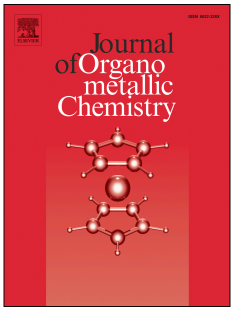

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Agro Waste DerivedNanosilica SupportedPd(ll) Complex: A Protocol for Copper Free Sonogashira Reaction in Water

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Abstract: A palladium (II) complex immobilized onto nanosilica(Pd-imine@nanoSiO$_2$) has been developed and evaluated as a highly efficient, retrievable catalyst for carbon-carbon triple bond activation reactions between aryl halides and terminal alkynes. Nanosilica has been derived from rice husk by simple and eco-compatible methodology. The catalyst has been extensively characterized by techniques such as FT-IR, UV-vis, powder XRD, XPS, SEM-EDX, thermogravimetric analysis, BET surface area measurement.The catalyst can be reused for five consecutive runs without compromising much with the activity.Easy preparation, its long shelf life, air-stability, wide substrate scope, ‘in water’ reactions,easy separability and good recyclability make it an ideal system for Sonogashira cross-coupling reaction. Moreover, various alkyne substrates were efficiently cross-coupled with a broad range of aryl iodides and aryl bromides to afford diaryl alkynes, providing improved yields with low catalyst loading in water. This protocol is also suitable for aliphatic alkynes.

Keywords:Aliphatic alkyne; Aryl halide; Diaryl alkyne; Sonogashira cross-coupling;Terminal alkyne;Thermogravimetric.

Introduction:

Sonogashira reaction belongs to the most powerful tool for the construction of C(sp)-C(sp^2) bond allowing the synthesis of different acetylene derivatives such as, pharmaceuticals, polymers, dyes , sensors, etc.[1-4]The acetylene derivatives find tremendous applications in material chemistry due to their unique electrical and optical properties.Therefore, remarkable efforts have been devoted to improve the synthetic methodologies of the reaction and also to increase its efficiency. Traditionally, this reaction was catalyzed by palladium salt in the presence of different ligands *viz*. phosphine based, N-based, Schiff-base, etc. along with a copper co-catalyst in an amine as a solvent. In the recent decades, however, several copper-free Sonogashira reaction methodologies have been proposed, since from environmental perspectives copper-mediated protocol is no longer viable as it produces a significant amount of unwanted homo coupling product of the terminal alkynes along with the desired product and needs an extra non environment friendly chemical CuX.[5-10]As a result several alternative methodologies were proposed time to time including designing of different ligand systems, use of additives, *viz.* tetra-n-butylammonium salt, sodium sulphide, Ag, Zn etc. However, most of these protocols were homogeneous in nature with advantages of higher yields but with distinct drawbacks like non-reusability, contamination of the products, catalyst loss and tedious workup procedures. These prompted researchers to develop ecofriendly, cheap and reusable heterogeneous systems.[11]Till now various heterogeneous catalysts such as silica, clay, zeolites and SBA-15 immobilized Pd complex/ Pd(0)nanoparticles ;bimetallic Pd-nanoparticles; polymer-supported N-heterocyclic carbene–palladium catalyst; poly(vinyl chloride)-supported Pd(II) complex; Pd(II) Schiff-base complex supported on multiwalled carbon nanotubes; Pd(II) supported on MCM-41 were reported for Sonogashira reactions.[12-16]Although significant advancements have been made, as per our literature review bio-derived silica supported Pd(II) complex has not been reported as catalyst for Sonogashira reaction till date. However, because of some specific characteristics like low cost, wide availability, high thermal stability and surface reactivity, high surface area, silica is one of the best candidates as solid support material.[17-22] Silica is found in various natural sources with different proportions. Agro waste such as rice husk ash is one of the cheapest and most eco-friendly sources of silica with 90-97%silica content.[23]So extraction of silica particle from rice husk ash benefits not only of producing valuable silica powder but also of reducing disposal and pollution problems.

Recently we have reported the efficiency of rice husk derived nanosilicasupported Pd(II) and Ru(III)complexes and montmorillonite K-10 supportedPd(0) nanoparticles in Suzuki–Miyaura, hydration of nitriles and selective oxidation of benzyl alcohols reactions, respectively.[23-24]So in order to extend the scope of bio-derived nanosilicaanchoredPd(II) complex, here we have reported a simple and efficient protocol for the Sonogashira reaction of aryl iodides in water under mild conditions .

Experimental

Materials and Methods

All the chemicals were commercially obtained and used as received. The substrates for Sonogashira reactions, bases and solvents were purchased from Merck, Sigma Aldrich, LobaChemie and Rankem and 3-aminopropyltriethoxysilane (APTES) and palladium acetate were from Sigma-Aldrich. Silica gel (particle size 60–120 mesh) used for column chromatography was purchased from Rankem, India.

FT-IR spectra were recorded using KBr pellets on a Shimadzu IR Prestige-21 FT-IR spectrophotometer(400-4000cm^{-1}). UV-vis (200-800nm) spectra were recorded on a Jasco V-750 spectrometer in solid state. The powder XRD patterns were recorded on RikaguUltima IV diffractometer with Cu-Kα (λ=1.541 Å) radiation. The SEM images were obtained with a JEOL, JSM IT-300 operating at an accelerating voltage of 20 kV. The EDX spectra were also recorded in the same instrument attached to the scanning electron microscope. The surface area measurement at liquid nitrogen temperature was obtained from the linear plot following Brunauer-Emmett-Teller (BET) method using Quantachrome instrument (Boynton Beach, FL 33426, USA).The X-ray photoelectron spectrum (XPS) of (Pd-imine@nanoSiO$_2$) was recorded on a XPS-AES Module, Model: PHI 5000 Versa Prob II. The C (1s) electron binding energy corresponding to graphitic carbon was used for calibration of the Pd (3d) core-level binding energy. Thermogravimetric analyses (TGA) were done with a Perkin Elmer STA 8000 thermal analyzer in the temperature range 35 ºC-850 ºC at a heating rate 20 ºC min^{-1} in air. The palladium content of the catalyst was determined by Inductively Coupled Plasma Atomic Emission Spectrometric (ICP-AES) analysis with a ARCOS, Simultaneous ICP Spectrometer at SAIF, IIT Bombay. The reaction products were characterized by recording^{1}H NMR spectra and comparing with authentic sample.

Synthesis of materials

Synthesis of nanosilica: From green chemistry and eco-compatibility point of view, the use of waste material is one of the major concerns in recent time. Keeping this in mind, we have used rice husk derived nanosilica[17] for immobilization of the Pd (II) complex. This process mainly involves the following steps and can be schematically represented as shown in **Scheme 1.**[25]

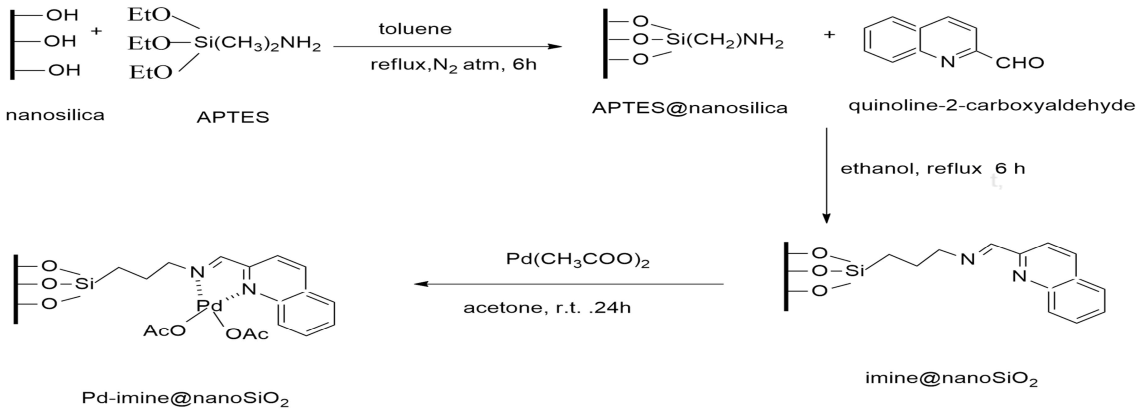
Synthesis of Pd-imine@nanoSiO$_2$catalyst

Step I: Immobilization of APTES onto nanosilica(APTES@nanoSiO$_2$):4g of nanosilica (dried at 250ºC for 20 h) was added to a 100 mL of dry toluene followed by addition of APTES

(0.04g, 2.0 mmol). The resulting mixture was refluxed under N_2 for 6 h, followed by cooling, whereupon a solid product was formed. It was separated by filtration, washed repeatedly through Soxhlet extraction with toluene and finally dried at 120^{o}C for 24 h to obtain APTES immobilized nanosilica.

Step II: Synthesis of imine funtionalizednanosilica [imine@nanoSiO$_2$]: In a suspension of 2.3 g of APTES@nanoSiO$_2$ in 60mL ethanol, 0.033g (0.21 mmol) of quinoline-2-carboxyaldehyde was added and was refluxed for 6 h. A solid precipitated was formed, which was filtered off, and washed several times through Soxhlet extraction with ethanol and acetone. The resulting compound was dried at 120^{o}C for 24 h and designated as imine@nanoSiO$_2$.The amount of the imine ligand attached to the imine@nanoSiO$_2$ was measured from the TGA analysis and was found to be 2.14 mmol/g.

StepIII: Immobilizationof Pd metal onto imine funtionalizednanosilica [Pd-imine@nanoSiO$_2$]:0.2 g of imine@nanoSiO$_2$ and0.060 g (0.026mmol) of Pd(OAc)$_2$were added in 40 mL acetone and stirred at room temperature for 24 h. The product was filtered off and washed through soxhlet extraction with acetone. The product was dried in an oven at 70^{o}C for 24h, whereupon a light brown color material was obtained and was designated as Pd-imine@nanoSiO$_2$.The palladium content of Pd-imine@nanoSiO$_2$ based on ICP analysis was estimated to be 0.9 mol % per 10mg.



Scheme 1: Synthesis of Pd-imine@nanoSiO$_2$

Procedure for Sonogashira Cross-Coupling reaction

In a typical reaction, a mixture of alkyne (1.1mmol),aryl halide(1.3mmol), amine (2 mmol), catalyst (10mg, 0.9 mol% of Pd) were added in water (4mL) and stirred at 70°C for required time.After completion of the reaction (monitored by GC-MS at different time intervals) it was cooled to room temperature and the catalyst was separated by simple centrifugal precipitation. The filtrated was diluted with water and extracted with 15mL acetic acid. To obtain the desired product the organic phase was washed with brine(2×10mL) and dried over anhydrous Na_2SO_4, then filtered and evaporated under reduced pressure. The products were isolated by silica gel column chromatography using hexane as eluent. The FT-IR and ^{1}H NMR data of isolated products were compared with previously reported literatures.[26-27]To check the reusability of the catalyst, the recovered catalyst was dried overnight at 100°C and reused in a new coupling reaction under identical conditions.

Results and Discussion

The X-ray diffraction pattern of the complex (**Fig** 1) is in good agreement with the reported literatures.[28-30]The PXRD of silica exhibits peaks at 2θ value of 19.26°, 29.82° , 39.62° , 49.04° and 60.68° corresponds to (100), (101), (012), (112) and (211) planes of hexagonal unit cell[29,31].The XRD patterns of the silica, nanosilica and the Pd-imine@nanoSiO_2 revealed that crystalline nature of silica changes to amorphous in both nanosilica and the complex. A broad peak corresponding to the silica phase was observed at 22° for both the materials, nanosilica and complex [25].The XRD patterns of nanosilica and the complex are similar, however a prominent decrease in peak intensity for the complex is consistent with the immobilization of Pd and ligand onto the nanosilica as reported by Komura *et al.*[29].

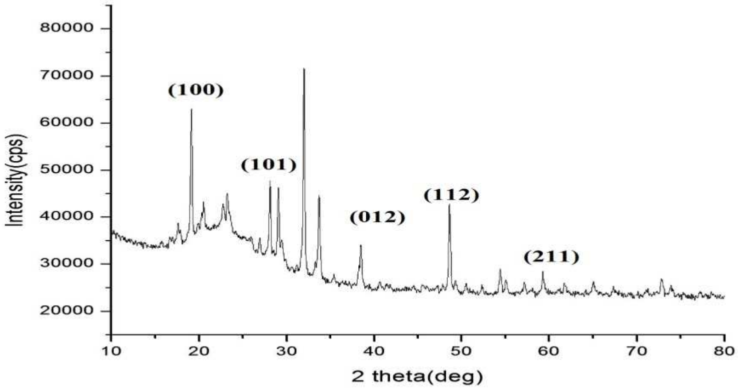


Fig.1a: XRD pattern of silica

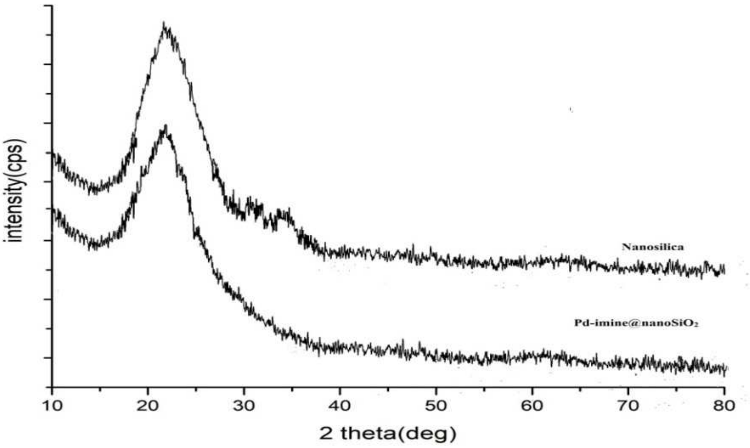


Fig.1b :XRD patterns of nanosilica and Pd-imine@nanoSiO_2

FT-IR study:The FTIR spectra of nanosilicaand silica are almost similar, however the bands for $\upsilon_{Si\text{-}O\text{-}Si}$, $\gamma_{Si\text{-}O\text{-}Si}$, υ_{OH} and γ_{OH} are shifted slightly either higher or lower frequency compared to that of silica(**Fig 2a& 2b**)[23,24]. The spectrum of APTES@nanoSiO_2 demonstrated a peak at 1621 cm^{-1} due to γ_{NH_2} indicating immobilization of APTES on nanosilica(**Fig 2c**) .The FTIR spectrum of imine@nanoSiO_2 showed a new band at 1600 cm^{-1} which could be assigned to $\nu_{C=N}$, suggesting the formation of Schiff base anchored nanosilica (**Fig 2d**). Interestingly, it was observed that this band was shifted from 1600 cm^{-1} to 1528cm^{-1}on complexation with Pd(II)(**Fig 2e**). In the far-IR region a band at 455 cm^{-1}($\nu_{Pd\text{-}O}$) and 585 cm^{-1} ($\nu_{Pd\text{-}N}$) clearly suggest that Pd is coordinated through N-and O-atom[23,24].

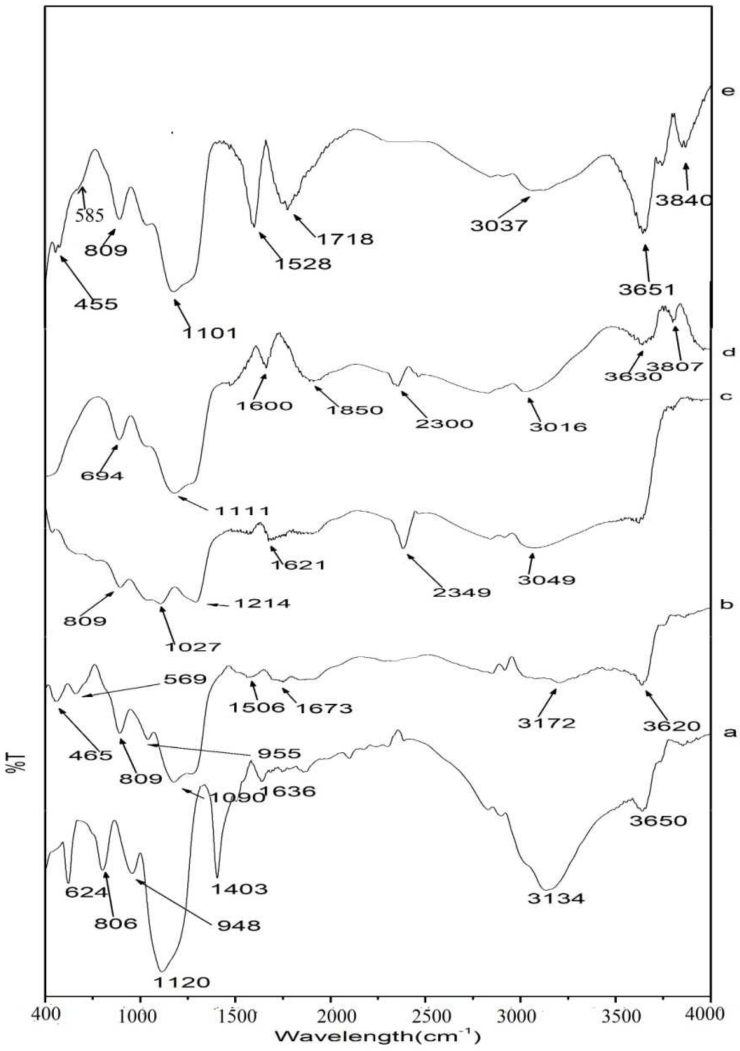


Fig. 2 : FT-IR spectra of (a) silica, (b) nanosilica, (c) APTES@nanoSiO$_2$, (d) imine@nanoSiO$_2$, (e) Pd-imine@nanoSiO$_2$

BET analysis: With the exception of nanosilica, the surface area of silica, APTES@nanoSiO$_2$and Pd-imine@nanoSiO$_2$ decreases successively, indicating successful immobilization of APTES, imine and Pd onto the silica. As compared to the catalysts reported by Nikoorazm *et al.* and Komura *et al.*, we have observed higher decrease of surface area of nanosilica with the successive immobilization of the ligand and Pd metal[28,29].

Table 1: BET surface area measurements of the silica based materials

Entry	Materials	Surface Area(m^2/g)
1	Silica	186
2	Nanosilica	280
3	APTES@nanoSiO_2	135
4	Pd-imine@nanoSiO_2	111

SEM-EDX and ICP analysis: Surface morphology of nanosilica was changed after immobilization of APTES, imine and Pd onto nanosilica (**Fig 3a & Fig 3b**).EDX patterns of nanosilica and Pd-imine@nanoSiO_2(**Fig 3c & Fig 3d**) invariably showed the presence of Pd, N elements and suggested the successful grafting of Pd complex with the anchored ligand. ICP-AES analysis revealed 0.9 mol% of Pd content per 10mg of Pd-imine@nanoSiO_2.

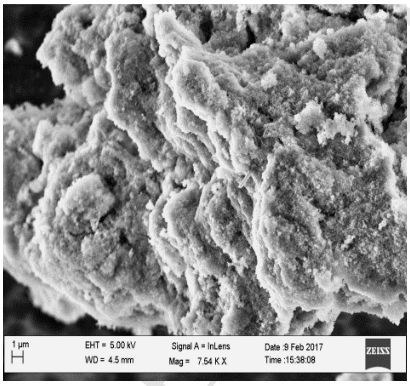


Fig. 3a: SEM image of nanosilica

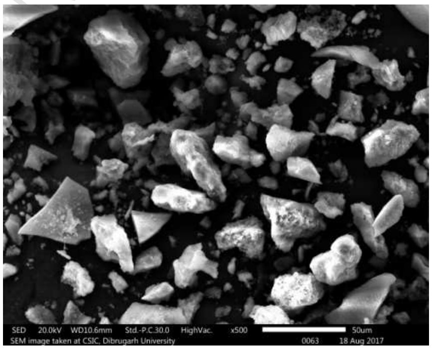


Fig. 3b: SEM image of Pd-imine@nanoSiO_2

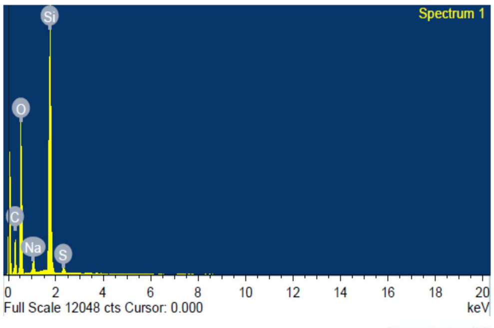


Fig. 3c: EDX of nanosilica

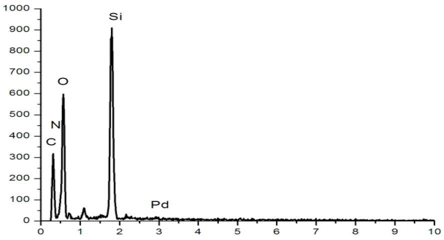


Fig. 3d: EDX of Pd-imine@nanoSiO_2

X-ray photoelectron spectroscopy study:

The XPS study for Pd 3d core of Pd-imine@nanoSiO_2 is demonstrated in **Fig 4.** The catalyst exhibited two peaks at binding energy 337.4eV and 342.6eV, could be assigned to the Pd^{2+} 3d core-level peaks corresponding to the palladium 5/2and 3/2 spin-orbit components, respectively. This enumerates the presence of Pd(II)in the complex.[11,28,29,32]

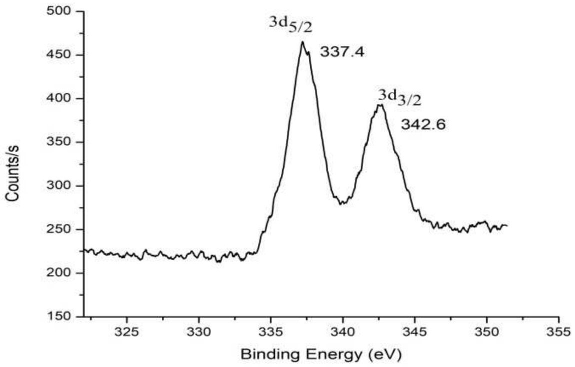


Fig 4: Pd 3d core level XPS spectrum Pd-imine@nanoSiO_2

TGA: The TGA analysis of nanosilica,APTES@nanoSiO_2 and imine@nanoSiO_2 revealed a initial weight loss of approximately 4.5, 5.3 and 4.6%, respectively in the temperature range 100-250°C, could be attributed to adsorbed water(**Fig S1-S3**). [28,33]With further increase in temperature the APTES@nanoSiO_2 and imine@nanoSiO_2 showed 3.80 and 5.94% wt loss corresponding to the decomposition of APTES and APTES- imine, respectively. The quantity of imine ligand attached to the Pd was measured from the TGA analysis and was found to be 2.14 wt% or 0.013 mmol in the catalyst (ESI).

UV-vis spectra: The electronic spectrum of the complex was recorded in the range 200-800nm in solid state. The bands observed in the region 220-250 nm and 355 nm could be assigned to the intraligand transitions (**Fig 5**).

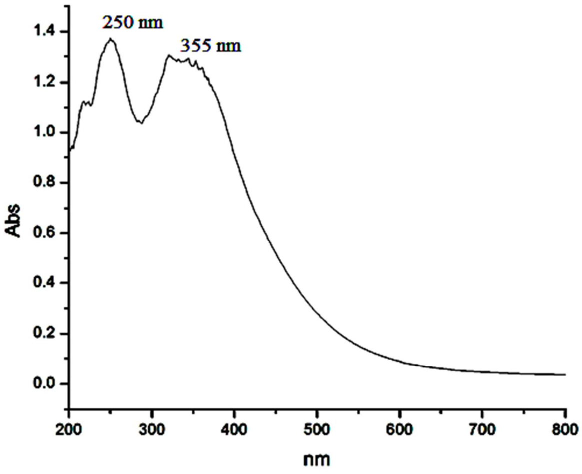


Fig 5: Solid UV-vis spectrum for Pd-imine@nanoSiO_2

Pd-imine@nanoSiO_2 Catalyzed Sonogashira Cross-Coupling reaction:

After characterization of the complex extensively we want to check the potentiality of the complex as a catalyst for Sonogashira cross-coupling reaction with various alkynes and aryl halides.For this purpose a model reaction was carried out between phenylacetylene and iodobenzene at different temperatures using triethylamine as an additive in copper free condition. As we know solvent plays an important role in product formation we have screened various solvents for the reaction. From the table it is clear that water is the most suitable solvent for the reaction as other solvents gave comparatively low percentage yield (table 2, entry1). Water may readily solvate other substrates present in the reaction medium due to high polarity index. We have also performed the reaction at different temperatures, *viz.* room temperature (25 ºC), 50 ºC, 70 ºC, 80 ºC, 100 ºC and observed that80 ºC was the optimum temperature for better product yield (table 2, entry1). Likewise, a number of runs were performed with a various amounts of Pd loadings such as 0.45, 0.9, 1.08, 1.35, 1.8 and 2.25 mol% and found that 0.9 mol% of Pd was the sufficient amount to produce the highest yield in water (table 2, entry1). It was clear that increase of Pd loading did not improve the product yield, while decrease of Pd loading to 0.45 mol% led to decrease the yield significantly (table 2, entries 13-17). In the absence of catalyst and solvent only trace amount of product was formed (table 2, entries 9, 10 & 11).

Table2:Optimization of the reaction conditions for the Sonogashira reaction of phenyl acetylene and iodobenzene using Pd-imine@nanoSiO$_2$ as a catalyst ^{a}

Entry	Solvent	Catalyst (mg; Pd loading)	Temperature(°C)	Time (h)*	Isolated yield(%)
1	H_2O	10 (0.9mol% Pd)	80	2	95
2	Isopropanol	10 (″)	80	2	65
3	DMF	10(″)	80	2	55
4	EtOH	10(″)	80	4	50
5	CH_3CN	10(″)	80	2	70
6	EtOH/H_2O	10(″)	100	3	85
7	H_2O	10(″)	25 (r.t.)	24	trace
8	H_2O	10(″)	50	4	60
9	H_2O	-	100	2	trace
10	H_2O	-	100	4	trace
11	-	10(″)	100	24	trace
12	H_2O	10(″)	70	4	80
13	H_2O	5(0.45 mol% Pd)	80	5	65
14	H_2O	12(1.08 mol% Pd)	80	2	95
15	H_2O	15(1.35	80	2	95

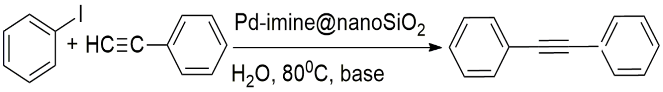
		mol% Pd)			
16	H_2O	20(1.80 mol% Pd)	80	2	95
17	H_2O	25(2.25 mol% Pd)	80	2	95

[a]Reaction conditions: Aryl halide (1.3 mmol), phenyl acetylene (1.0 mmol), triethylamine (2.0 mmol), catalyst (Pd-imine@nanoSiO_2) and solvent (3ml) .

*all reactions were carried out for 24h however, the time required to get maximum conversion is reported here.

Previous studies suggested that bases play a significant role in absorption of hydrogen halide in this reaction as well as inhibits the formation of homo-coupling product[34]. The reaction did not occur in absence of any base (Table 3, entry 5). We have examined both organic and inorganic bases like K_2CO_3, $NaHCO_3$, NaOH, Et_3N and water extract of banana (WEB) to find out the most efficient base for the reaction and found Et_3N as the most efficient base for the reaction (Table 3, entry 4).This might be due to the fact that amines trap hydrogen halide readily compared to inorganic bases[35-36] . The results are summarized in the **Table-3**.

Table 3: Optimization of bases for the Sonogashira cross-coupling reaction[a]

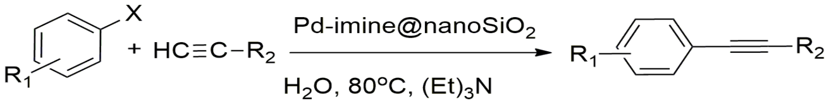


Entry	Base	Isolatedyield(%)
1	K_2CO_3	60
2	$NaHCO_3$	55
3	NaOH	50
4	Et_3N	95
5	-	-
6	WEB[b]	30

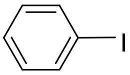
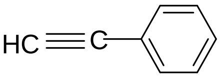
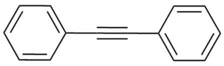
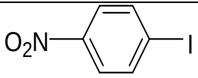
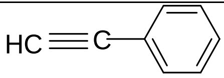
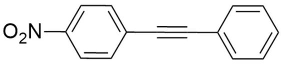
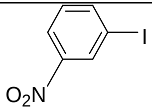
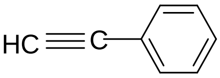
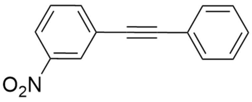
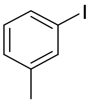
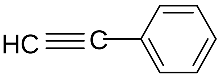
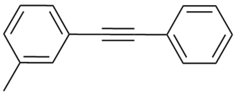
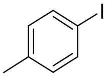
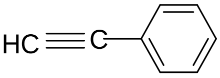
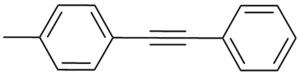
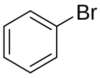
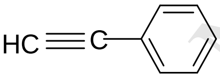
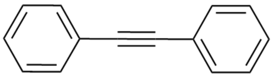
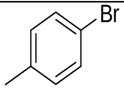
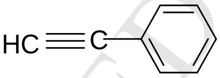
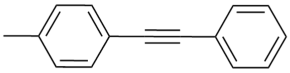
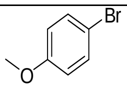
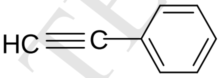
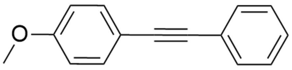
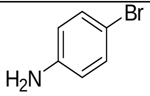
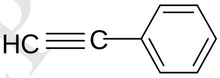
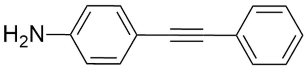
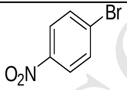
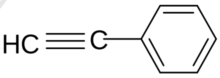
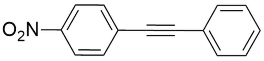
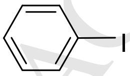
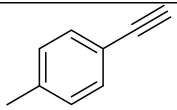
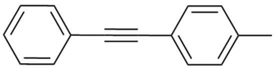
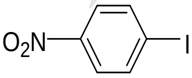
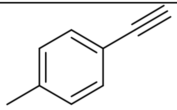
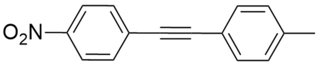
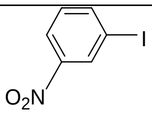
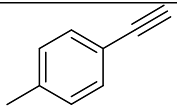
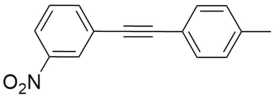
[a]Reaction conditions: iodobenzene(1.0 mmol),phenyl acetylene(1.1 mmol)], H_2O(2 ml), Pd-imine@nanoSiO$_2$ (10mg ; 0.9 mol% of Pd) at 80°C for 2 h; [b] Water extract of banana (WEB)

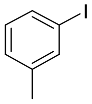
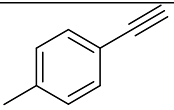
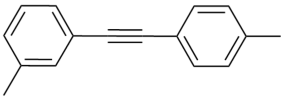
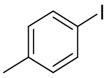
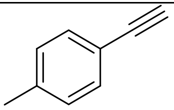
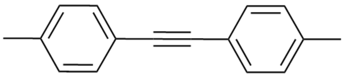
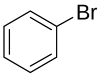
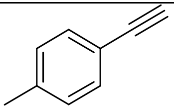
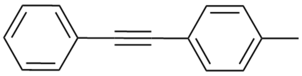
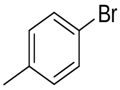
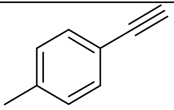
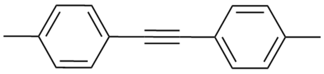
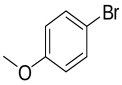
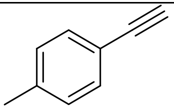
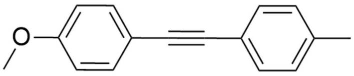
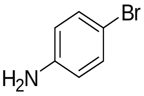
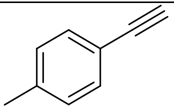
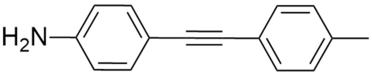
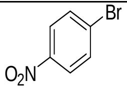
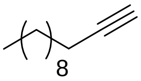
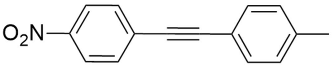
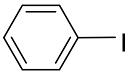
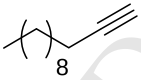
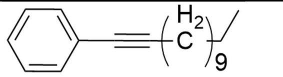
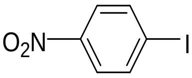
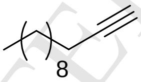
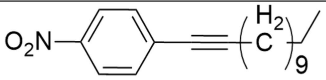
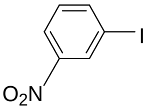
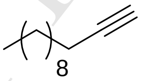
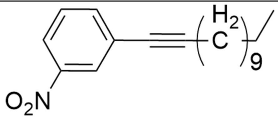
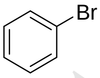
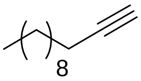
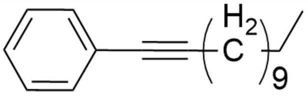
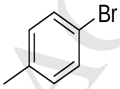
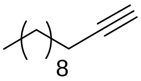
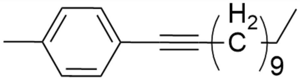
To widen the scope of the reaction we have carried out Sonogashira cross-coupling reaction between a wide range of substrates with Pd-imine@nanoSiO$_2$ as the catalyst. Water as a solvent tolerates very hardly both aryl iodides and aryl bromides as substrate to give good yield, however our catalytic system showed high tolerance for both aryl iodides and aryl bromides. Aryl bromides gave comparatively lower isolated yield than the aryl iodides (Table 4, entries 6-10 & 16-20) and aryl iodides with electron donating groups gave higher yield compared to electron withdrawing groups (Table 4, entries 4,5&15).Aliphatic alkynes coupled less effectively with aryl halides and afforded low yields, might be attributed to the presence of less acidic terminal hydrogen which results slow coordination of alkyneto aryl palladium intermediate to form aryl alkynyl palladium species (Table 4, entries 20-25).

Table 4: Sonogashira cross- coupling reactions of different aryl halides and alkynes in water[a]



Entry	Aryl halide		Product	Isolated yield

		Alkyne		(%)
1				85
2				80
3				75
4				92
5				96
6				85
7				87
8				85
9				88
10				77
11				90
12				85
13				87

14				85
15				90
16				80
17				82
18				77
19				81
20				81
21				78
22				80
23				78
24				73
25				75

[a]Reaction conditions: aryl halide(1.0 mmol), alkyne(1.1 mmol) , Pd-imine@nanoSiO_2(10mg ; 0.9 mol% of Pd) ,Et_3N(2.0 mmol), H_2O (2ml) .

Catalyst leaching and reusability of the catalyst

Hot filtration test

We have carried out a hot filtration test to know whether these catalytic reactions are truly heterogeneous or not by using phenyl acetylene and iodobenzene in the presence of Pd-imine@nanoSiO_2 catalyst (10mg; 0.9mol% of Pd) and stirred at 80 °C. After 30 min the reaction was stopped and the catalyst was filtered off (55% yield found from GC-MS). The reaction was allowed to progress without the catalyst for another 1and1/2 h, which eventually showed no increase in product yield. This clearly suggested non-leaching of Pd during reaction which was further confirmed by ICP-AES analysis with the filtrate.

Reusability test

Retrievability of a catalyst is of utmost concern to evaluate the efficiency of the catalyst as well as from the economic point of view. We therefore conducted the recyclability experiment by taking iodobenzene and phenyl acetylene as coupling partners with10 mg (0.9 mol% of Pd) of the catalyst. After completion of the reaction (monitored by GC-MS) the catalyst was separated with centrifugal precipitation and dried at temperature 120°C in an oven for 24h. Then the catalyst was reused in a new coupling reaction .To our delight the catalyst showed good recyclability for five consecutive runs without significant loss in activity (**Fig 6**).

To check the chemical change of the catalyst during subsequent runs we have performed a SEM-EDX analysis of the catalyst recovered after the fifth catalytic cycle (**Fig 7a & 7b**). It revealed that the catalyst retains its initial chemical composition even after 5th catalytic cycle.

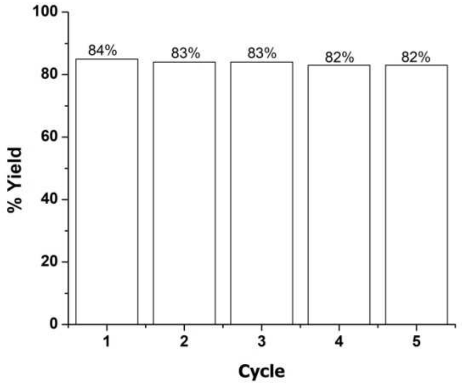


Fig 6: Reusability of Pd-imine@nanoSiO$_2$ in the Sonogashira cross-coupling reaction

Reaction conditions: Catalyst (10 mg;0.9 mol %);iodobenzene (6.3 mmol); phenyl acetylene (6.0 mmol);(Et)$_3$N (12mmol); H$_2$O (9 ml); temperature: 80 ◦C.

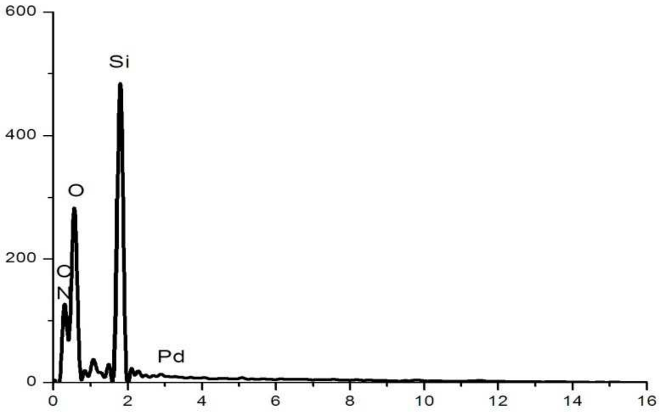
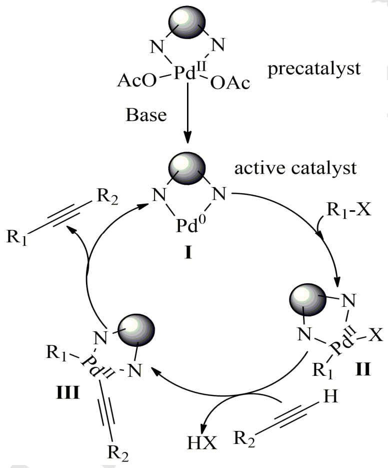


Fig.7a: SEM of catalyst after 5th cycle Fig.7b: EDX spectrum of the catalyst

A plausible mechanism for the catalytic performance of Pd-imine@nanoSiO_2 in copper free condition for Sonogashira reaction is demonstrated in **Scheme 2**.In analogy with the earlier reports , the mechanism initially may be started with the activation of Pd-imine@nanoSiO_2 and generating acetate free Pd(0) real catalytic species **I** in basic medium[4]. This was followed by the oxidative addition of aryl halide to the species **I** through the oxidation of Pd(0) to Pd(II). The coordination of terminal alkyne to intermediate **II** producing palladium acetylide complex **III** . At the final step Sonogashira reaction product was released through the reductive elimination of complex **III** with the simultaneous release of the active catalyst for the next catalytic cycle. To confirm the nature of the real catalytic species we have recorded TEM image of the catalyst after completion of the reaction, which clearly showed the formation of Pd(0) nanoparticles (**Fig S4**).



Scheme 5: The probable mechanism of copper free Sonogashira reaction

To know the actual catalytic performance of our catalyst with respect to the reported ones we have performed a literature survey (**Table 5**) and our catalyst was found to be effective with wide substrate scope at mild reaction conditions.

Table 5: Comparative study on Sonogashira cross-coupling reactions with different catalytic systems

Catalyst	**Reaction Conditions**	**Yield/Conversion (%)**	**Literature reference**
Pd(II)Cl_2-	DIPEA, DMF/H_2O,RT,	80-95	[4]

BTP@TMSP-nSiO_2	2-3h,0.15mol%		
Nano-Pd(0)/SDPP	K_2CO_3, PEG 200, 100°C, 1.5-4 h,0.5mol%	50-91	[3]
Pd-LHMS-3	Hexamine, H_2O, reflux, 10-15 h,0.52 mol%	70-90	[2]
nSiO_2-Dendrimer-Pd(0)0	$(Et)_3N$,H_2O,reflux,4-12h, 0.085mol%	82-96	[5]
Pd-2QC-MCM	Piperidinen,NMP,80^0C, 3h,1.8mol%	49-100	[29]
Pd-ABA-MCM-41	K_2CO_3, PEG 200, 60°C,1-7h,1.6 mol%	92-97	[28]
CuNPs@MP-3	Et_3N, H_2O, 40^0C, 8h,1 mol%	70-96	[35]
Co-MS@MNPs/CS	KOH,DMSO,140^0C,10-12h, 1.1 mol %	45-80	[37]
Pd/ICCP	K_2CO_3,EtOH,100^0C,4h, 1 mol %	64-92	[38]
Pd-BIP-γ-Fe_2O_3@SiO_2	Et_3N,DMF,100^0C,1.5-6h,0.5 mol %	71-96	[39]
Pd(II)-PMO-SBA-16	DBU,CuI,H_2O,90^0C,4-10h, 0.9 mol %	85-93	[40]
Pd-imine@nanoSiO_2	$(Et)_3N$, H_2O, 80ºC,2h, 0.9 mol%	50-97	Our work

Conclusion:

We have developed an eco-friendly, novel protocol for Sonogashira cross-coupling reaction using Pd-imine@nanoSiO_2. The catalyst exhibited excellent catalytic efficiency for carbon-carbon triple bond activation reactions between arylhalides(both iodides and aryl bromides) and terminal alkynes in water. Our catalyst could be easily recovered from the reaction mixture by simple centrifugal precipitation and reused for five consecutive catalytic cycles without profound loss in activity. This protocol is also moderately suitable for aliphatic alkynes.

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References

[1] A. Gogoi, A. Dewan, G. Borah, U. Bora, New J. Chem., 39 (2015) 3341.

[2] A. Modak, J. Mondal, A. Bhaumik, Green Chem., 14 (2012) 2840.

[3] N. Iranpoor, B.H. Firouzabadi, B.S. Motevalli,Aust. J. Chem.,68 (2015) 926.

[4] Z. Dehbanipour, M. Moghadam, S. Tangestaninejad, V. Mirkhani, I. Mohammadpoor-Baltork, J. Organomet. Chem., 853 (2017) 5.

[5] M. Esmaeilpour, A. Sardarian, J. Javidi, Catal. Sci. Technol., 6 (2016) 4005.

[6] M. Lamblin, L. Nassar-Hardy, J.C. Hierso, E. Fouquet, F.X. Felpin, Adv. Synth. Catal., 352 (2010) 33.

[7] Z. Mandegani, M. Asadi, Z. Asadi, Appl. Organomet. Chem., 30 (2016) 657.

[8] W. He, F. Zhang, H. Li, Chem. Sci., 2 (2011) 961.

[9] S.N. Jadhav, A.S. Kumbhar, S.S. Mali, C.K. Hong, R.S. Salunkhe, New J. Chem., 39 (2015) 2333.

[10] P. Veerakumar, P. Thanasekaran, K.L. Lu, S. Bin Liu, S. Rajagopal, ACS Sustain. Chem. Eng., 5 (2017) 6357.

[11] J. Baruah, R. Gogoi, N. Gogoi, G. Borah, Transit. Met. Chem., 42 (2017).

[12] J.H. Kim, J.W. Kim, M. Shokouhimehr, Y.S. Lee, J. Org. Chem., 70 (2005) 6714.

[13] M. Bakherad, A. Keivanloo, S. Samangooei, Chinese J. Catal., 35 (2014) 324.

[14] M. Navidi, N. Rezaei, B. Movassagh, J. Organomet. Chem., 743 (2013) 63.

[15] S.M. Sarkar, M.M. Yusoff, M.L. Rahman, J. Chinese Chem. Soc., 62 (2015) 33.

[16] S. Diyarbak, H. Can, and O.Metin, Appl. Mater. Interfaces., 7 (2015) 3199.

[17] A. Khalafi-Nezhad, F. Panahi, Green Chem., 13 (2011) 2408.

[18] D.A. Kotadia, U.H. Patel, S. Gandhi, S.S. Soni, RSC Adv., 4 (2014) 32826.

[19] M. Opanasenko, P. Stepnicka, J. Cejka, RSC Adv., 4 (2014) 65137.

[20] M. Pagliaro, V. Pandarus, F. Béland, R. Ciriminna, G. Palmisano, P.D. Carà, Catal. Sci. Technol., 1 (2011) 736.

[21] N. Pal, A. Bhaumik, RSC Adv., 5 (2015) 24363.

[22] S. Cui, S. Yu, B. Lin, X. Shen, X. Zhang, D. Gu, J. Porous Mater., 24 (2017) 455.

[23] N. Gogoi, U. Bora, G. Borah, P.K. Gogoi, Appl. Organomet. Chem., 31 (2017) 1.

[24] S. Sultana, G. Borah, P.K. Gogoi, Appl. Organomet. Chem., 33 (2018) doi:10.1002/aoc.4595.

[25] N. Gogoi, T. Begum, S. Dutta, U. Bora, P.K. Gogoi, RSC Adv., 5 (2015) 95344.

[26] Q. Zhu, L. Liao, G. Cheng, W. Yang, Y. Deng, D. Yang, Mod. Res. Catal., 06 (2017) 121.

[27] B.N. Lin, S.H. Huang, W.Y. Wu, C.Y. Mou, F.Y. Tsai, Molecules., 15 (2010) 9157.

[28] M. Nikoorazm, N. Noori, B. Tahmasbi, S. Faryadi, Transit. Met. Chem., 42 (2017) 469.

[29] K. Komura, H. Nakamura, Y. Sugi, J. Mol. Catal. A Chem., 293 (2008) 72.

[30] P. Wang, G.Y. Wang, W.L. Qiao, Y.S. Feng, Catal. Letters., 146 (2016) 1792.

[31] M. Mishra, A.P. Singh, P. Sambyal, S.K. Dhawan, Indian J. Pure Appl. Phys., 52 (2015) 478.

[32] Y.H. Ng, M. Wang, H. Han, C.L.L. Chai,Chem. Commun., 0 (2009) 5530.

[33] R. Kotcherlakota, A. K. Barui, S. Prashar, M. Fajardo, D. Briones, A. Rodríguez-Diéguez, C. R. Patra, S. Gómez-Ruiz,Biomater. Sci., 4 (2016) 448.

[34] T. Ljungdahl, T. Bennur, A. Dallas, H. Emtenäs, J. Mårtensson, Organometallics., 27 (2008) 2490.

[35] K. Wang, L. Yang, W. Zhao, L. Cao, Z. Sun, F. Zhang, Green Chem., 19 (2017) 1949.

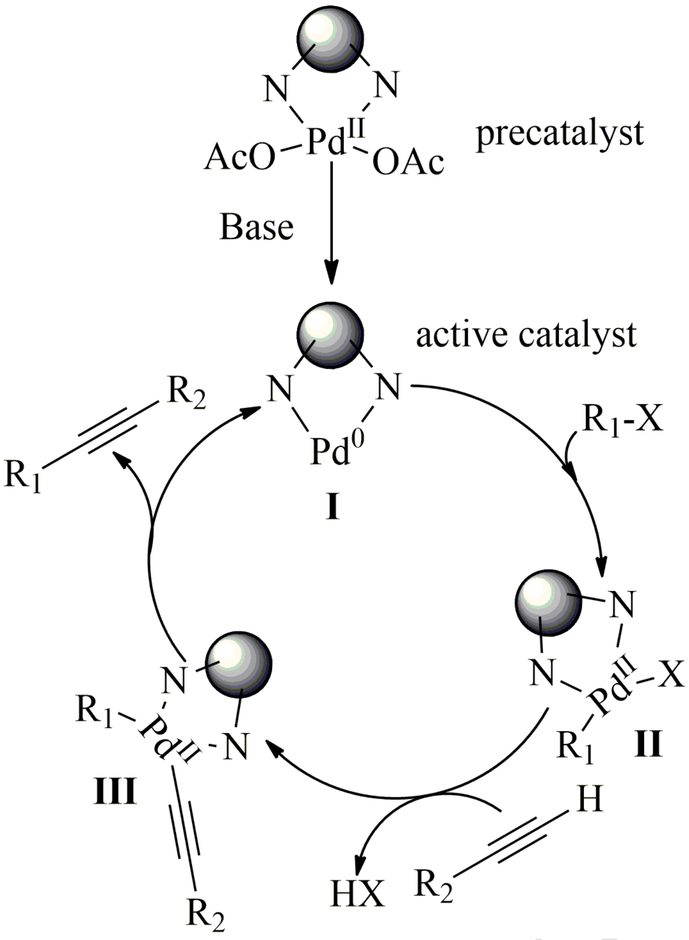
[36] M. Bakherad, Appl. Organomet. Chem., 27 (2013) 125.

[37] A.R. Hajipour, F. Rezaei, Z. Khorsandi, Green Chem., 19 (2017) 1353.

[38] T. Saetan, C. Lertvachirapaiboon, S. Ekgasit, M. Sukwattanasinitt, S. Wacharasindhu, Chem. An Asian J., 12 (2017) 2221.

[39] S. Sobhani, Z. Zeraatkar, F. Zarifi, New J. Chem., 39 (2015) 7076.

[40] F. Zhu, L. Zhu, X. Sun, L. An, P. Zhao, H. Li, New J. Chem., 38 (2014) 4594.


precatalyst
AcO
Pd^II
OAc
N
N
Base
active catalyst
Pd^0
I
R1-X
II
Pd^II
X
R1
III
R1
Pd^II
R2
H
HX
R2
R1
R2

Highlights

- Rice husk derived nanosilica supported Pd-imine@nanoSiO_2 catalyst can be synthesized easily.
- This is the first example of a nanosilica anchored Pd catalyst for Sonogashira cross-coupling reaction in aqueous medium in copper free condition and gave good to excellent isolated yields of the products.
- Activate both aryl iodides and aryl bromides to afford diaryl alkynes. This protocol was also suitable for aliphatic alkynes.
- The catalyst could be easily recovered and can be reused for five consecutive cycles without profound loss in activity.