solid supports.[23, 24]

Grafting of the ionic liquids on the solid surfaces gives a material with a charged surface. It is found that ILs are able to stabilize metal NPs through electrostatic interaction,but the most applications of the reaction are using 1,2,3-triazolyl[25, 26] and ionic liquid[27] alone as stable linkages for the connection of two chemical/biological components. The combination of ionic liquids and 1,2,3-triazolyl coordination group is expected to lead to the optimum balance between stability and reactivity of metal NPs, resulting from the highly synergistic effect of coordination and electrostatic interactions from 1,2,3-triazolyl and imidazolium group. Niu et al.[28] used Multiwalled Carbon Nanotubes-IL to support Au nanoparticles. Wang et al.[29] reported a click-imidazolium- modified copolymer as a solid support to stabilize the pd- NPs. They also prepared a series of click ionic salts through click reaction of organic azides with alkynefunctionalized imidazolium or 2-methylimidazolium salts.[30]

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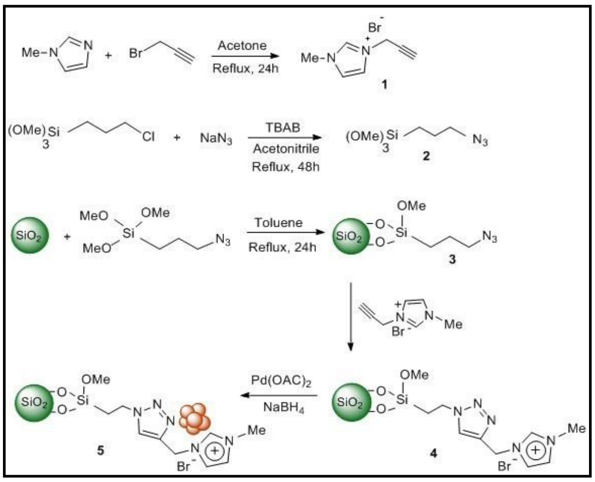
In continuation of our efforts to develop eco-friendly catalytic protocols, and catalysts containing quaternary ammonium and phosphonium salts.[31-34] herein, we present the synthesis and characterization of a click ionic-silica supported Pd–NPs, in which the NPs are immobilized by synergetic effect of coordination and electrostatic interactions from nitrogen-rich 1,2,3-triazolyl ligands and imidazolium salts, respectively. The as-prepared material was evaluated as a solid catalyst in Heck and Suzuki-Mura coupling reactions.

Result and Discussion

Preparation and characterization of the catalysts

The pathway to synthesize Si–IL@Pd(0)NPs was depicted in Scheme 1. Firstly, imidazolium salt was prepared from the reaction of N-methylimidazole and propargyl bromide. In the following step, silica was functionalized with 3-azidopropyltrimethoxysilane, which was subsequently reacted with N-propargylimidazolium via click reaction in the presence of $CuSO_4·5H_2O$ and sodium ascorbate as a catalytic system. Afterwards, the immobilization of palladium was carried out by the reduction of $Pd(OAc)_2$ in the presence of $NaBH_4$ as reducing agent, in CH_3CN/H_2O as the solvent system.

The Suzuki–Miyaura reaction of 4-bromonitrobenzene with phenylboronic acid was chosen as a model to evaluate the catalytic activity. To begin this investigation, we initially used immoblilized-palladium (II) click ionic support, which obtained without using any reducing agent like $NaBH_4$. It was found that by employing 0.12 mol% of catalyst, and K_2CO_3 (0.2 mmol) in the mixed solvent EtOH/H_2O (1:1) at 50 ^{o}C, the corresponding suzuki product was obtained in 40% yield after 3 h. However, under the same reaction conditions, the use of Si–IL@Pd(0)NPs as the catalyst, gave better conversions and improved the yield well, up to 97%. This result indicated that the effect of the palladium (0)-NPs was a significant factor in promoting the reaction. Hence, Si–IL@Pd(0)NPs was selected as the benchmark catalyst for further studies on the reaction parameters. The catalyst was well characterized using techniques including elemental analysis (EA), inductively coupled plasma analysis (ICP), FT-IR, TEM, SEM, EDX, XPS and XRD. The progress of the immobilization of the functional groups was confirmed by FT-IR Spectroscopy. As shown in Fig. 1a, in the spectrum of propargylimidazolium, a typical band at about 2934 cm^{-1} should be ascribed to C–H stretching vibrations. The characteristic peaks of 1573, 1432, 1163, 752 and 850 cm^{-1} were corresponding to the FT-IR spectra of the imidazolium cation. In addition, the absorption at 2124 cm^{-1} was attributed to CH stretching vibration of the propargyl group. In Fig. 1b, the absorption peak at 1098 cm^{-1} corresponded to the Si–O–Si vibration. Furthermore, the presence of an absorption band at 2100 cm^{-1} in FT-IR spectrum of compound 3 revealed the successful immobilization of N_3 on silica. In Fig. 1c, after the click reaction the peaks of azide and alkyne were disappeared, which demonstrated that the click reaction was successfully completed. In Fig. 1d, the intensity of the peaks is weaker than that of Silica-Click-IL (Fig. 1c) due to the formation of a metal–ligand bond. These characteristic absorption peaks confirm the successful attachment of organic groups and subsequent coordination of palladium nanoparticles within the hybrid material. In this catalyst system, since there were no significant shifts or evidences which have been reported for the NHC-Pd complex based catalysts, [35, 36] we could not certainly conclude that *N*-heterocyclic carbene/Pd complex (Pd (0)/NHC) is formed. According to the results of elemental analysis, the loading of click-methylimidazolium bromide ligand on the silica surface was determined to be 0.3 mmol g^{-1}. The content of palladium was measured by inductively coupled plasma (ICP) analysis, which was 0.12%. Energy dispersive X-ray (EDX) analysis of the obtained catalyst approved the presence of the expected elements such as;



Scheme 1 The nanocatalyst preparation

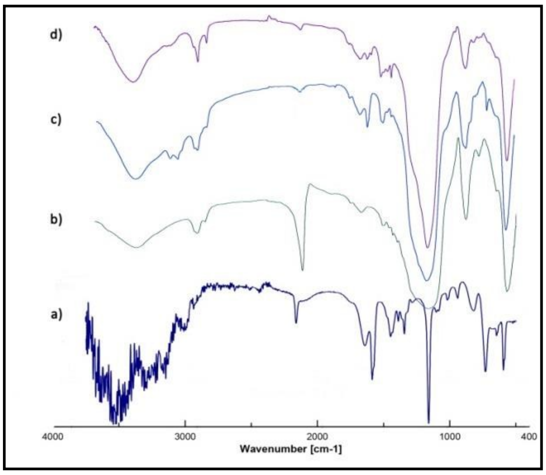


Fig.1 FT-IR spectra of 1-propargyl-3-methylimidazolium bromide (a), SiO_2-N_3 (b), Silica-Click-IL (c), Silica-Click-IL-Pd (d)

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silicon, bromide, carbon and palladium (Fig. 2). As shown in Fig. 3a, X-ray diffraction spectroscopy (XRD) pattern of catalyst that matched well with that of it (Reference code: 01-087-0643) shows the presence of Pd (0) particles on the amorphous silica support. The wide diffraction peak at $2\theta = 23^{O}$ attributed to SiO_2 and other peaks in the sample at 2θ of 39.9^{O}, 46.4^{O}, 67.7^{O}, 81.6^{O} can be assigned to the diffraction of (111), (200), (220), (311) crystal planes of Pd (0). XPS measurement was also performed to elucidate the oxidation state of Pd in the catalyst. The XPS spectra reveal that Pd is present in the zero oxidation state (Fig. 3b). The observed binding energy peaks of Pd $3d^{5/2}$ and Pd $3d^{3/2}$ electrons at about 335.48 and 340.9 eV, respectively, clearly indicate the presence of Pd(0) species in the Si-IL@Pd catalyst.

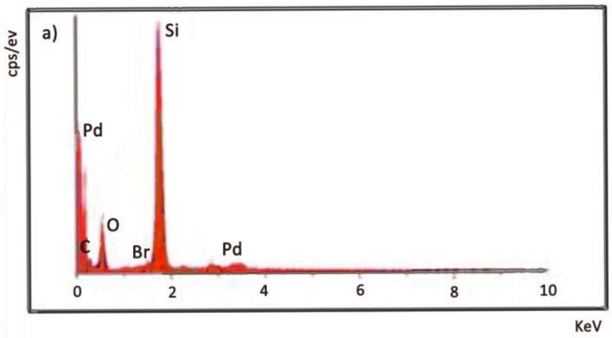

Fig.2 EDX spectrum of the catalyst

As displayed in Fig 4 (A and B), TEM images of the fresh catalyst reveals that palladium nanoparticles were produced in discrete spherical shape without any signs of aggregations. The particle size histogram shows that these nanoparticles have average diameter ranging about 13 nm (Fig. 4c), indicating that Silica-Click-IL can effectively isolate adjacent Pd nanoparticles. The information about the surface of catalyst was also investigated by scanning electron microscopy (SEM). As shown in Fig. 4d, the organic components were created with sphere-shaped morphology and monotonic nanometer-sized particles. The elemental mapping images for the synthesized catalyst reveals that Pd nanoparticles are well dispersed on the surface of silica. The selected-area elemental analysis figure shows the presence of Si, O and Pd throughout the composite in a homogeneous manner.The result indicated that the prepared sample was dispersed uniformly onto the surface of silica (Fig. 4e).

Catalytic tests

The catalytic performance of the nanocatalyst was evaluated in Suzuki–Miyaura cross-coupling. In order to obtain appropriate conditions, the efficiency of the various parameters such as solvent, bases, catalyst loading and temperature were examined on the reaction of 4-bromonitrobenzene with phenylboronic acid as the model reaction (Table 1). Firstly, we studied efficiency of the different solvent in Suzuki reaction. Among the tested solvents, a mixture of H_2O/EtOH (1:1, V/V) was chosen as the most effective solvent, which might be attributed to the good solubility of the organic reactants and the inorganic base. In the following step, to obtain the proper base for the cross-coupling, we examined different bases. The results of this experiment demonstrated that K_2CO_3 gave rise to the most suitable activity of the catalyst in the reaction among other bases such as K_3PO_4, $NaHCO_3$ and KOH. Subsequently, we investigated different amounts of catalyst ranging from 0.05 mol% to 0.2 mol%. On the basis of this study, 0.1 mol% was found to be the most efficient and suitable amount of catalyst for the reaction. For the higher amounts of catalyst, there was no significant increase in the yield of the reaction. However, the yield of the reaction was decreased in 0.05 mol% of Pd loading. In continuation, we investigated the optimum temperature for the cross-coupling reaction. It was found that, the reaction was not completed in room temperature, and only 52% of conversion was observed after 12 h. Therefore, the reaction temperature was raised to 50 ^{o}C; in which the reaction afforded the coupled product in 97% yield. Finally, the effect of the molar ratio of phenylboronic acid to 4-bromonitrobenzene on the cross-coupling reaction was

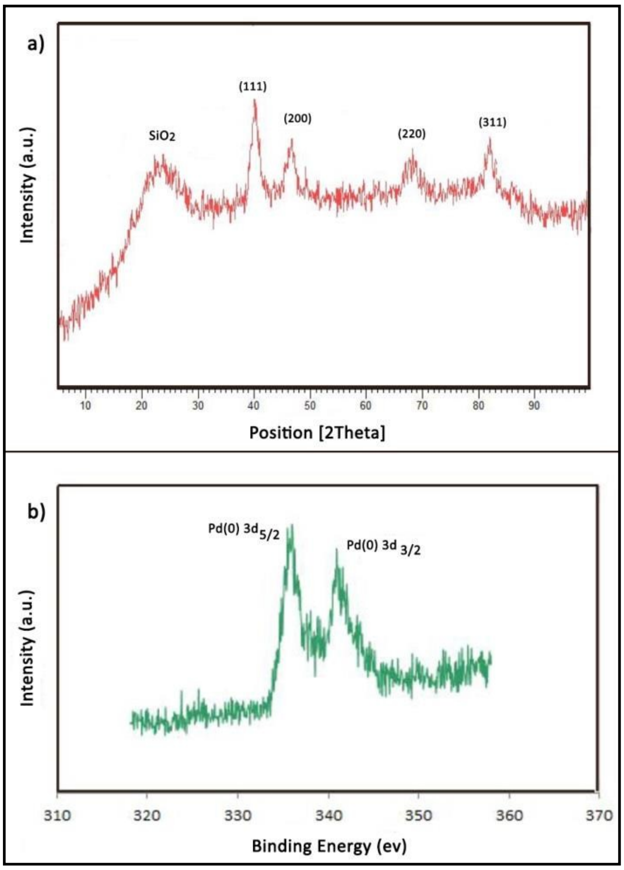

Fig. 3 XRD pattern of the catalyst (a), XPS spectra of the catalyst (b)

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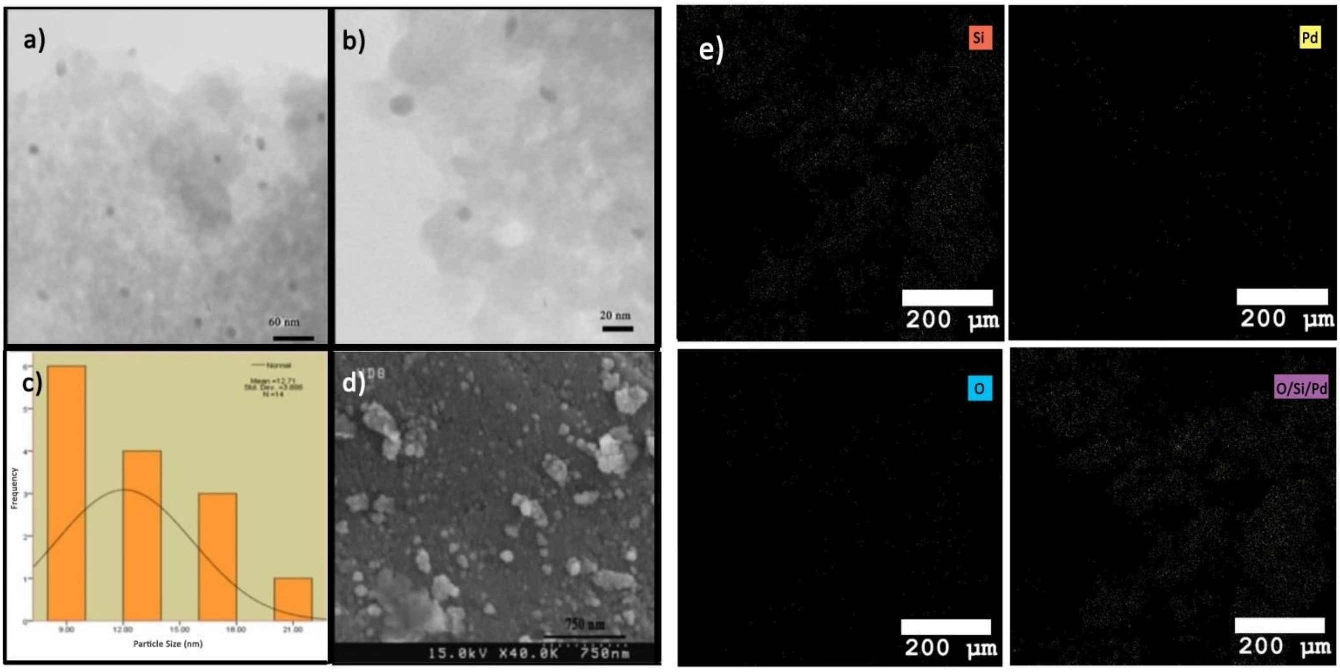

Fig. 4 TEM images of the catalyst (a and b), Histogram of the catalyst (c), SEM images of the catalyst (d), the corresponding elemental mapping images of the catalyst (e)

explored (Table 2). As shown in Table 2, the isolated yield 97% was obtained when the molar ratio was 1.2, while higher substrate ratios did not provide any improved yields under the investigated conditions. After optimization, we applied the nanocatalyst for the reaction of various aryl halides with phenylboronic acid under optimized conditions. The results depicted in Table 5 clearly exhibit that the protocol was amenable to various substrates (iodo, bromo and chloro-derivatives) and substituents, providing very good to excellent yields to products. In order to clarify the generality of the protocol, the reactions of different aryl halides with phenylboronic acid were checked and the results are shown in Table 5. Aryl iodides were rapidly converted into the desired biphenyl products in excellent yields. The reaction of aryl bromides with phenylboronic acid under the optimized conditions afforded the desired products in high yields. Also, for aryl chlorides a little more time was needed to obtain substantial yields. Overall, the coupling reaction of phenylboronic acid with electron withdrawing aryl halides gave better conversions in shorter reaction times. For the nitro-substituted aryl bromides (Table 5, Entry 4), the position of the nitro group has a large effect on the reaction, and moderate yields were obtained when the methyl group was at the meta position. Steric hindrance of the procedure was examined using 2-bromoacetophenone as hindered substituted aryls (Table 5, Entry 7). As expected, an increasing steric hindrance of ortho substituents can cause a decrease in the reaction conversion.

Table 1 Effect of different parameters for the reaction of 4-bromonitrobenzene with phenylboronic acid catalyzed by Si–IL@Pd(0)NPs catalyst[a]

Entry	Solvent	T(°C)	Base	Time (h)	Yield[b]
1	EtOH	50	K_2CO_3	3.5	62
2	H_2O	50	K_2CO_3	4	55
3	$EtOH/H_2O$ (1:1, V/V)	50	K_2CO_3	3	97
4	PEG-400	50	K_2CO_3	5	85
5	$EtOH/H_2O$ (1:1, V/V)	50	K_3PO_4	3	93
6	$EtOH/H_2O$ (1:1, V/V)	50	$NaHCO_3$	4.5	86
7	$EtOH/H_2O$ (1:1, V/V)	50	KOH	6	73
8	$EtOH/H_2O$ (1:1, V/V)	rt	K_2CO_3	12	52
9	$EtOH/H_2O$ (1:1, V/V)	40	K_2CO_3	3	88

[a] Reaction conditions: 4-bromonitrobenzene (0.1mmol), phenylboronic acid (0.12mmol), Si-IL@Pd(0)NPs catalyst 0.1 mol%, base (0.2 mmol)
[b] GC yield

Reusability and heterogeneity test

The recyclability of the solid catalyst was also examined in the coupling of 4-bromoacetophenone with phenylboronic

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acid using 0.1 mol% of catalyst in solvent mixture of H_2O/EtOH (1:1) at 50 °C in the presence of 2 mmol of K_2CO_3. For this, at the end of each reaction, the catalyst was separated by centrifugation from the reaction mixture, washed with water and ethanol several times, dried under vacuum and used for the next cycle. As shown in Table 3, no significant decrease catalyst performance was observed until the fourth reuse. To determine the nature of the reactive species, i.e., surface or leached Pd, we have also performed the hot filtration test by using 4-bromoacetophenone and phenylboronic acid as coupling partners. The solid catalyst was separated from the solution after 20 min reaction(~32% conversion) and the reaction was then allowed to continue stirring to react for another 3 h. After this time, no further progress in product yield was observed upon catalyst removal. The ICP analysis only showed 0.02 ppm palladium in solution, indicating that essentially no Pd species was leached out into the reaction mixture and the reaction has truly been catalyzed by the heterogeneous system. On the other hand, TEM image of the seventh cycle of the catalyst showed that the structure of Pd/silica has no significant change in comparison with fresh catalyst (Fig. S1, ESI†). The XRD measurements of the recovered catalysts showed that the metallic state of palladium was kept after the catalytic reaction Fig. S2, (ESI†). Both the TEM and XRD results indicate that the attachment between palladium nanoparticles and silica matrix is sufficiently strong. To further evaluate the efficiency of our catalyst, a comparison was made with the reported heterogeneous Pd-catalysts in the Suzuki and Heck reactions. The results for the reactions of bromobenzene with phenylboronic acid and methyl acrylate are listed in Table 7. It can be clearly seen that our catalyst is superior to others in terms of reaction condition, reaction time, and yield.

Table 2 Effect of the molar ratio of substrates on the cross-coupling reaction[a]

Entry	Molar ratio[b]	Yield(%)[c]
1	1	88
2	1.2	97
3	1.2	95[d]
4	1.5	97
5	1.75	97

[a] Reaction conditions: 4-bromonitrobenzene (0.1 mmol), catalyst 0.1mol%, base (0.2 mmol), 50 ^{0}c, 3h

[b] The ratio of phenylboronic acid to 4-bromonitrobenzene

[c] GC yield

[d] At 90 °C for 1.5 h

Experimental

All chemical reagents were purchased from Merck Chemical Company and used without further purification. ^{1}H-NMR spectra were recorded on a Bruker 400 spectrometer using deutrated $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. X-ray diffraction (XRD) powder patterns were obtained using an X'PERT MPD, with Cu Kα radiation (40 kV, 30 mA). X-ray photoelectron spectroscopy (XPS) were obtained using twin anode XR3E2 X-ray source system operating at a vacuum by X-ray 8025-BesTec spectrometer. The XPS peaks were deconvoluted by using Voigt function which is combination of Lorentzian and Gaussian.Transmission electron microscopy (TEM) images were obtained using a Philips CM10 microscope. FT-IR spectroscopy (JASCO FT-IR 680-Plus spectrophotometer) was employed for characterization of products. Also we used Inductive coupled plasma Perkin Elmer Optima 7300 DV. Gas chromatography (GC) (BEIFIN 3420 gas chromatograph equipped with a Varian CP SIL 5CB column: 30 m, 0.32 mm, 0.25 mm) was used for consideration of reaction conversions and yields. Elemental mapping images and scanning electron micrographs of the catalyst were taken on [FE-SEM, HITACHI (S-4160)].

Table 3 Reusability of the catalyst in the Suzuki-Miyaura

Run	Time (h)	Yield(%)[a]
1	3	95
2	3	95
3	4	93
4	4	89
5	4	78
6	5	75
7	6	76

[a] GC yield

Synthesis of propargyl imidazolium bromide

The propargylimidazolium bromide was prepared according to the literature method.[37] Propargyl bromide (20.09 mmol, 80 wt% solution in toluene) was added dropwise to N-Methylimidazole (18.27 mmol) at room temperature, and then the reaction mixture was stirred overnight. Afterward, the solvent was removed and the obtained product was washed thoroughly with acetone. IR (KBr, cm^{-1}): 3425, 3228, 3080, 2934, 2124, 1629, 1573, 1432, 1334, 1163, 1088, 1014, 850, 752, 620.

Synthesis of 3-azidopropyltrimethoxysilane

To a solution of sodium azide (0.33 g, 5 mmol) and tetrabutylammonium bromide (TBAB, 0.32 g, 1 mmol) in dry acetonitrile (10 mL), 3-chloropropyltrimethoxysilane (0.92 mL, 5 mmol) was added and the mixture was refluxed for 48 h under a nitrogen atmosphere. After that, the solvent was removed under vacuum. The residue was then diluted in Et_2O, filtered and washed twice with Et_2O.[38]
FT-IR (KBr, cm^{-1}): 2948, 2870, 2840, 2100, 1469, 1356, 1259, 1091, 895, 820, 424.

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Synthesis of azide-functionalized silica

Before immobilization, Silica-gel (60-120 mesh) (1.5 g) was immersed in hydrochloric acid for 12 h, and washed several times with deionized water to reach pH=7, and dried under vacuum at 120 °C for 12 h. Afterward, the activated silica was suspended in toluene (10 mL), and 3-azidopropyltriethoxysilane was added. The solution was refluxed for 24 h under nitrogen atmosphere.[39]

FT-IR (KBr, cm^{-1}): 3419, 2927, 1639, 1098, 799, 468.

Click Reaction

The propargyl IL grafted silica was synthesized via click reaction. Briefly, (1.5 g) azide functionalized silica was dispersed in 10 mL methanol/water (1:1, V/V) solution and propargyl IL (5 mmol, 1.5 g) was added. Then, $CuSO_4{\cdot}5H_2O$ (0.08 mmol, 0.02 g) and (0.48 mmol, 0.092 g) sodium ascorbate were added to the above solution. The mixture was stirred for 72 h at room temperature. The completion of the reaction was monitored by IR. Finally, the solid particles were separated from the mixture by centrifugation, washed several times with ethanol, HCl solution (5% solution in water), water and acetone and dried in vacuum at 60 °C.

FT-IR (KBr, cm^{-1}): 3430, 2925, 1637, 1100, 800, 467.

Preparation of palladium NPs

At first, silica–IL (0.25 gr) was dispersed in acetonitrile/H_2O (3:2 V/V, 20 ml). Afterward, $Pd(OAc)_2$ (0.045 mmol, 0.01 gr) solution was added to this solution and stirred for 5 h at room temperature. $NaBH_4$ solution (0.45 mmol, 0.016 g) was then dropwise added to the above solution with vigorous stirring. After 2 h, the catalyst was separated from the mixture by centrifugation, washed several times with methanol to remove unreacted $Pd(OAc)_2$ and dried under vacuum to obtain a black solid powder.

Heck–Mizoroki Reaction

The palladium-catalysed Mizoroki–Heck cross-coupling reaction has become a powerful strategy for the synthesis of carbon–carbon bonds. In this section, we applied this catalyst for the Heck–Mizoroki coupling reaction of a variety of aryl halides with methyl acrylate. For this purpose, the effect of different solvents, bases and reaction Temperature in the presence of 10 mg of the catalyst were surveyed for the reaction of iodoanisole with methyl acrylate. As shown in Table 4, DMF was the most effective solvent and K_2CO_3 was a suitable base for this reaction. The model coupling reaction was also studied at different temperatures. On the basis of this study, the quantitative conversion and shorter reaction times can be obtained with increasing the temperature from room temperature to 80 °C. This catalytic system was also applied to the reaction of varieties of aryl halides with methyl acrylate. As clearly shown in Table 6, aryl iodides are successfully converted to the corresponding Heck products in excellent yields. Also, the reaction of aryl bromides and aryl chlorides proceeded smoothly and the desired products were obtained in 64–88% yields (Table 6, Entries 4–12). We also surveyed the electronic on the yields and reaction times of the couplings. Generally electron-poor aryl halides, in comparison to electron-rich aryl halides, transform to the corresponding coupled products with better conversion and shorter reaction times. For the reaction of 4-bromoacetophenon with metyl acrylate, elongations of the reaction times with the decrease of the yields of the products were observed. This result is rather unexpected.

Table 4 Optimization of conditions for the Heck–Mizoroki reaction for the reaction of 4-iodoanisole and methyl acrylate using Si–IL@Pd(0)NPs catalyst[a]

Entry	Solvent	T(°C)	Base	Time(h)	Yield[b]
1	NMP	80	K_2CO_3	4	79
2	DMF	80	K_2CO_3	4	95
3	Toluene	80	K_2CO_3	6	76
4	EtOH	80	K_2CO_3	6	69
5	DMF	80	K_3PO_4	5	84
6	DMF	80	KOH	5	63
7	DMF	80	$NaHCO_3$	5	76
8	DMF	rt	K_2CO_3	12	28
9	DMF	70	K_2CO_3	5	83

[a] Reaction conditions: 4-iodoanisole (0.1 mmol), methyl acrylate (0.12 mmol), Si–IL@Pd(0)NPs catalyst 0.1 mol%, base (0.2 mmol)
[b] GC yield

Conclusions

The click ionic-silica supported Pd-NPs were successfully synthesized and well characterized by different techniques. The obtained product was then applied as solid catalyst in the Suzuki–Miyaura and Heck–Mizoroki cross-coupling reaction and exhibits a high catalytic activity under mild reaction conditions. The recyclability of the catalyst was successfully examined in the Suzuki–Miyaura reaction for seven consecutive runs.

Acknowledgements

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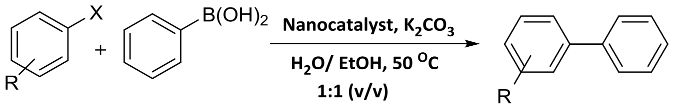
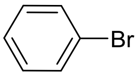
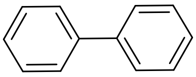
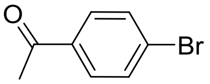
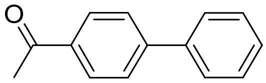
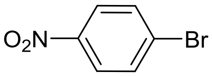
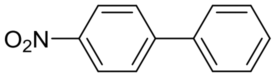
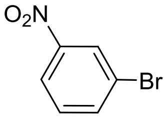
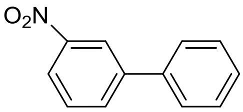
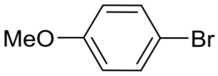
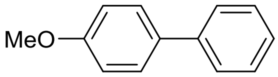
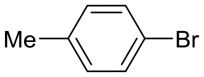
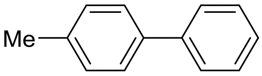
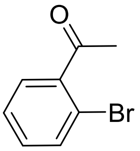
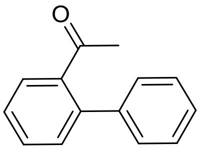
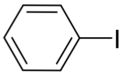
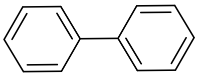
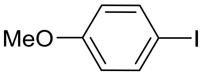
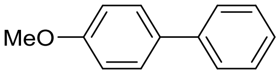
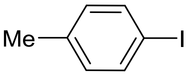
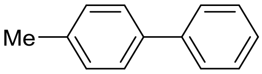
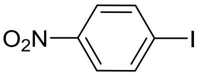
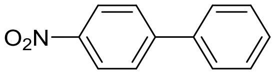
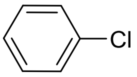
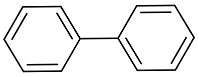
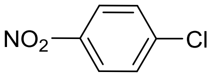
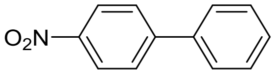
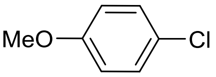
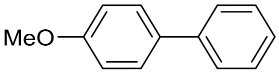
Table 5 Suzuki cross-coupling reaction of various aryl halides with phenylboronic acid[a]



Entry	Ar–X	Product	Time/ h	Yield[b]	TON[c]
1			4	92	920
2			3	95	950
3			3	97	970
4			4.5	68	680
5			3.5	95	950
6			4.5	81	810
7			6	32	320
8			2	100	1000
9			2	93	930
10			2	90	900
11			1.5	100	1000
12			6	91	910
13			5	95	950
14			6	87	870

[a] Reaction conditions: aryl halide (0.1 mmol), phenylboronic acid (0.12 mmol), K_2CO_3 (0.2 mmol), catalyst (0.1 mol%)

[b] GC yield

[c] TON: product mole /Pd mole

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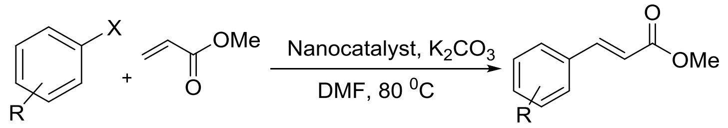
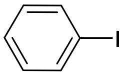
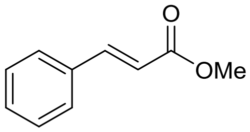
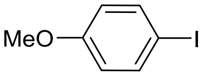
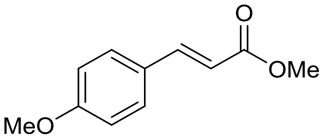
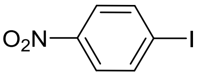
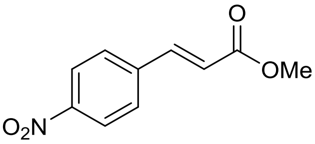
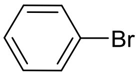
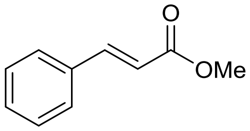
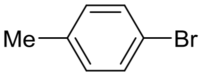
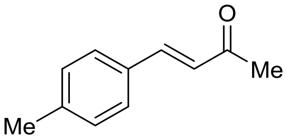
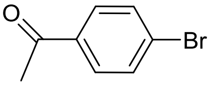
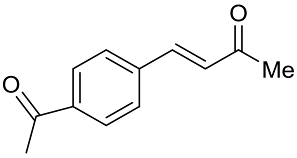
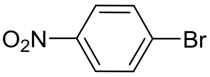
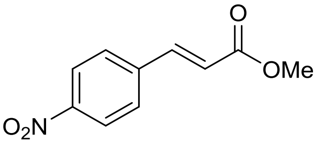
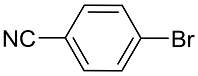
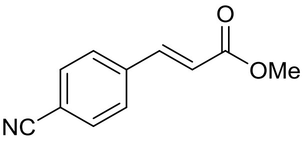
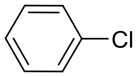
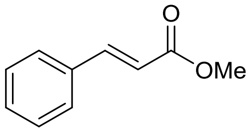
Table 6 Heck cross-coupling reaction of various aryl halides with methyl acrylate[a]



Entry	Ar–X	Product	Time/ h	Yield[b]	TON[c]
1			3	90	900
2			4	95	950
3			3	93	930
4			5	82	820
5			5	78	780
6			9	64	640
7			5	88	880
8			5	85	850
9			6	79	790

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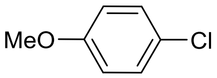
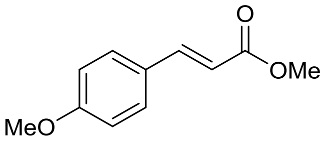
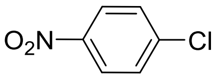
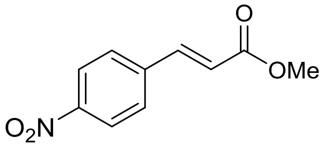
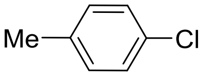
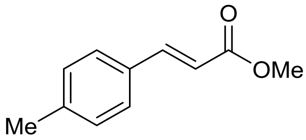
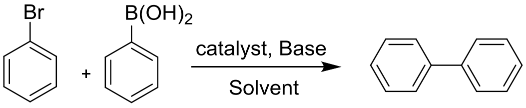
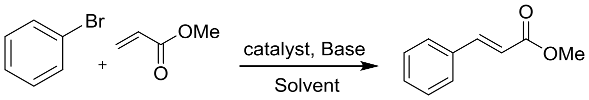
10			6	73	730
11			6	84	840
12			6	71	710

[a] Reaction conditions: aryl halide (0.1 mmol), methyl acrylate (0.12 mmol), K_2CO_3 (0.2 mmol), catalyst (0.1 mol%)

[b] GC yield

[c] TON: product mole /Pd mole

Table 7. Comparison of catalytic activity of the Si-IL@Pd(0)NPs catalyst with literature examples for Suzuki and Heck reactions

Entry	Catalyst	conditions	Yield(%)^{ref}
			
1	Silica-Pd(0) (0.1 mol% Pd)	K_2CO_3, H_2O:EtOH, 4h, 50 °C	92 (This work)
2	PFG-Pd(0) (1.2 mol% Pd)	K_2CO_3, H_2O:EtOH, 10h, 80 °C	95[40]
3	Fe_3O_4@PUVS-Pd (0.09 mol% Pd)	K_2CO_3, H_2O, 1h, 90 °C	93[41]
4	Polymer–iminophosphine- Pd (0.05 mol% Pd)	K_2CO_3, Dioxane, 1h, reflux	95[42]
5	Pd@agarose–Fe_3O_4	K_2CO_3, PEG 200, 0.75h, 80°C	92[43]
6	Fe_3O_4/P(GMA-AA-MMA-Pd) (0.2 mol% Pd)	K_2CO_3, EtOH/H_2O, 3h, 80 °C	96[44]
7	Pd/Fe_3O_4@SiO_2@KCC^{-1}(0.2 mol% Pd)	K_2CO_3, EtOH, 6h, 80 °C	90.8[45]
			
8	Silica-Pd(0) (0.1 mol% Pd)	K_2CO_3, DMF, 5h, 80 °C	82 (This work)
9	PFG-Pd(0) (1.7 mol% Pd)	K_2CO_3, DMF, 6h, 120 °C	88[40]
10	Fe_3O_4@PUVS-Pd (0.09 mol% Pd)	K_2CO_3, H_2O, 12 h, reflux	93[41]
11	Polymer –iminophosphine- Pd (0.5 mol%)	Et_3N, Dioxane, 5h , reflux	70[42]
12	Fe_3O_4/SiO_2/HPG-Pd (3 mol% Pd)	NaOAc, DMF, 140 °C, 12 h	67[46]
13	Fe_3O_4/DAG/Pd	Et_3N, DMF, 110 °C, 3h	85[47]
14	Cell–$OPPh_2$-Pd(0) (0.1 mol% Pd)	Bu_3N, DMF, 110 °C, 7h	81[48]

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References

1 M. E. Davis, *Top. Catal.*, 2015, **58**, 405.

2 M. J. Climent, A. Corma, S. Iborra and M. J. Sabater, *ACS Catal*, 2014, **4**, 870.

3 F. Zaera, *Chem. Soc. Rev.*, 2013, **42**, 2746.

4 V. Polshettiwar and R. S. Varma, *Green Chem.*, 2010, **12**, 743.

5 D. Habibi, A. R. Faraji, D. Sheikh, M. Sheikhi and S. Abedi, *RSC Adv.*, 2014, **4**, 47625.

6 F. Ye, S. Qu, L. Zhou, C. Peng, C. Wang, J. Cheng, M. L. Hossain, Y. Liu, Y. Zhang and Z.-X. Wang, *J. Am. Chem. Soc.*, 2015, **137**, 4435.

7 S. M. McAfee, J. S. McCahill, C. M. Macaulay, A. D. Hendsbee and G. C. Welch, *RSC Adv.*, 2015, **5**, 26097.

8 V. Polshettiwar and R. S. Varma, Green Chem., 2010, **12**, 743.

9 E. Amadio, A. Scrivanti, G. Chessa, U. Matteoli, V. Beghetto, M. Bertoldini, M. Rancan, A. Dolmella, A. Venzo and R. Bertani*, J. Organomet. Chem.*, 2012, **716**, 193.

10 K.V. Ranganath, S. Onitsuka, A.K. Kumar and J. Inanaga, *Catal. Sci. Tech.,* 2013, **3**, 2161.

11 Y. Xu, Z. Zhang, J. Zheng, Q. Du and Y. Li, *Appl. Organomet. Chem.,* 2013, **27**, 13.

12 C. Ornelas, J. Ruiz, L. Salmon and D. Astruc, *Adv. Synth. Catal.*, 2008, **350**, 837.

13 R.L. Oliveira, W. He, R.J.K. Gebbink and K.P. de Jong, *Catal. Sci. Tech.*, 2015, **5**, 1919.

14 D. Sahu and P. Das, *RSC Adv.*, 2015, **5**, 3512.

15 S. Bahadorikhalili, L. Ma'mani, H. Mahdavi and A. Shafiee, *RSC Adv.*, 2015, **5**, 71297.

16 H. Veisi, A. Sedrpoushan and S. Hemmati, *Appl. Organomet. Chem.,* 2015, **29**, 825.

17 E. Nehlig, B. Waggeh, N. Millot, Y. Lalatonne, L. Motte and E. Guénin, *Dalton Trans.*, 2015, **44**, 501.

18 M. Meldal and C. W. Tornøe, *Chem. Rev.*, 2008, **108**, 2952.

19 H. C. Kolb, M. Finn and K. B. Sharpless, *Angew. Chem. Int. Ed.*, 2001, **40**, 2004.

20 Z. Cai, B. T. Li, E. H. Wong, G. R. Weisman and C. J. Anderson, *Dalton Trans.*, 2015, **44**, 3945.

21 H. C. Kolb and K. B. Sharpless, *Drug discovery today*, 2003, **8**, 1128.

22 A. R. Hajipour and F. Abrishami, *J. Appl. Polym. Sci*., 2012, **124**, 1757.

23 Q. Zhang, H. Su, J. Luo and Y. Wei, *Catal. Sci. Tech*., 2013, **3**, 235.

24 E. Mieczyńska, T. Borkowski, M. Cypryk, P. Pospiech and A. Trzeciak, *Appl. Catal. A: Gen*, 2014, **470**, 24.

a) B. Helms, J.L. Mynar, C.J. Hawker, J.M. Fréchet, *J. Am. Chem. Soc.,* 2004, **126**, 15020; b) M. Munteanu, S. Choi, H. Ritter, *Macromolecules,* 2008, **41**, 9619; c) E. Díez-Barra, J. Guerra, V. Hornillos, S. Merino, J. Tejeda, *Organometallics,* 2003, **22**, 4610; d) D. Maity, T. Govindaraju, *Chem. Commun.,* 2010, **46**, 4499.

a) P.L. Golas, K. Matyjaszewski, *Chem. Soc. Rev.,* 2010, **39**, 1338; b) Y. He, C. Cai, *Chem. Commun.,* 2011, **47**, 12319.

25 M.-J. Jin, A. Taher, H.-J. Kang, M. Choi and R. Ryoo, *Green Chem.*, 2009, **11**, 309.

26 Z. Wang, Q. Zhang, D. Kuehner, X. Xu, A. Ivaska and L. Niu, *Carbon*, 2008, **46**, 1687-1692.

29 D. Zhang, C. Zhou and R. Wang, *Catal. Commun.*, 2012, **22**, 83-88.

30 L. Li, J. Wang, T. Wu and R. Wang, Chem. Eur. J., 2012, **18,** 7842-7851.

31 A. R. Hajipour and F. Mohammadsaleh, *Tetrahedron Lett.,* 2014, **55**, 3459.

32 A. R. Hajipour S. H. Nazemzadeh and F. Mohammadsaleh, *Tetrahedron Lett*, 2014, **55**, 654.

33 A. R. Hajipour, R. Pourkaveh, *Synlett*, 2014, **25**, 1101.

34 A. R. Hajipour and F. Rafiee, *Appl. Organomet. Chem.,* 2015, **29***,* 147.

35 A. Z. Wilczewska, I. Misztalewska, *Organometallics,* 2014, **33**, 5203.

36 A. R. Hajipour, N. S. Tadayoni, Z. Khorsandi, *Appl. Organomet. Chem*, 2016, **30**, 590.

37 N. Gonsior, H. Ritter, *Macromol. Chem. Phys.,* 2011, **212**.

38 Q. Zhang, H. Su, J. Luo and Y. Wei, *Catal. Sci. Technol.,* 2013, **3**, 235.

39 G. Zhang, Y. Wang, X. Wen, C. Ding and Y. Li, *Chem. Commun.,* 2012, **48**, 2979.

40 R. Fareghi-Alamdari, M. G. Haqiqi, N. Zekri, *New J. Chem.* 2016, **40**, 1287.

41 D. Wang, W. Liu, F. Bian, W. Yu, *New J. Chem.* 2015, ***39***, 2052.

42 X. Liu, X. Zhao, M. Lu, *J. Organomet. Chem.,* 2014, **768**, 23.

43 H. Firouzabadi, N. Iranpoor, M. Gholinejad, S. Akbari, N. Jeddi, *RSC Adv.,* 2014, **4**, 17060.

44 D. Z. Yuan and H. P. Zhang, Appl. Catal., A, 2014, **475**, 249.

45 X. Le, Z. Dong, Y. Liu, Z. Jin, T.-D. Huy, M. Le, J. Ma*J. Mater. Chem. A,* 2014, **2**, 19696.

46 L. Zhou, C.Gao andW. J. Xu, Langmuir, 2010, **26**, 11217.

47 H. Veisi, J. Gholami, H. Ueda, P. Mohammadi, M. Noroozi, *J. Mol. Catal. A: Chem.* 2015. **396**, 216.

48 Q. Du and Y. Li, *Res. Chem. Intermed.*, 2012, **38**, 1807

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