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Synthesis and applications of polymeric N-heterocyclic carbene palladium complex-grafted silica as a novel recyclable nano-catalyst for Heck and Sonogashira coupling reactions†

Bahman Tamami,^{*a} Fatemeh Farjadian,^{ab} Soheila Ghasemi^a and Hamed Allahyari^a

A new catalytic system based on palladium nanoparticles supported on polymeric N-heterocyclic carbene-grafted silica (Si-PNHC-Pd) is introduced. Aminopropylsilica was reacted with benzoylchloride to form acrylamidopropylsilica. Onto this functionalized silica, vinylimidazole monomer was copolymerized by free radical polymerization. Poly(vinylimidazole)-grafted silica was treated with methyl iodide to form a quaternary salt of poly(vinylimidazole). Si-PNHC-Pd was obtained by subsequent treatment of imidazolium salt with PdCl₂. Determination of Pd content was performed using an inductively coupled plasma (ICP) analyzer and the crystalline character was determined by an XRD technique. The topography and particle size of the catalyst was studied by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM). TEM images showed that palladium was dispersed through the polymer surface in nano particle size. This catalytic system exhibited excellent activity in Heck and Sonogashira coupling reactions with various aryl halides. The catalyst was successfully re-used up to 12 runs without appreciable change in its activity. High efficiency of the catalyst along with high yields of products, easy purification, large scale synthesis and high TON and TOF are among the advantages of this heterogeneous catalyst.

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Introduction

The use of N-heterocyclic carbenes (NHCs) as ligands and their metal complexes have been receiving wide attention recently.¹ Some of the beneficial features of these compounds that make them unique in organometallic chemistry and are responsible for their rapid growing are; σ -electron-donation and to a lesser degree π -back-donation properties that lead to stronger bonds with metal centers than most classical ligands, resistance of metal complexes to decomposition, thermal and oxidative stability and better steric protection of the active site within the inner metal coordination sphere.² These properties make them the only class of ligands that has been able to challenge the widely employed tertiary phosphines.³ The first metal complex with a NHC ligand was reported in 1968 by Ofele and Wanzlick.⁴ Since then, many complexes of transition metals with enhanced catalytic performance and higher stability have been introduced.⁵

Palladium-catalyzed cross-coupling reactions are one of the most employed organic transformations.⁶ Among these transformations, the coupling of aryl, vinyl, benzyl or allyl halides, acetates or triflates with alkenes in the Heck–Mizoraki reaction,⁷ and the reaction of terminal alkynes with organic halides in the Sonogashira reaction⁸ for the synthesis of substituted arylated alkyne compounds, are interesting examples of carbon–carbon [C(sp²)–C(sp)] bond formations. These reactions are carried out in the presence of Pd catalysts involving ligands such as phosphines, amines, NHCs, dibenzylideneacetone (dba), *etc.*^{6a} Among various ligands, NHCs have gained attention due to their capability to form moisture- and air-stable catalysts with remarkable activity in carbon–carbon bond formation reactions.^{5a} The NHC ligand Pd complex was first introduced by Herrmann and Kocher in 1997 to the Suzuki and Heck reactions⁹ and is now widely applied in C–C bond formation reactions.¹⁰ Many homogeneous palladium complexes of NHC ligands are reported as potential alternatives to phosphine ligands for cross-coupling reactions.^{10b}

However, homogenous systems are accompanied with limitations such as inefficient separation of products from the reaction mixture and the loss of expensive metal complexes. On the other hand, the immobilization of homogeneous catalysts onto insoluble supports, polymeric organics¹¹ or inorganics,¹² is an expanding

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research area offering the advantages of easy product separation, catalyst recovery, recycling and the inhibition of metal loss. Silica or modified silica-supported catalysts are good alternatives to traditional homogeneous catalysts; they are environmentally friendly, have excellent (chemical and thermal) stability, good accessibility, and good dispersion of catalytic sites.¹² Several advantages of the immobilization of homogeneous catalysts, and the preparation and use of NHC Pd complexes supported either on polymeric¹³ or silica¹⁴ supports have also been investigated. Other inspiring work in this field, was preparation of a main-chain NHC–palladium polymer as a recyclable self-supported catalyst for the Suzuki reaction, which was reported by Karimi *et al.*¹⁵

Grafting polymer chains onto the silica surface provide a system that can be completely compatible with solvents and substrates, with good dispersion. Polymer-grafted silica has found applications in practical and fundamental studies of interfacial phenomena.¹⁶ There are some reports in the literature on the applications of polymeric metal complex-grafted silica as catalysts in organic transformations. The first concept of this type appeared in 1991 by Challa *et al.*, who used Cu(II) complexes of poly(styrene-*co*-*N*-vinylimidazole) grafted on silica in an oxidative coupling reaction.¹⁷ Other reports are on the use of Co(II) tetraphenylporphyrins immobilized on poly(4-vinylpyridine-*co*-styrene)-grafted silica for the aerobic oxidation of ethylbenzenes,¹⁸ a poly(4-vinylpyridine)-Cu(II) complex for use in oxidation reactions,¹⁹ and poly(*N*-vinyl-2-pyrrolidone)-Ru(0) complex-grafted silica for the hydrogenation of aromatic compounds.²⁰ However, as far as we know there is no report in the literature on heterogeneous polymeric *N*-heterocyclic carbene–Pd complex-grafted silica for use in cross-coupling reactions. In continuation of our studies on heterogeneous Pd catalysts based on polymer-grafted silica,²¹ herein, we report the synthesis and applications of a novel polymeric *N*-heterocyclic carbene–palladium complex based on poly(*N*-methyl vinylimidazolium)-type polymer-grafted silica as a recoverable catalyst in Heck and Sonogashira coupling reactions.

Results and discussion

Synthesis and characterization of polymeric *N*-heterocyclic carbene–Pd complex-grafted silica (Si–PNHC–Pd)

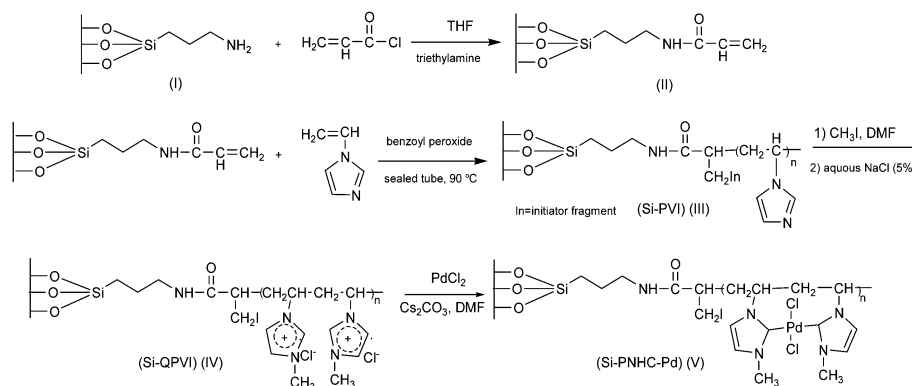
In this study we disclose a new type of polymeric NHC–Pd complex grafted onto silica (Scheme 1).

Aminopropylsilica (AMPS) (**I**) was reacted with acryloylchloride to form acrylamidopropylsilica (**II**). This modified silica, with a polymerizable double bond, was copolymerized with vinylimidazole monomer through a free radical polymerization reaction. FT-IR spectrum of the polyvinylimidazole-grafted silica (Si–PVI) (**III**) showed the characteristic band of the N–C=N group at 1647 cm^{−1} and C=C group of imidazole at 1504 cm^{−1} respectively (Fig. 1).

The amount of PVI-grafted silica was determined by TGA and was found to be 1.3 mmol g^{−1} (Fig. 2). Polymer-grafted silica (**III**) was treated with methyl iodide followed by stirring with sodium chloride solution to form a quaternary salt of polyvinylimidazole (Si–QPVI) (**IV**). The FT-IR spectrum of (**IV**) exhibit two bands at 1677 and 1522 cm^{−1}, which are assigned to the C–H bending of the imidazolium group, and at 1141 cm^{−1} was the C–H band of the C2 position of the imidazolium ring (Fig. 1). The permanent charge density of the imidazole groups was determined using argentimetric titration and was calculated to be 1.1 mmol g^{−1}. The imidazolium chloride salt was reacted with PdCl₂ in the presence of cesium carbonate as a base and DMF as a solvent to obtain the polymeric *N*-heterocyclic carbene–palladium-grafted silica (Si–PNHC–Pd) (**V**) (Scheme 1). The FT-IR Spectrum of (**V**) showed the absorption frequencies of a double bond at 1642 and the C–Pd absorption frequency at 792 cm^{−1}, along with the disappearance of the C–H band of the C2 position of the imidazolium ring due to NHC–Pd formation (Fig. 1).^{13b} Determination of Pd content of (**V**) was performed by digestion of the catalyst followed by ICP analysis, which revealed the presence of 0.26 mmol Pd g^{−1} for this heterogeneous catalyst.

The powder X-ray diffraction (XRD) patterns for (**V**) showed the expected crystallinity of Pd(0) nanoparticles and amorphous silica (Fig. 3). The diffraction rings can be ascribed to the (111), (200), (220) and (311) crystallographic planes of the Pd(0) nanoparticles.

Scanning Electron Microscopy (SEM) images of the catalyst are shown in Fig. 4. The SEM images show the smooth surface of the cubic like Si–PNHC–Pd. According to the Transmission Electron Microscopy (TEM) image (Fig. 5a), the palladium particles are well dispersed through the catalyst surface, with a certain degree of homogeneity. The average size of the palladium particles were measured from the TEM image and



Scheme 1 Synthesis of the polymeric *N*-heterocyclic carbene–Pd complex-grafted silica (Si–PNHC–Pd).

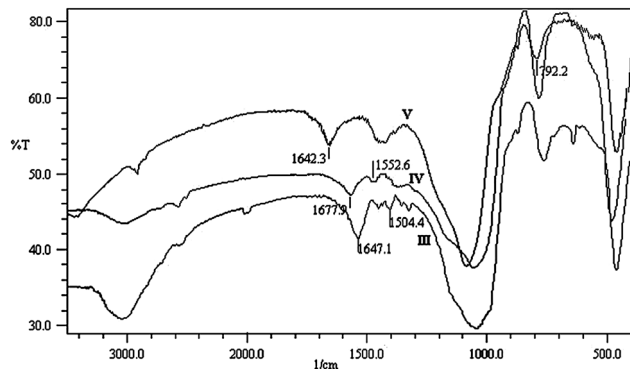


Fig. 1 FT-IR Spectrum of poly(*N*-vinylimidazole)-grafted silica (Si-PVI) (III), quaternary chloride salt of polyvinylimidazole-grafted silica (Si-QPVI) (IV) and polymeric *N*-heterocyclic carbene-Pd complex-grafted silica (Si-PNHC-Pd) (V).

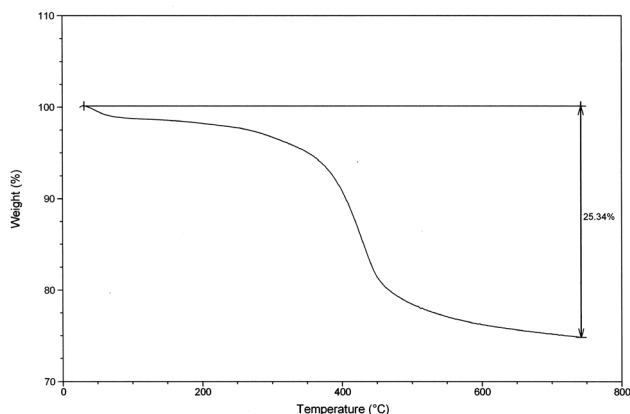


Fig. 2 Thermogravimetric analysis of poly(*N*-vinylimidazole)-grafted silica (Si-PVI) (III).

found to be in the range of 7–10 nm. AFM was used to study the topography of the elements in micro and nano scales.²³ By means of this digital instrument nanoscope, several scans

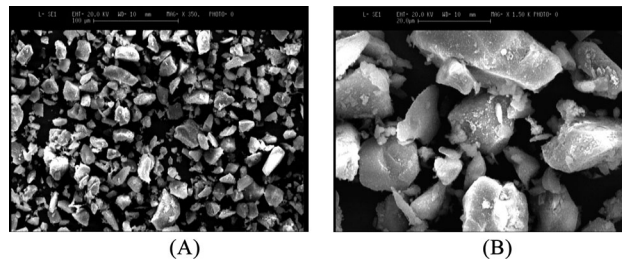


Fig. 4 (A) SEM image of polymeric *N*-heterocyclic carbene-Pd complex-grafted silica (Si-PNHC-Pd) (V) (B) SEM close-up of image (A).

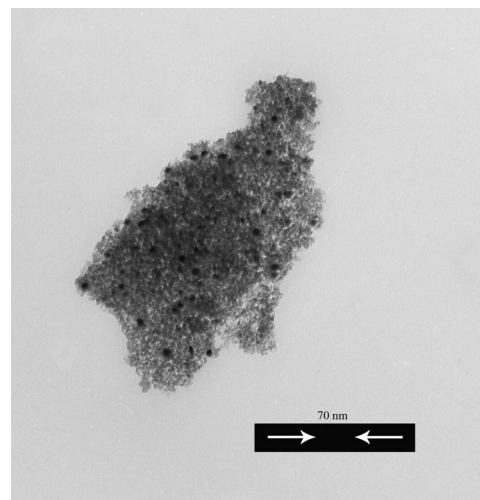


Fig. 5 (a) TEM image of polymeric *N*-heterocyclic carbene-Pd complex-grafted silica (Si-PNHC-Pd) (V).

were performed from (V) to obtain the topography of the Pd particle dispersion in 3 dimensions of *x*, *y*, *z*. In (Fig. 6a) there is a two dimensional (2-D) AFM image, which shows that the average diameter of the Pd nanoparticles is between 6–7 nm.

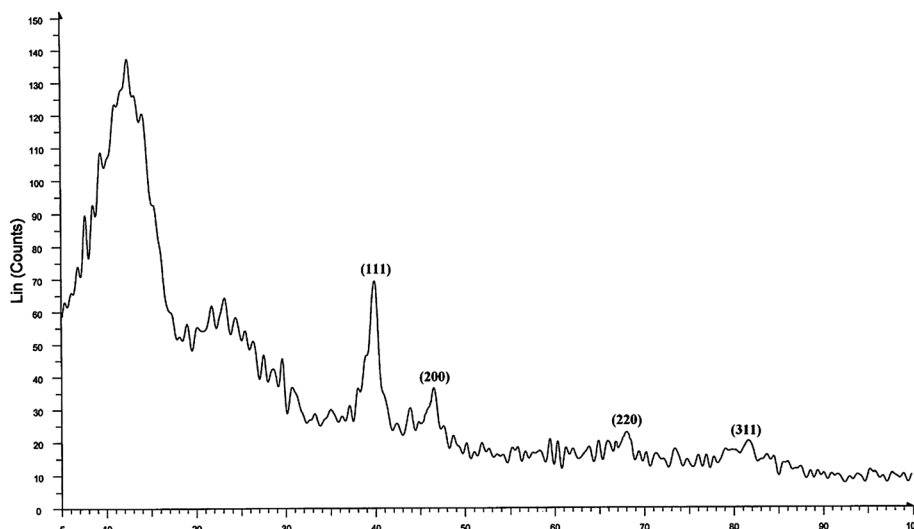


Fig. 3 XRD spectrum of polymeric *N*-heterocyclic carbene-Pd complex-grafted silica (Si-PNHC-Pd) (V).

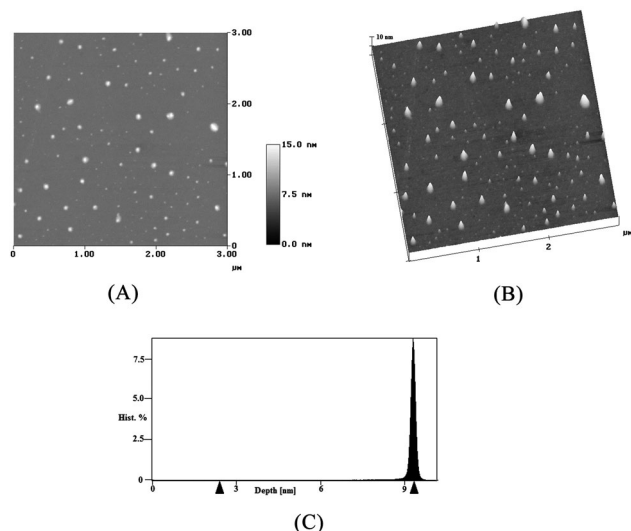


Fig. 6 AFM images of the polymeric N-heterocyclic carbene-Pd complex-grafted silica (Si-PNHC-Pd) (**V**) (a) 2-D image, (b) 3-D image and (c) voltage profile.

This concept was also confirmed by the TEM image. In the 3-D image (Fig. 6b) more details were obtained about the height of the Pd particles. The maximum height scanned was 10 nm. The corresponding histogram (Fig. 6c) shows a symmetric distribution of scanned depth. The maximum height of the particles was 9.3 nm. By the symmetric shape of the histogram, we can conclude that the Pd nanoparticles dispersed smoothly, without or with a negligible amount of agglomeration.

Pd nanoparticle formation during NHC-Pd complexation is inevitable, since **IV** was reacted with PdCl₂ in the presence of CsCO₃ as base and DMF as solvent. Although these conditions are favored for NHC-Pd complexation, it can also prompt Pd nanoparticle formation by implementing the transformation of Pd(II) to Pd(0) in the presence of the base^{6c} and DMF,²² which are also working as reducing agents. We also observed stabilized Pd nanoparticles by TEM and AFM without aggregation, as a result, we concluded that the ionic structure of **IV** protected the Pd nanoparticles from aggregation, as suggested and confirmed by Burguete *et al.*, who had the same observation in their NHC-Pd complex formation.^{13g}

Heck and Sonogashira coupling reactions

The catalytic activity of the Pd catalyst (**V**) was tested for a Heck reaction of aryl halides with styrene and *n*-butyl acrylate. In a model reaction, the coupling of iodobenzene with *n*-butyl acrylate was studied in the presence of a base and the catalyst in a solvent at 120 °C. The reaction conditions were optimized, and the results are presented in Table 1. It was found that the best system was NMP as the solvent and K₂CO₃ as the base using 0.5 mol% of catalyst at 120 °C. The amount of catalyst can be reduced down to 0.2 mol% of Pd by prolonging the reaction time to 3 h.

The generality of this reaction system was shown when other coupling reactions were carried out using *n*-butyl acrylate or

Table 1 Optimization of base, solvent and Pd catalyst (**V**) for the Heck reaction of iodobenzene with *n*-butyl acrylate^a

Entry	Base	Solvent	Pd (mol%)	Time (h)	Conversion ^b (%)
1	K ₂ CO ₃	DMF	0.5	3.5	100
2	K ₂ CO ₃	EtOH	0.5	8	90
3	K ₂ CO ₃	THF	0.5	4	60
4	K ₂ CO ₃	NMP	0.5	2	100
5	LiF	NMP	0.5	10	70
6	NaOAc	NMP	0.5	4	90
7	NaOH	NMP	0.5	7	80
8	K ₂ CO ₃	NMP	0.3	2.5	90
9	K ₂ CO ₃	NMP	0.2	3	87

^a Reaction conditions: iodobenzene (1.0 mmol), *n*-butyl acrylate (1.2 mmol), base (2.0 mmol), Pd catalyst (0.5–0.2 mol%) and 3 mL of solvent at 120 °C. ^b Conversions based on iodobenzene.

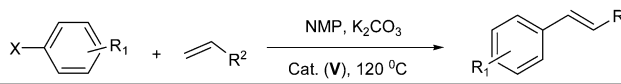
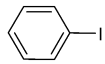
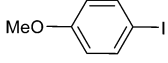
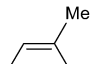

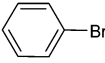
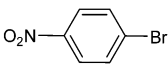
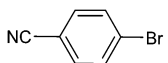
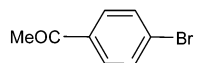
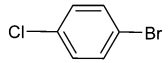
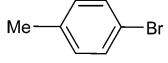
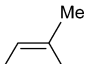
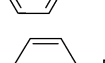
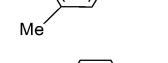
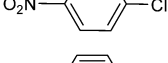
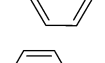
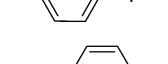
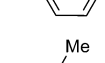
styrene as the olefinic substrate with different aryl halides (Table 2). The electron-neutral, electron-rich and electron-poor aryl iodides and bromides reacted with *n*-butyl acrylate very well to generate the corresponding cross-coupling products in good to excellent yields; however, aryl chlorides were inert under the same conditions. We used tetrabutylammonium bromide (TBAB) as the Jeffery catalyst²⁴ in the reaction of aryl chlorides with *n*-butyl acrylate, but they were unreactive and remained intact even after long reaction times. Only 4-chloro nitro benzene, as an activated substrate, transformed to the coupled product in low yield after 24 h (Table 2, entry 13).

We also examined the Sonogashira cross-coupling reaction for the generation of arylated-alkyne compounds. The copper-, amine- and phosphine-free Sonogashira reaction of phenylacetylene with aryl iodides, bromides and some chlorides were performed with this catalyst. In a model reaction, the coupling of iodobenzene with phenylacetylene was studied in the presence of different bases and solvents in the presence of the catalyst. The reaction parameters were optimized. DMF as solvent and K₂CO₃ as base using 0.5 mol% of the catalyst at 120 °C gave the best result. The amount of the catalyst could be reduced to 0.1 mol% by prolonging the reaction time to 2.5 h. The generality of this reaction was shown when other coupling reactions were carried out using phenylacetylene with different aryl halides (Table 3). The electron-neutral, electron-rich and electron-poor aryl halides reacted with phenylacetylene very well to generate the corresponding cross-coupling products in good to excellent yields. Although aryl chlorides are not as reactive and are less commonly employed in palladium-catalyzed coupling reactions, Sonogashira reactions could be performed with this catalyst using phenylacetylene and aryl chlorides in the presence of a catalytic amount of TBAB (Table 3, entries 11–13).

Heterogeneity test and recycling of the catalyst

For practical applications of a heterogeneous catalytic system, the reusability of the supported catalyst is very important. Thus, the recovery and reusability of the supported catalyst (**V**) was investigated using iodobenzene and *n*-butyl acrylate as model substrates. We could successfully use this catalyst in 12 subsequent

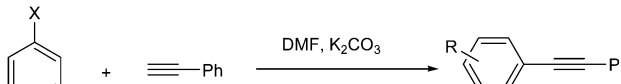
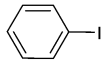
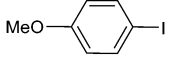
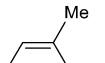

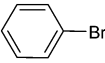
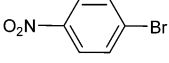
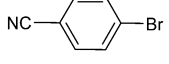
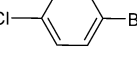
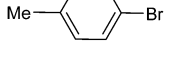
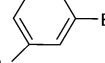
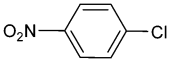
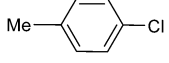
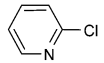
Table 2 Heck reaction of *n*-butyl acrylate or styrene with aryl halides^a

				
Entry	Aryl halide	R ²	Time (h)	Isolated yield ^b (%)
1		CO ₂ Bu ⁿ	2	95
2		CO ₂ Bu ⁿ	6	95
3		CO ₂ Bu ⁿ	1.5	87
4		CO ₂ Bu ⁿ	1.45	78
5		CO ₂ Bu ⁿ	8	80
6		CO ₂ Bu ⁿ	5	90
7		CO ₂ Bu ⁿ	4	93
8		CO ₂ Bu ⁿ	5	80
9		CO ₂ Bu ⁿ	3	75
10		CO ₂ Bu ⁿ	24	50
11		CO ₂ Bu ⁿ	24	30
12		CO ₂ Bu ⁿ	24	40
13		CO ₂ Bu ⁿ	24	30 ^c
14		CO ₂ Bu ⁿ	24	Trace ^c
15		Ph	7	90
16		Ph	12	80
17		Ph	10	88

^a Molar ratios of ArX: *n*-butyl acrylate or styrene: K₂CO₃: palladium catalyst = 1.0:1.2:2.0:0.005. Reaction conditions: NMP at 120 °C.

^b The characterization of products was performed by comparison of their FT-IR, ¹H-NMR, ¹³C-NMR and physical data with those of authentic samples.²⁵ ^c With additional tetrabutylammonium bromide (0.01 mmol).

Table 3 Sonogashira reaction of phenylacetylene with aryl halides^a

			
Entry	Aryl halide	Time (h)	Isolated yield ^b (%)
1		1.25	93
2		1.5	85
3		1.5	77
4		1.45	70
5		1.5	77
6		1	92
7		1	95
8		2	85
9		2	78
10		24	70
11		24	85 ^c
12		24	65 ^c
13		24	80 ^c

^a Molar ratios of ArX: phenylacetylene: K₂CO₃: palladium catalyst = 1.0:1.2:2.0:0.005. Reaction conditions: DMF at 120 °C. ^b The characterization of products was performed by comparison of their FT-IR, ¹H-NMR, ¹³C-NMR and physical data with those of authentic samples.²⁶ ^c With additional tetrabutylammonium bromide (0.01 mmol).

reactions and the catalyst retained its catalytic activity in these repeating cycles. The Pd catalyst did not show an appreciable change in its catalytic activity but prolonging the reaction time was necessary to achieve full conversion. The results are presented in Table 4. To check the heterogeneity of this catalyst, which is an important factor, the filtrate of each cycle was analyzed by an ICP technique. Very low palladium contamination was observed during these experiments. The turn over number (TON = mmole of product/mmole of Pd catalyst) of the catalyst was calculated for 12 runs of recycling to be 2130 and an average turnover

Table 4 Recycling of Pd catalyst (V) for the Heck reaction of iodobenzene with *n*-butyl acrylate^a

Entry	Cycle	Time (h)	Isolated yield (%)	TON ^b	TOF ^c (h ⁻¹)
1	1st	2	95	190	95
2	2nd	2.5	95	190	76
3	3rd	2.5	95	190	76
4	4th	2.5	93	186	74.4
5	5th	2.75	93	186	67.6
6	6th	3	90	180	60
7	7th	3.5	87	174	49.7
8	8th	3.5	87	174	49.7
9	9th	3.5	85	170	48.5
10	10th	4	85	170	42.5
11	11th	4.25	80	160	37.6
12	12th	4.25	80	160	37.6
TON for twelve runs			2130	Av. TON (h ⁻¹)	59.5

^a Reaction conditions: molar ratio of iodobenzene: *n*-butyl acrylate: K₂CO₃: Pd catalyst = 1.0:1.2:2.0:0.005 in NMP at 120 °C. ^b TON = mmol of products/mmol of Pd catalyst. ^c TOF = TON/time.

frequency (TOF (h⁻¹) = TON/time) for 12 runs was calculated to be 59.5.

A hot filtration test was also used to ascertain whether the catalyst was behaving in a truly heterogeneous manner, or whether it was merely a reservoir for a more active soluble form of Pd. In a typical experiment, Pd complex (0.5 mol%), iodobenzene (1.0 mmol), *n*-butyl acrylate (1.2 mmol), K₂CO₃ (2.0 mmol) and NMP (3 mL) were taken in a round-bottomed flask and stirred at 120 °C for 15 min. At this stage, the catalyst was filtered off and the experiment was continued with the filtrate for another 24 h. There was no detectable increase in the product concentration, as is evident from the GC analysis. Furthermore, the ICP analysis does not show any Pd leaching in this stage. This experiment confirmed the heterogeneous character of the catalytically active species.

Experimental section

General remarks

Materials were purchased from Fluka AG and Merck Chemical Companies. Aminopropylsilica, with an average particle size of 0.015–0.035 mm (>400 mesh ASTA) and a loading of 0.95 mmol g⁻¹, was supplied by Fluka AG. All products were characterized by comparison of their IR and NMR spectra and physical data with those reported in the literature. Thin-layer chromatography was performed on silica-gel Polygram SIL/UV 254 plates. Petroleum ether boiling point used for TLC monitoring is in the range of 40–60 °C. Gas chromatographic analyses were performed on a Shimadzu GC 10-A instrument with hydrogen flame ionization detector. Infrared spectra were recorded on a Shimadzu FT-IR-8300 spectrophotometer. NMR spectra for ¹H and ¹³C were recorded on a Bruker Avance DPX instrument (250 MHz). Thermogravimetric analysis (TGA) was performed using Perkin Elmer instrument under N₂ gas and a heating rate of 20 °C min⁻¹. X-ray diffraction data obtained with XRD, D8, Advance, Bruker, axs. TEM analysis was performed on a Philips model CM 10 instrument. Scanning electron micrographs were obtained

by SEM, XL-30 FEG SEM, Philips, at 20 kV. Pd loading and leaching tests were carried out with an Inductively Coupled Plasma (ICP) analyzer (Varian, vista-pro). Particle size distribution (PSD) was determined by a dynamic light scattering particle size analyzer Horiba-LB-550 instrument. Atomic force microscopy (AFM) analysis was performed with Nanoscope IIIa Multimode AFM (from Veeco) and images are recorded in Tapping Mode using a 10 micron scanner and standard silicon cantilevers.

Preparation of poly(*N*-vinylimidazole)-grafted silica (Si-PVI) (III)

Acrylamidopropylsilica was prepared according to our reported procedure.²¹ To a suspension of acrylamidopropylsilica (2.0 g), *N*-vinylimidazole (4 mL) and recrystallized benzoyl peroxide (0.05 g) were added in a 10 mL sealed tube. The mixture was heated at 90 °C in an oven for 15 h. The polymer-grafted silica was Soxhlet-extracted with CHCl₃ (200 mL) for 24 h, followed by washing and drying. The amount of poly(*N*-vinylimidazole)-grafted silica was determined by TGA to be 1.3 mmol g⁻¹.

Preparation of polymeric *N*-heterocyclic carbene-Pd complex-grafted silica (Si-PNHC-Pd) (V)

To a suspension of (Si-PVI) (2.0 g) in DMF (30 mL) was added methyl iodide (5 mmol, 0.311 mL). The slurry was stirred at 80 °C for 20 h and then filtered off. The corresponding solid was washed with DMF and ethanol and then dried under reduced pressure. The resulting powder stirred in NaCl solution (5%) (35 mL) at room temperature for one day. The mixture was filtered off, washed thoroughly with H₂O and acetone and then dried in an oven under vacuum at 60 °C for 10 h. The chloride ion capacity of the imidazolium type polymer was found using an argentimetric titration method.²⁷ It was calculated to be 1.1 mmol g⁻¹.²⁸ The resulting imidazolium chloride salt (2.0 g) was reacted with PdCl₂ (5 mmol) in the presence of Cs₂CO₃ (10 mmol) as base and DMF (30 mL) as solvent at 80 °C for 20 h. The mixture was filtered and washed thoroughly with DMF, H₂O and acetone. The black powder was then treated for 24 h in DMF solvent in order to remove any physisorbed palladium particles. According to the ICP analysis, the Pd content in the heterogeneous catalyst was determined to be 0.26 mmol g⁻¹.

General procedure for the Heck reaction

A suspension of aryl halide (1.0 mmol), K₂CO₃ (2.0 mmol), Pd complex (0.005 mmol) in NMP (5 mL) was mixed in a reaction flask and *n*-butyl acrylate or styrene (1.2 mmol) was added. The reaction mixture was stirred at 120 °C for an appropriate length of time. The progress of the reaction was monitored by TLC using a petroleum ether–ethyl acetate (95/5) and/or GC until no traces of starting aryl halide was observed. On completion of the reaction, the mixture was filtered and the filtrate poured into water (50 mL) and extracted with CH₂Cl₂ (3 × 15 mL). The combined organic phases were dried over Mg₂SO₄, filtered and the solvent evaporated under vacuum. The product was isolated by flash chromatography using a mixture of petroleum ether and ethyl acetate as eluent. Characterization of the products was performed by comparison of their FT-IR, ¹H-NMR, ¹³C-NMR, and physical data with those of the authentic samples. The used

catalyst was washed with DMF, water and acetone. It was dried under vacuum and reused without any pretreatment for repeating cycles.

General procedure for the Sonogashira reaction

To a suspension of aryl halide (1.0 mmol), K_2CO_3 (2.0 mmol), Pd complex (0.005 mmol) in DMF (5 mL), phenylacetylene (1.2 mmol) was added. The reaction mixture was stirred at 120 °C for an appropriate length of time. The progress of the reaction was monitored by TLC using a petroleum ether–chloroform mixture (90 : 10) and/or GC until no traces of starting aryl halide was observed. Upon completion of the reaction, the procedure outlined above was followed.

Conclusion

In conclusion, we introduced a novel heterogeneous catalyst based on polymeric N-heterocyclic carbene–Pd complex-grafted silica. The XRD technique was used to ascertain the presence of Pd(0). TEM image showed the presence of Pd nanoparticles dispersed through the surface of this polymer. In addition, the AFM histogram confirmed the presence of palladium in the nanoparticle size range. The high efficiency and stability of this catalytic system was shown for Heck and Sonogashira coupling reactions with a number of aryl halides. The catalyst showed high thermal stability and could be successfully reused for 12 reaction cycles giving a total TON = 2130. Simple filtration of the catalyst, excellent dispersity of Pd particles, short reaction times and high yields are among the other advantages of this catalytic system.

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- 28 0.1 g of imidazolium chloride (Si-QPVI) (**IV**) salt was suspended in 10 mL of 0.1 M HNO₃. After adding 1 mL of 0.1 M AgNO₃, the mixture was stirred for 10 h at room temperature. The chloride counter ions precipitated as AgCl. The amount of remaining Ag⁺ was back titrated using 0.1 M HCl. The permanent charge density of imidazole groups was calculated to be 1.1 mmol g⁻¹.