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Pyridinyl Functionalized MCM-48 Supported Highly Active Heterogeneous Palladium Catalyst for Cross-Coupling Reactions

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MCM-48 supported 2-pyridinylmethanimine Pd-catalyst was found to be a highly efficient catalyst in the Mizoroki-Heck, Suzuki-Miyaura and copper-free Sonogashira cross-coupling reactions of aryl halides in aqueous reaction conditions. The catalyst was efficiently promoted these coupling reactions with ppm level of palladium to afford the corresponding coupling products in up to 98% yield. The supported Pd-catalyst was readily recovered and reused several times without significant loss of its catalytic activity.

Keywords: Pyridinecarboxaldehyde, Mizoroki-Heck reaction, Suzuki-Miyaura reaction, Sonogashira reaction, Pd-Catalyst.

1. Introduction

Palladium is the most popular metal catalyst widely used in numerous organic syntheses due to their applications in organic synthesis [1–3] materials science [4] photochemistry [5], and in the pharmaceutical industry [6-10]. Among them, the Mizoroki-Heck [11-15], Suzuki-Miyaura [16-20], and Sonogashira [21-25] coupling reactions play important roles in modern synthetic chemistry. These cross-coupling reactions are generally proceed in the presence of a homogeneous palladium catalyst. One practical limit to perform homogeneous catalysis reactions is difficult to separate the product from catalyst and reuse of the catalyst. From the standpoint of environmentally benign organic synthesis, the development of highly active and easily reusable immobilized catalysts, solvent-free reactions are significant interest to chemists. To overcome these problems, chemists have investigated the employment of various heterogeneous palladium species [26, 27]. The development of heterogeneous metal supported on materials such as carbon [28] nanotubes [29, 30] graphene [31-33] silicates [34-37], polymers [38, 39], metal oxides [40, 41] and various hybrid nanocrystals composed of different materials have been reported [42-45]. Alternatively, metal complexes bound to a ligand anchored on a support have also been studied as a recyclable catalyst [46, 47]. Palladacycles have recently emerged as one of the most promising classes of catalysts or catalyst precursors in the Pd-catalyzed C-C bond formation reactions such as the Mizoroki-Heck [48-51], Suzuki-Miyaura [52-55], and Sonogashira reactions [56-58]. Nevertheless, only a few examples of Suzuki-Miyaura, Mizoroki-Heck, and Sonogashira reactions by using water as the solvent have been reported in the literature [59, 60]. The common strategy to prepare a heterogeneous catalyst consists of anchoring the conveniently modified transition metal complexes onto an insoluble support provided the anchoring procedure and maintains the intrinsic activity and selectivity of the catalytic center [61, 62].

Recently, mesoporous MCM materials with uniform nanosized pore diameters and high specific surface areas have become of high interest as inorganic supports [63-65]. MCM-41 silica has recently been used as a solid support for the immobilization of the catalysts [66, 67]. On the other hand, cubic-structured mesoporous MCM-48 silica has received less attention due to difficulties in the synthesis [68-70]. Owing to its unique three-dimensional pore structure, MCM-48 may be more advantageous than MCM-41. MCM-48 with three-dimensional nanosized pore networks and high specific surface areas would be highly interesting in this area. Herein, we report MCM-48 supported Pd-catalyzed Mizoroki-Heck, Suzuki-Miyaura and Sonogashira cross-coupling reactions where the quantitative products were achieved with 130 to 400 mol ppm of catalyst in aqueous reaction conditions. The ease preparation of the catalyst, its long shelf-life, its stability toward air, and its compatibility with a wide variety of aryl halides make it ideal for the above-mentioned reactions.

2. Experimental

2.1 General Information

All manipulations were performed under atmospheric conditions unless otherwise noted. Reagents and solvents were obtained from commercial suppliers and used without further purification. Water was deionized with a Millipore system as a Milli-Q grade. $PdCl_2$ was purchased from Aldrich chemical industries, Ltd. Proton nuclear magnetic resonance (^1H NMR, 500/400 MHz) and carbon nuclear magnetic resonance (^{13}C NMR, 125 MHz) spectra were measured with a JEOL JNM ECA-500/400 spectrometer. The ^1H NMR chemical shifts were reported relative to tetramethylsilane (TMS, 0.00 ppm). The ^{13}C NMR chemical shifts were reported relative to deuterated chloroform ($CDCl_3$ 77.0 ppm). Elemental analyses were performed on a Yanaco CHN Corder MT-6 elemental analyzer by the chemical analysis team in Rikagaku Kenkyūjo (RIKEN), Wako, Japan. Inductively coupled plasma atomic emission spectrometry (ICP-AES) was performed on a Shimadzu ICPS-8100 equipment by the chemical analysis team in RIKEN Wako, Japan. N_2 adsorption-desorption isotherms were measured with a BEL SORP mini II analyzer at liquid N_2 temperature. Surface area (S_{BET}) was calculated by the BET method, the pore volume (V_p) was determined by nitrogen adsorption at a relative pressure of 0.98, and average pore

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size (D) was determined from the desorption isotherms using the Barrett-Joyner-Halenda (BJH) method. XPS spectra were measured with an ESCALA 250 (Thermo Fisher Scientific K.K.) by the cooperative support team in RIKEN. The energy dispersive spectroscopy (EDX) was examined using JEM-2100F, Inha University, Korea. The gas chromatography-mass spectrometry (GC-MS) was measured by an Agilent 7860A/JEOL JMS-T100GC equipped with a capillary column (DB-Wax, 0.25 mm i.d. × 30 m or HP-1, 0.32 mm i.d. × 30 m). Thin layer chromatography (TLC) analysis was performed on Merck silica gel 60 F_{254}. Column chromatography was carried out on silica gel (Wakogel C-300).

2.2 Preparation of the MCM-48 silica

MCM-48 silica was prepared according to the literature method [71]. The resultant silicate mixture was stirred for 1 h at room temperature and the samples were then collected by filtration and transferred to a Teflon lined steel vessel. The sample was then heated at 100 °C for 4 days. The mixture was cold at room temperature and the precipitated products were washed with DI water and calcinated at 500 °C for 8 h. The MCM-48 was characterized by XRD and TEM.

2.3 Preparation of the 3-aminopropylated MCM-48 silica 1

Fresh calcinated MCM-48 silica (1.0 g) was added to a solution of 3-(aminopropyl)triethoxysilane (0.65 mmol) in toluene (20 mL). The mixture was stirred at 105 ºC for 12 h. The amino functionalized MCM-48 silica **1** was collected by filtration, washed repeatedly with CH_2Cl_2, and dried under vacuo at 70 ºC. Weight gain showed that 0.43 mmol of aminopropyl moiety was immobilized on 1.0 g of MCM-48 silica **1**.

2.4 Preparation of the MCM-48 supported 2 pyridinylmethanimine

To a stirred solution of 2-carboxypyridine (0.5 mmol) and Et_3N (0.5 mmol) in toluene (25 mL) was added **3**-aminopropylated MCM-48 silica **1** (1 g, 0.43 mmol). The mixture was stirred at 50 ^{o}C for 3 h. After filtration, the powder was washed several times with methylene chloride and dried under vacuum at 70 ^{o}C to give 3-aminopropylated MCM-48 silica supported pyridinylmethanimine **2**. Weight gain showed that 0.38 mmol of 2-carboxypyridine was immobilized on 1.0 g of mesoporous MCM-48 silica **2**.

2.5 Preparation of the MCM-48 supported Pd-catalyst 3

To a stirred solution of **2** (1 g, 0.38 mmol) in CH_2Cl_2 (25 mL) was added 0.3 mmol of $PdCl_2$ and stirred at 50 °C for 6 h. The MCM-48 supported Pd catalyst was then collected by filtration and washed with CH_2Cl_2 and methanol. After drying in vacuo at 80 °C, the MCM-48 supported Pd-catalyst **3** was obtained as a reddish color solid. Weight gain and ICP analyses showed that 0.26 mmol of Pd was immobilized onto 1.0 g of MCM-48 supported **3**.

2.6 General procedure for the Heck reaction

All reactions were carried out in a 4 mL glass vial equipped with a Teflon screw cap. A mixture of aryl halide (1 mmol), olefin (1.2 mol equiv), Na_2CO_3 (2 mol equiv), and the Pd catalyst **3** (0.5 mg, 0.013 mol%, 130 mol ppm) in aqueous DMA (1:1) was stirred at 130 °C for 5 h, and monitored periodically by GC analysis. After completion of the reaction, it was cold at room temperature and diluted with EtOAc. The immobilized Pd-catalyst **3** was separated by filtration and washed by EtOAc. The organic layer was washed by H_2O, brine, dried over $MgSO_4$ and evaporated under reduced pressure. The residue was purified by short column chromatography on silica gel eluted with *n*-hexane/EtOAc afforded the desired coupling products in 87-96% isolated yields.

2.7 General procedure for the Suzuki reaction

A mixture of aryl halide (1 mmol), boronic acid (1.1 mol equiv), K_2CO_3 (2 mol equiv), and the Pd-catalyst **3** (0.013-0.025 mol%) in aqueous ethanol (1:1) was stirred at 90 ºC for 5 h. The reaction was monitored with GC until the complete consumption of the aryl halide. The Pd-catalyst **3** was separated by filtration and the reaction mixture was diluted with H_2O and EtOAc. The organic layer was separated, dried over $MgSO_4$ and evaporated under reduced pressure. The residue was purified by short column chromatography on silica gel to give the corresponding coupling products in up to 96% yield.

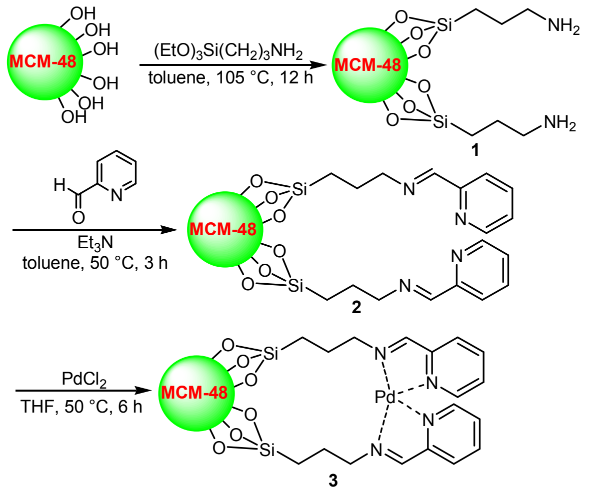
2.8 General procedure for the Sonogashira reaction

Aryl halide (1 mmol), phenylacetylene (1.1 mol equiv), piperidine (2 mol equiv) and the Pd-catalyst **3** (0.013-0.025 mol%) was stirred at 80 °C for 4 h and the reaction progress was monitored periodically by GC analysis. The reaction mixture was cold at room temperature and diluted with EtOAc and the immobilized Pd-catalyst was separated by filtration. The organic layer was washed by H_2O, dried over $MgSO_4$ and solvent was evaporated under reduced pressure. The residue was purified by short column chromatography on silica gel eluted with *n*-hexane/EtOAc to afford the corresponding coupling products in up to 96% yield.

3. Results and discussion

3.1 Characterization of the MCM-48 supported Pd-catalyst 3

The immobilization of Pd-catalyst onto nanostructured mesoporous MCM-48 silica was performed in three steps (Scheme 1). Treatment of MCM-48 silica with (3-aminopropyl)triethoxysilane in refluxing toluene gave aminopropylated silica gel **1** (0.43 mmol, $(CH_2)_3NH_2$/g). The loading ratio of the aminoproplylated moiety can be adjusted by changing the amount of (3-aminopropyl)triethoxysilane in the immobilization process. The ^{13}C NMR is indicated that the bond formation between triethoxysilane and MCM-48 silica (Fig. 1c).



Scheme 1. Preparation of the MCM-48 supported heterogeneous Pd-catalyst **3**.

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Reaction of **1** with 1.16 equiv excess of 2-carboxypyridine in toluene at 50 ºC afforded MCM-48 supported 2-pyridinylmethanimine **2** (0.38 mmol/g). The MCM-48 supported Pd-catalyst **3** was prepared by treatment of **2** with $PdCl_2$ in CH_2Cl_2 at 50 °C for 6 h. Based on the inductively coupled plasma (ICP) analysis, the loaded Pd content was 2.71% (0.26 mmol/g). The TEM images were obtained before (Fig 1a) and after (Fig. 1b) modification of the MCM-48 silica. Both images showed the hexagonal symmetry of the pore arrays is conserved after immobilization of the Pd-catalyst onto the MCM-48 silica. The 3D cubic structure and the pore arrays are conserved after the anchoring of the MCM-48 silica, which is also confirmed by XRD (Fig. 1d). The fresh MCM-48 shows a strong diffraction peak and five small diffraction peaks for the 211, 220, 321, 400, 420 and 332 planes. The presence of Pd $3d_{3/2}$ (343 eV) and Pd $3d_{5/2}$ (337 eV) peaks in XPS image (Fig 1e) suggested that the successful incorporation of the Pd(II) onto the MCM-48 supported Pd-catalyst **3**. Moreover, EDX image also revealed that the presence of Pd-metal onto the Pd-catalyst **3**. The presence of guest moieties on the mesoporous framework of MCM-48 resulting in the decrease of intensity of the peaks. However, the surface area, pore volume and pore size decreased due to the grafting of organic moieties onto the mesoporous MCM-48 silica (Table 1).

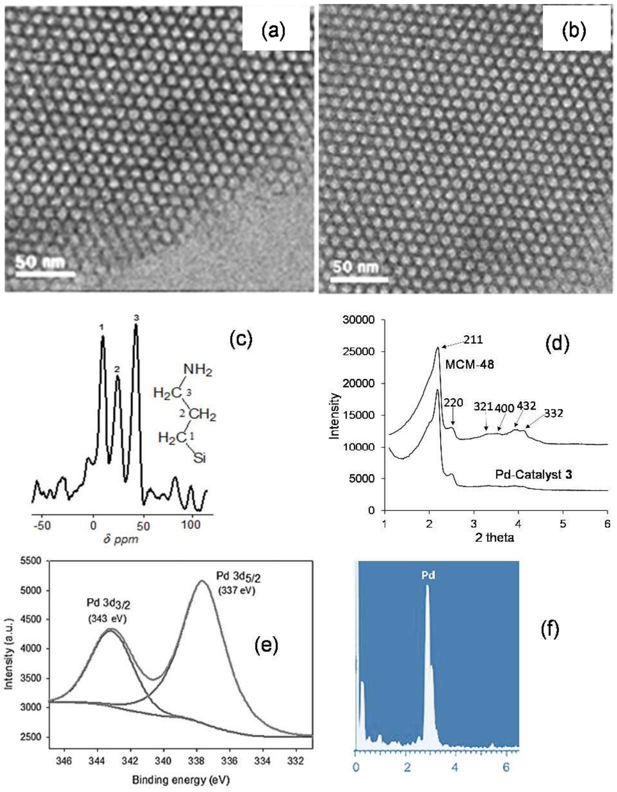


Fig. 1 (a) TEM image of Parent MCM-48; (b) TEM image of MCM-48 supported Pd-catalyst **3**; (c) ^{13}C NMR of MCM-48 supported **1**; (d) XRD of MCM-48 and Pd-catalyst **3**; (e) XPS and (f) EDX image of **3**.

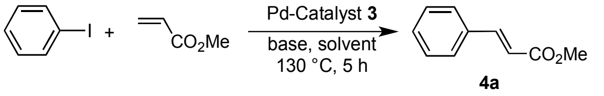
Table 1. Loading information of the MCM-48

Sample	Surface area (m^2/g)	Pore diameter (nm)	Pore volume (cm^3/g)	Functional group (mmol/g)
MCM-48	1250	3.25	0.71	-
1	865	2.82	0.62	0.43
2	790	2.35	0.48	0.38
3	465	2.12	0.35	0.26

3.2 Mizoroki-Heck reaction

The prepared MCM-48 supported heterogeneous Pd-catalyst **3** was first used in the Mizoroki-Heck coupling reaction of iodobenzene. The coupling of iodobenzene with methyl acrylate in the presence of Na_2CO_3 in aqueous DMA with 0.1 mol% of **3** was initially studied as a model reaction, which delivered 99% conversion with 96%, isolated yield of the product within 5 h without using any additive. (Table 2, entry 1). The reaction conditions were then systematically optimized, and the results are presented in Table 2. The catalyst loading could be decreased even further 0.013 to 0.01 mol% (130 to 100 mol ppm), where the catalyst was still efficiently promoted the coupling reaction (entries 2, 3). High conversion could be still maintained at 0.01 mol% of ultra-low Pd-catalyst loading (entry 3). Then we surveyed this coupling reaction using 130 mol ppm of **3** by changing solvents and bases. When the reaction was conducted in DMSO, NMP, DMF instead of DMA, in the presence of different bases similar results were obtained under the same reaction conditions (entries 4-10). In the presence of non-polar solvent octane, the reaction showed slow conversion rate compare to other polar solvents used (entry 11).

Table 2. Optimization of the Heck reaction[a]



Entry	Solvent (1:1)	Base	**3** (mol%)	Yield (%)[b]
1	DMA:H_2O	Na_2CO_3	0.1	99(96)[c]
2	DMA:H_2O	Na_2CO_3	0.013	98(95)[c]
3	DMA:H_2O	Na_2CO_3	0.01	86(82)[c]
4	DMA:H_2O	K_2CO_3	0.03	93
5	DMA:H_2O	NaOMe	0.03	93
6	DMA:H_2O	Na_2PO_4	0.03	94
7	DMA:H_2O	K_2PO_4	0.03	92
8	DMSO:H_2O	Na_2CO_3	0.03	91
9	NMP:H_2O	Na_2CO_3	0.03	92
10	DMF:H_2O	Na_2CO_3	0.03	93
11	Octane:H_2O	Na_2CO_3	0.03	78

[a] All reactions were carried out using 1 mmol of iodobenzene, 1.2 mmol of methyl acrylate, a catalytic amount of **3** and 2 mmol of base in 2 mL of solvent. [b] GC yield determined using *n*-dodecane as an internal standard and based on the amount of iodobenzene employed. [c] Isolated yield.

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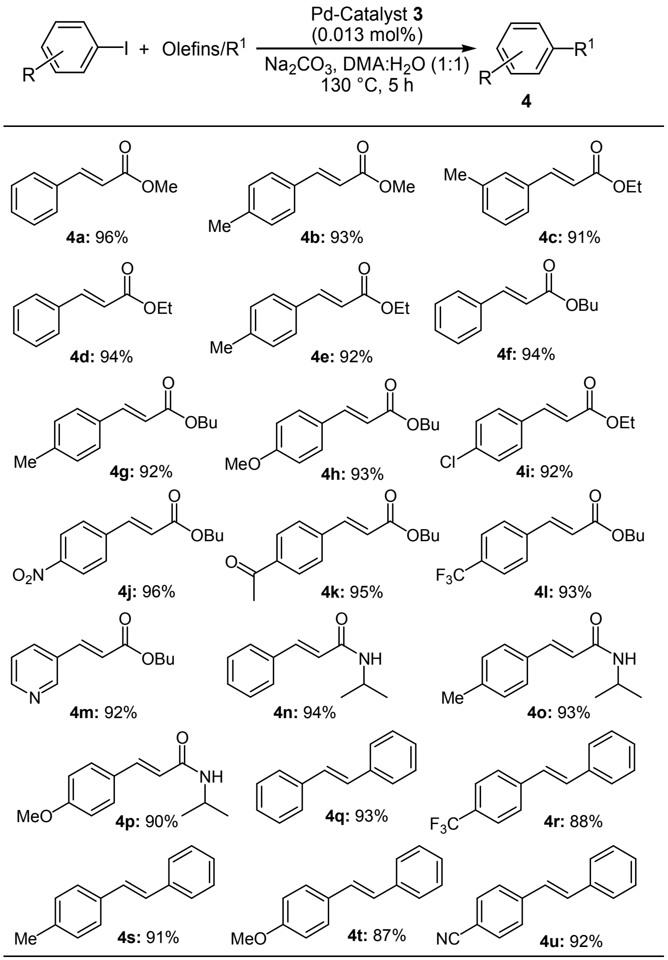
The complex is very stable to oxygen and moisture; less change of its activity was observed when the Pd-catalyst was exposed to air and water in the Heck reaction. With these results in hand, several Heck coupling of aryl halides with different olefins were then tested, and the results are summarized in Table 3. Aryl iodides react with methyl, ethyl, butyl acrylate, isopropyl acrylamide, and styrene, to give the corresponding coupling products with high yield. Excellent catalytic activity was observed in the couplings of deactivated iodotoluene, 4-iodoanisole (**4b-h**) as well as activated 4-chloroiodobenzene, 4-nitroiodobenzene, 4-iodoacetophenone and 4-trifluoromethyl iodobenzene with acrylates (**4i-l**). The deactivated aryl iodides possessing electron-donating group showed a slight drop in reactivity compared to the activated aryl iodides possessing electron-withdrawing group. The heterocyclic compound such as 3-iodopyridine was efficiently promoted the coupling reaction to give the corresponding predicts (**4m**) in 92% yield. Moreover, the catalyst showed outstanding activity in the coupling of iodobenzene with isopropyl acrylamide and styrene to give the corresponding coupling products in up to 94% yield (**4n-u**).

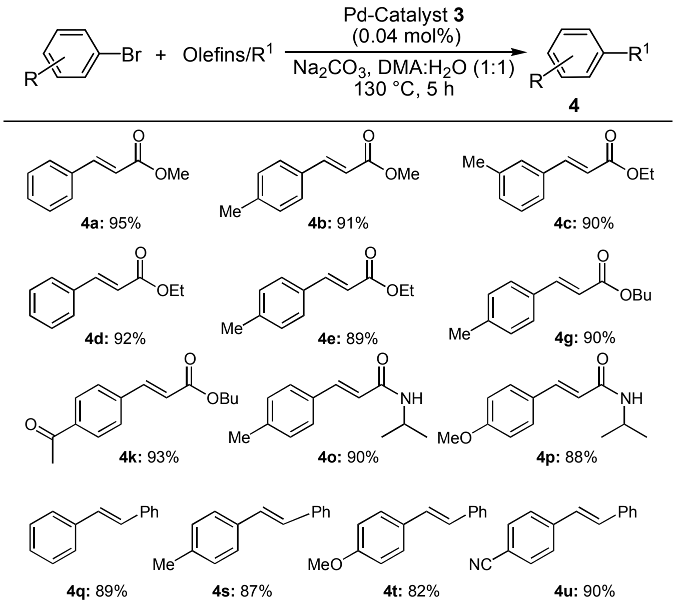
Table 3. Heck reaction of aryl iodides with olefins using Pd-catalyst **3**[a]



[a]All reactions were carried out using 1 mmol of aryl iodide, 1.2 mol equiv of olefin, 0.013 mol% of **3**, 2 mol equiv of Na_2CO_3, in 2 mL of DMA/H_2O (1:1) at 130 °C for 5 h.

The development of effective catalysts for the C-C bond formation of olefins with aryl bromides is highly important, since these are interesting substrates for industrial applications. Using diol-functionalized imidazolium ionic liquids along with $PdCl_2$, Cai et al. [72] observed moderate yields in the Heck reaction of aryl bromides with various olefins but the reaction rates were quite slow. By observing the promising catalytic activity of **3** for various aryl iodides, the catalyst was investigated for the coupling of aryl bromides with olefins. It was found that the catalyst showed outstanding activity in the coupling of aryl bromides with acrylates (Table 4, entries **4a-e**, **g**, **k**). A catalyst loading of 0.04 mol% was sufficient to achieve the high conversion within 5 h. Moreover, the catalyst also showed outstanding activity in the coupling of arylbromides with isopropyl acrylamide and styrene smoothly afforded the corresponding coupling products in up to 90% yield (**4o-q**, **s-u**). Recently, R. Pleixats et. al [73] have been reported hybrid silica materials containing di-(2-pyridyl)methylamine-palladium dichloride complex catalyzed (0.2 mol%) Heck reaction of activated aryl bromide (4-bromoacetophenone) with butyl acrylate in refluxing DMF with significance decreased of catalytic activity (1st run 100%, 4th run 47% yield). Hence, our catalyst (0.04 mol%) showed better activity (1st run 96%, 5th run 83% yield) compared to their hybrid silica supported Pd-complex.

Table 4. Heck reaction of aryl bromides with olefins using Pd-catalyst **3**[a]



[a]All reactions were carried using 1 mmol of aryl bromide, 1.2 mol equiv of olefin, 0.04 mol% of **3**, 2 mol equiv of Na_2CO_3, in 2 mL of DMA/H_2O (1:1) at 130 °C for 5 h.

3.3 Suzuki-Miyaura cross-coupling reaction

Heterogeneous silica-supported Pd-catalysts are extensively studied for the C-C bond formatin reaction of aryl halides with aryl boronic acids, often referred as Suzuki-Miyaura cross-coupling reaction [74]. The properties of such Pd-catalysts can be tuned by ligands, such as phosphines, amines, carbenes, dibenzylideneacetone, imidazol-2-ylidenes and so on [75]. Silica-immobilized *N*-heterocyclic carbine-Pd-complex has recently been reported as a catalyst for Suzuki cross-coupling reaction [76, 77]. By observing the high catalytic activity of MCM-48 supported Pd-catalyst **3** in the Heck reaction hence, we turned our attention to further testify our Pd-catalyst **3** for the Suzuki-Miyaura cross-coupling reaction. With the heterogeneous Pd-catalyst **3** (0.013 mol%) in hand, we then tested Suzuki-Miyaura cross coupling reaction of 4-iodoanisole with phenylboronic acid in aqueous ethanol at 90 ºC to for 5 h to give the corresponding biaryl

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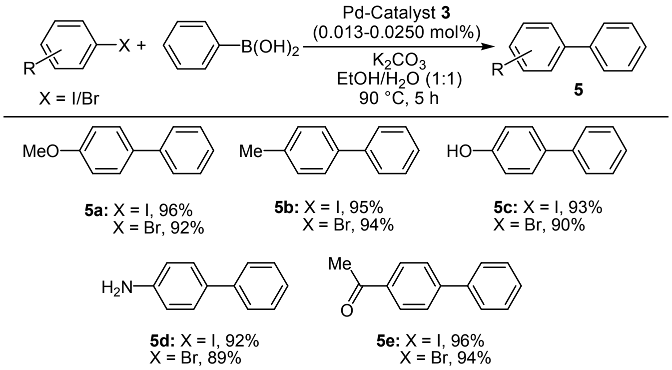
product in 96% yield (Table 5, **5a**). High catalytic activity was observed in the coupling of deactivated aryl iodides such as 4-iodotoluene, 4-iodophenol and 4-iodoaniline as well as activated 4-iodoacetophenone (**5b-e**). In order to investigate the scope of aryl halides in the coupling with phenylboronic acid, various aryl bromides were used in the coupling reaction. The coupling of activated or deactivated aryl bromides proceeded cleanly with 0.025 mol% of Pd to give the corresponding coupling product in up to 96% yield (**5a-e**). J. H. Clark [76] reported pyridinyl functionalized silica gel supported Pd(OAc)$_2$ catalyzed (0.4 mol%) Suzuki-Miyaura cross-coupling reaction of aryl bromide in *o*-xylene at 110 °C under N$_2$ atmosphere. The reaction proceeded smoothly but the catalytic activity was decreased (1st run 1.5 h 100%, 4th run 2.5 h 95% yield). Hence, we used 0.025 mol% of the catalyst which is sixteen times lower loading of catalyst. Moreover, we performed this cross-coupling reaction in aqueous condition at 90 °C with no significance loss of catalytic activity (1st run 5 h, 95%, 4th run 5 h 87% yield).

Table 5. Suzuki-Miyaura coupling reaction with MCM-48 supported Pd-catalyst **3**[a]

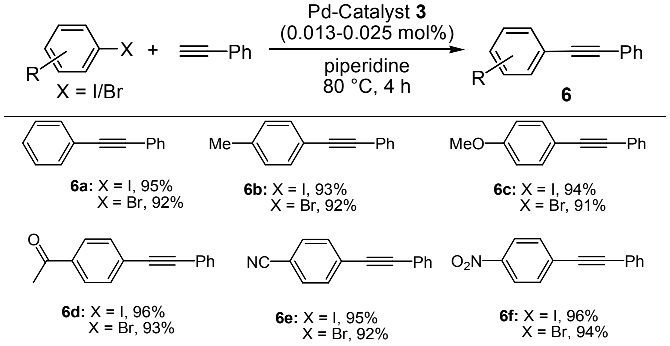


[a]All reactions were carried using aryl halide (1 mmol), Pd-catalyst **3** (0.013 mol% for aryl iodides, 0.025 mol% for aryl bromides), boronic acid (1.1 mol equiv), K$_2$CO$_3$ (2 mol equiv), EtOH/H$_2$O (1:1) at 90 °C for 5 h.

3.4. Heterogeneous Sonogashira cross-coupling reaction

Sonogashira cross-coupling of an aryl halides and a terminal alkynes are useful tool for the synthesis of aryl-substituted acetylene compounds [78]. This method has been widely used for the synthesis of natural products [79], biologically active molecules [80] nonlinear optical materials and molecular electronics [81] dendrimeric and polymeric materials [82] macrocycles with acetylene links [83] and polyalkynylated molecules [84]. With the heterogeneous Pd-catalyst **3** in hand, we investigated its catalytic activity towards Sonogashira coupling reaction of various aryl halides with phenylacetylene in the presence of piperidine. The results are summarized in Table 6. The supported Pd-catalyst **3** with 0.013 mol% efficiently promoted the Sonogashira coupling reaction of aryl iodides under solvent and copper free reaction conditions within 4 h. It is worth to note that the catalytic activities (0.025 mol%) in the coupling of bromobenzene and substituted bromobenzenes were also excellent (**6a-f**). R. Pleixats et. al [73] reported hybrid silica materials containing di-(2-pyridyl)methylamine-palladium dichloride complex catalyzed (0.2 mol%) Sonogashira cross-coupling reaction of 4-iodoanisole with phenylacetylene in refluxing DMF with significance decreased of catalytic activity (1st run 100%, 5th run 43% yield). Hence, we used 0.013 mol% of the catalyst which is fifteen times lower loading of catalyst. Moreover, we performed this cross-coupling reaction without presence of copper salt under solvent free reaction condition at 80 °C with no significance loss of catalytic activity (1st run 95%, 5th run 79% yield). Therefore, our catalyst showed better results compared to their report.

Table 6. SBA-16 supported Pd-catalyst **3** catalyzed Sonogashira reaction[a]



[a]All reactions were carried using 1 mmol of aryl halide, 1.2 mol equiv of phenyl acetylene, Pd-catalyst **3** (0.013 mol% for aryl iodides, 0.025 mol% for aryl bromides), 2 mol equiv of piperidine under solvent free reaction conditions at 80 °C for 4 h.

4. Recycling of the catalyst

The recycling of the catalyst is an important issue in heterogeneous catalysis system. Again, we turn our attention to reuse our Pd-catalyst. The catalyst was used five times without significance loss of its catalytic activity. The Pd-catalyst **3** was recovered and reused by the following steps: the reaction mixture was cooled to room temperature and diluted with EtOAc and filtered. The solid catalyst was washed with dichloromethane and dried at 80 °C under vacuum, and then used it in the next run without changing of the reaction conditions.

Table 7. Heck, Suzuki and Sonogashira reactions catalyzed by recycled Pd-catalyst **3**

Cycle	Mizoroki-Heck yield (%)[a]	Suzuki-Miyaura yield (%)[b]	Sonogashira yield (%)[c]
1	96	95	95
2	94	93	90
3	90	90	86
4	88	87	81
5	83 (<0.16 mol ppm Pd was leached out)	84	79

[a]Reaction was carried out according to Table 3, **4a** using 0.5% of **3.** [b]Reaction was carried out according to Table 5, **5b**, X = I, using 0.5% of **3**. [c]Reaction was carried out according to Table 6, **6a**, X = I, using 0.5% of **3**.

After carrying out the reaction, the catalyst had consistent catalytic activity as shown in Table 7. Only slight loss of catalytic activity was observed under the same reaction conditions as for initial run. The slight loss of catalyst activity after five cycles due to the loss of palladium from the support during reaction time (<0.16 mol ppm of Pd, ICP-AES). Thus, it is reasonable to believe that the immobilized catalyst can be repeatedly used for large-scale production without significant loss of its catalytic activity.

5. Heterogeneity test

In order to check the heterogeneity of the Pd-catalyst **3** we were carried out in a similar manner as the general procedure for Suzuki reaction (Table 5, **5a**, X = I). After 52% conversion the reaction mixture was filtered off at hot condition and the aqueous solution was heated under identical reaction conditions for 2 h and GC analyzed for the further conversions. No starting material was converted to the corresponding product after removal of the catalyst (Fig. 2). This experiment is indicated that the Suzuki-Miyaura reactions were followed a heterogeneous pathway.

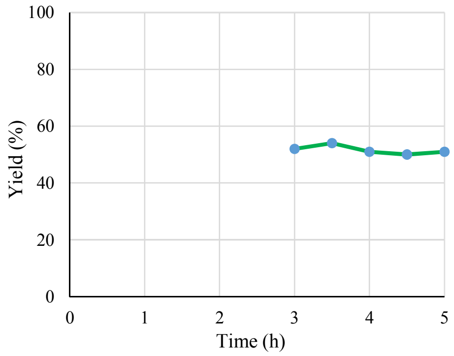


Fig. 2 Hot filtration test of Suzuki-Miyaura reaction (Table 5, **5f**).

6. Conclusions

In conclusion, we have developed nanostructured MCM-48 supported Pd-catalyst **3** for Mizoroki-Heck, Suzuki-Miyaura and Sonogashira cross coupling reactions. The heterogeneous Pd-catalyst was found to be highly active for these coupling reactions of aryl iodide and bromide in aqueous conditions. The Sonogashira cross coupling reaction was performed under copper and solvent-free reaction conditions. Furthermore, this catalytic system was simply recovered and reused several times without a significant loss of its activity.

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Notes and references

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