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Recyclable palladium(□) imino-pyridine complex immobilized on mesoporous silica as a highly active and recoverable catalyst for Suzuki-Miyaura coupling reactions in aqueous medium

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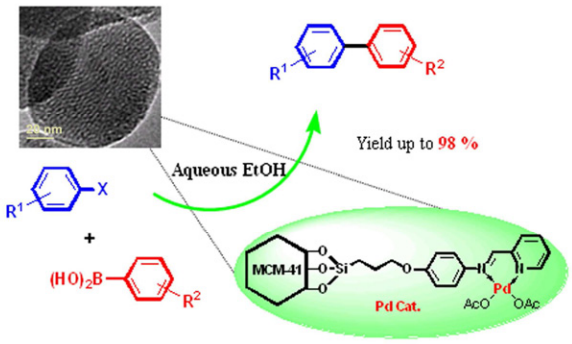


Abstract: A new mesoporous silica supported palladium imino-pyridine complex was successfully prepared by attaching palladium acetates to a novel imino-pyridine ligand functionalized MCM-41. The as-prepared catalyst was characterized by ICP-AES, XRD, FT-IR, SEM and TEM. It was found to be an efficient catalyst for Suzuki-Miyaura coupling reactions in

aqueous medium. The reactions of various aryl bromides with arylboronic acids could be carried out under aerobic and low Pd loading (0.1 mol%) conditions with good to excellent yields, and very low Pd leaching (<0.2 ppm) was detected. Moreover, the supported catalyst could be simply recovered and reused several times without significant loss of efficiency.

Keywords: imino-pyridine complex; supported palladium catalyst; mesoporous silica; Suzuki-Miyaura coupling

1. Introduction

The palladium-catalyzed Suzuki-Miyaura coupling of aryl halides with arylboronic acids, is one of the most successful methods for the construction of carbon-carbon bonds in organic synthesis.[1] And the produced biaryl units are important and versatile building blocks in the field of natural products, pharmaceuticals, agrochemicals, and functional materials.[2] Catalysts used in the reaction process are usually based on homogenous palladium-phosphine complexes[3] or oxime-carbapalladacycles.[4] More recently, palladium-*N*-heterocyclic carbene complexes have attracted considerable attention as valuable catalysts for this transformation.[5] However, separation of the catalyst from the product is often problematic in the homogeneous systems. Moreover, from environmental and economic points of view, catalyst recovery is highly desirable, in particular, if precious metal catalysts are used in large-scale synthesis. In this regard, heterogeneous catalysis seems particularly well suited since the palladium catalyst immobilized on a support could be easily separated from the product free of metal residues and recycled. Thus, a variety of supports, such as polymers,[6] silica,[7] metal oxides,[8] carbon,[9] and ionic liquids,[10] have been explored. Among silica supports, the mesoporous silica MCM-41 has aroused considerable interest because it has a

regular large pore and a extremely high surface area.[11] To date, a few palladium complexes on functionalized MCM-41 support have been prepared and used in the Suzuki coupling.[12]

Schiff bases, a sort of powerful organic ligands in coordination chemistry, have been widely used in transition metal-catalyzed reactions.[13] Furthermore, some supported Pd Schiff base complex were prepared and used as heterogeneous catalysts in Suzuki-Miyaura coupling.[14] Nevertheless, most of these transformations catalyzed by the supported Pd Schiff base complexes were performed in high Pd loading, toxic organic solvents or longer reaction time. In recent years, imino-pyridine chelating ligands, a new kind of Schiff bases, have emerged as attractive ligands for Cu catalyzed C-O or C-N coupling [15] and Pd catalyzed Heck reactions, cyclization, or ethylene polymerization.[16] In continuation of our efforts in designing greener supported catalysts, herein, we would like to present a simple preparation of mesoporous silica MCM-41 supported Pd imino-pyridine complex *via* anchoring a novel silane-functionalized imino-pyridine ligand onto MCM-41 by covalent bonds and its application for Suzuki-Miyaura coupling reactions in aqueous medium. High activity was observed and the catalyst could be simply recovered and reused several times without significant loss of efficiency.

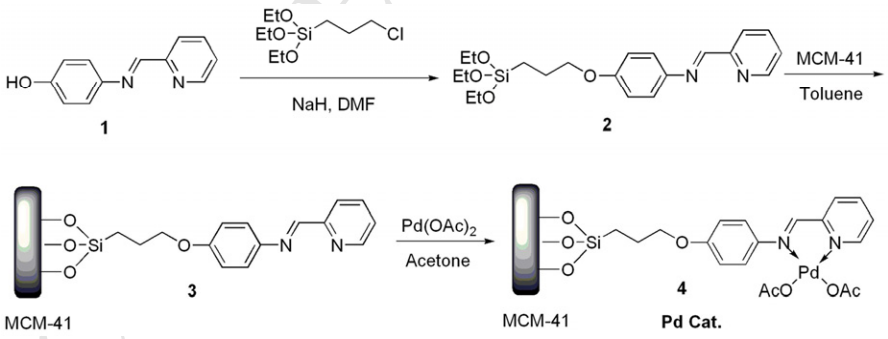
2. Results and discussion

2.1 Preparation and characterization of the catalyst

It should be mentioned at this point that Clark and co-workers previously prepared similar imino-pyridine ligands immobilized on amino-functionalized silica and amino-modified starch, respectively.[17] However, the propyl chain as the linker between the bidentate nitrogen donor and the silicon based anchoring group is short, which might favor additional interactions between the

framework walls and active sites. Additionally, the results of application for the Suzuki reaction were not representing the best of advance in this area, due to the harsh conditions, such as the use of toxic xylene, high reaction temperature and Pd loading. Thus, we focused on immobilizing a novel imino-pyridine ligand onto silica *via* a prolonged alkyl chain contained a aryl ring and its application for a milder Pd-catalyzed process.

The MCM-41 supported palladium catalyst was prepared following the simple procedure shown in Scheme 1. The precursor silane-functionalized imino-pyridine ligand **2** was synthesized by nucleophilic substitution of imino-pyridine ligand **1** and (3-chloropropyl)triethoxysilane under basic conditions. Then the MCM-41 with a toluene solution of complex **2** was refluxed for 24 h to undergo a condensation reaction, which afforded imino-pyridine ligand functionalized MCM-41 **3**. The loading amount of the imino-pyridine ligand was then determined to be 0.25 mmol·g^{-1} by elemental analysis of the nitrogen content, which was also supported by TGA analysis (see Supporting Information).



Scheme 1 Preparation of MCM-41 supported Pd catalyst

In order to warrant the successful functionalization of MCM-41, FT-IR was firstly employed to give a detailed investigation of the blank MCM-41, free precursor **2**, and functionalized MCM-41 **3** (Fig. 1). The Si-O-Si stretching modes of the MCM-41 could be observed as a strong peak at 1078 cm^{-1} and broad peaks at around 3440 and 1635 cm^{-1}, which are attributed to the

Si-OH group and adsorbed water, respectively. The IR curve of free precursor 2 shows typical bands at around 1590 cm^{-1} (C=N vibration), 1500 cm^{-1} (C=C vibration of aryl ring), 2930, 2880 and 1468 cm^{-1} (alkyl chain stretching and deformation vibrations). While in the spectrum of functionalized MCM-41 **3**, these characteristic peaks are at the same wavenumbers, with a small shift because of the interaction with the support. However, all of these significant features cannot be observed in the blank MCM-41. The functionalized MCM-41 **3** was further confirmed by solid-state ^{13}C NMR spectra (see Supporting Information). The ^{13}C CP/MAS NMR spectrum clearly shows the signals for saturated C at 6, 22 and 69 ppm, and for the aryl and pyridine rings in the range of 115-160 ppm. The resonances at 58 and 16 ppm are attributed to $(EtO)_3Si$- groups that did not completely hydrolyze. Thus, the above results indicate that the precursor **2** was successfully grafted onto the MCM-41.

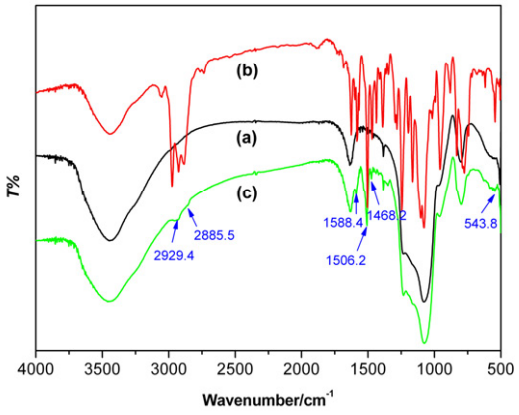


Fig.1 FT-IR spectra of blank MCM-41 (a), free precursor **2** (b), functionalized MCM-41 **3** (c).

Ultimately, the obtained **3** was reacted with palladium acetate in acetone at room temperature for 12 h to give the target catalyst, MCM-41 supported Pd imino-pyridine complex **4**, with a loading of 0.18 mmol of Pd per gram based on inductively coupled plasma (ICP) analysis. X-ray power diffraction (XRD) patterns of the parent MCM-41 and the catalyst **4** are shown in Fig. 2.

Small angle XRD of the parent MCM-41 gives the peaks corresponding to hexagonally ordered mesoporous phases. The characteristic (100) reflection of the parent MCM-41 is remained after functionalized, indicating that the basic mesoporous structure is not damaged in the whole process of catalyst preparation. While the (110) and (200) reflections become weak and diffuse, which can be due to the organic moieties anchored inside the channel of MCM-41.[12c] Furthermore, the morphology of the catalyst **4** was investigated by TEM and SEM. Periodic hexagonal porous tubules can be clearly observed, further confirming that the highly ordered mesopores are present and these findings are well consistent with the XRD results (Fig. 3). This catalyst exhibited an ellipsoidal particle shape with a range of particle size from 150 to 250 nm as depicted in the SEM micrograph (see Supporting Information). The as-prepared catalyst **4** was also characterized by FT-IR, and the IR spectrum of the catalyst **4** demonstrates that no obvious change occurs after immobilization of Pd salts on the functionalized MCM-41 **3** due to the low Pd loading on the support (see Supporting Information).[18]

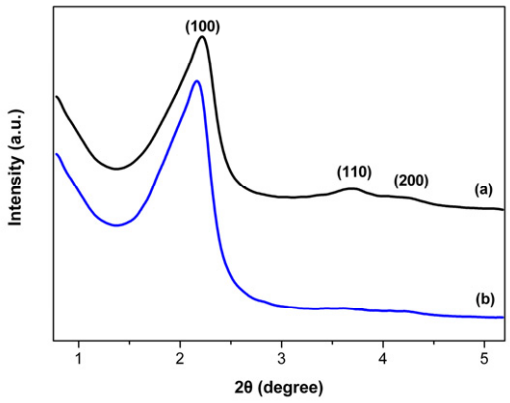


Fig. 2 XRD patterns of MCM-41 (a), MCM-41 supported Pd catalyst **4** (b).

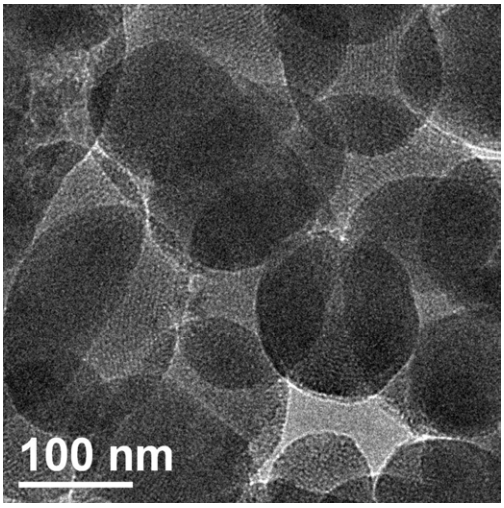
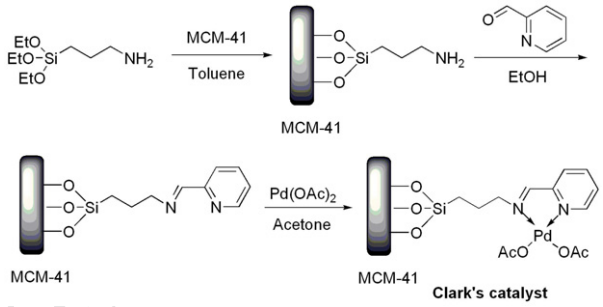


Fig. 3 TEM image of the catalyst **4**

For comparison, an analogous mesoporous silica supported Pd catalyst (Clark's catalyst) was also prepared using the previously reported procedure (Scheme 2).[17a] The ICP analysis of this silica-bound catalyst showed there to be 2.13% Pd on the silica, corresponding to a catalyst loading of 0.20 mmol Pd per gram.



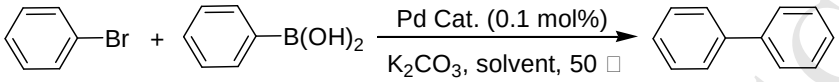
Scheme 2 Preparation of the Clark's catalyst

2.2 Catalytic activity of the catalyst in Suzuki-Miyaura coupling

The catalytic property of the MCM-41 supported Pd imino-pyridine complex **4** was initially tested in Suzuki-Miyaura coupling. The coupling of bromobenzene and phenylboronic acid was chosen as the model reaction. Firstly, the effect of solvent was examined, and a significant effect was observed (Table 1). The aprotic solvent such as DMF, toluene, THF, CH_3CN, acetone, and dioxane, gave low to moderate yields for this model reaction (Table 1, entries 1-6). While the

reactions were carried out in ethanol and pure water, moderate to good yield were obtained (Table 1, entries 7 and 8). Interestingly, the use of organic/aqueous co-solvent, resulted in good to excellent yields for a shorter time (Table 1, entries 9-12). It was worth noting that the best result was observed when the reaction was performed in EtOH/H_2O (1:1, v/v) (Table 1, entry 10).

Table 1 Effect of the solvent on Suzuki–Miyaura reaction [a]



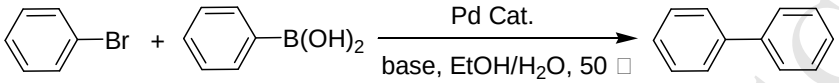
Entry	Solvent	Time (h)	Yield [b] (%)
1	DMF	3	41
2	Toluene	3	26
3	THF	3	7
4	CH_3CN	3	13
5	Acetone	3	10
6	Dioxane	3	<5
7	EtOH	3	90
8	H_2O	6	54
9	EtOH/H_2O (3:1, v/v)	1.5	89
10	EtOH/H_2O (1:1, v/v)	1.5	96
11	EtOH/H_2O (1:3, v/v)	2	72
12	DMF/H_2O (1:1, v/v)	1.5	93

[a] Reaction conditions: bromobenzene (1.0 mmol), phenylboronic acid (1.2 mmol), K_2CO_3 (2.0 mmol), catalyst **4** (0.1 mol% Pd) in 6.0 mL of solvent at 50 □ under air.
[b] Isolated yield.

Secondly, a series of bases were taken into consideration for the model reaction in the aqueous EtOH. With regard to other bases, K_2CO_3 was found to act as an excellent base (Table 2, entry 1). Na_2CO_3, Cs_2CO_3, and K_3PO_4 were also effective (Table 2, entries 2-4). Moreover, the organic bases, NEt_3 and dimethylaminopyridine (DMAP), were also studied, the unsatisfied yields were obtained (Table 2, entries 7 and 8). Lastly, the different catalyst loading were also investigated, and 0.1 mol% loading of Pd was found to be optimal (Table 2, entries 9-11). In

addition, the model reaction could be well carried out in the presence of even much less amount of Pd (0.005 mol%) for a extended time, which corresponds to a turnover number of 15200, indicating that this novel MCM-41 supported Pd catalyst **4** is highly efficient for the Suzuki-Miyaura coupling.

Table 2 Effect of the base and catalyst loading on Suzuki–Miyaura reaction [a]



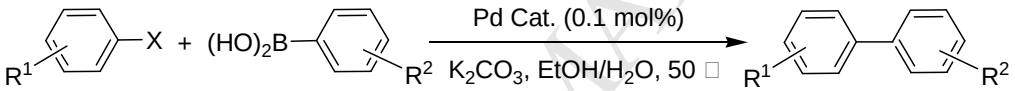
Entry	Base	Time (h)	Yield [b] (%)
1	K_2CO_3	1.5	96
2	Na_2CO_3	1.5	93
3	Cs_2CO_3	1.5	89
4	K_3PO_4	1.5	92
5	KOAc	1.5	25
6	KF	1.5	47
7	NEt_3	3	23
8	DMAP	3	36
9 [c]	K_2CO_3	1	98
10 [d]	K_2CO_3	8	92
11 [e]	K_2CO_3	24	76

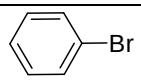
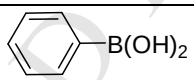
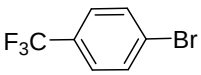
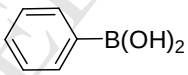
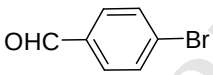
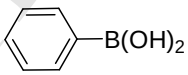
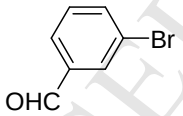
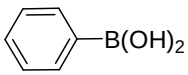
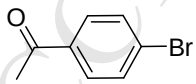
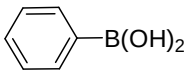
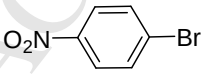
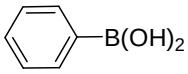
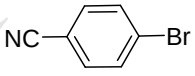
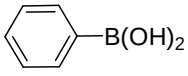
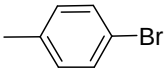
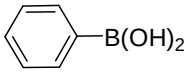
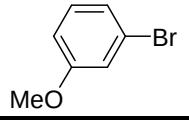
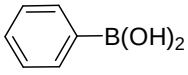
[a] Reaction conditions: bromobenzene (1.0 mmol), phenylboronic acid (1.2 mmol), base (2.0 mmol), catalyst **4** (0.1 mol% Pd) in 6.0 mL of EtOH/H_2O (1:1, v/v) at 50 □ under air.
[b] Isolated yield.
[c] Catalyst (0.5 mol% Pd) was used.
[d] Catalyst (0.01 mol% Pd) was used.
[e] Catalyst (0.005 mol% Pd) was used.

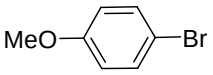
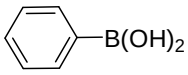
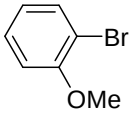
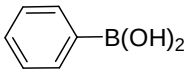
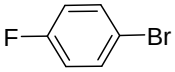
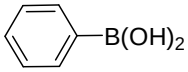
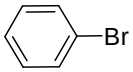
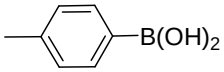
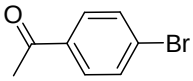
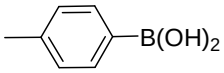
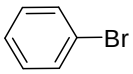
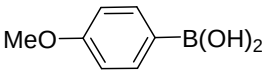
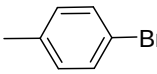
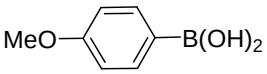
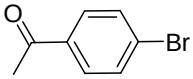
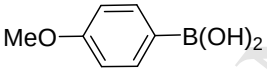
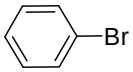
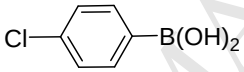
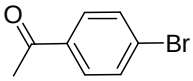
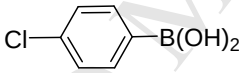
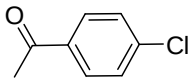
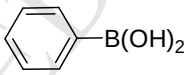
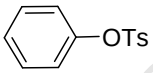
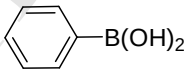
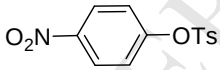
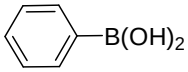
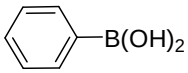
With the optimized reaction conditions in hand, several representative coupling reactions of a variety of aryl halides with arylboronic acids were investigated in the presence of 0.1 mol% of supported Pd catalyst **4** and 2 equiv of K_2CO_3 in aqueous EtOH (1:1, v/v) at 50 ℃ under air, and the results are summarized in Table 3. The coupling between aryl bromides and phenylboronic acid, which contained electron-donating as well as electron-withdrawing groups, proceeded

effectively to afford the corresponding products in good to excellent yields (Table 3, entries 1-12). And a wide range of functional groups, such as nitryl, acyl, cyano, methoxy and aldehyde, could be well tolerated in the reaction. Some substituted arylboronic acids were also tested, and they all reacted smoothly with aryl bromides and generated the desired products in high yields (Table 3, entries 13-19). Unfortunately, the catalytic system was less effective with the challenging substrate such as aryl chloride, aryl tosylate, or aryl mesylate. Although the coupling of phenyl tosylate with phenylboronic acid could generate a 21% yield of biphenyl, it might be caused by homocoupling of the phenylboronic acid (Table 3, entries 20-23).

Table 3 Suzuki–Miyaura coupling reaction of aryl halide with arylboronic acid [a]



Entry	Aryl halides	Arylboronic acids	Time (h)	Product	Yield [b] (%)
1			1.5	**3a**	96
2			1	**3b**	94
3			1.5	**3c**	97
4			1.5	**3d**	95
5			1.5	**3e**	97 (69)[d]
6			1	**3f**	98
7			1	**3g**	94
8			2	**3h**	93 (56)[d]
9			2.5	**3i**	92

10			3	**3j**	91 (50)[d]
11			4.5	**3k**	86
12			1.5	**3l**	90
13			1.5	**3h**	92
14			1.5	**3m**	97
15			1.5	**3j**	91
16			2	**3n**	87
17			1.5	**3o**	97
18			2	**3p**	92
19			1.5	**3q**	97
20[c]			12	**3e**	0 (15)
21[c]			24	**3a**	21
22[c]			24	**3f**	<5 (19)
23[c]			24	**3f**	<5 (17)

[a] Reaction conditions: aryl halide (1.0 mmol), arylboronic acid (1.2 mmol), K_2CO_3 (2.0 mmol), catalyst **4** (0.1 mol% Pd) in 6.0 mL of EtOH/H_2O (1:1, v/v) at 50 □ under air.

[b] Isolated yield.

[c] Catalyst (0.5 mol% Pd) was used (yield of biphenyl in parentheses).

[d] The corresponding yields were given in parentheses when Clark's catalyst (0.1 mol% Pd) was used.

Interestingly, although the Clark's catalyst with a shorter propyl chain possesses the similar active

sites, while it was used for some above Suzuki reactions, the corresponding products were obtained in only moderated yields (Table 3, entries 5, 8 and 10). We carried out an further effect of the time on the reaction of *p*-methylbromobenzene with phenylboronic acid using 0.1 mol% Pd of our catalyst 4 and Clark's catalyst, respectively (Fig. 4). Obviously, the Clark's catalyst was less active than our designed catalyst **4**. These results can be rationalized by our designed catalyst **4** possesses the active sites which are more accessible to the reactants due to a extended hydrocarbon chain as compared to the Clark's catalyst.

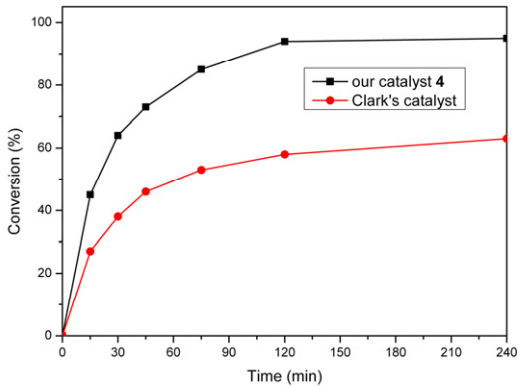


Fig. 4 effect of the time on Suzuki-Miyaura reaction

The recovery and reuse of a catalyst is highly preferable for a greener process. Thus, the recyclability of this supported Pd catalyst **4** was investigated by using *p*-bromoacetophenone and phenylboronic acid as model substrates. After the reaction, the catalyst 4 was separated by simple filtration and washed. After drying, it could be reused in the next run directly without further purification. It was found that the recovery can be successfully achieved in a test of five cycles with a slight loss of its activity (Fig. 5). Darkening of the recovered catalyst in successive runs took place under the reaction conditions and the morphology of the recovered catalyst was then investigated by TEM (see Supporting Information). After the first cycle, Pd nanoparticles with a

size of about 5 nm were formed and well distributed inside the regular meso-channels. However, after the fifth cycle, few parts of the mesopores were collapsed in a longtime basic aqueous medium and then some Pd nanoparticles aggregated outside the meso-channels, which might be a main reason responsible for a slight deactivation of the catalyst after several cycles.

Furthermore, Pd leaching in the catalyst **4** was also determined. ICP analysis of the clear filtrate showed that the Pd content was less than 0.2 ppm, which revealed that the immobilized Pd catalyst **4** was very stable and could endure this coupling conditions. For comparison, we also examined the reusability of a similar Pd catalyst supported on the pristine MCM-41 without functionalized by imino-pyridine **2** (designated as Pd@MCM-41). In this case, the catalyst Pd@MCM-41 was extensively deactivated after the first run and more Pd leaching was found in the filtrates, which indicated that the imino-pyridine nature within the catalyst **4** played a crucial role in anchoring active Pd pieces. In order to exclude that the catalyst **4** was only an initial source for the homogeneous Pd, a new reaction was carried out in the clear filtrate at 50 ℃ for 24 h, whereas no desired product **3e** was detected.

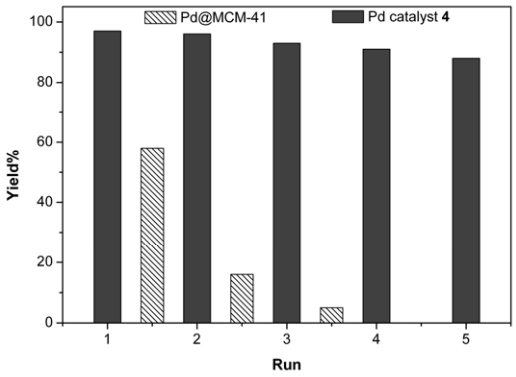


Fig. 5 Recycling experiment of supported Pd catalyst **4**

3. Conclusions

In summary, we have prepared a novel MCM-41 supported Pd imino-pyridine complex **4**, which was used as a heterogeneous catalyst for Suzuki-Miyaura coupling reactions in aqueous medium under air. The catalyst was proved to be highly efficient in the synthesis of a diverse range of biphenyls in excellent yields. Moreover, it offered many practical advantages, such as oxygen insensitivity, thermal stability, and recyclability. The catalyst could be recovered by simple filtration and reused for several runs without obvious loss of activity. It was worth noting that the presence of the imino-pyridine **2** was necessary for the excellent recyclability of the catalyst and the catalytic activity could be improved when the chain tether in the catalyst structure was prolonged.

4. Experimental

4.1 General

Melting points were determined with a WRS-1B apparatus and were uncorrected. The IR spectra were run on a Nicolete spectrometer (KBr). Thermogravimetric analysis was carried out in nitrogen using a Shimadzu TGA-50 spectrometer. ^{1}H NMR spectra were recorded on a Bruker DRX500 (500MHz) and ^{13}C NMRspectra on Bruker DRX500 (125 MHz) spectrometer. Solid-state ^{13}C CP/MAS NMR spectra were measured on a Bruker DRX-400 spectrometer with a 4.0 mm zirconia rotor spinning at 5 kHz. Mass spectra were obtained with an automated Fininigan TSQ Advantage mass spectrometer. Elemental analysis was performed on an Elementar Vario EL recorder. Palladium content of the catalyst was measured by inductively coupled plasma (ICP) on L-PAD analyzer (Prodigy). Transmission electron microscopy (TEM) images were performed with a JEM-2100 instrument. The mesoporous silica MCM-41 was prepared according to a

literature procedure.[19] All solvents used were strictly dried according to standard operations and stored over 4A molecular sieves. All other chemicals (AR grade) were commercially available and used without further purification.

4.2 Synthesis of imino-pyridine ligand (1): *4-[(Pyridine-2-ylmethylene)amino]phenol*

Pyridine-2-carbaldehyde (5.35 g, 50.0 mmol) and *p*-aminophenol (5.46 g, 50.0 mmol) were added into 25 mL of Methanol and the resulting mixture was stirred under reflux for 3 h. The mixture was slowly cooled to room temperature and the pure solid product **1** (6.44 g, 32.5 mmol) was obtained by filtration immediately (yield: 65%). Yellow crystals, Mp (℃): 186-187; ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.64 (s, 1H), 8.63 (s, 1H), 8.67-8.58 (m, 1H), 8.50 (s, 1H), 8.09 (d, J = 8.0 Hz, 1H), 7.92-7.88 (m, 1H), 7.48-7.45 (m, 1H), 7.30-7.26 (m, 2H), 6.82-6.79 (m, 2H).

4.3 Synthesis of silane-functionalized imino-pyridine ligand (2): *N-(pyridin-2-ylmethylene)-4-(3-(triethoxysilyl)propoxy)benzenamine*

A round-bottom flask was charged with compound **1** (3.97 g, 20.0 mmol), NaH (0.72 g, 30.0 mmol) and dry DMF (30 mL) and the solution was stirred at room temperature for 2 h. 3-chloropropyltriethoxysilane (5.06 g, 21 mmol) was then added dropwise. The resulting mixture was stirred at 85 ℃ under nitrogen atmosphere for 24 h, and then cooled and filtered. Finally, the solvent was removed by rotatory evaporation under reduced pressure, and the crude oil was purified by flash chromatography (5:1 hexane-EtOAc) to give 5.80 g of product (yield: 72%). FT-IR (KBr, cm^{-1}): 3055.2, 2079.1, 2926.5, 2879.6, 1627.7, 1589.0, 1497.5, 1466.8, 1231.3, 1169.9, 1085.0, 963.6, 780.8, 543.9; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.69 (d, J = 4.4 Hz, 1H), 8.63 (s, 1H), 8.18 (d, J = 7.5 Hz, 1H), 7.78 (t, J = 7.5 Hz, 1H), 7.34-7.31 (m, 3H), 6.94 (d, J = 8.5 Hz,

2H), 3.97 (t, *J* = 6.5 Hz, 2H), 3.84 (q, *J* = 7.0 Hz, 6H), 1.95-1.89 (m, 2H), 1.23 (t, *J* = 7.0 Hz, 11H), 0.78 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.51, 157.96, 154.88, 149.58, 143.45, 136.62, 124.76, 122.66, 121.62, 115.03, 70.09, 58.41, 22.77, 18.30, 6.47; ESI-MS: m/z 425.0 $[M+Na]^+$.

4.4 Synthesis of MCM-41 supported imino-pyridine ligand (3)

The compound **2** (1.00 g, 2.48 mmol) and pyridine (0.5 mL, 6.15 mmol) were added dropwise to a suspension of MCM-41 (2.00 g) in dry toluene (20 mL), under nitrogen atmosphere. The resulting mixture was refluxed for 24 h. After cooling, the suspension was filtered and the solid residue was washed with acetone and ether. The resulting solid was dried under vacuum at room temperature, giving a pale yellow powder (2.35 g). FT-IR (KBr, cm^{-1}): 3444.4, 2929.4, 2885.5, 1634.9, 1588.4, 1506.2, 1468.2, 1077.7, 795.4, 543.8.

4.5 Preparation of supported Pd catalyst (4)

To a round-bottomed flask, palladium acetate (67.2 mg, 0.30 mmol) and acetone (30 mL) were added. The solution was stirred at room temperature for 30 min under nitrogen atmosphere, and then 1.0 g of the above imino-pyridine ligand functionalized MCM-41 **3** was added. The mixture was stirred at room temperature for 24 h, and filtered. The solid was washed several times with acetone, dried under vacuum for 4 h to afford the corresponding supported Pd catalyst **4** (1.02 g). The loading of Pd was 1.88 % as determined by ICP-AES. For comparison, palladium salts were also immobilized on unmodified mesoporous MCM-41 *via* wet impregnation under the above conditions. The resulting sample was designated as Pd@MCM-41.

4.6 Preparation of Clark's catalyst[17a]

Anchoring the amino group onto MCM-41 was achieved by the stirring of 1.0 g of

mesoporous silica with 1.8 g of 3-aminopropyltriethoxysilane in toluene at reflux temperature for 18 h under nitrogen. A white solid was obtained, filtered and washed with dichloromethane. This solid was then reacted with an excess pyridine-2-carbaldehyde (1.0 g) in ethanol at room temperature for 18 h. The resulting yellowish solid was then collected by filtration and was dried overnight at 90 ℃. Lastly, a solution of palladium acetate (67.2 mg, 0.30 mol) in acetone was added to the above obtained yellowish solid (1.0 g) and the mixture was stirred at room temperature for 24 h, and filtered. The solid was washed several times with acetone, dried overnight at 90 ℃ to afford the corresponding Clark's catalyst. The loading of Pd was 2.13 % as determined by ICP-AES.

4.7 General procedure for Suzuki-Miyaura coupling reaction

Under air atmosphere, a round-bottom flask was charged with aryl halide (1.0 mmol), arylboronic acid (1.2 mmol), Pd catalyst (5.6 mg, 0.1 mol%), K_2CO_3 (2.0 mmol) and EtOH/H_2O (1:1, v/v, 6.0 mL). The reaction mixture was stirred at 50 ℃ for a certain time as monitored by GC. After completion of the reaction, water (5 mL) and ether (10 mL) was added. The catalyst was separated by filtration, washed with ether and water, and dried under vacuum for the next run. The combined organic layers were dried over Na_2SO_4, filtered, concentrated, and the residue was purified by flash chromatography on silica gel to afford the corresponding products.

4.8 Analytical data for the Suzuki-Miyaura coupling products

*4.8.1. 1,1'-Biphenyl (**3a**)*. White solid, Mp (℃): 70-71; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61 (d, *J* = 7.5 Hz, 4H), 7.44 (t, *J* = 7.5 Hz, 4H), 7.35 (t, *J* = 7.5 Hz, 2H).

*4.8.2. 4-(Trifluoromethyl)biphenyl (**3b**)*. White solid, Mp (℃): 69-70; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.69 (s, 4H), 7.60 (d, *J* = 7.5 Hz, 2H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 1H).

*4.8.3. 1,1'-Biphenyl-4-carbaldehyde (**3c**)*. White solid, Mp (℃): 58-59; ^{1}H NMR (500 MHz, $CDCl_3$): 10.09 (s, 1H), 7.98 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.68-7.66 (m, 2H), 7.53-7.49 (m, 2H), 7.46-7.43 (m, 1H).

*4.8.4. 1,1'-Biphenyl-3-carbaldehyde (**3d**)*. White solid, Mp (℃): 53-54; ^{1}H NMR (500 MHz, $CDCl_3$): 10.11 (s, 1H), 8.13 (d, *J* = 1.5 Hz, 1H), 7.89 (dd, *J* = 7.5, 1.5 Hz, 2H), 7.66-7.62 (m, 3H), 7.52-7.49 (m, 2H), 7.43 (t, *J* = 7.5 Hz, 1H).

*4.8.5. 1-(Biphenyl-4-yl)ethanone (**3e**)*. White solid, Mp (℃): 120-121; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.06 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 7.5 Hz, 2H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 1H), 2.67 (s, 3H).

*4.8.6. 4-Nitrobiphenyl (**3f**)*. Pale yellow solid, Mp (℃): 114-115; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.33 (d, *J* = 8.5 Hz, 2H), 7.77 (d, *J* = 8.5 Hz, 2H), 7.65 (d, *J* = 7.5 Hz, 2H), 7.53 (t, *J* = 7.5 Hz, 2H), 7.48 (t, *J* = 7.5 Hz, 1H).

*4.8.7. 1,1'-Biphenyl-4-carbonitrile (**3g**)*. White solid, Mp (℃): 85-86; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74-7.68 (m, 4H), 7.59 (d, *J* = 7.0 Hz, 2H), 7.50-7.43 (m, 3H).

*4.8.8. 4-Methylbiphenyl (**3h**)*. White solid, Mp (℃): 47-48; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57 (d, *J* = 7.5 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 2.39 (s, 3H).

*4.8.9. 3-Methoxybiphenyl (**3i**)*. Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63 (d, *J* = 7.0 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.41-7.37 (m, 2H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.17 (t, *J* = 7.0 Hz, 1H), 6.94 (dd, *J* = 8.0, 2.5 Hz, 1H), 3.89 (s, 3H).

*4.8.10. 4-Methoxybiphenyl (**3j**)*. White solid, Mp (℃): 87-88; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59-7.55 (m, 4H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.01 (d, *J* = 8.5 Hz, 2H), 3.88

(s, 3H).

*4.8.11. 2-Methoxybiphenyl (**3k**)*. Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.39-7.36 (m, 3H), 7.09 (t, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 8.5 Hz, 1H), 3.86 (s, 3H).

*4.8.12. 4-Fluorobiphenyl (**3l**)*. White solid, Mp (℃): 73-74; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72-7.69 (m, 4H), 7.59 (s, 2H), 7.49-7.43 (m, 3H).

*4.8.13. 1-(4'-Methylbiphenyl-4-yl)ethanone (**3m**)*. White solid, Mp (℃): 120-121; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04 (d, *J* = 8.5 Hz, 2H), 7.70 (d, *J* = 8.5 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 2.66 (s, 3H), 2.43 (s, 3H).

*4.8.14. 4-Methoxy-4'-methylbiphenyl (**3n**)*. White solid, Mp (℃): 109-110; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.5 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 8.5 Hz, 2H), 3.87 (s, 3H), 2.41 (s, 3H).

*4.8.15. 1-(4'-Methoxybiphenyl-4-yl)ethanone (**3o**)*. White solid, Mp (℃): 154-155; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.5 Hz, 2H), 7.65 (d, *J* = 8.5 Hz, 2H), 7.60 (d, *J* = 8.5 Hz, 2H), 7.0 (d, *J* = 8.5 Hz, 2H), 3.87 (s, 3H), 2.64 (s, 3H).

*4.8.16. 4-Chlorobiphenyl (**3p**)*. White solid, Mp (℃): 76-77; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56 (d, *J* = 7.5 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.46-7.40 (m, 4H), 7.36 (t, *J* = 7.5 Hz, 1H).

*4.8.17. 1-(4'-Chlorobiphenyl-4-yl)ethanone (**3q**)*. White solid, Mp (℃): 102-103; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 8.5 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 2.66 (s, 3H).

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Supporting Information

Supporting information related to this article can be found online at…

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