



Pyridine-derived palladium complexes immobilized on ordered mesoporous silica as catalysts for Heck-type reactions

Jana Horniakova^a, Thirumalaiswamy Raja^b, Yoshihiro Kubota^a, Yoshihiro Sugi^{a,*}

^a Department of Materials Science and Technology, Faculty of Engineering, Gifu University, Gifu 501-1193, Japan

^b Catalysis Division, National Chemical Laboratory, Pune 411 008, India

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Abstract

Palladium complexes with pyridine–carboimine and quinoline–carboimine ligands immobilized on ordered mesoporous silica (FSM-16) were prepared by the following reactions: (1) surface modification of FSM-16 with 3-aminopropyl group via silylation; (2) preparation of pyridine–carboimine and quinoline–carboimine ligands on FSM-16; (3) formation of palladium complex on FSM-16 with PdCl₂. The palladium complexes were characterized by X-ray diffraction (XRD), N₂-adsorption, FT-IR, ²⁹Si and ¹³C MAS NMR, inductively coupled plasma (ICP) and TG analysis. These catalysts were found to be active in the Heck vinylation of aryl iodides and activated aryl bromides with methyl acrylate. Conversion of 100% in 1–5 h reaction and selectivity for *trans*-stereoisomer higher than 99% have been achieved. In the case of less reactive aryl bromides, addition of quaternary ammonium salt increased activity of catalysts, but significant leaching of palladium into solution has been observed. The palladium complexes showed high catalytic activity even for Suzuki coupling of aryl iodides and aryl bromides with the yield of coupling products 50–100% after 1.5 h reaction. Hindered substrates such as 9-bromoanthracene and 9,10-dibromoanthracene were also coupled in yield of 40–65%. Nevertheless, slightly higher concentration of Pd (1.5 times as high as for mono-coupling) is required for complete di-coupling in the case of 9,10-dibromoanthracene. These immobilized catalysts can be easily separated from the reaction mixture by filtering and re-used for further reaction. Catalysis by these palladium complexes can offer an alternative to homogeneous catalysts.

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1. Introduction

Heck-type reactions, such as the Heck vinylation and the Suzuki coupling, one of the most important C–C coupling reactions in organic synthesis, are mostly catalyzed in solution by palladium species generated from either Pd(0) or Pd(II) compounds [1]. High activity for coupling of aryl halides can be achieved using homogeneous palladium catalysts [2] and extremely good conversions can be obtained for aryl bromides using Herrmann's palladacycle. Turnover numbers (TONs) of 10⁶ were reported for the coupling of 4-bromoacetophenone in the presence of additives [3]. However, these catalysts, in general, suffer from recovery and

recycling of an active homogeneous palladium catalyst because of the inherent problems of air-sensitive character of the catalysts, difficulty in separation of catalysts and products, etc.

The heterogenization of homogeneous catalysts can help their use for practical processes to overcome these problems. In the last years, numerous methods have been developed for the synthesis of large variety of heterogeneous palladium catalysts [4,5]. Metallic palladium species supported on carbon [6], metal oxides [7,8], mesoporous silica [9] and zeolites [10–13] were found to be suitable catalysts for the Heck reaction of aryl iodides and/or activated bromides in polar solvents. Nevertheless, the deactivation of catalysts by leaching of palladium species into solution under the reaction conditions and the oxidation of active palladium complexes is the major drawback of these catalysts because palladium species leached from supports are

* Corresponding author. Fax: +81-58-293-2597.

E-mail address: sugi@apchem.gifu-u.ac.jp (Y. Sugi).

stabilized in polar solvent [12,14]. The combination of tributylamine as base and toluene as solvent in the Heck vinylation of 4-bromoacetophenone with butyl acrylate can prevent conditions in which Pd⁰ and Pd²⁺ may be extracted to the solution, although reaction rate was considerably slower than in conventional polar aprotic solvents [12]. Toluene was reported as a suitable solvent to avoid palladium leaching in the Suzuki coupling catalyzed by palladium-containing basic zeolites [13].

The immobilization of palladium complexes on organic or inorganic supports has been shown to be an efficient method for preventing palladium leaching. Kosslick et al. [15] has shown possibility to immobilize palladium phosphine complexes on mesoporous MCM-41 appropriately functionalized to obtain an active catalyst for the Suzuki coupling of *p*-iodoanisole with *p*-tolylboronic acid. However, leaching of metal moiety due to oxidation of phosphine ligands cannot be suppressed during the reaction, especially in polar solvents.

Nitrogen chelating ligands have been shown an effective replacement of phosphine ligands in the Heck type of reactions. In addition, these ligands are air stable, less expensive, and non-toxic. Among the available supports for homogeneous catalysts, silica is chosen most frequently as support due to its chemical neutrality and relatively easy immobilization procedure. The amino-functionalized silica supported palladium catalysts have been successfully tested in the Heck reaction of iodobenzene with olefins [16]. Palladium complexes immobilized on silica functionalized with acetylpyridines [17] have been found to be active and stable catalysts in the Heck reaction of iodobenzene with ethyl acrylate (TON of 350 ethyl cinnamate/mmol Pd in the first cycle and 4100 mmol ethyl cinnamate/mmol Pd for the 14 cycle in Heck reaction of iodobenzene with ethyl acrylate) as well as in the carbonylation of iodobenzene. Clark et al. [18] has reported C–C coupling of iodobenzene using pyridinium palladium complexes immobilized on MCM-41 with minimal level of palladium leaching and turnover numbers around of 2000 mmol of methyl cinnamate/mmol Pd in the fifth cycle.

Herein, we report the preparation and characterization of palladium complexes immobilized on pyridine–carboimine and quinoline–carboimine functionalized mesoporous FSM-16. These immobilized complexes can be sufficiently applied even for the Heck vinylation and the Suzuki coupling of aryl bromides as active and re-usable catalysts with a minimal leaching of palladium species into solution and with stability at higher reaction temperature. Quinoline–carboimine as ligand can offer higher conversions than pyridine–carboimine: differences in the activity between pyridine–carboimine and quinoline–carboimine palladium complexes were much more evident in the Suzuki reaction of aryl bromides with phenylboronic acid. Very recently, the Suzuki coupling of aryl bromides with arylboronic acids was reported using the same catalytic system using pyridine–carboimine ligand as ours

after we completed our work and prepared the article [19].

2. Experimental

2.1. Materials

FSM-16 [20] was supplied from Toyota Central Laboratory. 3-Aminopropyltrimethoxysilane was purchased from Aldrich, Japan. All chemicals were used as received without further purification.

2.2. Measurements

The catalysts were characterized by powder X-ray diffraction (XRD), sorption measurement, FT-IR spectroscopy, inductively coupled plasma atomic emission spectroscopy (ICP), and thermal analysis (TG/DTA). X-ray diffractograms were recorded on a Shimadzu XRD-6000 diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). Nitrogen adsorption–desorption isotherms were obtained at 77 K using a Belsorp 28SA apparatus (Bel, Japan). TG/DTA measurement was performed on a Shimadzu DTG-50 apparatus. IR spectra were recorded on a Nexus 470 (Thermo Nicolet) FT-IR spectrometer by KBr technique. The solid NMR spectra (¹³C and ²⁹Si MAS NMR) were obtained using a Varian Inova 400 FT-NMR spectrometer. Solution NMR spectra of the organic compounds were recorded on a JEOL α -400 FT-NMR spectrometer. Elemental analysis by ICP was performed using a JICP-PS-1000UV (Leeman Labs. Inc.) analyzer.

2.3. Catalyst preparation

2.3.1. Surface modification of FSM-16 with 3-aminopropyltrimethoxysilane

FSM-16 (1.0 g) vacuum dried at 250 °C for 1 h was suspended in dry toluene (30 ml). Then, 1.35 mmol of 3-aminopropyltrimethoxysilane was added, and the mixture was stirred under reflux for 2 h. Toluene containing methanol was distilled off, toluene (10 ml) was added and the reflux was continued for another 0.5 h. 3-Aminopropylated FSM-16 was recovered by filtration, washed with toluene and dried at 40 °C over night [21].

2.3.2. Preparation of pyridine and quinoline–carboimine ligands on FSM-16

The reaction of 2-pyridinecarbaldehyde as well as 2-quinolinecarbaldehyde with 3-aminopropylated FSM-16 was performed as follows: 3-aminopropylated FSM-16 obtained above was suspended in ethanol (15 ml). To this suspension, corresponding carboaldehyde was added and the whole mixture was stirred at room temperature for 24 h under N₂ atmosphere. The functionalized FSM-16 was

filtered off, carefully washed with ethanol and dried at 40 °C over night [18].

2.3.3. Preparation of palladium complex on FSM-16 with PdCl₂

Appropriate amount of PdCl₂ was dissolved in acetone. One drop of conc. HCl was added to improve solubility of PdCl₂. Then, functionalized FSM-16 was added to the prepared solution, and the suspension was stirred at room temperature for 4 h. Physisorbed palladium species was removed by extraction with refluxing dichloromethane for 5 h.

2.4. Catalytic reactions

2.4.1. Heck vinylation

In a typical reaction, aryl halide (2 mmol), methyl acrylate (5 mmol), base (2 mmol), solvent (5 ml), and the catalyst were taken in a round bottom flask. The mixture was degassed by argon flow followed by heating at 130 °C for required time. After the reaction, the reaction mixture was cooled to room temperature, and allowed to stand for about 10 min until the solid materials precipitated. Then, the liquid phase containing NMP, triethylamine, substrates, products and HX-base salt was separated by decantation, and analyzed by GC using biphenyl as an internal standard. Products were characterized by GC–MS analysis. The conversion was determined from the amount of aryl halide consumed in the reaction. For recycling studies, the catalyst was separated from the reaction mixture by filtration, washed with dichloromethane to remove organic compounds, and re-used for the reaction after drying at 90 °C overnight.

2.4.2. Suzuki reaction

Aryl halide (2.5 mmol), phenylboronic acid (3.75 mmol), potassium carbonate as base (5 mmol), benzene as solvent (5 ml) and the catalyst were taken in a round bottom flask. The mixture was degassed by argon flow followed by heating at 80 °C for required time. GC analysis of reaction mixture

was performed as described above for the Heck reaction using cumene as internal standard.

Products of the Suzuki coupling of 9-bromoanthracene, 9,10-dibromoanthracene, and 4-bromobiphenyl were purified by column chromatography (silica gel, eluent: hexane/benzene = 9/1), and their structures were confirmed by ¹H and ¹³C NMR spectroscopies (CDCl₃ solvent).

3. Results and discussion

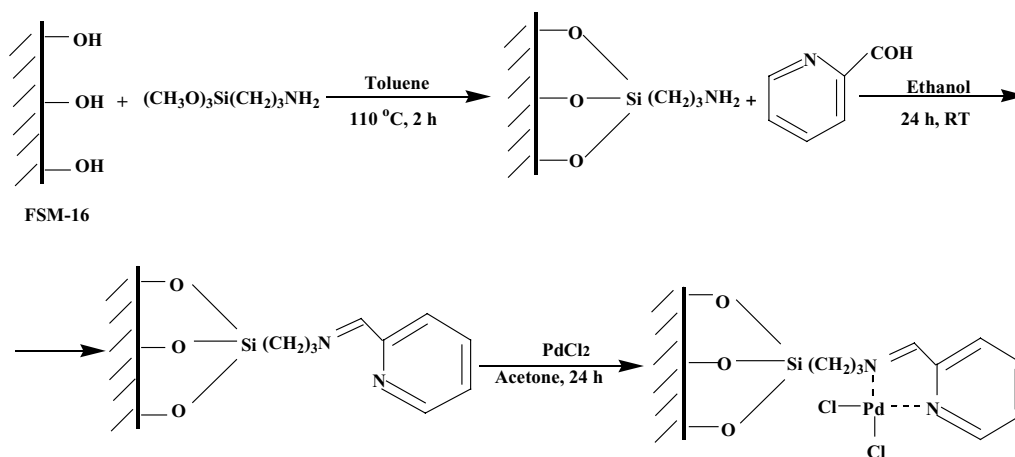
3.1. Preparation and characterization of catalysts

Immobilization of palladium complexes on FSM-16 consists of the following steps as illustrated in Scheme 1:

- surface modification of FSM-16 with 3-aminopropyltrimethoxysilane;
- preparation of pyridine and quinoline–carboimine ligands on FSM-16; and
- preparation of palladium complex on FSM-16 with PdCl₂.

XRD patterns of calcined FSM-16, palladium complexes with pyridine–carboimine (Pd-2PC) and quinoline–carboimine (Pd-2QC) functionalized FSM-16 are shown in Fig. 1. X-ray diffraction pattern for FSM-16 shows characteristic low angle peaks attributed to *d*₁₀₀, *d*₁₁₀, and *d*₂₀₀ reflections assuming a hexagonal lattice [22]. As for the catalysts Pd-2PC and Pd-2QC, *d*₁₁₀ and *d*₂₀₀ peaks became less prominent, while the *d*₁₀₀ peak was almost unchanged. These results indicate that periodicity of FSM-16 was maintained well in the palladium catalysts. Thus, immobilization of palladium complexes on FSM-16 did not significantly affect the structure of ordered mesoporous silica.

Physicochemical properties of the catalysts are listed in Table 1. Nitrogen isotherms of Pd-2PC and Pd-2QC catalysts are of the type IV as it is typical for mesoporous materials (Fig. 2). Decrease in their surface areas in comparison with



Scheme 1. Preparation of catalyst.

Table 1
Physicochemical properties of catalysts

Catalyst	Surface area ($\text{m}^2 \text{g}^{-1}$) ^a	V_p ($\text{cm}^3 \text{g}^{-1}$) ^b	Amount of ligand ($\text{mmol g}_{\text{cat}}^{-1}$) ^c	Pd content (wt.%) ^d
FSM-16	997	0.472	–	–
Pd-2PC	456	0.412	1.08	1.9
Pd-2QC	420	0.357	0.99	2.2

^a BET method.

^b Kelvin equation.

^c TG analysis.

^d ICP analysis.

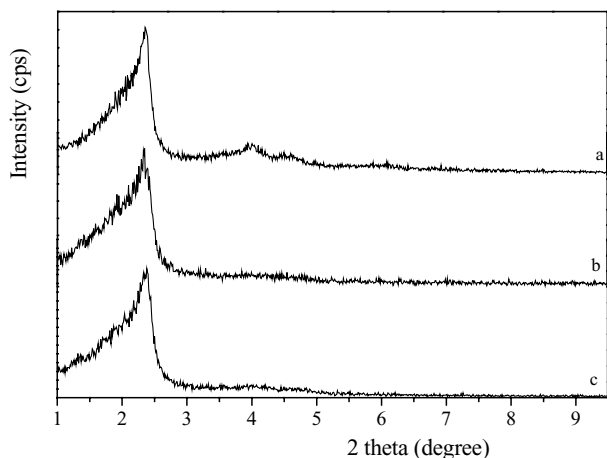


Fig. 1. XRD patterns of: FSM-16 (a); Pd-2PC (b) and; Pd-2QC (c).

FSM-16 is due to surface modification. No essential difference in pore volume among FSM-16, pyridine–carboimine and quinoline–carboimine on functionalized FSM-16 were observed.

TG/DTA was used to determinate the amount of ligand incorporated into 3-aminopropylated FSM-16. TG/DTA profile of 2QC is shown in Fig. 3. Weight loss is mainly divided into three temperatures regions: below 150 °C, 150–620 °C and above 620 °C. Weight loss during heating from 25 to

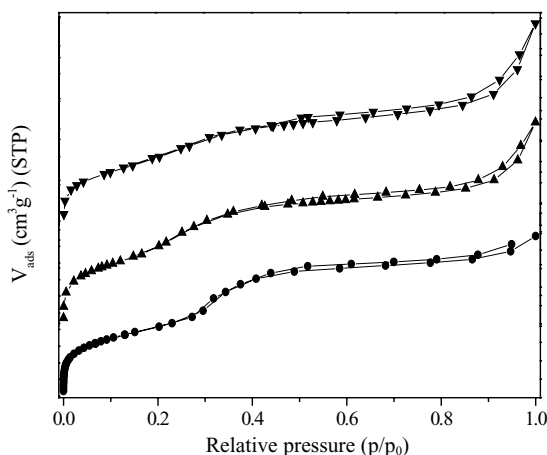


Fig. 2. N_2 adsorption–desorption isotherms for FSM-16, Pd-2PC and Pd-2QC samples. (●) FSM-16; (▲) Pd-2PC; (▼) Pd-2QC.

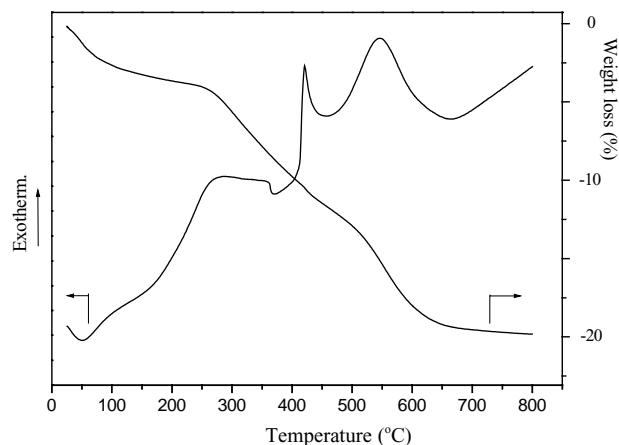


Fig. 3. TG-DTA profile of 2QC.

150 °C was assigned to the loss of loosely bound water (3.7%). Large weight loss of around 16–19% at temperature between 470 and 620 °C was due to the decomposition of covalently bonded organics. Similar result was obtained for 2PC.

The introduction of a 3-aminopropyl group on FSM-16 was confirmed by ^{29}Si and ^{13}C CP MAS NMR and FT-IR spectroscopies. ^{29}Si MAS NMR spectra of unmodified FSM-16 and 3-aminopropylated FSM are shown in Fig. 4. As for unmodified FSM (Fig. 4a), two distinct resonances at –109.9 and –101.3 ppm were observed for the siloxane units ($Q^n = \text{Si}(\text{OSi})_n(\text{OH})_{4-n}$, $n = 3, 4$). After

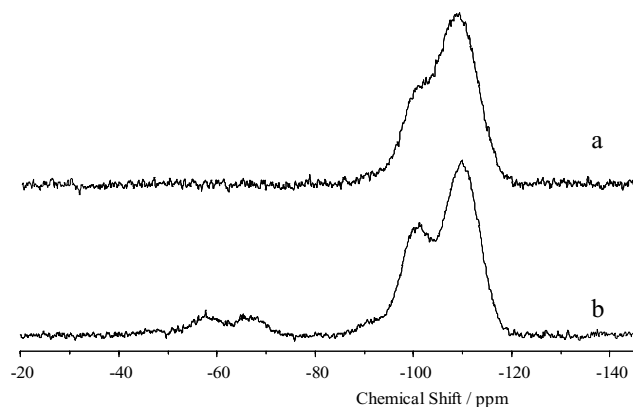


Fig. 4. ^{29}Si MAS NMR spectra of unmodified FSM-16 (a) and 3-aminopropylated FSM (b).

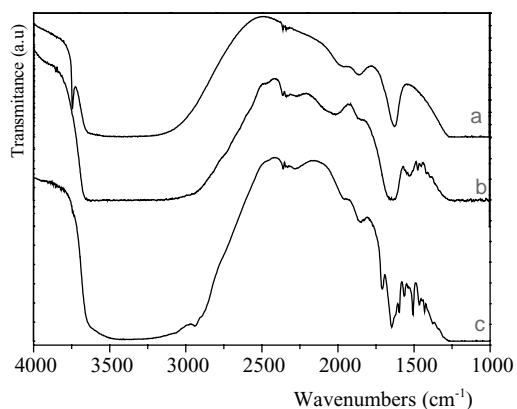


Fig. 5. FT-IR spectra at room temperature in region 4000–1000 cm^{-1} of FSM-16 (a) (peaks at 3746 and 1625 cm^{-1}), AMP-FSM (b) (peaks at 1635, 1527, 1474, 1448 cm^{-1}) and functionalized 2QC-FSM (c) (peaks at: 1706, 1646, 1598, 1563, 1506 and 1430 cm^{-1}).

modification of FSM-16 with 3-aminopropyltrimethoxysilane, two new resonances appeared at lower field (Fig. 4b) that are assigned to surface bonds of silicon: $T^3 = \text{RSi}(\text{OSi})_3$ at -66.9 ppm and $T^2 = \text{RSi}(\text{OSi})_2(\text{OH})$ at -57.8 ppm [23]. The nature of the 3-aminopropyl group incorporated into FSM-16 was confirmed by ^{13}C CP MAS NMR spectra, in which three typical resonances for 3-aminopropyl group were observed (chemical shifts: 8.8, 21.7 and 42.6 ppm).

Fig. 5 shows FT-IR spectra of FSM-16 in each step of the preparation of immobilized carboimine in the range of 4000–1000 cm^{-1} . IR spectra of freshly calcined FSM-16 have an adsorption band at 3746 cm^{-1} , which is ascribed to the OH stretching vibrations of isolated (single) silanol groups [24], and a band at 1625 cm^{-1} , which is assigned to the OH bending vibration of adsorbed water [25]. The band at 3746 cm^{-1} disappeared after the aminopropylation, indicating that single silanol groups reacted with the silane. The aminopropylation of FSM-16 was also confirmed by ^{29}Si MAS NMR spectra (as discussed above). Nevertheless, attempts to identify the small number densities of amines in the modified FSM-16 by IR spectroscopy proved inconclusive (no peak assigned to the amino group (ν_{NH}) is observed in the spectra of 3-aminopropylated FSM-16 (Fig. 5b) and a series of peaks that appeared at 1450–1530 cm^{-1} are due to C–H stretches of hydrocarbon chain (ν_{CH_2}). On the con-

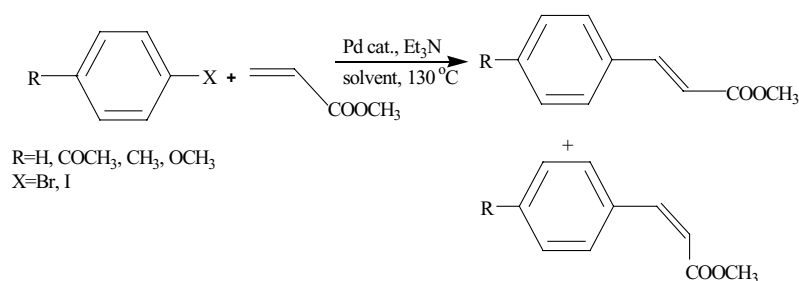
trary, carboimines formed by the reaction of carboaldehydes (2-quinolinecarbaldehyde and 2-pyridinecarbaldehyde, respectively) with the amino group on FSM-16 have strong characteristic IR bands, which are easy to follow via IR spectra unlike the case of amino group. The formation of quinoline–carboimine bases by the reaction of 2-quinolinecarbaldehyde with 3-aminopropylated FSM-16 is demonstrated by the presence of the absorption peak at 1646 cm^{-1} in FT-IR spectra (Fig. 5c), assignable to the C=N double bond. A shoulder at 1706 cm^{-1} is probably due to adsorbed unreacted aldehyde. Sharp peaks at 1600–1500 cm^{-1} correspond to C=C stretches of quinoline.

3.2. Heck vinylation

The activity of palladium-complexes immobilized on FSM-16 (Pd-2PC and Pd-2QC) was tested in the Heck reaction of aryl halides, namely the reactivity of aryl iodides and aryl bromides with methyl acrylate in polar and non-polar solvents using triethylamine as a base (Scheme 2).

Polar aprotic solvents, such as *N,N*-dimethylformamide (DMF), *N*-methylpyrrolidone (NMP) and acetonitrile are commonly used for homogenous Heck reactions [1,2]. They provide high rates due to stabilization of active palladium species by forming clusters coordinated by solvent [26]. Efficiency of polar solvents was also confirmed in comparison with non-polar ones for the Heck vinylation of 4-bromoacetophenone with methyl acrylate over Pd-2QC catalyst (Fig. 6). Conversion of 4-bromoacetophenone reached 100% in polar solvents (NMP and DMF) after 2 h. The conversion of 4-bromoacetophenone was 20% after 24 h reaction in non-polar solvents (mesitylene and *p*-xylene). However, no increase in the conversion of 4-bromoacetophenone was observed by increasing the reaction time to 48 h in the case of non-polar solvents.

Conversions of various aryl iodides and aryl bromides in their reaction with methyl acrylate over Pd-2QC and Pd-2PC catalysts are listed in Table 2. Both catalysts were active for aryl iodides and activated aryl bromides with 100% conversion in 1–5 h (Table 2, entries 1–5) and the products of the vinylation were highly selective (selectivity higher than 99% for the corresponding *trans*-stereoisomer was observed). Aryl bromides with electron-donating substituents ($-\text{OCH}_3$, $-\text{CH}_3$, $-\text{H}$) on the benzene ring were particularly



Scheme 2. Heck vinylation of aryl halides with methyl acrylate to methyl *trans*-3-arylacrylate and methyl *cis*-3-arylacrylate.

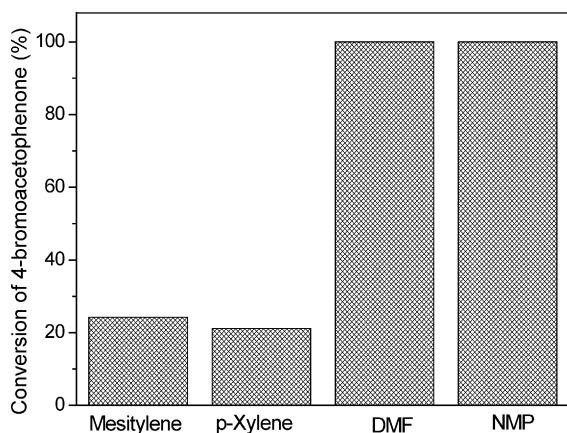


Fig. 6. Conversion of 4-bromoacetophenone in polar (DMF, NMP) and non-polar solvents (mesitylene, *p*-xylene). Reaction conditions: 130 °C, catalyst (Pd-2QC) 0.2 mol%, Et₃N as base 2 mmol, solvent 5 ml, reaction time; 24 h for non-polar solvents, 2 h for polar solvents.

sluggish in their activity (Table 2) with 10–30% conversion after 24 h (Table 2, entries 6, 8, 10). This trend is in agreement with the gradation of aryl bromides conversion in homogeneous catalysis [1].

Addition of quaternary ammonium salts is often used to enhance the reactivity and selectivity of the Heck reactions [12,27–30]. Bu₄NBr used as an additive (15 mol% based on aryl bromide) in the Heck vinylation of aryl bromides with electron-donating substituents over Pd-2PC and Pd-2QC catalysts increased effectively the reaction rate and yield of desired products (yield of coupling products 50–70% was obtained after 17 h reaction; Table 2, entries 7, 9, 11). To confirm the possibility of leaching of the palladium species, reaction mixture was filtered under hot conditions after 30 min reaction (bromobenzene conversion of 16% in the filtrate was determined by GC). Then, fresh methyl acrylate was added to the filtrate and the reaction was allowed to continue for 3 more hours. Bromobenzene conversion of 38% after 3 h reaction in filtrate indicates that significant

Table 2
Heck vinylation of aryl halides with methyl acrylate over Pd-2QC and Pd-2PC catalysts^a

No.	Substrate	Pd (mol%)	Time (h)	Conversion (%)	
				Pd-2QC	Pd-2PC
1	4-Iodoanisole	0.1	1	100	100
2	4-Iodoanisole	0.01	3	98	99
3	4-Iodotoluene	0.1	1	100	100
4	4-Bromonitrobenzene	0.1	1	95	90
5	4-Bromoacetophenone	0.1	1	51	46
6	Bromobenzene	0.2	24	32	30
7	Bromobenzene ^b	0.2	17	63	–
8	4-Bromotoluene	0.2	24	30	29
9	4-Bromotoluene ^b	0.2	17	68	–
10	4-Bromoanisole	0.2	24	19	13
11	4-Bromoanisole ^b	0.2	17	50	–

^a Reaction conditions: halide, 2 mmol; methyl acrylate, 2 mmol; catalyst (Pd against halide); Et₃N, 2 mmol; solvent, NMP; temperature, 130 °C.

^b 15 mol% Bu₄NBr based on aryl bromide was mixed as additive.

Table 3
Catalytic activity of Pd-2QC in Heck vinylation of bromobenzene with methyl acrylate^a

No.	Solvent	Pd (mol%)	Bu ₄ NBr (mol%)	Cycle	Conversion (%)
1	NMP	0.2	15	1	49.5
2		0.2	15	2	0.1
3	Toluene	0.2	15	1	4.5
4		0.2	60	1	22.8
5		0.2	100	1	21.7
6		0.52	100	1	42.3
7		0.52	100	2	0.5
8	H ₂ O–toluene (1:5)	0.2	30	1	0
9	1,4-Dioxane	0.2	15	1	3.6
10	H ₂ O	0.2	15	1	0

^a Reaction conditions: 130 °C; Et₃N, 2.5 mmol; bromobenzene, 2 mmol; methyl acrylate, 5 mmol; catalyst, Pd-2QC; 5 h.

amount of palladium reacts in homogeneous phase. Moreover, in the second cycle, only negligible (0.1% conversion, Table 3, entry 2) formation of methyl cinnamate is observed. These results show that the increase in the activity by adding Bu₄NBr was due to leaching of palladium into the solution. It has been reported that palladium species may react with polar solvents and an organic base to leach into the solution [12,14]. Consequently, some palladium species may react in homogeneous phase, especially at higher palladium loadings and leaching of palladium cannot be totally excluded when polar solvents was used. The Heck reaction of 4-iodoanisole with methyl acrylate with fresh catalyst (Pd-2QC, 0.05 mol%) gave the conversion of 44% after 30 min reaction in suspension, and 53% of conversion for the reaction in filtrate recovered from the first experiment after 5 h reaction. These results also support that the addition of Bu₄NBr strongly increases leaching of palladium.

The use of appropriate solvent systems has been investigated to suppress palladium leaching after the addition of quaternary ammonium salt. Table 3 shows the Heck vinylation of bromobenzene with methyl acrylate in various solvents using Bu₄NBr as additive. Very low activity of Pd-2QC catalyst was obtained in the solvent other than NMP under the same reaction conditions for NMP (Table 3, entries 3, 8–10). An increase in the amount of Bu₄NBr to the amount of bromobenzene together with increase in the amount of catalyst to 0.52 mol% of Pd in toluene led to significant increase of bromobenzene conversion (42%, Table 3, entry 6). Similarly, no activity of catalyst in the second cycle of Pd-2QC catalyst was observed in toluene (0.5% conversion, Table 3, entry 7). These results suggest that such increase in the conversion is accompanied by leaching of palladium into the solution by addition of Bu₄NBr.

Pd-2PC and Pd-2QC catalysts have shown high activity in the recycling experiments (Table 4) in the Heck vinylation of 4-bromoacetophenone with methyl acrylate. After the separation from reaction mixture by filtration, they were re-used in seven reaction cycles without significant loss of the activity.

Table 4

Recycling and re-use of Pd-2QC and Pd-2PC in reaction of 4-bromoacetophenone with methyl acrylate^a

Ligand	Conversion of 4-bromoacetophenone in cycle (%)						
	1	2	3	4	5	6	7
2QC	100	100	99	99	99	98	97
2PC	93	94	93	92	91	93	91

^a Reaction conditions: 4-bromoacetophenone, 2 mmol; methyl acrylate, 2 mmol; 130 °C; catalyst, 0.1 mol%; Et₃N, 2 mmol; NMP, 5 ml; 10 h.

Table 5

Suzuki coupling of aryl bromides with phenylboronic acid over Pd-2QC and Pd-2PC catalysts^a

No.	Substrate	Time (h)	Yield (%)	
			Pd-2QC	Pd-2PC
1	4-Bromonitrobenzene	1.5	100	98
2	4-Bromoacetophenone	1.5	91	83
3	4-Bromoanisole	1.5	64	50
4	4-Bromobiphenyl	16	43 ^b	32 ^b
5	9-Bromoanthracene	24	65 ^b	48 ^b
6	9,10-Dibromoanthracene ^c	16	50 (33) ^{b,d}	37 (35) ^{b,d}

^a Reaction conditions: aryl bromide, 2.5 mmol; phenylboronic acid, 3.75 mmol; catalyst, 0.55 mol% (Pd against halide); K₂CO₃, 5 mmol; solvent benzene; temperature, 80 °C.

^b Isolated yields.

^c 9,10-Dibromoanthracene, 2.5 mmol; phenylboronic acid, 6 mmol; K₂CO₃, 10 mmol; catalyst, 0.55 mol% (Pd against halide).

^d Yield of di-coupled product in the brackets.

3.3. Suzuki coupling

Table 5 summarizes the Suzuki coupling of aryl bromides with phenylboronic acid in benzene over Pd-2PC and Pd-2QC catalysts (Scheme 3). Potassium carbonate, rather than triethylamine, was used as a base promoter. Pd-2PC and Pd-2QC catalysts were active and selective catalysts for the Suzuki coupling as in the case of the Heck vinylation. The coupling reaction occurred in a short time under mild conditions to give the corresponding biphenyl derivatives in moderate to high yields for aryl bromides with electron-donating as well as electron-withdrawing groups. Coupling products were obtained quantitatively for aryl halides with electron-donating groups over Pd-2QC catalyst after 1.5 h (Table 5, entries 1 and 2), and the yield of coupling products was 40–60% (Table 5, entries 1–4) for aryl bromides with electron-withdrawing groups. The formation of biphenyl by homo-coupling of phenylboronic acid has been found to be less than 1%. These catalysts have shown catalytic activity also for the coupling of 9-bromoanthracene and 9,10-dibromoanthracene that are less reactive than mononuclear aryl bromides

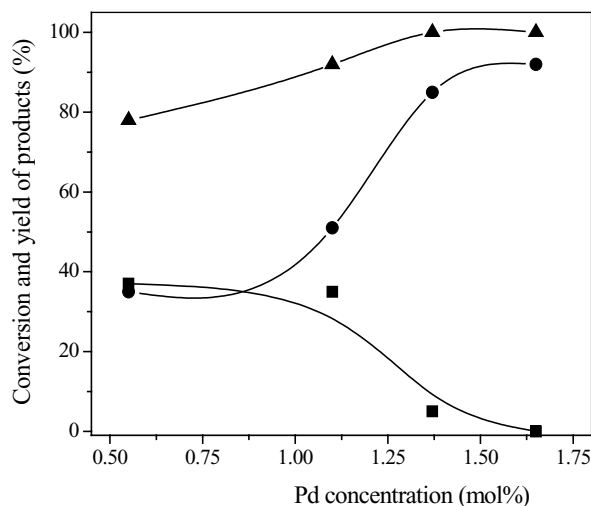
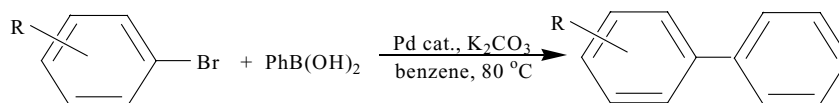


Fig. 7. Influence of catalyst concentration on the amount of coupling products of 9,10-dibromoanthracene with phenylboronic acid. Reaction conditions: 9,10-dibromoanthracene 2.5 mmol, phenylboronic acid 6 mmol, K₂CO₃ 10 mmol, catalyst Pd-2PC (Pd against halide), benzene 5 ml, 80 °C. Legend: (▲) conversion; (■) yield of 9-phenyl-10-bromoanthracene; (●) yield of 9,10-diphenylanthracene.

with a yield of desired products from 40 to 65% (Table 5, entries 5 and 6). Coupling of 9,10-dibromoanthracene with phenylboronic acid gave a mixture of mono- and di-coupled products. The influence of catalyst concentration on the di-coupling of 9,10-dibromoanthracene is shown in Fig. 7. Although the increase in the catalyst concentration to 1.1 mol% resulted in the increase in the yield of 9,10-diphenylanthracene (yields of 9,10-diphenylanthracene were 35% for Pd 0.55 mol% and 51% for Pd 1.1 mol%), mono-coupling product was still formed in 36% yield. Further increase in the catalyst concentration to 1.37 mol% increased the yield of 9,10-diphenylanthracene to 85%. Moreover, only 5% yield of mono-coupled product was obtained. Thus, more than 1.37 mol% of Pd is required for complete di-coupling of 9,10-dibromoanthracene into 9,10-diphenylanthracene.

Our results achieved for the Suzuki couplings are comparable with those recently reported for the Suzuki reaction of various aryl halides with *p*-tolylboronic acid [31] using homogeneous palladium imidazole catalysts. Nevertheless, palladium catalysts with quinoline-carboimine as ligand can offer slightly higher conversions compared to the case of pyridine-carboimine. The same effect was observed in the case of methyl substituted 1-methylimidazole that gave slightly better results compared to 1-methylimidazole. Moreover, our results correlate very well with the latest re-



Scheme 3. Suzuki coupling of aryl bromides with phenylboronic acid.

ported results for the Suzuki reaction over a similar catalytic system [19] (yields coupling products near 100% within 2 h have been reported for aryl bromides with electron-withdrawing groups at 95 °C using 0.02 mmol of Pd and 50–70% for biaryls at 120 °C after 20 h), although we have used less amount of palladium (0.0129 mmol Pd) and the reaction was performed at lower temperature (80 °C).

4. Conclusions

Palladium with pyridine and quinoline–carboimines immobilized on FSM-16 (Pd-2PC and Pd-2QC) were found to be active and selective catalysts for the Heck vinylation of aryl iodides and activated aryl bromides with methyl acrylate as well as the Suzuki coupling of aryl halides with phenylboronic acid. These heterogenized catalysts were easily separable from reaction mixture by filtration. The recovered Pd-2PC and Pd-2QC catalysts were able to be used in more than seven reaction cycles without losing activity. In the case of less reactive aryl bromides, the addition of the quaternary ammonium salt increased catalytic activity of catalysts, but significant leaching of palladium into the solution has been observed.

These catalysts very effectively catalyzed the coupling reaction of aryl bromides with phenylboronic acid to give desired products in high yields. Moreover, they showed catalytic activity for the Suzuki coupling of more hindered substrates such as 9-bromoanthracene and 9,10-dibromoanthracene to give coupling products in 40–65% yield. Nevertheless, more than 1.37 mol% of Pd was required for complete di-coupling of 9,10-dibromoanthracene.

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