A new functionalized mesoporous matrix supported Pd(II)-Schiff base complex: an efficient catalyst for the Suzuki–Miyaura coupling reaction†

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A new Pd(II) bounded 2D-hexagonally ordered functionalized MCM-41 type material (**IV**) has been synthesized. Functionalization was carried out by the anchoring of 3-aminopropyltriethoxysilane in the MCM-41 type mesoporous material, followed by grafting with 2,6-diacetylpyridine (DAP) to give a N_3-type Schiff base chelating attachment for the Pd(II) species. Fourier transform infrared (FTIR), powder X-ray diffraction (PXRD) and high resolution transmission electron microscopy (HRTEM) studies have been used to characterize the material. Material **IV** behaves as a highly active catalyst towards Suzuki–Miyaura cross-coupling reaction for the synthesis of biaryl organics. In addition, **IV** acts as a true heterogeneous catalyst in coupling reaction. It was found that this catalyst is highly efficient and recyclable towards Suzuki–Miyaura reaction with high turn over frequencies. X-Ray photoelectron spectroscopic (XPS) analysis was employed to understand the oxidation state of the palladium atom in the catalyst (**IV**) and its loading in the material.

Introduction

Palladium is one of the most crucial metals in catalysis and it is commonly used to catalyze a large variety of carbon–carbon bond forming reactions.[1] Of these reactions, the Suzuki–Miyaura reaction is very important for constructing unsymmetrical biaryl compounds compared to other coupling reactions, which employ more reactive organometallics such as organozinc or Grignard reagents. Complexes of palladium(II) with nitrogen containing ligands are well-known catalysts for Suzuki–Miyaura coupling reactions and thus there is a large interest to employ this reaction in the formation of C–C bonds.[2] The organoboronic acids (and esters) commonly employed in the Suzuki–Miyaura reaction, which are air- and moisture-stable and have relatively low toxicity.[3] However, common catalysts for the Suzuki–Miyaura reaction are generally based on homogeneous palladium complexes of Pd(0) or Pd(II), which causes difficulties in purification of the final product, recycling of the catalyst, and deactivation *via* aggregation into Pd nanoparticles. Further removal of residual palladium offers considerable complexity to the reaction that may render it industrially unacceptable.[4] Thus the heterogenization of a Pd-catalyst is a logical step to avoid these problems, as it allows for easy removal from the reaction mixture. However, inorganic heterogeneous Pd-catalysts show low stability due to leaching of palladium from the surfaces.[5] In fact the leached homogeneous Pd species is responsible for the catalytic activity in most of the cases.[6] Therefore the search for new efficient and recyclable heterogeneous catalysts has received much attention.[7] Different approaches like encapsulation or immobilization of catalytically active metal complexes in solid supports such as zeolites,[8] covalent grafting of such active complexes onto reactive polymer surfaces[9] or inorganic porous matrices[10] *etc.* have been utilized in developing an efficient heterogeneous catalyst. Thus, functionalized ordered mesoporous silica with high surface area, *e.g.* MCM-41, MCM-48 and SBA-15 having attractive nanoscale pore structure are the natural choice for heterogenization.[11]

Modified Pd-silica catalysts have been investigated by Molnar *et al.*[12] and found that Pd immobilized on silica modified with methyl or phenyl groups exhibited high activity and selectivity in the Mizoroki–Heck coupling reaction. So the choice of ligand for functionalization of silica matrices has an important role on catalytic activity and stability. Mandal *et al.*[13] and Bedford *et al.*[14] reported the immobilization of Pd nanoparticles on amine-functionalized zeolites and mesoporous silica, respectively, and observed high activity and stability of both catalysts in the Mizoroki–Heck reaction. Tsai *et al.*[15] and Gonzalez-Arellano *et al.*[16] investigated the nanosized Pd-bipyridyl complex and a Pd(II)-Schiff base complex anchored onto MCM-41 which showed high reactivity and recyclability for the Mizoroki–Heck reaction. An active catalyst for the Ullmann reaction of iodobenzene was phenyl-PMO supported Pd(II) complex that was reported by Wan *et al.*[17] Recent developments on the mesoporous material

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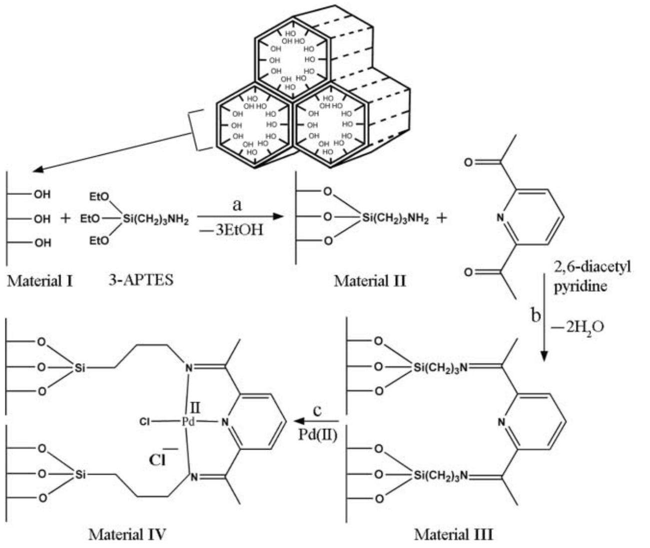
SBA-15 provided a new possible candidate for a solid support for immobilization of homogeneous catalysts.[11f,18] Crudden *et al.*,[19] Shimizu *et al.*,[20] and Ji *et al.*[21] reported that Pd complexes immobilized on mercapto-functionalized SBA-15 and FSM-16 also displayed high activity and excellent recyclability in the Suzuki–Miyaura reaction. Recently Sarkar *et al.*[22a] reported facile Suzuki coupling over *ortho*-metalated Pd(II) complex anchored on 2D-hexagonal mesoporous organosilica. It is generally believed that high surface area of a heterogeneous catalyst results in high catalytic activity. Considering the fact that MCM-41 support has an extremely high surface area and the catalytic palladium species is anchored on the inner surface of the mesopores of the MCM-41 support, we expect that a MCM-41 supported palladium catalyst will exhibit high activity, stability and good reusability. To the best of our knowledge for the reaction of organoboron compounds with organic halides, only very few palladium(II) complexes anchored on functionalized MCM-41 support have been prepared and successfully used in organic reactions.[22]

In this paper, we report the synthesis (Scheme 1) of a new Pd(II) bound heterogeneous catalyst (**IV**) *via* functionalization of 2D-hexagonally ordered MCM-41 type material with 3-aminopropyltriethoxysilane followed by the grafting with 2,6-diacetylpyridine (DAP). Fourier transform infrared (FTIR), powder X-ray diffraction (PXRD), high resolution transmission electron microscopy (HRTEM) and X-ray photoelectron spectra (XPS) studies have been used to characterize the material. We wish to focus the application of this Pd(II)-complex supported on functionalized MCM-41, which involves the use of DAP based N_3-Schiff base as a chelating attachment, for the Suzuki–Miyaura coupling. This functionalized mesoporous material (**IV**) acts as a true heterogeneous catalyst together with high reactivity and recycling efficiency towards Suzuki–Miyaura C–C coupling reaction.



Scheme 1 (a) Functionalization of the pore wall of the MCM-41 type material with 3-aminopropyltriethoxysilane (3-APTES), (b) grafting of the 2,6-diacetylpyridine (DAP) to the surface of **II** and (c) Pd(II) ($PdCl_2$) binding with **III**. All three Si–OH groups, attached to the mesopore surface, are shown in the scheme for clarity.

Results and discussion

Fourier transform IR spectroscopy analysis

FTIR spectra of **I**, **II**, **III** and **IV** are shown in Fig. 1. C–H and N–H vibration bands in the 3500–2800 cm^{-1} and 1650–1500 cm^{-1} regions were found in the FTIR spectra of **II** and these bands are surely absent in the case of **I**. This result shows that 3-APTES has been attached into the mesoporous silica (**I**) matrix. Now, **II** is allowed to react with the 2,6-diacetylpyridine (DAP) and it produces a functionalized mesoporous Schiff-base compound (**III**) (Scheme 1).[23] The bands observed at 1670 cm^{-1} and 1527 cm^{-1} for **III** could be attributed to the C=N and C=C (pyridine ring) stretching frequency respectively. The free C=O (acetyl group) of DAP shows a band at 1695 cm^{-1} and is absent in the case of **III** which indicates the absence of free $-CH_3C=O$ in **III**. Thus it is evident from the FTIR spectrum that both the acetyl groups are converted into Schiff base. The spectrum of isolated Pd(II)-bound complex (**IV**) is shown in Fig. 1 where the C=N stretching frequency is red shifted by 64 cm^{-1} and appears at 1606 cm^{-1}. The stretching frequency at 564 cm^{-1} in **IV** indicates υ_{Pd-N}.[11e] In order to establish the homogeneous distribution of functional groups inside material **II**, FTIR spectra have been carried out in a quantitative manner. Percentage transmittances ($-CH_2-$ groups taken as probe) have been plotted against the weight taken of the sample and a linear curve fit (Fig. 2) is obtained, signifying nearly homogeneous distribution of functional groups.[23]

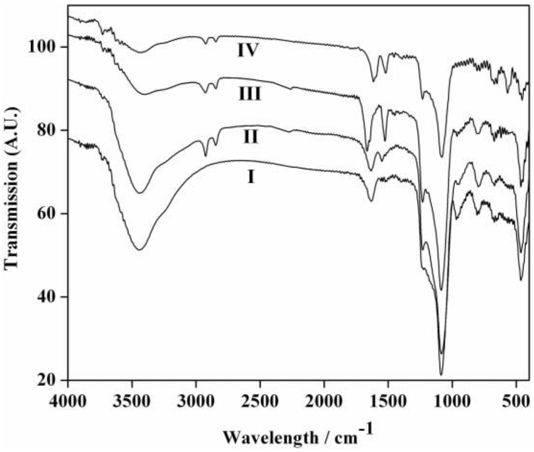


Fig. 1 FTIR spectra of samples **I**–**IV**.

Powder XRD

The small angle powder X-ray diffraction patterns for **I**, **II**, **III** and **IV** are shown in Fig. 3. Sample **I** is highly ordered, showing three strong diffractions for the 100, 110, 200 planes and a weak one for the 210 plane of 2D-hexagonal mesophase.[11a,24] Comparison of the diffraction patterns for samples **I**–**III** indicates that the 2D-hexagonal ordering have been almost retained after the binding of 3-APTES and also after the grafting of DAP molecule. An overall decrease in the intensity of the peaks is observed after the binding with DAP. This is attributed to the lowering of local order, such as variations in the wall thickness, or it may be due to the reduction of scattering contrast between the channel wall of the silicate framework and Schiff base ligand present in **III** mentioned

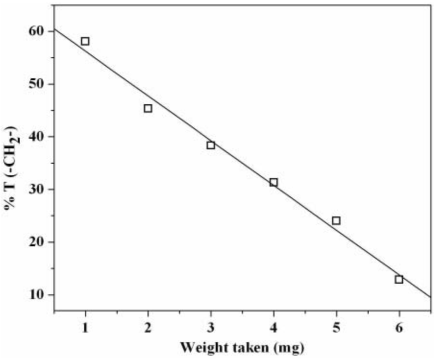


Fig. 2 % Transmittance (T) *vs.* weight of the material **II** obtained from FTIR.

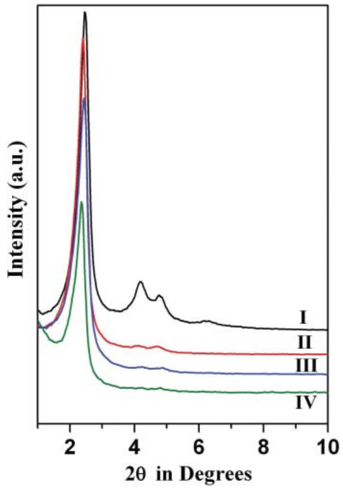


Fig. 3 Small angle XRD patterns for samples **I**–**IV**.

previously by Lim and Stein.[25] XRD pattern is retained in the case of Pd(II)-bounded material **IV**, where the d-spacing is found to increase a little, and this is caused probably due to the coordination of the Pd(II) with the chelating N_3-type ligand unit inside the pore. No wide-angle XRD peak (not shown here) was seen in material **IV** suggesting the absence of metallic Pd in the material.

HRTEM

High resolution transmission electron micrographs (HRTEM) of Pd(II)-catalyst (**IV**) are shown in Fig. 4 in the perpendicular direction of the pore axis. The 2D-hexagonal arrangement of the pores with a different contrast than that of the pore walls throughout the specimen is quite clear. Hexagonal pore ordering after the DAP grafting and also for Pd(II)-binding with the composite has been observed. It is further confirmed by the respective SAED (selected-area electron diffraction) pattern (Fig. 4, inset) corroborating with the hexagonal ordering of the pores. From the TEM image and XRD data, it can be concluded that the ordered mesoporous silica based matrix remains almost intact throughout all the reaction steps starting from the surface functionalization to the binding of Pd(II). The metal content of the material **IV** was investigated using EDS. EDS spectra at different points of the image (Fig. 5) confirm the presence of Pd in the mesoporous silica matrix.

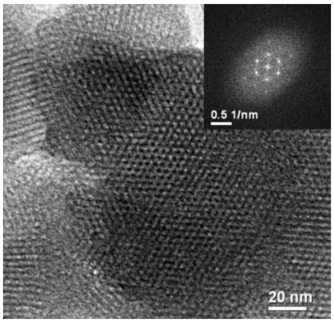


Fig. 4 HRTEM images of material **IV** in the direction of the pore axis. FFT pattern is shown in the inset.

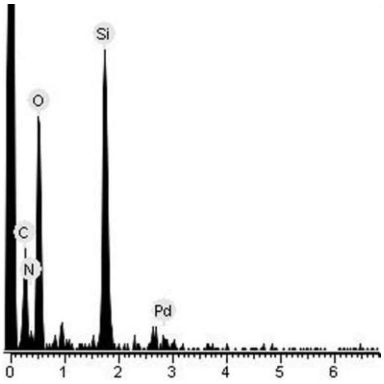


Fig. 5 EDS pattern of material **IV**. [Signals of Cu are due to the sample grid.]

N_2 sorption

Fig. 6(a) indicates the N_2 adsorption/desorption isotherms of materials **I** and **IV**. The isotherm of material **I** could be classified as type IV characteristic of the mesoporous materials.[24–26] Sharp capillary uptake is observed for the adsorption of N_2 at $P/P_0 =$ 0.3–0.5, indicating the mesopores were uniform in size. Pore size distribution (PSD) of these samples **I** and **IV** estimated by the non-local density functional theory (NLDFT) is shown in Fig. 6(b). This PSD pattern suggested the peak pore diameter of 4.0 nm and 2.4 nm for samples **I** and **IV**, respectively. Pore diameter estimated from the respective TEM image analysis resembles nicely

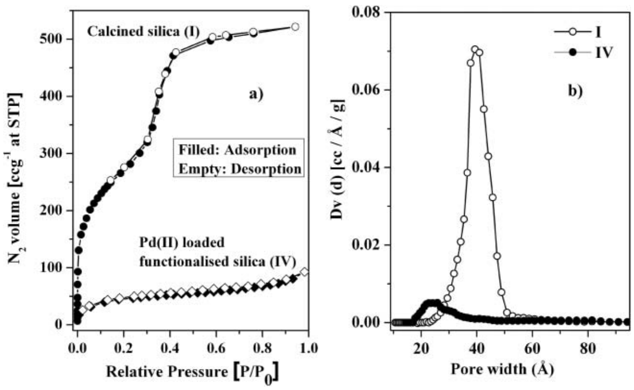


Fig. 6 (a) N_2 adsorption/desorption isotherms of **I** and **IV**, (b) pore size distributions, determined by the non-local density functional theory (NLDFT) method.

Table 1 XPS results for different elements present in catalyst (**IV**)

Elements			Pd		
Binding energy	Si	C	$3d_{5/2}$	$3d_{3/2}$	N
Observed/eV	107	289	342	347	404
Corrected/eV[a]	103	285	338	343	400
Literature/eV[b]	103.5	285	337.5	343	402

[a] Corrected to C 1s with binding energy of 285 eV using adventitious carbon. [b] *Handbook of X-Ray Photoelectron Spectroscopy*, Physical Electronics, Perkin Elmer.

with these values. The BET surface area and pore volume of sample **I** was 952 m^2g^{-1} and 0.79 ccg^{-1}, whereas for sample **IV** this value decreased to 154 m^2g^{-1} and 0.14 ccg^{-1}, respectively. During functionalization *via* 3-APTES and later grafting by the DAP, the pore volumes are drastically reduced. This could be attributed to the more loading of organics, which occupy the void space inside the mesopores. It is clearly suggested that the chromophores are grafted inside the mesopores.

X-Ray photoelectron spectra

X-Ray photoelectron spectra (XPS) were carried out for material **IV** in order to define the oxidation state of the palladium atom in the catalyst (**IV**) and also to detect the presence of the desired element in the catalyst (**IV**). Fig. 7 showed the typical Pd(II) oxidation state (Pd $3d_{5/2}$ = 338 eV, Pd $3d_{3/2}$ = 343 eV) and no cluster formation of Pd metal in the catalyst.[11e] Table 1 shows the XPS binding energy values for different elements present in the catalyst (**IV**). These results suggest a nice correlation of the observed and literature binding energies and thus the presence of Pd(II), Si, C and N for material **IV** as shown in Scheme 1.

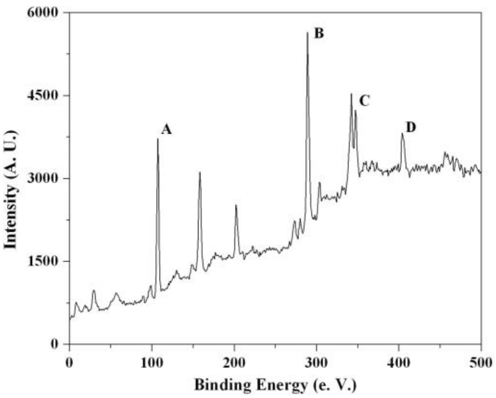


Fig. 7 X-Ray photoelectron spectra (XPS) of catalyst (material **IV**) (**A**: Si $2p_{3/2}$; **B**: C $1s_{1/2}$; **C**: Pd $3d_{5/2}$, $3d_{3/2}$; **D**: $2p_{3/2}$).

Catalytic testing

Initially, a solvent/base optimization study was carried out for the coupling of phenylboronic acid with 4-bromoanisole catalyzed by catalyst **IV**, using 1,4-dioxane, toluene and DMF as solvents and KF : K_3PO_4 (1 : 1), KF, K_2CO_3, K_3PO_4 and Cs_2CO_3 as bases. 4-Bromoanisole was chosen as the test substrate because it is electronically deactivated with respect to oxidative addition and therefore gives a more accurate assessment of catalyst activity as compared to more easily coupled electron-deficient species, such as aryl iodides, and the data are depicted graphically in Fig. 8. The optimum activity (measuring percentage conversion in 8 h) of the catalyst (**IV**) was found in DMF solvent together with KF acting as base. These conditions were thus used for all further studies.

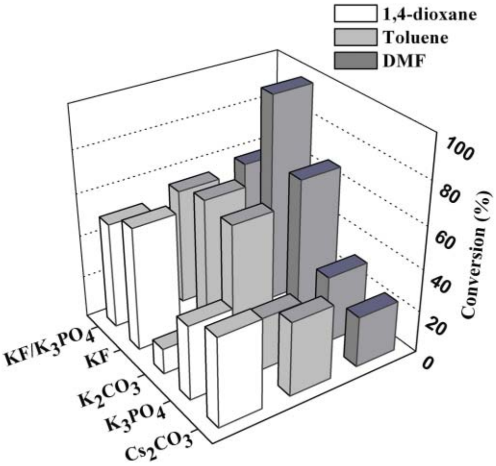


Fig. 8 Bar diagram of catalyst activity in the solvent/base optimization for catalyst **IV** (coupling of phenylboronic acid with 4-bromoanisole in DMF/KF at 100 °C).

Suzuki–Miyaura reaction

To evaluate the activity of the catalysts, the Suzuki–Miyaura coupling reaction of organoboron compounds with organic halides was studied. The choice of the conditions was based on those frequently employed for homogeneous and heterogeneous catalyzed Suzuki–Miyaura coupling reactions. A range of substituted aryl bromides were used as substrates. The entries in Table 2 reveal that both electron withdrawing (entries 1–6) and electron-donating (entries 8–12) substituents yielded excellent results. Even 2-substituted aryl bromides (5, 10) led to excellent yield of the desired biaryl.

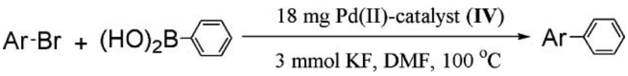
Heterogeneity test

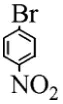
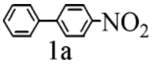
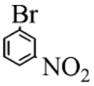
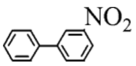
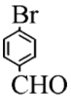
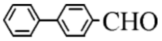
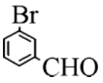
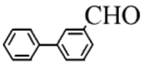
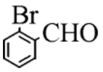
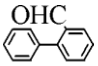
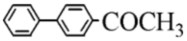
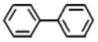
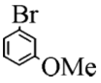
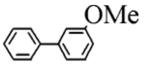
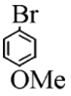
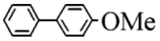
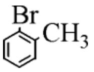
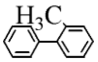
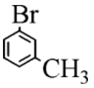
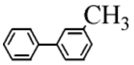
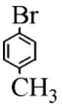
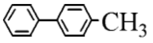
Leaching of palladium in solution and also recovery and reuse of the catalyst are the vital topics in coupling reaction especially in heterogeneous reaction condition.[27] To elucidate this matter, we have performed a series of tests as described below.

Hot filtration test[28]

After completion of 30% of the coupling reaction the liquid phase is collected by filtration at the reaction temperature. If palladium is leaching from the solid surface during the reaction, the liquid phase should contain palladium. Atomic absorption spectrometric analysis of the liquid phase reveals that any detectable palladium is absent in the reaction mixture. Simultaneously the coupling reaction does not proceed further after the filtration of the Pd(II)-catalyst (**IV**) from the batch reactor at the same reaction temperature. It is further noted that palladium is also not detected in the liquid phase after the completion of the reaction and remarkably the filtrate remains completely colorless. These results

Table 2 Suzuki–Miyaura cross-coupling[a] reaction of organoboron compounds with organic halides over Pd(II)-catalyst (**IV**)



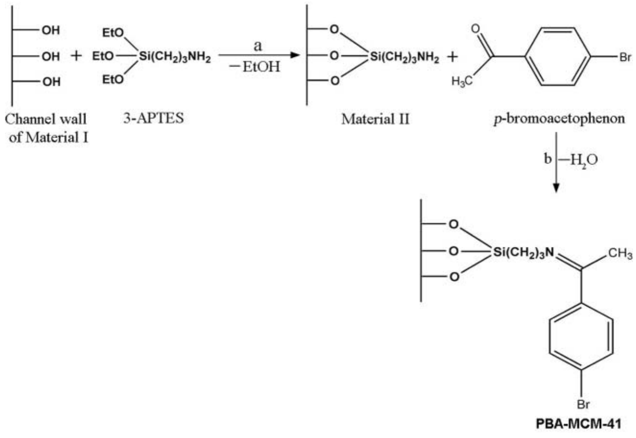
Entry	Aryl halide	Product	Time/h	%Yield[b]	TOF[c]/h^{-1}
1		 1a	3.5	95	5354
2		 1b	3.5	92	5184
3		 1c	4.0	95	4684
4		 1d	4.0	90	4438
5		 1e	4.0	95	4684
6		 1f	3.5	98	5522
7		 1g	4.0	98	4832
8		 1h	8.0	90	2219
9		 1i	8.0	98	2416
10		 1j	5.0	90	3550
11		 1k	4.5	90	3945
12		 1l	4.5	95	4164

[a] Reaction conditions: aryl bromide (1 mmol), phenyl boronic acid (1.5 mmol), Pd catalyst (**IV**): 18 mg, base KF: 3 mmol, DMF: 3.5 mL, temp: 100 °C. [b] Yields are based on isolated pure product. [c] TOF (turn over frequency) = mols converted/mol of active site/time.

suggest that the Pd is not being leached out from the solid surface of the catalyst during coupling reactions.

Three-phase test[29]

To establish whether the reactions are truly heterogeneous, we have carried out the three-phase test for Suzuki–Miyaura coupling reaction. To perform this test, we have chosen aryl halide, *p*-bromoacetophenone (PBA) that is anchored on the surface of the 3-APTES functionalized MCM-41 to give PBA-MCM-41 as shown in Scheme 2. A solution of 1 mmol of *p*-nitrobromobenzene, 1.5 mmol of phenyl boronic acid, and 3 mmol base in 3.5 mL of DMF was stirred in the presence of 18 mg of Pd(II)-catalyst (**IV**) and 1 g of PBA-MCM-41 at 100 °C for 4 h. The reaction mixture was then cooled to room temperature, then filtered and washed with ether and water. The collected filtrate was purified and analyzed by GC and ^{1}H NMR, which showed about 95% of *p*-nitrobromobenzene converted to 4-nitrobiphenyl as expected for Suzuki–Miyaura coupling reaction. The residue obtained from the filtration was then hydrolyzed by 2 N aqueous HCl under refluxing condition. It was neutralized and extracted with ethyl acetate and finally analyzed by GC and ^{1}H NMR. The only compound obtained in this process was *p*-bromoacetophenone. The expected product of *p*-bromoacetophenone in Suzuki–Miyaura coupling reaction is 4-phenylacetophenone and it was not detected from the liquid phase test. So it is clearly evident that the *p*-bromoacetophenone remains unreacted inside the mesopores of PBA-MCM-41. Hence, the *p*-bromoacetophenone has not participated in the coupling reaction, while anchored on the functionalized MCM-41. If there will be any leaching of palladium species from Pd(II)-catalyst (**IV**), the anchored *p*-bromoacetophenone would have also participated in the above Suzuki–Miyaura coupling reaction. However, this is not the case for our present catalyst.



Scheme 2 (a) Organic modification of the channel wall of **I** with 3-aminopropyltriethoxysilane (3-APTES) and (b) anchoring of the *p*-bromoacetophenone (PBA) on material **II**.

Furthermore the same reaction has been repeated in the absence of *p*-nitrobromobenzene and also employing longer reaction time (24 h). The collected filtrate was purified and analyzed by GC/^{1}H NMR. We have not found any coupling products. The residue obtained from the filtration was also analyzed and the only compound obtained in this process was *p*-bromoacetophenone. Hence, further *p*-bromoacetophenone has not been involved in the coupling reaction, while anchored on the functionalized MCM-41. So, it is further evident from the results that there is no leaching of palladium species from the catalyst.

Recycling of the catalyst

Furthermore, we have studied the recyclability of Pd(II)-catalyst (**IV**) in the model Suzuki–Miyaura cross-coupling reaction using electronically deactivated substrate, 4-bromoanisole (1.0 mmol equiv.) and phenylboronic acid (1.5 mmol) in the presence of catalyst (18 mg) in DMF (3.5 mL) at 100 °C under argon, and KF (3 equiv.) as base. Each time, after completion of the reaction, the catalyst was recovered by centrifugation and then washed thoroughly with DMF followed by copious amounts of water to remove the base present in the used catalyst and finally by dichloromethane. The recovered catalyst was dried under vacuum at 100–110 °C overnight. This used catalyst was re-employed in six successive cycles under identical conditions. The percentage conversions with respect to the time for the consecutive runs are shown in Fig. 9. It was seen that for the fresh catalyst the reaction was completed within 8 h, but for the other 2–6 cycles the desired conversion was achieved within 10 h.

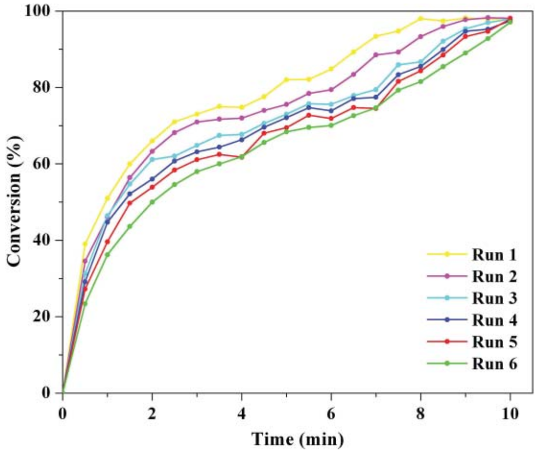


Fig. 9 Plot of catalytic activity of the catalyst (**IV**) over six consecutive cycles in the Suzuki–Miyaura cross-coupling reaction (coupling of phenylboronic acid with 4-bromoanisole in DMF/KF at 100 °C).

Conclusions

In summary, a new mesoporous silica supported palladium(II) catalyst (**IV**) has been successfully prepared through sequential grafting of several organic molecules. Fourier transform infrared (FTIR), powder X-ray diffraction (PXRD), high resolution transmission electron microscopy (HRTEM) and X-ray photoelectron spectra (XPS) studies suggested the functionalization of Pd(II) in the surface of the mesopores. The prepared catalyst has shown high activity towards Suzuki–Miyaura cross-coupling reaction. In addition, **IV** acts as a true heterogeneous and recyclable catalyst in coupling reaction with high turn over frequencies. Hot filtration test suggests that mesoporous silica supported palladium(II) catalyst catalyzes the C–C coupling reactions in truly heterogeneous manner. High catalytic activity and efficiency in this coupling reaction suggested potential application of this catalyst in the synthesis of a large variety of targeted organic molecules. Moreover due to its recyclability and true heterogeneous nature, material **IV** might be a potential catalyst for industry.

Experimental

Materials and physical methods

All reagents and chemicals were purchased from Sigma-Aldrich and used without further purification. FTIR spectra were obtained on a Nicolet MAGNA-IR 750 spectrometer with samples prepared as KBr pellets. Powder X-ray diffraction patterns were recorded on a Bruker D-8 Advance diffractometer operated at 40 kV voltage and 40 mA current and calibrated with a standard silicon sample, using Ni-filtered Cu-Kα ($\lambda = 0.15406$ nm) radiation. Transmission electron microscope (TEM) with an EDS attachment was used to investigate the morphology and nanostructure and chemical composition of these materials. TEM images were recorded in a Jeol JEM 2010 transmission electron microscope operated at an accelerated voltage of 200 kV. Nitrogen adsorption/desorption isotherms were obtained using a Bel Japan Inc. Belsorp-HP at 77 K. Prior to gas adsorption measurements materials were degassed for 6 h at 423 K. A Shimadzu AA-6300 double beam atomic absorption spectrophotometer (AAS) was used for wet chemical analysis of different metal ions. Gas chromatography analysis was performed with an Agilent Technologies 6890 N network GC system equipped with a fused silica capillary column (30 m × 0.32 mm) and a FID detector. ^{1}H NMR (300 MHz) spectra were recorded on a Bruker-Avance DPX300 for a $CDCl_3$ solution and reported in ppm (δ). X-Ray photoelectron spectroscopic (XPS) measurements were conducted on an Omicron Multiprobe (Omicron NanoTechnology Gmbh., UK) spectrometer fitted with an EA125 (Omicron) hemispherical analyzer. Monochromatic Al-Kα source operated at 150 W was used and the pass energy of the analyzer was kept at 40 eV. A low-energy electron gun (SL1000, Omicron) with a large spot size was used for sample neutralization. The voltage of the electron gun was fixed at −3 V.

Synthesis of the mesoporous material (I)

The mesoporous material (**I**) was prepared by a little modification of the procedure described previously.[30] In this present procedure, 2.96 g cetyltrimethylammonium bromide (CTAB) (0.0082 mol) and 1.5 g Brij-35 ($C_{12}H_{25}$–$(OC_2H_4)_{23}$–OH, a polyether and aliphatic hydrocarbon chain surfactant) were dissolved in an aqueous solution of tartaric acid (TA, 0.78 g TA in 60.00 g H_2O) under vigorous stirring at room temperature over a period of 30 min. After that, 3.50 g TEOS (tetraethyl orthosilicate) (0.016 mol) was added to the mixture under continuous stirring for 1 h. Tetramethylammonium hydroxide (TMAOH, 25% aqueous solution) was thereby added drop wise and the pH was maintained at *ca.* 11.0. The resulting mixture was aged overnight under stirring at room temperature and finally heated at 353 K for 72 h without stirring. Then the solid product was recovered by filtration, washed several times with water and dried under vacuum in a lypholyzer. The resulting powder was calcined in the flow of air at 723 K for 8 h to remove all the organic surfactants. The molar ratio of the constituents of the synthesis gels were: 25 TEOS : 12.5 CTAB/(Brij-35) : 2.5 TA : 5556 H_2O.

Preparation of the 3-APTES functionalized mesoporous material (II)

The functionalization of the mesoporous silica (**I**) material with 3-APTES has been done by stirring 0.1 g of **I** in 0.18 g of 3-APTES in chloroform at room temperature over a period of 12 h under N_2 atmosphere. Details on the synthesis and characterization of these materials are given elsewhere.[31] A white solid was obtained and it was filtered and washed repeatedly with chloroform and dichloromethane, and finally dried in air.

Grafting of 2,6-diacetylpyridine (DAP) on functionalized silica (III)

A methanolic solution (20 cm^3) of 2,6-diacetylpyridine (DAP) (25 mmol, 4.08 g) was refluxed with 3-APTES functionalized silica (**II**) for 6 h at 333 K. The resulting light yellow solid was collected by filtration, repeatedly washed with hot methanol and finally dried in a vacuum desiccator.

Synthesis of the Pd(II)-MCM-41 catalyst (IV)

A methanolic solution of $PdCl_2$ (0.135 mmol, 0.024 g) was added to a suspension of material **III** (1.0 g) in methanol (30 cm^3). The resulting mixture was then stirred under reflux for 10 h, cooled to room temperature and filtered. The resulting light brownish solid was washed several times with methanol and dried in desiccator. The Pd content of the Pd(II)-MCM-41 as well as the catalyst was 0.03 wt%.

Preparation of PBA-MCM-41[32]

Anchoring of 3-APTES has been achieved into MCM-41 by the stirring of 0.1 g of mesoporous silica (**I**) with 0.18 g of 3-APTES in chloroform at room temperature for 12 h under N_2 atmosphere. A white solid was obtained, filtered and washed with chloroform and dichloromethane. This solid was then refluxed with 10 g *p*-bromoacetophenone (50 mmol) in methanol (10 cm^3) for 3 h at 60 °C. The resulting yellowish solid PBA-MCM-41 was then collected by filtration and was dried in a desiccator (Scheme 2).

Suzuki–Miyaura cross-coupling reaction

An oven dried round bottomed flask was cooled under argon and charged with arylhalide (1 mmol), phenylboronic acid (1.5 mmol), Pd-catalyst (**IV**) (18 mg) and base (KF) (3 mmol). The flask was evacuated and flushed with argon once again and DMF (3.5 mL) was added to the reaction mixture by a syringe. The reaction mixture was stirred at 100 °C for the specified time. The reaction mixture was then cooled to room temperature, filtered and washed with ether and water. The crude material was purified by flash chromatography using petroleum ether or acetone/petroleum ether as eluent.

Time-dependent studies on the coupling of phenylboronic acid with 4-bromoanisole

These were performed as described above at 100 °C, and aliquots of the supernatant liquid (0.2 mL) were removed at various stages throughout the reaction for analysis by a gas chromatography (Agilent 4890D GC, fitted with a capillary column).

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