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# Anchoring of palladium(II) in chemically modified mesoporous silica: An efficient heterogeneous catalyst for Suzuki cross-coupling reaction

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#### ABSTRACT

The synthesis and characterization of a highly efficient and reusable catalyst, Pd(II) immobilized in mesoporous silica MCM-41, are described. Pd(II) Schiff-base moiety has been anchored onto mesoporous silica surface via silicon alkoxide chemistry. The catalyst has been characterized by small-angle X-ray diffraction (SAX), FTIR and electronic spectroscopy as well as elemental analysis. The catalyst is used in Suzuki cross-coupling reaction of various aryl halides, including less reactive chlorobenzene, and phenylboronic acid to give biaryls in excellent yields without any additive or ligand. High selectivity for the biaryl products containing both electron-donating and electron-withdrawing substituents, mild reaction conditions and possibility of easy recycle makes the catalyst highly desirable to address the industrial needs and environmental concerns.

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#### 1. Introduction

Suzuki coupling is an important reaction in organic chemistry for the selective synthesis of biaryls [1]. Biaryls have widespread applications in the synthesis of natural products, pharmaceuticals, and advanced materials [2-5]. The utility of the Suzuki reaction comes from its relative thermal stability, insensitivity to air or moisture, broad functional group tolerance, as well as low toxicity associated with boron compounds. Many palladium complexes have been used as homogeneous catalysts for Suzuki reaction [6-8]. Although homogeneous catalytic systems are known to exhibit better activity than heterogeneous systems but for the large scale applications in liquid phase reactions, it causes greater difficulties such as purification of the final product, recycling of the catalyst, and deactivation via aggregation into inactive Pd particles. Further removal of Pd from organic products at the end of the reaction is highly desirable because of its high cost and toxicity. So the development of heterogeneous systems where the metal is grafted on inorganic or organic supports has attracted much attention in recent years [9-11]. The mesoporous silica-based materials designated as M41S have attracted a lot of attention in catalysis study [12] since its invention by the scientists of Mobil Corporation [13,14]. MCM-41 is one of the members of this family having uniform hexagonal arrays of one-dimensional channels of mesopores with a pore diameter in the range of 20–100 Å. As regards the preparation and characterization of porous silica-based heterogeneous catalyst for cross-coupling reactions few studies deserve particular mention. It is reported that catalysts derived from anchoring of Pd(II) complex into MCM-41 showed high catalytic activity and recyclability for the Mizoroki-Heck reaction [15,16]. High activity and selectivity in the carbon-carbon coupling reaction is also obtained using catalyst prepared by immobilization of Pd on silica modified with methyl or phenyl groups [17]. Pd nanoparticles dispersed on amine-functionalized zeolites and mesoporous silica are found to be highly active in Heck reactions [18,19]. Recently, we have developed Pd(0) immobilized mesoporous silica catalyst which efficiently catalyzes various C-C coupling reactions like Heck, Sonogashira, Suzuki, Stille reactions [20,21]. Palladium complexes have been immobilized on mercaptopropylfunctionalized SBA-16 and KIT-6 to catalyze Suzuki-Miyaura reaction [22].

Wiedermann reported a series of square-planar *trans*-dichloro palladium(II) complexes containing N-(2-thienylmethylene)-aniline and N-(2-thienylmethyl)-aniline ligands that exhibit high catalytic activity in the Suzuki cross-coupling reaction [23]. Inspired by this ligand system, we have synthesized heterogeneous catalyst using similar type of ligand system.

Herein, we describe preparation, characterization and catalytic efficacy of a new heterogeneous palladium based catalyst for Suzuki cross-coupling reaction. The catalyst is active towards various aryl halides including less active chlorobenzene as well as *para*chloroacetophenone under mild reaction conditions.





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#### 2. Experimental

#### 2.1. Materials

PdCl<sub>2</sub>. (>99.9%), tetraethyl orthosilicate (TEOS, 98%), the cationic surfactant cetyltrimethylammonium bromide (CTAB, 98%), 3-mercaptopropyl-functionalized silica (SH–SiO<sub>2</sub>) [sulfur content of SH–SiO<sub>2</sub> = 3.95 wt%], and all other reagents were purchased either from Sigma–Aldrich/Fluka or Alfa-Aesar and were used as received without further purification. The solvents were purchased from Merck (India) and were distilled and dried before use.

#### 2.2. Synthesis of siliceous MCM-41

MCM-41 was synthesized according to the literature method [24] by the hydrolysis of the structure directing agent CTAB (cetyl-trimethylammonium bromide) and tetraethyl orthosilicate (TEOS), in basic solution with a molar composition of the reactants 1.0 CTAB:7.5 TEOS:1.8 NaOH:500 H<sub>2</sub>O. The gelatinous mixture was then hydrothermally treated at 110 °C for 60 h in a Teflon lined autoclave. After cooling to room temperature the resultant solid was recovered by filtration, washed with deionized water and dried in air. The collected product was calcined at 823 K for 8 h to remove the occluded polymeric surfactants.

#### 2.3. Organic modification of MCM-41 with (3-aminopropyl)triethoxysilane (3-APTES)

Post synthesis organic modification of the mesoporous material was performed by stirring 0.3 g of MCM-41 with 0.004 mmol of 3-APTES in dry chloroform (20 ml) at room temperature for 12 h under nitrogen atmosphere. The resulting white solid MCM-41-(SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>x</sub> was filtered, and washed with chloroform followed by dichloromethane and dried in air.

# 2.4. Schiff base generation in APTES modified MCM-41 using 2-thiophenecarboxaldehyde

The white solid, MCM-41-(SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>x</sub> was refluxed with 50 mg (0.45 mmol) of 2-thiophenecarboxaldehyde in methanol at 60 °C for 8 h. The resulting cream colored solid was filtered, washed with methanol followed by dichloromethane and dried in air.

#### 2.5. Anchoring of Pd(II) in modified MCM-41

Pd(II)–MCM-41 was prepared by refluxing Schiff base containing cream colored solid with 5 mg of PdCl<sub>2</sub> in 20 ml acetone for 72 h. The light yellow solid thus formed was then filtered, dried and washed with acetone using Soxhlet for 12 h to remove any unanchored palladium species and dried under vacuum. The Pd content of the catalyst found to be 0.3 (wt%) ( $2.82 \times 10^{-3}$  mol%). Elemental analysis showed Pd:C and Pd:N were 15.62 and 1.84, respectively.

#### 2.6. Catalyst characterization

The powder X-ray diffraction (XRD) patterns of the samples were recorded on a Scintag XDS-2000 diffractometer using Cu K $\alpha$  radiation. Fourier transform infrared (FTIR) spectra of KBr pellets were measured on a Perkin Elmer RX1 FTIR spectrometer. Electronic spectra were measured on a Shimadzu CP-3101 UV–Vis spectrophotometer. The palladium content of the sample was determined by Perkin Elmer A-Analyst 200 atomic absorption spectrometer. Elemental analysis, for carbon, hydrogen, and

nitrogen (CHN), was undertaken on a Perkin Elmer 240C elemental analyzer. Other instruments used in this study were the same as reported earlier [25,26]. <sup>1</sup>H NMR spectra were measured on a Bruker Avance DPX 300 NMR (300 MHz) spectrometer using TMS as the internal standard. To study the progress of the reaction the products were collected at different time intervals and identified and quantified by a Varian CP-3800 Gas chromatograph using a CP-Sil 8 CB capillary column.

#### 2.7. General experimental procedure for Suzuki cross-coupling reaction

The coupling reaction was carried out in a glass batch reactor. At first aryl halide (3 mmol) and phenylboronic acid (0.4 g, 3.3 mmol) were dissolved in 4 ml ethanol. This reactant mixture was then added to the solution of Na<sub>2</sub>CO<sub>3</sub> (0.318 g, 3 mmol) in 1 ml of water under stirring condition. To this 0.01 g of Pd(II)-MCM-41 catalyst was added and the reaction mixture was heated to 60 °C in an oil bath. For isolation of products at the end of the catalytic reaction, the catalyst was first separated out by filtration and then the filtrate was extracted four times with diethyl ether  $(4 \times 10 \text{ ml})$ . The organic layers thus collected were combined and washed with water to remove excess Na<sub>2</sub>CO<sub>3</sub> and finally washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated in vacuo. The residue was purified by column chromatography over silica gel (mesh 60–120) using *n*-hexane/ethyl acetate mixture as eluent to give the desired product. The product was analyzed by GC and <sup>1</sup>H NMR. All of the products were well-known and reported in the literature. The spectroscopic data (<sup>1</sup>H NMR) of these products are consistent with those previously reported values.

#### 2.8. Heterogeneity tests

#### 2.8.1. Hot filtration test

A mixture of iodobenzene (3 mmol), phenylboronic acid (0.4 g, 3.3 mmol), Na<sub>2</sub>CO<sub>3</sub> (0.318 g, 3 mmol), Pd(II)–MCM-41 (2.82 × 10<sup>-3</sup> mol%) in 5 ml of 20% H<sub>2</sub>O/EtOH was stirred at 60 °C and the progress of the reaction was monitored by GC analysis. After 30% completion of the reaction (analyzed by GC), the catalyst was separated at the reaction temperature (to avoid re-deposition of leached Pd species on the catalyst surface during cooling of the reaction mixture) by centrifugation and the reaction solution was stirred at that temperature for another 2 h. There was no further increase in the product concentration, as determined by GC analysis.

#### 2.8.2. Solid-phase poisoning test

A mixture of SH–SiO<sub>2</sub> (0.10 g, 0.12 mmol) and 0.01 g of Pd(II)–MCM-41 catalyst were taken in the solution containing arylhalides (3 mmol), phenylboronic acid (0.4 g, 3.3 mmol) and Na<sub>2</sub>CO<sub>3</sub> (0.318 g, 3 mmol) in 5 ml of 20% H<sub>2</sub>O/EtOH. The mixture was stirred continuously maintaining the temperature of the oil bath at 60 °C. The progress of the reactions was monitored by the method described above.

#### 3. Results and discussion

#### 3.1. XRD studies

The small-angle X-ray diffraction patterns of MCM-41 and the catalyst Pd(II)–MCM-41 are shown in Fig. 1. The pristine MCM-41 shows a typical three-peak pattern [14,27] with a very intense  $d_{100}$  = 38.85 Å diffraction peak at  $2\theta \approx 2.27^{\circ}$  and two other weaker peaks at  $2\theta \approx 3.99^{\circ}$  and  $2\theta \approx 4.58^{\circ}$  for  $d_{110}$  and  $d_{200}$ , respectively. MCM-41 shows an additional peak at  $2\theta \approx 6.16^{\circ}$  which can be assigned to  $d_{210}$  reflection. All the peaks are well-resolved



Fig. 1. Small-angle XRD pattern of: (a) MCM-41; (b) Pd(II)-MCM-41.

indicating MCM-41 has a well defined hexagonal symmetry and have long-range ordering of structure. Comparison of X-ray powder diffraction patterns of Pd(II)-MCM-41 and MCM-41 indicates that the mesoporosity of the material remains intact even after formation of the Pd complex in MCM-41 matrix although some degree of amorphization takes place in the catalyst. Upon post synthetic grafting, the diffraction lines are shifted to the higher angles and broadening of the diffraction lines occurs. This is possibly due to the lowering of the local order, such as variations in the wall thickness, or might be the result of the reduction of scattering contrast between the channel wall of silicate framework and palladium complex present in the pores. A similar type of behavior was observed by Burkett et al. in phenyl modified mesoporous sieves [28,29] and by Lim and Stein for directly synthesized thiol-MCM-41 [30]. Therefore, the changes of the diffraction lines upon anchoring of Pd(II) into MCM-41 are not inconsistent.

#### 3.2. FTIR spectra study

The FTIR spectra of the MCM-41, MCM-41-(SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>x</sub> and Pd(II)–MCM-41 are shown in Fig. 2. Presence of various N–H and C–H vibration bands appeared in the 3100–2800 and 1550–1250 cm<sup>-1</sup> region in the IR spectrum of MCM-41-(SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>x</sub> that are absent in the case of MCM-41 clearly indicates that 3-APTES has been anchored into the MCM-41 matrix. The expected vibration band for azomethine group appears at ca. 1690 cm<sup>-1</sup> in Pd(II)–MCM-41.

#### 3.3. UV-Vis spectra

The solid-state electronic spectra of the catalyst Pd(II)–MCM-41 shown in Fig. 3, featured a strong band in the region of 290–370 nm. This band can be ascribed to both the  $\pi \to \pi^*$  and



Fig. 2. IR spectra of: (a) MCM-41; (b) MCM-41-(SiCH\_2CH\_2CH\_2NH\_2)\_x; (c) Pd(II)-MCM-41.



Fig. 3. UV-Vis spectrum of Pd(II)-MCM-41.

 $n \rightarrow \pi^{-1}$  transitions of C=N and charge transfer transition arising from  $\pi$  electron interactions between the metal and ligand which involves ligand to metal electron transfer typical for Pd–Schiff base complex [31]. Relatively weak band appearing in the visible region for d–d transitions could not be resolved owing to its very low extinction coefficient and low palladium content of the catalyst.

Recently Pd(II) Schiff base complexes have been synthesized and characterized by X-ray structure analysis and employed in C–C cross-coupling reactions in homogeneous condition [23]. Similar type of ligand arrangement is expected in this case also. Spectroscopic results and elemental analysis indicates that the coordination geometry of the complex anchored to the silica wall of MCM-41, where the nitrogen atom of azomethine group coordinates to the metal centre in monodentate fashion leading to *trans*-N–Pd–N and the central metal ion possesses the square-planar geometry having *trans*-Cl–Pd–Cl arrangements (Scheme 1).



Scheme 1. (a) Modification of MCM-41 channel wall: APTES/chloroform; (b) condensation with 2-thiophenecarboxaldehyde in methanol; (c) metal complex formation: PdCl<sub>2</sub>/acetone/reflux.

#### 3.4. Suzuki cross-coupling reaction

In Suzuki cross-coupling reaction, the catalyst is able to activate the non-substituted as well as substituted aromatic halides containing both electron-withdrawing and electron-donating groups giving high yield of products under mild reaction conditions (60 °C). The results of Suzuki cross-coupling reactions are shown in Table 1. Among non-substituted arvl halides, iodobenzene and bromobenzene (Table 1, entries 1 and 2) showed 100% conversion with a 99% yield in 2-3 h. Aryl chlorides are of great interest due to their low price and large availability. Generally it is difficult to activate C-Cl bonds because of their relative inertness. Suzuki coupling of chlorobenzene with phenylboronic acid under both homogeneous and heterogeneous conditions over a variety of catalysts has been studied in the recent past (Table 2). Zhou et al. have shown Suzuki coupling of chlorobenzene by water-soluble Pd(II)-diimine complex gives only 20% yield [32]. Further, [PdBr<sub>2</sub>{et(impy)}<sub>2</sub>] complex of ligand yields no desired products in case of chlorobenzene [33]. Palladium-guanidine complex immobilized on SBA-16 has been used as catalyst in Suzuki coupling of chlorobenzene that affords a yield of ca. 8% [34]. Recently Dey et al. have used molecular sieves-supported palladium chloride in Suzuki coupling reaction of chloroarenes [35]. The yield of chlorobenzene is satisfactory, but the reaction occurs at high temperature (120 °C) in DMF medium. However, it is established that leaching of Pd often occurs in C-C coupling reaction if DMF is used as a solvent [36]. It is, therefore, desirable to avoid DMF being used as solvent. It is noteworthy to mention that we have succeeded to improve the yield of chlorobenzene in contrast to our recent work using Pd(0)-MCM-41 as catalyst [21]. Chlorobenzene exhibited a comparable yield in Suzuki reaction using (tert-butylarylphosphino)-polystyrene supported Pd catalyst under non-anhydrous heterogeneous conditions [37]. Among the para-substituted substrates, 4-bromoanisole, 4-iodoanisole, 4-nitro bromobenzene, 4-bromophenol, 4-iodophenol and *para*-bromoacetophenone afford enhanced activity in Suzuki reactions. Pd(II)-MCM-41 is able to activate para-chloroacetophenone also in the same reaction condition. However, *para*-chlorophenol gives low yield in this reaction. For Pd(II)–MCM-41, sodium carbonate is the best choice as base, although triethylamine gave comparable yield in the coupling reaction between iodobenzene and phenylboronic acid (yield ~ 97%). In case of sodium acetate yield was very poor (yield ~ 10%). In order to compare the efficacy of the catalyst Pd(II)–MCM-41 with the analogous Pd(II)–Schiff base complex used in homogeneous medium, we have synthesized the complex containing similar [PdN<sub>2</sub>Cl<sub>2</sub>] chromophore (namely dichlorobis- $\kappa$ -N-[N-(2-thienylmethylene)-1-propaneamine] palladium(II)) according to the literature method [23] and its catalytic activities have been studied (Table 3). Although the conversion in Suzuki coupling reactions for both the catalysts is comparable, Pd(II)–MCM-41 showed markedly higher turnover.

Pd incorporated NaY zeolite [38] and Pd/CeO<sub>2</sub> [39] have been used as heterogeneous catalyst in cross-coupling reactions. Cai et al. have used MCM-41 supported sulfur palladium(0) complex in Suzuki coupling reaction [40]. However, the turn over numbers (TON) in C–C coupling reaction for these catalysts are reported to be low.

The catalyst Pd(II)–MCM-41 is not thermal, air or moisture sensitive and so there was no need to carry out the reaction under inert atmospheric condition. The catalyst is easily recoverable by filtration and can be reused several times without any loss of catalytic activity. For the recycling study, Suzuki coupling reaction was performed with iodobenzene and phenylboronic acid maintaining the same reaction condition. After first cycle of reaction the catalyst was recovered by centrifugation and then washed thoroughly with diethylether followed by copious amount of water to remove the base present in the used catalyst and finally by dichloromethane. The recovered catalyst was dried under vacuum at 110 °C overnight. The performance of the recycled catalyst in C–C coupling reactions up to four successive runs is summarized in Table 4. The catalytic efficacy of the recovered catalyst remains almost same in every run as shown in Fig. 4.

To ascertain the catalysis is indeed heterogeneous we have performed hot filtration test and solid phase poisoning test. In

#### Table 1

Pd(II)-MCM-41 catalyzed Suzuki cross-coupling reaction of aryl halides and phenylboronic acid.<sup>a</sup>



 $R = H, OCH_3, COCH_3, NO_2, OH$ X = I, Br, Cl

Entry Aryl halide Product Time (h) Conversion<sup>b</sup> (wt%) Yield<sup>c</sup> (wt%)  $TOF^{d}(h^{-1})$ 1 2 100 99 5320 Ph 2 3 100 99 3546 Ph B 3 24 93 60 414 Ph 98 872 4 12 96 Ph OMe MeO 5 20 97 92 518 Ph OMe B MeO 6 24 74 54 329 Ph COCH<sub>3</sub> B H<sub>3</sub>COC 93 7 24 21 17 Ph COCH3 H<sub>3</sub>COC 8 12 100 99 890 Ph 102  $O_2N$ 9 24 61 57 271 P٢ ОH НО 10 24 100 99 445 Ph ЭH HO 11 19 2 84 24 Ph OH HO

<sup>a</sup> Reaction conditions: 3 mmol of aryl halide, 3.3 mmol of phenylboronic acid, 3 mmol of Na<sub>2</sub>CO<sub>3</sub>, 0.01 g of Pd(II)–MCM-41 (Pd content:  $2.82 \times 10^{-3}$  mol%) in 20% H<sub>2</sub>O/EtOH at 60 °C temperature.

Conversion of reactant is determined by GC.

с Isolated yields were calculated from the mass of the product after separation by column chromatography. All the isolated products showed more than 99% of GC purity. <sup>d</sup> TOF (turnover frequency) = moles converted/(mol of active site  $\times$  time).

Entry	Catalyst	Time (h)	Base	Temp. (°C)	Yield (wt%)	Ref.
1	Pd(II)-MCM-41	24	$Na_2CO_3$	60	60	This study
2	Pd(0)-MCM-41	24	K <sub>2</sub> CO <sub>3</sub>	80	24	[21]
3	Pd(II)–diimine complex	24	K <sub>2</sub> CO <sub>3</sub>	120	20	[32]
4	[PdBr <sub>2</sub> {et(impy)} <sub>2</sub> ]	16	Cs <sub>2</sub> CO <sub>3</sub>	85	0	[33]
5	Pd-L/SBA-16	3	K <sub>3</sub> PO <sub>4</sub>	50	8	[34]
6	Molecular sieves-supported Pd catalyst	18	K <sub>2</sub> CO <sub>3</sub>	120	84	[35]

Table 2				
Suzuki coupling of chlorobenzene with	phenylboronic acid	catalyzed by	a variety	of catalysts.

L = 1,1,3,3-tetramethyl-2-(3-trimethoxysilylpropyl)-guanidine, et(impy) = ethylene bridged imidazo[1,5-a]pyridine-3-ylidenes.

#### Table 3

Suzuki coupling of aryl halid	es and phenylboronic	acid catalyzed by Pd-Schift	f base complex and Pd(II)–MCM-41 <sup>a</sup>
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Entry	Substrate	Time (h)	Catalyst	Conversion <sup>b</sup> (wt%)	Yield <sup>c</sup> (wt%)	$TOF^{d}(h^{-1})$
1		2	Pd–Schiff base complex Pd(II)–MCM-41	100 100	100 99	362 5320
2	ci	24	Pd-Schiff base complex Pd(II)-MCM-41	71 93	49 60	21 414
3	Br — OH	24	Pd–Schiff base complex Pd(II)–MCM-41	93 61	64 57	28 271
4		24	Pd–Schiff base complex Pd(II)–MCM-41	83 74	62 54	25 329
5	Br-OMe	20	Pd–Schiff base complex Pd(II)–MCM-41	98 97	84 92	36 518
6	Br-NO <sub>2</sub>	12	Pd–Schiff base complex Pd(II)–MCM-41	99 100	92 99	61 890

<sup>a</sup> Reaction conditions: 3 mmol of aryl halide, 3.3 mmol of phenylboronic acid, 3 mmol of Na<sub>2</sub>CO<sub>3</sub>, 0.004 mmol of Pd–Schiff base complex (or 0.01 g of Pd(II)–MCM-41: Pd content 2.82  $\times$  10<sup>-3</sup> mol%) in 20% H<sub>2</sub>O/EtOH at 60 °C temperature.

<sup>b</sup> Conversion of reactant is determined by GC.

<sup>c</sup> Isolated yields were calculated from the mass of the product after separation by column chromatography. All the isolated products showed more than 99% of GC purity. <sup>d</sup> TOF (turnover frequency) = moles converted/(mol of active site × time).

hot filtration test, the solid catalyst was filtered off after 30% of the coupling reaction was completed and the liquid phase of the reaction mixture was kept in reaction condition for another 2 h. No increase in the amount of product was noticed. This result suggests that Pd is not being leached out from the solid catalyst during the cross-coupling reactions.

According to Richardson and Jones [41] solid-phase poisoning test is one of the important tests to ascertain the true heterogeneity of the Pd-based catalyst in C–C coupling reactions. We have performed solid-phase poisoning tests using commercially available (purchased from Sigma–Aldrich) 3-mercaptopropyl-functionalized silica (SH–SiO<sub>2</sub>) as an effective palladium scavenger which

#### Table 4

Recycling of Pd(II)-MCM-41 catalysts in the Suzuki and cross-coupling reaction with iodobenzene and phenylboronic acid<sup>a</sup>.

Entry	Run	Conversion <sup>b</sup> (wt%)	Yield <sup>c</sup> (wt%)	$TOF^{d}(h^{-1})$
1	1st	100	99	5320
2	2nd	100	99	5320
3	3rd	99	98	5267
4	4th	98	97	5213

<sup>a</sup> Reactions were carried out in air using 3 mmol of aryl halide, 3.3 mmol of phenylboronic acid, 3 mmol of Na<sub>2</sub>CO<sub>3</sub>, and 0.01 g of Pd(II)–MCM-41 (Pd content:  $2.82 \times 10^{-3}$  mol%) in 20% H<sub>2</sub>O/EtOH at 60 °C temperature.

<sup>b</sup> Conversion of reactant is determined by GC.

<sup>c</sup> Isolated yields were calculated from the mass of the product after separation by column chromatography. All the isolated products showed more than 99% of GC purity.

<sup>d</sup> TOF (turnover frequency) = moles converted/(mol of active site  $\times$  time).

selectively coordinates and deactivates the leached out palladium [42]. Thereby, cessation of the reaction is expected if catalysis of the coupling reaction is catalyzed by leached palladium species from the solid support. A comparison of percentage of conversion in absence and in presence of solid poison in C–C coupling reactions (Table 5) clearly indicates that the catalytic activity of Pd(II)–MCM-41 is not affected even in the presence of poisoning agent SH–SiO<sub>2</sub>. The kinetic profiles of the typical Suzuki reactions in the presence or absence of SH-SiO<sub>2</sub> are shown in Fig. 5.



Fig. 4. Chart showing recyclability of the catalyst.

## Table 5 Performance of the Pd(II)-MCM-41 catalyst in solid-phase poisoning test.

Aryl halide	Phenylboronic acid	Coupling Reaction	T (°C)	SH-SiO <sub>2</sub> added	Conversion <sup>b</sup> (yield) (wt%)
	B(OH)2		60	No Yes	100 (99) 99 (98)
Br — OMe	B(OH)2	Suzuki <sup>a</sup>	60	No Yes	97 (92) 96 (91)

<sup>a</sup> Reactions were carried out in air using 3 mmol of aryl halide, 3.3 mmol of phenylboronic acid, 3 mmol of Na<sub>2</sub>CO<sub>3</sub>, 0.12 mmol of SH-SiO<sub>2</sub>, and 0.01 g of Pd(II)–MCM-41(Pd content:  $2.82 \times 10^{-3}$  mol%) in 20% H<sub>2</sub>O/EtOH at 60 °C temperature.

<sup>b</sup> Conversion of reactant is determined by GC.



**Fig. 5.** Kinetic profiles for the Suzuki coupling reaction of iodobenzene with phenylboronic acid in the absence of solid poison ( $\blacksquare$ ) and in the presence of SH–SiO<sub>2</sub> as solid poison ( $\bullet$ ).

From the above results it may be concluded that there were no leaching of Pd species occurring in the Pd(II)–MCM-41 catalyzed Suzuki cross-coupling reaction.

#### 4. Conclusion

In conclusion, we have succeeded to design a new heterogeneous catalyst for carbon–carbon coupling reaction by anchoring Pd(II) Schiff-base moiety into mesoporous silica, MCM-41. The catalyst shows high activity towards Suzuki cross-coupling reaction in environmentally friendly solvent (20% H<sub>2</sub>O/EtOH) under mild reaction conditions. The catalytic system tolerates a broad range of functional groups. Notably, Pd(II)–MCM-41 is able to activate less reactive chlorobenzene as well as *para*-chloroacetophenone without any additives. Possibility of easy recycle and mild reaction condition make the catalyst cheap and highly desirable to address the environmental concerns.

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#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.07.076.

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