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Heck, Suzuki and Sonogashira Cross-Coupling Reactions using ppm Level of SBA-16 Supported Pd-Complex

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SBA-16 supported 1,2-diaminocyclohexane Pd-complex (100-500 mol ppm of Pd) was found to be an efficient catalyst in the palladium-catalyzed Mizoroki-Heck, Suzuki-Miyaura and copper-free Sonogashira cross-coupling reactions of aryl halides under mild reaction conditions. The Pd-complex was efficiently promoted all of these coupling reactions with apporpiate coupling partners to afford the corresponding coupling products with almost quantitative yield. The supported Pd-complex was readily recovered and used five tiemes without significance loss of its catalytic activity.

Keywords: 1,2-diaminocyclohexane, Mizoroki-Heck, Suzuki-Miyaura, Sonogashira, SBA-16, Pd-complex

1. Introduction

Palladium catalyst is the most popular transition metal catalyst widely used in numerous organic syntheses and synthetic transformations [1-3]. Palladium catalyzed Suzuki-Miyaura [4, 5], Mizoroki-Heck [6-8], and Sonogashira [9-11] cross-coupling reactions play important roles in modern synthetic chemistry. The original Heck, Suzuki, and Sonogashira reactions are generally proceed in the presence of homogeneous palladium catalyst. Purification of the product and reuse of catalyst are quite difficult when homogeneous catalyst is used. In this context, heterogeneous metal catalysts are emerging as an alternative to the homogeneous one that suffers various limitations both commercially and environmentally. On the otherhand heterogeneous catalysts have many advantages such as heat stability, reusability, and ease to purify the product. One common strategy to prepare a heterogeneous catalyst by covalently anchoring of transition metal complexes onto an insoluble support provided the anchoring procedure and maintains the intrinsic activity and selectivity of the catalytic center [12-14]. From these perspectives, heterogeneous metal catalysts are particularly well suited since the metal catalyst immobilized on a support could be easily removed by filtration leaving products virtually free of metal residues. A number of supports such as zeolite [15], metal oxides [16], silica-starch [17], polymers [18, 19], carbon nanofiber [20], clay [21], montmorillonite [22], and magnetic mesoporous silica [23-25] have been used. Alternatively, metal complexes anchored to a solid support have also been studied as a recyclable catalyst [26-30]. Palladacycles have recently emerged as one of the most promising classes of catalyst or catalyst precursors in the Pd-catalyzed C-C bond formation reactions such as Mizoroki-Heck [31, 32], Suzuki-Miyaura [33-36], and Sonogashira cross-coupling reactions [37-41]. Nevertheless, only a few examples of Suzuki-Miyaura, Mizoroki-Heck, and Sonogashira reactions were carried out using water as the solvent [42, 43].

Here we report the synthesis of SBA-16 supported Pd(II) complex and its application to the cross-coupling reactions of Mizoroki-Heck, Suzuki-Miyaura, and copper free Sonogashira reactions under aerobic conditions. Our approach is guided by three imperatives: (i) the solid support should be easily accessible; (ii) developing an efficient synthetic route for the facile conversion of the Heck, Suzuki, and Sonogashira coupling reactions; and (iii) the ligand anchored on the support should have thermal and air-stable at room temperature. The ease of preparation of the Pd-complex, 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 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 (^{1}H 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 ^{1}H 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 size (D) was determined from the desorption isotherms using the Barrett-Joyner-Halenda (BJH) method. The gas chromatography-mass spectrometry (GC-MS) was measured by an Agilent

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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 SBA-16 silica

SBA-16 silica was synthesized at room temperature under acidic condition using Puronic F127 ($EO_{106}PO_{70}EO_{106}$, M_w = 12.6 K) as a structure-directing agent (SDA) [44]. The acidic solution was made by adding 1.5 g of deionized (DI) water to 120 g of 2 M HCl solution at room temperature. Subsequently, 8.5 g of Tetraethoxysilane (TEOS) was added onto the solution and continued to stirring for 20 h. The reaction mixture was kept at 100 °C for 48 h. During this time the solid SBA-16 was produced under static conditions in a Teflon-lined vessel. The solid product was recovered and washed with DI water. The calcination was carried out at 500 °C for 6 h.

2.3 Preparation of the 3-chloropropylated SBA-16 silica 1

To a solution of 3-(chloropropyl)triethoxysilane (200 mg, 0.9 mmol) in toluene (15 mL) was added mesoporous silica SBA-16 (1.0 g) and the mixture was stirred at 105 ℃ for 12 h. The modified silica was collected by filtration and washed with CH_2Cl_2. After drying in vacuo at 80 ℃, 3-chloropropylated silica **1** was obtained. Weight gain showed that 0.73 mmol of 3-chloropropyl moiety was immobilized onto 1.0 g of SBA-16 mesoporous silica **1**.

2.4 Preparation of the SBA-16 supported bis-cyclodiamine 2

To a starred solution of **1** (1 g, 0.73 mmol) in CH_2Cl_2 (30 mL) was added 1.5 mol equiv of DIPEA and 1.3 mol equiv of 1,2-diaminocyclohexane at room temperature and stirred was continued for 8 h. The modified silica was then collected by filtration and washed with CH_2Cl_2. After drying in vacuo at 80 ℃, the SBA-16 supported diamine **2** was obtained as a lite yellow color solid. Weight gain showed that 0.40 mmol of cyclodiamine was immobilized on 1.0 g of SBA-16.

2.5 Preparation of the SBA-16 supported Pd-complex 3

To a solution of **2** (1 g, 0.4 mmol) in THF (20 mL) was added 0.2 mmol of $PdCl_2$ and stirred at 50 °C for 6 h. The SBA-16 supported Pd-complex was then collected by filtration and washed with THF and methanol. After drying in vacuo at 80 °C, the SBA-16 supported Pd-complex **3** was obtained as an orange color solid. Weight gain and ICP analyses showed that 0.25 mmol of Pd was immobilized on 1.0 g of SBA-16 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 (1.3 mol equiv), Na_2CO_3 (2 mol equiv), and the Pd-complex **3** (2.5 mg, 0.05 mol%, 500 mol ppm) in aqueous DMA (1:1) was stirred at 125 °C for 4 h. The reaction progress was monitored periodically by GC analysis. After completion of the reaction, it was cold at room temperature and diluted with ethyl acetate (EtOAc). The immobilized Pd-complex **3** was separated by filtration and washed with EtOAc. The organic layer was washed by H_2O, brine and 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 coupled products in in up to 97% yield.

2.7 General procedure for the Suzuki reaction

A mixture of aryl halide (1 mmol), arylboronic acid (1.1 mol equiv), K_2CO_3 (2 mol equiv), and the Pd-complex **3** (0.5 mg, 0.01 mol%, 100 mol ppm) in aqueous ethanol (1:1) was stirred at 90 ºC for 6 h. The reaction was monitored by GC until the complete consumption of the aryl halide. The Pd-complex **3** was separated by filtration and the reaction mixture was diluted with H_2O and ether. 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 product in up to 94% isolated yield.

2.8 General procedure for the Sonogashira reaction

Aryl halide (1 mmol), phenylacetylene (1.2 mol equiv), piperidine (2 mol equiv) and the Pd-complex **3** (1 mg, 0.02 mol%, 200 mol ppm) was stirred at 80 °C for 2 h and reaction progress was monitored by GC analysis. After completion of the reaction it was cold at room temperature and diluted with EtOAc and the immobilized Pd-complex **3** was separated by filtration. The organic layer was washed by H_2O and dried over $MgSO_4$. Solvent was evaporated under reduced pressure and 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 SBA-16 supported Pd-complex 3

The immobilization of Pd-complex **3** onto mesoporous SBA-16 silica was performed in three steps (Scheme 1). Treatment of SBA-16 silica with (3-chloropropyl)triethoxysilane in refluxing toluene gave chloropropylated silica **1** with 0.73 mmol/g of chloropropyl moiety. In the FT-IR spectra bands ware observed at 752 (C-Cl), 1074 (Si-O-Si), 1275 (O-Si-C), 1474 (C-C) and 2924 cm^{-1} (C-H) which indicate the presence of chloropropyl group onto the SBA-16. The loading ratio of the chloroproplylated moiety can be adjusted by changing the amount of (3-chloropropyl)triethoxysilane in the immobilization process. Reaction of **1** with 1.3 equiv excess of 1,2-diaminocyclohexane in CH_2Cl_2 at room temperature afforded SBA-16 supported 1,2-diaminocyclohexane **2** (0.4 mmol/g).

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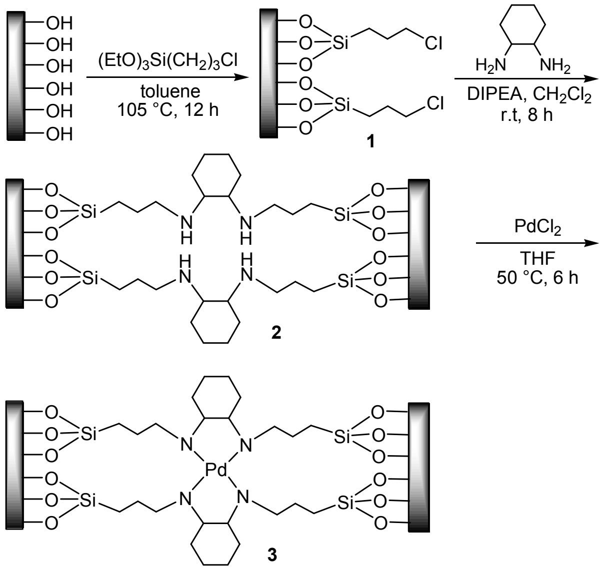


Scheme 1 Preparation of the SBA-16 supported heterogeneous Pd-complex **3**

The FT-IR bands of **2** ware observed at 1065 (Si-O-Si), 1152 (C-N), 1255 (O-Si-C), 1457 (C-C), and 2912 (C-H) cm^{-1} which indicate the incorporation of the cyclohexane moieties. The SBA-16 supported Pd-complex **3** was prepared by the treatment of **2** with $PdCl_2$ in THF at 50 °C for 6 h [45]. The content of Pd in the SBA-16 supported **3** was determined (2.46 wt%, 0.25 mmol/g) by weight gain and inductive coupled plasma emission spectrometer (ICP) analyses and no chlorine atom was found by the elemental analysis.

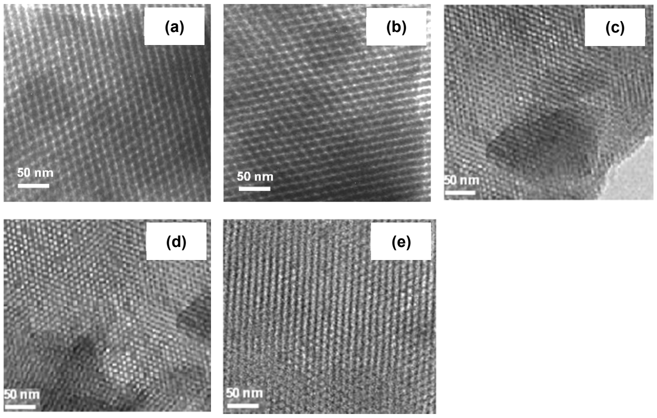


Fig. 1 (a) Parent SBA-16; (b) SBA-16 supported Pd-complex **3**; (c), (d), (e) After five cycles of Heck, Suzuki, and Sonogashira couplings respectively.

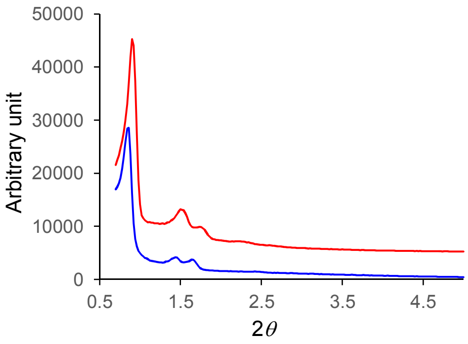


Fig. 2 Small angle XRD patterns of SBA-16 and SBA-16 supported Pd-complex **3**

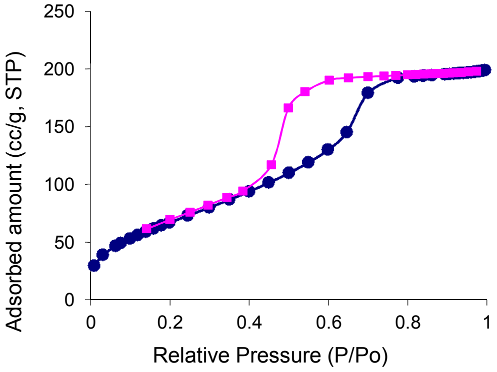


Fig. 3 Nitrogen absorption isotherm of SBA-16 supported Pd-complex **3**

The TEM images of SBA-16, Pd-complex **3** and after five runs of Pd-complex **3** are shown in Fig 1. For fresh SBA-16 (a), the highly ordered arrangements of mesopores reveal that the material consists of a high-quality body-centered cubic mesostructure. In Fig. (b), Pd-complex **3** presents a well-ordered mesopores structure characteristic of the SBA-16 material, which indicates the mesostructure of SBA-16 can be substantially conserved after grafting process. Moreover, the TEM images of reused Pd-complex **3** were also conserved the hexagonal symmetry of the pore arrays (c, d & e). The small-angle X-ray diffraction patterns of SBA-16 and the Pd-complex **3** are shown in Fig. 2. The fresh SBA-16 shows a strong diffraction peak at 110 and two small diffraction peaks at 200 and 211 planes. The intensity of these peaks are decreased due to incorporation of organic moieties onto the mesoporous SBA-16 but not collapse of the pore structure [46]. The structural information about the solid catalyst on a mesoscopic scale, the N_2 sorption isotherm plot for Pd-complex **3** show a type-IV isotherm with H_2 hysteresis loop, indicating that the Pd-complex **3** still maintains a good mesoporous cage-like structure (Fig. 3). The BET surface area and pore volume of SBA-16 is 820 m^2/g and 0.73 cm^3/g, whereas for Pd-complex **3**, these values decrease to 465 m^2/g and 0.28 cm^3/g, respectively (ESI, Table 1). The surface area, pore volume and pore size in Pd-complex **3** are reduced during the functionalization of organic moiety into the parent SBA-16 [47].

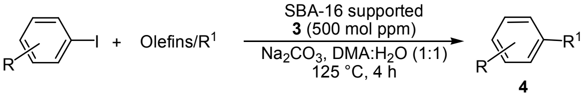
3.2 Mizoroki-Heck reaction

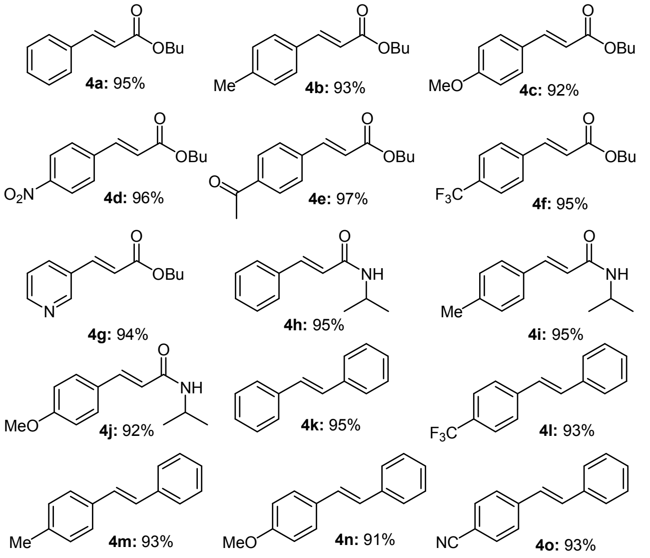
The prepared heterogeneous Pd-complex **3** was first used in Heck coupling reaction. The coupling of iodobenzene with butyl acrylate in the presence of Na_2CO_3 in aqueous DMA with 1.5 mol% of Pd-complex **3** was initially studied as a model reaction which delivered 100% conversion of the product within 0.8 h (ESI, Table 2, entry 1).

The catalyst loading could be decreased even further 1 to 0.01 mol%, when 1.5 to 5 h reaction times were required to complete the reaction (entries 2-6). High conversion could be still maintained at 0.01 mol% (100 mol ppm) of ultra-low Pd-complex **3** loading (entry 6). Solvents and bases effect on the activity of Pd-complex **3** were surveyed. When the reaction was conducted in DMF, DMSO, NMP instead of DMA, and using different bases similar results were obtained under the same reaction conditions (ESI, entries 7-13). The reaction showed slow conversion rate when non-polar solvent dodacane was used (entry 14). The complex is very stable to oxygen and moisture and less change of its activity was observed when the Pd-complex was exposed to air and water in the Heck reaction. With these results in hand, several Heck coupling of aryl iodides with different olefins were then tested, and the results are summarized in Table 1. Aryl iodides react with butyl acrylate, isopropylacrylamide, and styrene, to give the corresponding coupling products with high yield. Excellent catalytic activity was observed in the couplings of deactivated 4-iodotoluene (**4b**), 4- iodoanisole (**4c**) as well as activated 1-iodo-4-nitrobenzene (**4d**), 4- iodoacetophenone (**4e**) and 4-trifluoromethyl iodobenzene (**4f**) with butyl acrylates. 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 product (**4g**) in 94% yield. Moreover, the catalyst showed outstanding activity in the coupling of iodobenzene with isopropyl acrylamide and styrene to give the corrersponding coupling products in up to 95% isolated yield (**4h-o**).

The development of effective catalysts for the carbon-carbon 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. [48] observed moderate yields in the Heck reaction of aryl bromides with various alkenes but the reaction rates were quite slow. By observing the promising catalytic activity of **3** to various aryl iodides, the catalyst was then investigated for the coupling of aryl bromides and olefins. It was found that the Pd-complex **3** showed outstanding activity in the coupling of bromobenzene, 4-bromotoluene, 4-nitro-bromobenzene and 4-bromoacetophenone with butyl acrylate (Table 2, **4a**, **b**, **d**, **e**). A catalyst loading of 0.05 mol% (500 mol ppm) was sufficient to achieve the high conversion within 4 h reaction time.

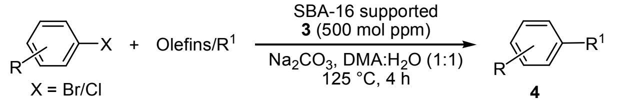
Table 1. Heck reaction of iodobenzene with olefins using Pd-complex **3**[a]

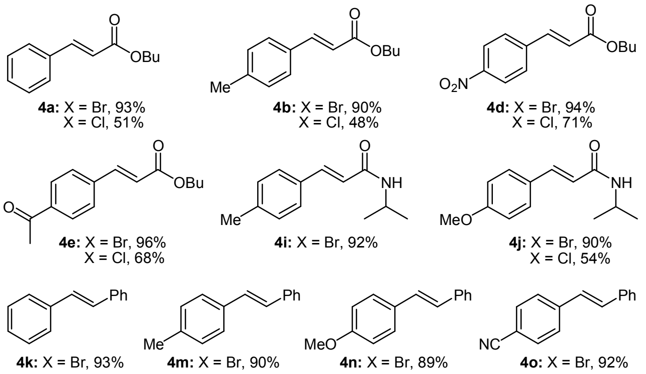




[a] All reactions were carried out using 1 mmol of aryl iodide, 1.3 mol equiv of olefin, 500 mol ppm of **3**, 2 mol equiv of Na_2CO_3, in 2 mL of DMA/H_2O (1:1) at 125 °C for 4 h.

Table 2. Pd-complex **3** catalyzed Heck reaction of aryl halides with olefins[a]





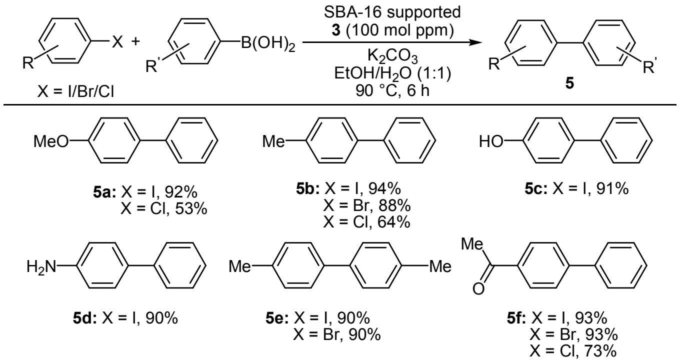
[a] All reactions were carried using 1 mmol of aryl halide, 1.3 mol equiv of olefin, 500 mol ppm of **3**, 2 mol equiv of Na_2CO_3, in 2 mL of DMA/H_2O (1:1) at 125 °C for 4 h.

The Heck reaction was also efficiently promoted of aryl bromides with isopropyl acrylamide and styrene to give the corresponding coupling products in up to 93% yield (**4i-k**, **m-o**). Interestingly, aryl chlorides were also promoted this coupling reaction under the similar reaction conditions (**4a**, **b**, **d**, **e**, **j**) with relatively poor yields. Recently, C. Nájera et al. [42] reported styrene-maleic anhydride co-polymer supported di(2-pyridyl)methylamine-palladium dichloride complex catalyzed Heck reaction of aryl bromides in water using 0.1 mol% of catalyst at 160 °C for 2 days. Here we used only 500 mol ppm of SBA-16 supported Pd-complex **3** which was efficiently promoted Heck reaction and exhibit higher catalytic activity compared to their newly prepared catalyst. Moreover, our catalyst also worked well in the aryl chloride systems.

3.3 Suzuki-Miyaura cross-coupling reaction

Heterogeneous silica-supported Pd-catalysts are extensively studied for the C-C bond formation reaction of aryl halides with arylboronic acids, often referred as Suzuki-Miyaura cross coupling reaction. The properties of such Pd-catalysts can be tuned by ligands, such as phosphines, amines, carbenes, dibenzylideneacetone, imidazol-2-ylidenes and so on. Silica-immobilized *N*-heterocyclic carbine Pd-complex has recently been reported as a catalyst for Suzuki cross-coupling reaction [49, 50]. By observing the high catalytic activity of SBA-16 supported Pd-complex **3** in the Heck reaction hence, we turned our attention to further testify our Pd-complex **3** for the Suzuki- Miyaura cross coupling reaction. With the heterogeneous Pd-complex **3** (0.01 mol%, 100 mol ppm) in hand, we then tested Suzuki-Miyaura cross coupling reaction of 4-iodoanisole with phenylboronic acid in aqueous ethanol at 90 ºC for 6 h provided the corresponding biaryl product in 92% yield (Table 3, **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-f**). 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 0.01 mol% of Pd-complex **3** to give the corresponding coupling products in up to 93% yield (**5b**, **e**, **f**). It should be noted that activated 4-chloroacetophenone and deactivated 4-chloroanisole and 4-chlorotoluene were also efficiently promoted the cross-coupling reaction to provide the corresponding coupling products in up to 73% yields (**5a**, **b**, **f**).

Table 3. Suzuki-Miyaura coupling reaction with Pd-complex **3**[a]



5a: X = I, 92%
X = Cl, 53%

5b: X = I, 94%
X = Br, 88%
X = Cl, 64%

5c: X = I, 91%

5d: X = I, 90%

5e: X = I, 90%
X = Br, 90%

5f: X = I, 93%
X = Br, 93%
X = Cl, 73%

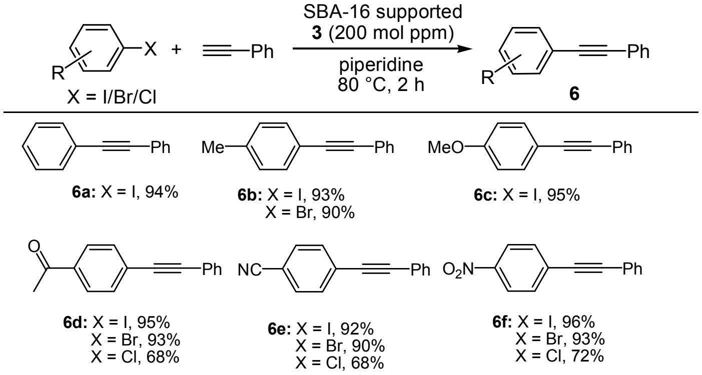
[a]Molar ratio: aryl halide (1 mmol), Pd-complex **3** (100 mol ppm), aryl boronic acid (1.1 mol equiv), K_2CO_3 (2 mol equiv), $EtOH/H_2O$ (1:1) at 90 °C for 6 h.

The SBA-16 supported heterogeneous palladium catalyst (0.01 mol%) showed better result compared to our previously reported silica-supported NHC-Pd (0.1 mol%) catalyst [51]. Moreover H. Yang et. al [24] reported that 0. 1 mol% of SBA-16 supported Pd-guanidine complex catalyzed Suzuki-Miyaura cross-coupling reaction of aryl iodides and bromides under aqueous conditions at 50 °C but their catalyst does not work well (8% yield) in the aryl chloride system also their catalyst quickly decreased the reactivity (1st run 99%, 35 min; 7th run 77%, 15 h). Herein our catalyst (100 mol ppm) efficiently promoted Suzuki reaction of aryl halides (iodo/bromo/chloro) using only 100 mol ppm of Pd without significance loss of catalytic activity (1st run 94%, 6 h; 5th run 87%, 6 h). From this data our SBA-16 supported Pd-complex **3** is superior than their SBA-16 supported Pd-guanidine complex.

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 [52, 53]. This method has been widely used for the synthesis of biologically active molecules [54] and nonlinear optical materials and molecular electronics [55]. With the heterogeneous Pd-complex **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 4. The supported Pd-complex **3** with only 0.02 mol% (200 mol ppm) efficiently promoted the Sonogashira coupling reaction of aryl iodides and bromides under solvent and copper free reaction conditions within 2 h (**6a-f**) reaction time. It is worth to note that the catalytic activities in the coupling of aryl chlorides were also excellent (**6d-f**). Recently B. Movassagh et al [56] reported Pd(II) Schiff base complex supported on multi-walled carbon nanotubes for Sonogashira cross-coupling reaction of aryl iodide using 1.2 mol% of Pd under copper free reaction conditions at 90 °C with prominent decreased of the catalytic activity (1st cycle 99, 4th cycle 82%). However our catalyst efficiently (200 mol ppm) promoted the Sonogashira reaction without significance loss of its catalytic activity (1st cycle 100, 4th cycle 96%).

Table 4. SBA-16 supported Pd-complex **3** catalyzed Sonogashira reaction of aryl halides[a]



6a: X = I, 94%

6b: X = I, 93%
X = Br, 90%

6c: X = I, 95%

6d: X = I, 95%
X = Br, 93%
X = Cl, 68%

6e: X = I, 92%
X = Br, 90%
X = Cl, 68%

6f: X = I, 96%
X = Br, 93%
X = Cl, 72%

[a]All reactions were carried using 1 mmol of aryl halide, 1.2 mol equiv of phenyl acetylene, 200 mol ppm of **3**, 2 mol equiv of piperidine under solvent free reaction condition at 80 °C for 2 h.

3.5 Recycling of the catalyst

The recycling of the catalyst is an important issue in heterogeneous catalysis system. Again, we turn our attention to reusability of our Pd-complex **3**. The complex was used five times without significance loss of its catalytic activity. The Pd-complex **3** was recovered and reused by the following steps: the reaction mixture was cold to room temperature and diluted with EtOAc and filtered. The solid catalyst was washed with EtOAc and dried at 80 °C under vacuum, and then used it in the next run without changing the reaction conditions. After carrying out the reaction, the catalyst had consistent catalytic activity as shown in Table 5. 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 case due to the loss of palladium (<0.18 ppm Pd, ICP-AES) from the support during the reaction. 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.

Table 5. Heck, Suzuki and Sonogashira reactions catalyzed by recycled Pd-complex **3**

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Cycle	Heck yield (%)[a]	Suzuki yield (%)[b]	Sonogashira yield (%)[c]
1	95	94	94
2	95	93	92
3	93	94	91
4	92	92	88
5	88 (<0.18 ppm Pd was leached out)	89	86

[a]Reaction was carried out according to Table 1, **4a**. [b]Reaction was carried out according to Table 3, **5b**, X = I). [c]Reaction was carried out according to Table 4, **6a**.

3.6 Heterogeneity test

In order to check the heterogeneity (Table 1, **4a**) of the Pd-complex **3** we were considered two experiments; (a) to determine the Pd content in the solution, a part of the filtrate was placed in a 50 mL crucible after removing the solvent it was calcined at 600 °C for 3 h. The residue was dissolved in 20 mL aqua-regia and diluted to 50 mL. The Pd leaching in solution was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) analysis. It revealed that the leaching of Pd from the complex into the solution was lower than 0.18 ppm, which suggests the heterogeneous nature of the prepared Pd-complex **3**. (b) The reaction was carried out in a similar manner as the general procedure for Suzuki reaction (Table 3, **5f**, X = I). After 50% conversion, the reaction mixture was filtered off at hot condition and the aqueous solution was heated under identical reaction conditions for an additional 3 h and analyzed for further conversions.

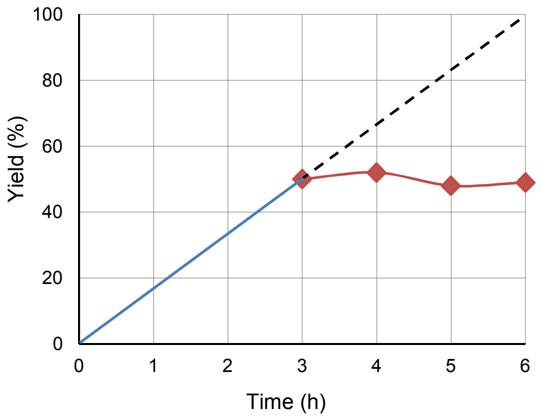

Fig. 4 Hot filtration test of Suzuki-Miyaura reaction (Table 3, **5f**).

No starting material was converted to the corresponding product after removal of the catalyst (Fig. 4). This experiment is indicated that the Suzuki-Miyaura reactions were followed a heterogeneous pathway.

4. Conclusion

In conclusion, we have developed nanostructured SBA-16 supported Pd-complex **3** for Mizoroki-Heck, Suzuki-Miyaura and Sonogashira cross-coupling reactions. The heterogenized Pd-complex **3** was found to be highly active catalyst for these coupling reactions of aryl halides in aqueous reaction conditions. The Sonogashira cross-coupling reaction was performed under copper and solvent-free reaction conditions. Furthermore, this Pd-complex was simply recovered and reused several times without a significant loss of its activity. Currently we are preparing heterogeneous chiral cyclohexyldiamine ligand for asymmetric transfer reactions.

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Notes and references

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Electronic Supplementary Information (ESI) available: [Loading amount of organic moieties onto the mesoporous silica SBA-16, optimization reaction conditions of Heck reaction and NMR data of the coupling products]. See DOI: 10.1039/b000000x/

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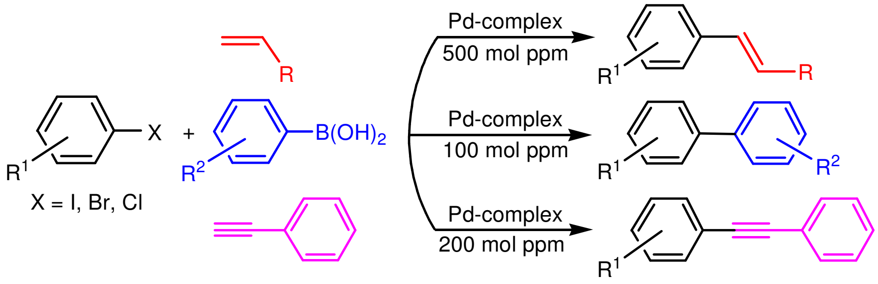
Graphical abstract

SBA-16-supported Pd-complex (100-500 mol ppm) catalyzed the Heck, Suzuki and Soonogashra cross-coupling reactions under mild reaction conditions without significance loss of its activity.



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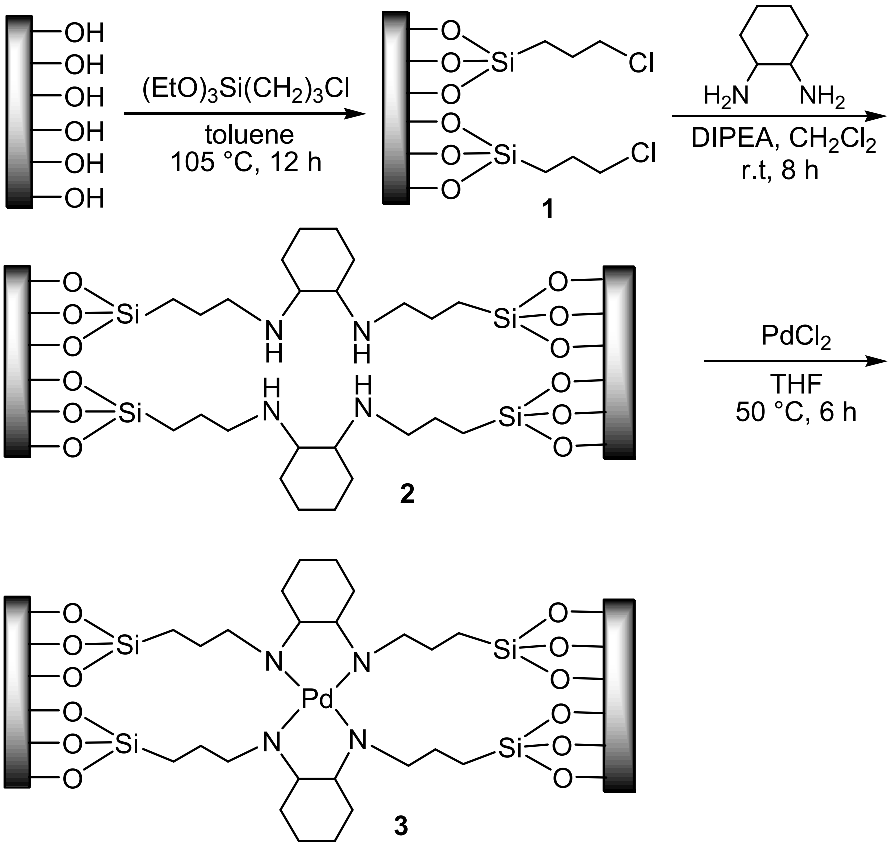

Scheme 1 Preparation of the SBA-16 supported heterogeneous Pd-complex **3**

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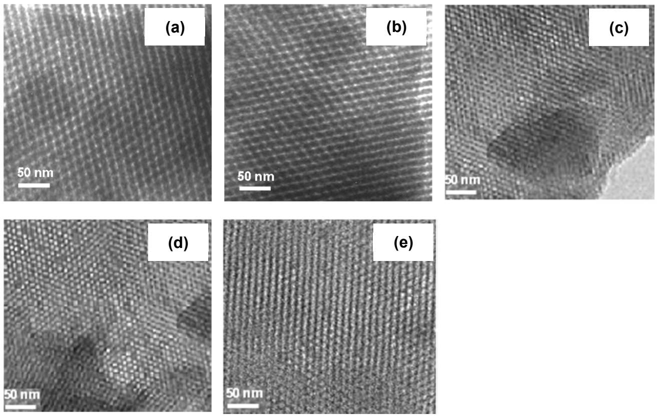

Fig. 1 (a) Parent SBA-16; (b) SBA-16 supported Pd-complex **3**; (c), (d), (e) After five cycles of Heck, Suzuki, and Sonogashira couplings respectively.

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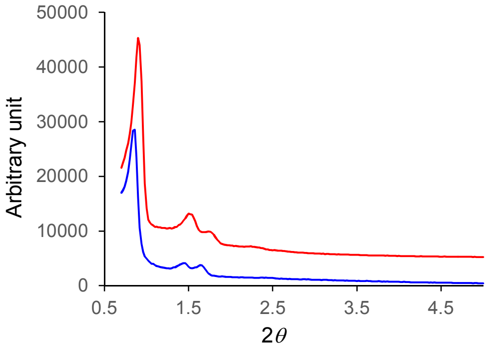

Fig. 2 Small angle XRD patterns of SBA-16 and SBA-16 supported Pd-complex **3**

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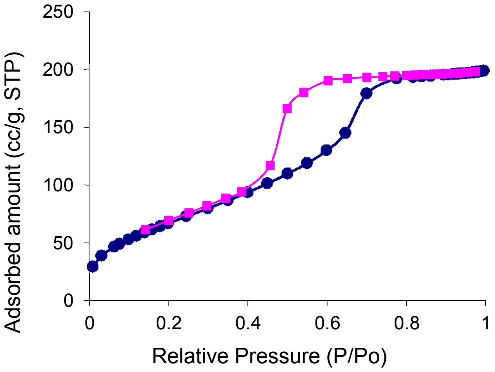

Fig. 3 Nitrogen absorption isotherm of SBA-16 supported Pd-complex **3**

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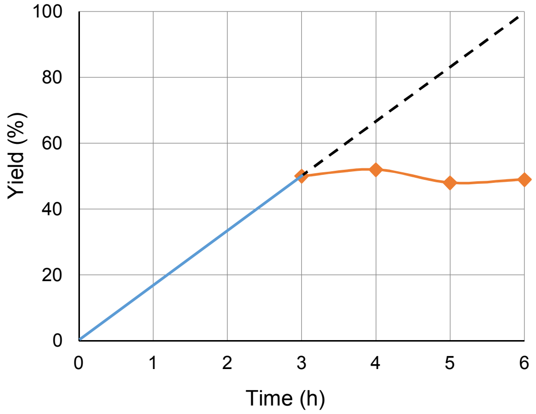
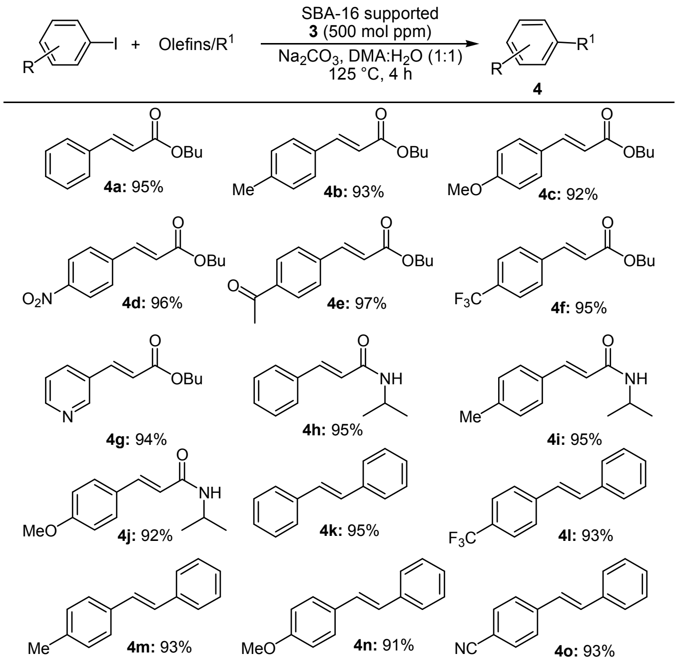


Fig. 4 Hot filtration test of Suzuki-Miyaura reaction (Table 3, **5f**).

Table 1. Heck reaction of iodobenzene with olefins using Pd-complex **3**[a]



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[a] All reactions were carried out using 1 mmol of aryl iodide, 1.3 mol equiv of olefin, 500 mol ppm of **3**, 2 mol equiv of Na_2CO_3, in 2 mL of DMA/H_2O (1:1) at 125 °C for 4 h.

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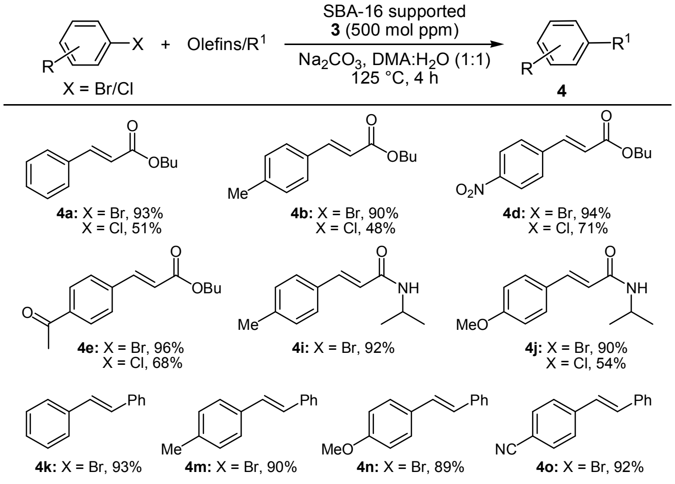
Table 2. Pd-complex **3** catalyzed Heck reaction of aryl halides with olefins[a]



4a: X = Br, 93%
X = Cl, 51%

4b: X = Br, 90%
X = Cl, 48%

4d: X = Br, 94%
X = Cl, 71%

4e: X = Br, 96%
X = Cl, 68%

4i: X = Br, 92%

4j: X = Br, 90%
X = Cl, 54%

4k: X = Br, 93%

4m: X = Br, 90%

4n: X = Br, 89%

4o: X = Br, 92%

[a] All reactions were carried using 1 mmol of aryl halide, 1.3 mol equiv of olefin, 500 mol ppm of **3**, 2 mol equiv of Na_2CO_3, in 2 mL of DMA/H_2O (1:1) at 125 °C for 4 h.

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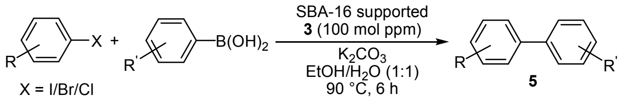
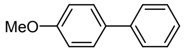
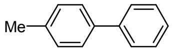
Table 3. Suzuki-Miyaura coupling reaction with Pd-complex **3**[a]

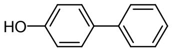




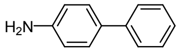
5a: X = I, 92%



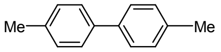
5b: X = I, 94%
X = Br, 88%



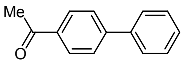
5c: X = I, 91%



5d: X = I, 90%



5e: X = I, 90%
X = Br, 90%



5f: X = I, 93%
X = Br, 93%
X = Cl, 73%

---

[a] Molar ratio: aryl halide (1 mmol), Pd-complex **3** (100 mol ppm), aryl boronic acid (1.1 mol equiv), K$_2$CO$_3$ (2 mol equiv), EtOH/H$_2$O (1:1) at 90 °C for 6 h.

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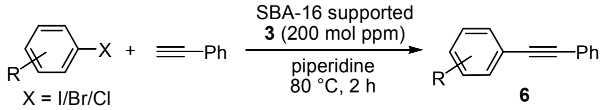
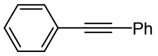
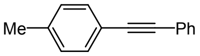
Table 4. SBA-16 supported Pd-complex **3** catalyzed Sonogashira reaction of aryl halides[a]

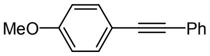




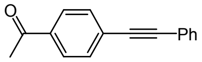
6a: X = I, 94%



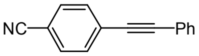
6b: X = I, 93%
X = Br, 90%



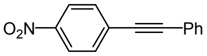
6c: X = I, 95%



6d: X = I, 95%
X = Br, 93%
X = Cl, 68%



6e: X = I, 92%
X = Br, 90%
X = Cl, 68%



6f: X = I, 96%
X = Br, 93%
X = Cl, 72%

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[a] All reactions were carried using 1 mmol of aryl halide, 1.2 mol equiv of phenyl acetylene, 200 mol ppm of **3**, 2 mol equiv of piperidine under solvent free reaction condition at 80 °C for 2 h.