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Immobilization of Palladium in Mesoporous Silica Matrix: Preparation, Characterization, and Its Catalytic Efficacy in Carbon−Carbon Coupling Reactions

Sreyashi Jana, Buddhadeb Dutta, Rajesh Bera, and Subratanath Koner*

Department of Chemistry, Jadavpur University, Kolkata 700 032, India

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Palladium(0) has been immobilized into the silica-based mesoporous material to develop catalyst Pd(0)-MCM-41, which is found to be highly active in carbon−carbon coupling reactions. $[Pd(NH_3)_4]^{2+}$ ions have been incorporated into the mesoporous material during synthesis of MCM-41 and subsequently upon treatments with hydrazine hydrate Pd^{2+} ions present in mesoporous silica matrix were reduced to Pd(0) almost instantaneously. The catalyst has been characterized by small-angle X-ray diffraction, N_2 sorption, and transmission electron microscopy (TEM). TEM and surface area measurements clearly demonstrate that the immobilization of Pd(0) into the mesoporous silica has a significant effect on pore structure of the catalyst. Nevertheless, after immobilization of palladium the meso-porosity of the material is retained, as evidenced in the nitrogen sorption measurement. The TEM micrograph shows that both MCM-41 and Pd(0)-MCM-41 have similar types of external surface morphology; however, Pd(0)-MCM-41 was less ordered. Pd(0)-MCM-41 showed high catalytic activity toward carbon−carbon bond formation reactions like Heck and Sonogashira coupling, as evidenced in high turn-over numbers. In contrast to many other Pd-based catalysts reported so far, Pd(0)-MCM-41 acts as a *truly heterogeneous* catalyst in C−C coupling reactions. Notably, the new heterogeneous catalyst is found to be efficient in the activation of arylchloride to give impressive conversion in cross coupling (15−45% for Heck and 30% for Sonogashira) reactions under mild conditions.

Introduction

Carbon−carbon coupling reactions, such as Heck and Sonogashira reactions, have profound importance for application in the industry. Both the reactions have been studied extensively in homogeneous condition using a variety of palladium-containing complexes as catalyst. The mechanistic pathways of palladium-catalyzed carbon−carbon coupling reactions in homogeneous medium are well established.[1,2] Homogeneous catalysts, however, suffer from the problems of separation of catalyst from reaction mixture, recycling of the catalyst and deactivation via the aggregation of metallic Pd particles formed in situ during the Heck reaction.[3,4] Recycling of catalysts is a task of great economic and environmental importance in the chemical and pharmaceutical industry, especially when expensive or toxic heavy metal complexes are employed.[5] In this context, heterogeneous catalysis reactions are far fetching in comparison to the homogeneous ones because the former process allows the production and ready separation of a large quantity of the desired products with the use of a small amount of catalyst. In addition, such catalysts can also be used in continuous-flow systems[6] or in flow-injection microreactors.[7] Consequently, the search of new efficient and recyclable heterogeneous catalysts has received much attention.[8,9] Different approaches like encapsulation or immobilization of catalyti-

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* To whom correspondence should be addressed. E-mail: snkoner@chemistry.jdvu.ac.in. Tel: +91 33 2414 6666, ext. 2505. Fax: +91 33 2414 6223.

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cally active metal complex in solid supports such as zeolites[10,11] and covalent grafting of such active complex onto reactive polymer surfaces[12] or inorganic porous matrices[13] have been used to develop the efficient heterogeneous catalyst. Ordered mesoporous silica, for example, MCM-41,[14] with high surface area and attractive pore structure are the natural choice to use as matrix.

In regard to the preparation and characterization of porous silica-based heterogeneous Heck catalysts, few studies deserve particular mention. Mehnert et al. have used vapor deposition technique for grafting of Pd-allyl complex into Nb-MCM-41 pretreated with trimethylchloro-silane.[15] Good to moderate activity was reported in a variety of Heck coupling reactions of arylbromide with styrene and *n*-butyl acrylate. Although no leaching of palladium was observed during catalytic reactions, recycling of the catalyst was not successful because of agglomeration of Pd(0) species, partial structural damage, and coke deposition. Pd(II) ions have been immobilized onto the dicyano-functionalized MCM-41 through complex formation for development of Heck catalyst.[16] Clark et al. have investigated the Heck reaction using Pd(II) Schiff-base complex catalyst−supported on porous silica and observed a high degree of recyclability in respect of both activity and selectivity.[17] Pd-bipyridyl complex has been immobilized into the nanosized channels of MCM-41 to catalyze Heck coupling reactions.[18] Djakovitch et al. have succeeded to prepare highly active Heck catalysts by entrapping Pd(0) and Pd(II) compounds in the micropores of a variety of zeolites (ZSM-5, Y and mordenite).[19,20] It has been proposed that dissolved active species of Pd(0) catalyze the Heck reaction and Pd species have been retained inside the zeolite pores after the reaction through dissolution-readsorption equilibria of Pd(0) and Pd(II). A similar mechanism is also described by Arai et al. for Pd/C catalysts.[21] Jacobs et al. have claimed that truly heterogeneous Heck catalyst can be obtained by in situ incorporation of metallic Pd particles into silica and zeolite (ZSM-5, Y and mordenite) matrices.[22] Pd(0) nanoparticles have been immobilized onto silica or aluminosilicate matrices in the last 4−5 years to prepare heterogeneous catalyst for C−C coupling reactions.[23,24] Bedford et al. investigated carbon−carbon coupling reactions using Pd nanoparticle catalyst immobilized onto the modified silica surface.[24] An enhanced catalytic activity was noticed in hydrogenation and Heck reactions using Pd nanoparticles encapsulated in dendrimer.[25] In addition, Pd nanoparticle catalysts have also been used in hydrogenation,[23g,26] Pauson−Khand reaction,[27] and oxidation of alcohols.[28] Immobilization of molecular species of palladium into the zeolite cage was found to be capable of activating aryl chlorides, which usually remain inactive in Heck reactions. Initially it was thought that the reactions occurred in zeolite cavity which effectively prevents the agglomeration of inactivate Pd particles, later it was ascertained that palladium species leached from the zeolite into bulk solution, catalyzed the reactions, and diffused back into the pores.[29] PdO particles have been generated on the surface of modified MCM-41, which catalyzes the hydrogenation reaction of cyclic olefins.[30] To our knowledge, no attempts have been made so far to immobilize the Pd(0) particles into the silica-based mesoporous materials, MCM-41.

In this paper we report the immobilization of Pd(0) into the mesoporous silica matrix to prepare a new catalyst, Pd(0)-MCM-41 and study its catalytic efficacy in carbon−carbon cross coupling reactions. Interestingly the prepared catalyst is capable of activating arylchloride both in Heck and Sonogashira coupling reactions under truly heterogeneous and mild conditions to afford an impressive conversion. While some of the Pd-containing catalysts showed only poor

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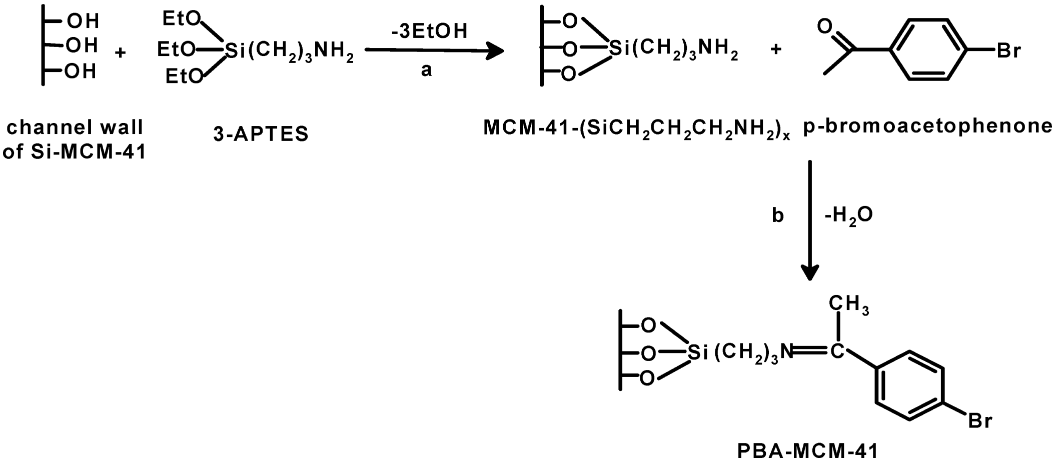
Scheme 1. (a) Organic Modification of Si-MCM-41: APTES/$CHCl_3$ and (b) Anchoring of *p*-Bromoacetophenone onto MCM-41 (in Methanol)



activity toward C−C coupling reactions, other Pd systems have failed to activate the aryl chlorides.[15−18,24,25]

Experimental Section

Materials. The precursor $PdCl_2$ (>99.9%), tetraethyl-orthosilicate (TEOS, 98%), 3-mercaptopropyl-triethoxysilane, the cationic surfactant cetyl-trimethylammonium bromide (CTAB, 98%), 3-mercaptopropyl-functionalized silica (SH-SiO_2) [sulfur content of SH-SiO_2 = 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. $[Pd(NH_3)_4]Cl_2$ complex has been prepared from $PdCl_2$ by following the reported procedure.[31]

Preparation of the MCM-41. Pure mesoporous silica MCM-41 was prepared as described by Grün et al.[32] The white solid obtained was then calcined at 813K in N_2 atmosphere (heating rate of 2 K min^{-1}) for 2 h and in air for 5 h to remove the template.

Preparation of the Catalyst, Pd(0)-MCM-41. Pd(0)-MCM-41 was prepared via simultaneous incorporation of palladium and self-assembling of mesoporous silica by following a method as described below. In the present procedure, Pd(II) ions were first incorporated into the mesoporous silica matrix followed by reduction to obtain Pd(0)-MCM-41. In a stoppered 250 mL conical flask, 0.025 g (0.1 mmol) of $[Pd(NH_3)_4]Cl_2$ complex was suspended in 60 cm^3 of distilled water, and then 5 mL of aqueous ammonia (0.07 mol) was added. After complete dissolution of the $[Pd(NH_3)_4]Cl_2$ complex, 1.2 g (0.003 mol) CTAB was added to the mixture. Then 5.5 mL of TEOS (0.03 mol) was added dropwise over a period of 10 min. The resulting gel had the molar composition TEOS/CTAB/NH_3/H_2O/$[Pd(NH_3)_4]Cl_2$ = 1.0:0.11:2.3:111.11:0.003. The mixture was stirred for 1 h, and then the off-white precipitate was filtered and washed with distilled water until the filtrate gets completely chloride free. After it was dried at room temperature, the prepared solid was calcined at 813 K in N_2 atmosphere (heating rate = 2 K min^{-1}) for 2 h and then in air for 5 h to remove the organic template. After calcination a light orange colored product Pd(II)-MCM-41 was obtained. To reduce the Pd(II) ions to Pd(0), 20 mL of 5% aqueous solution of hydrazine hydrate was added at room temperature with constant stirring in 15 min, and the stirring was then continued for another 2 h. The resulting product was filtered, washed with copious amount of methanol and, finally, with dichloromethane, and dried under vacuum to give a gray product, Pd(0)-MCM-41. The Pd content of the Pd(II)-MCM-41 as well as catalyst was 0.008 wt %.

Preparation of SH-MCM-41. To introduce thiol group into mesoporous matrix, organic modification of MCM-41 was achieved by using (3-mercaptopropyl)-triethoxysilane as reported by Richardson and Jones.[33] Prepared materials have been characterized by IR spectra and elemental analysis. The elemental analysis showed that the loading of sulfur was 0.5−3.3% (wt.) in SH-MCM-41.

Preparation of PBA-MCM-41. Anchoring of (3-aminopropyl)-triethoxysilane (3-APTES) into MCM-41 has been achieved by stirring 0.1 g of MCM-41 with 0.18 g (0.81 mmol) of 3-APTES in dry chloroform at room temperature for 12 h under N_2 atmosphere. The white solid MCM-41-$(SiCH_2CH_2CH_2NH_2)_x$ thus produced was 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 1).

Catalyst Characterization. The powder X-ray diffraction (XRD) patterns of the samples were recorded with a Scintag XDS-2000 diffractometer using Cu Kα radiation. Cell parameter of the mesoporous materials were calculated from XRD pattern using d_{100} values. The Pd content of the Pd(0)-MCM-41 samples was determined by PerkinElmer A-Analyst 200 atomic absorption spectrometer (sensitivity: up to parts per billion level). N_2 sorption measurements were performed on a Quantachrome Autosorb Automated Gas Sorption system. Prior to sorption experiments, samples were outgassed at 150° under vacuum until a final pressure of 10^{-2} Torr was reached. BET (Brunauer−Emmett−Teller) surface areas were determined over a relative pressure range of 0.005 to 0.20. Mesopore size distributions were calculated with BJH (Barrett−Joyner−Halenda) method of the adsorption branch of the isotherms. Transmission electron microscopic (TEM) images were recorded with a JEOL JEM 2100 transmission electron microscope equipped with lanthanum hexaboride (LaB_6) gun, operating at an accelerating voltage of 200 kV and with an objective aperture of 60 mm. The samples were ground and sonicated in ethanol and dispersed over carbon-coated copper grids. Other instruments used in this study were the same as reported earlier.[10c,13b]

Catalytic Reactions. The reactions were carried out in glass batch reactors. To study the progress of the catalytic reactions the

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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. The products of the catalytic reactions have also been isolated and purified by column chromatography and identified by ^{1}H NMR measurement. ^{1}H NMR spectra were measured on a Bruker Avance DPX 300 NMR (300 MHz) spectrometer using TMS as the internal standard. The detail experimental procedures that were undertaken to study the individual reactions are given below.

Heck Coupling Reactions. One millimole of arylhalide and 0.123 g (1.5 mmol) of sodium acetate (NaOAc) were mixed with 8 mL of *N*,*N*-dimethylformamide (DMF) and placed in a batch reactor. To this 0.05 g of Pd(0)-MCM-41 was added, and the mixture was heated to the desired temperature in an oil bath. Finally 1.5 mmol of styrene/*n*-butyl acrylate was added to start the coupling reaction. The products were collected at different time intervals and identified and quantified by GC. For isolation of products at the end of catalytic reaction, the catalyst was first separated out by filtration, and then the filtrate was treated with distilled water to remove the NaOAc. The organic layer was collected and dried over Na_2SO_4, and finally the remaining solvent was removed under vacuum at 25 °C. The purified desired products are then isolated by column chromatography.

Sonogashira Coupling Reactions. One millimole of arylhalide, 0.45 g (1.5 mmol) of tetra-*n*-butylammonium acetate (TBAA), and 0.001 g (0.05 mmol) of CuI were mixed with 6 mL of DMF and placed in a batch reactor. To this solution 0.05 g of Pd(0)-MCM-41 was added. The mixture was then heated to the desired temperature in an oil bath. The coupling reaction started once 1.5 mmol of phenylacetylene was added to the mixture. The products were collected at different time intervals and identified and quantified by GC. For isolation of products at the end of the catalytic reaction, the catalyst was first separated out by filtration. Twenty milliliters of distilled water was then mixed with the filtrate and extracted with hexanes (3 × 15 mL). The organic layers thus collected were combined and dried over anhydrous $MgSO_4$. Solid compounds were obtained on evaporation of the organic solvent under vacuum at 25 °C. The compounds were recrystallized from hot ethanol.

Results and Discussion

X-ray Diffraction Studies. The small-angle X-ray diffraction patterns of MCM-41, Pd(II)-MCM-41, and the catalyst Pd(0)-MCM-41 are shown in Figure 1. In the low-angle region ($2\theta \approx 1.5-5°$), three characteristics Bragg reflections were observed in all the three materials, namely, MCM-41, Pd(II)-MCM-41, and Pd(0)-MCM-41. These diffraction lines can be indexed by assuming a hexagonal symmetry of the materials.[14,32] The pronounced d_{100} reflections at $2\theta \approx 2.56-2.18°$ and the less intense d_{110} and d_{200} peaks at $2\theta \approx 4.42-3.76°$ and $5.06-4.32°$ correspond well to the hexagonally arranged pore structure of the MCM-41 framework, which confirms the long-range structural ordering of these materials. MCM-41 and Pd(II)-MCM-41 show additional peaks at $2\theta \approx 5.74$ and $6.26°$, respectively, that can be assigned to d_{210} reflection, while in the case of Pd(0)-MCM-41, the weakest reflection for d_{210} is buried in the background noise. All the peaks are well-resolved, indicative of good quality of the material. The values of XRD unit cell parameter for MCM-41, Pd(II)-MCM-41, and Pd(0)-MCM-41 were 4.05, 3.65 and 3.45 nm, respectively. Comparison of X-ray powder diffraction patterns of MCM-41, Pd(II)-MCM-41, and Pd(0)-MCM-41 shows that the typical three peak pattern of MCM-41 has been retained after the incorporation of Pd(II) and subsequent immobilization of Pd(0) into the mesoporous silica. However, all the diffraction lines shifted to the higher angles. The d_{100} spacing of the materials decreased from MCM-41 to Pd(II)-MCM-41 to Pd(0)-MCM-41. A similar type of behavior was observed by Brukett et al. in phenyl modified mesoporous sieves[34] and by Lim and Stein for directly synthesized thiol-MCM-41.[35] In our case, upon immobilization of Pd(0), a broadening of the diffraction lines was also noticed. This result can be attributed to the lowering of 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 present in the pores, as was previously mentioned by Lim and Stein.[35] Therefore, the changes of the diffraction lines upon incorporation of Pd(II) into MCM-41 and its subsequent reduction to form Pd(0) are not inconsistent. Diffraction lines for palladium metal, which appear at $2\theta \approx 40.1°(111)$ and $46.7°(200)$, were not observed in the XRD pattern of Pd(0)-MCM-41, indicating that the palladium sites are highly dispersed in the matrix.

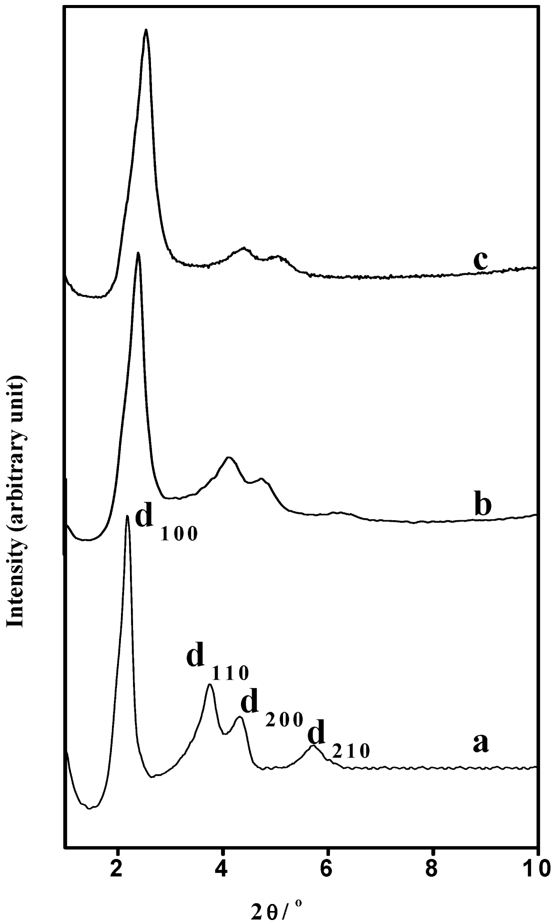

Figure 1. Small angle XRD pattern of (a) MCM-41, (b) Pd(II)-MCM-41, and (c) Pd(0)-MCM-41.

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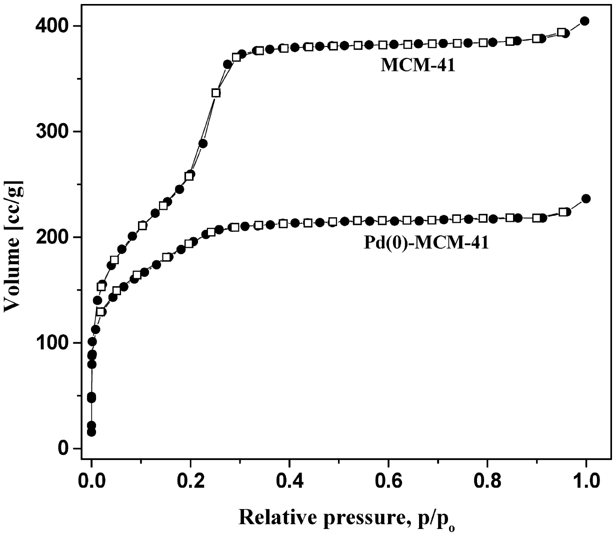

Figure 2. N_2 adsorption/desorption isotherms of MCM-41 and Pd(0)-MCM-41. Adsorption points are marked by filled circles and desorption ones are by open square.

N_2 Sorption Studies. The nitrogen sorption experiments showed that the MCM-41 has the BET surface area (A_{sBET}) of 1136 m^2g^{-1} and the primary mesopore volume (V_p) of 0.61 cm^3 g^{-1} (Figure 2). The average pore diameter is calculated to be 22.6 Å for MCM-41 using the BJH method. All the calculated values are in agreement with those reported for good quality mesoporous MCM-41.[36] The N_2 adsorption isotherm, as well as pore size distribution of the Pd(0)-MCM-41, was considerably different from that of MCM-41. Pd(0)-MCM-41 displays a considerably lower BET surface area in comparison to the MCM-41 (Figure 2). The BET surface area of Pd(0)-MCM-41 was 676 m^2 g^{-1}, while the mesoporous volume (V_p) was ~0.31 cm^3 g^{-1}. The BJH pore size distribution illustrated a narrow peak centered at around 20.3 Å for Pd(0)-MCM-41.

The pore wall thickness of MCM-41 and Pd(0)-MCM-41 has been calculated assuming a hexagonal pore geometry for both of these materials.[37–39] The pore walls are considered to be amorphous, and in several studies, the density of pore walls is taken as the density of amorphous silica,[35,38,40] that is, equal to 2.2 cm^3 g^{-1}.[41] Accordingly, the pore wall thickness values were calculated to be 0.96 and 1.32 nm for MCM-41 and Pd(0)-MCM-41, respectively. The decrease in BET surface area and V_p value and increase of wall thickness of Pd(0)-MCM-41 in comparison to the corresponding values for MCM-41 clearly demonstrate that the immobilization of Pd(0) into the mesoporous silica has a significant effect on pore structure of the catalyst. One of the possible reasons for this remarkable difference in the BET surface area, V_p, and b_d values between MCM-41 and Pd(0)-MCM-41 might be the immobilization of significant amount of Pd(0) into the nanosized pores of the mesoporous material. However, considering the amount of palladium present in Pd(0)-MCM-41 the pore volume loss is significantly high. This can be caused by partial amorphization[42] of the layered phase of mesoporous material during palladium incorporation and calcination of Pd(0)-MCM-41. It is well-known that mesoporous materials often tend to collapse during calcination of sample because of their low stability.[43]

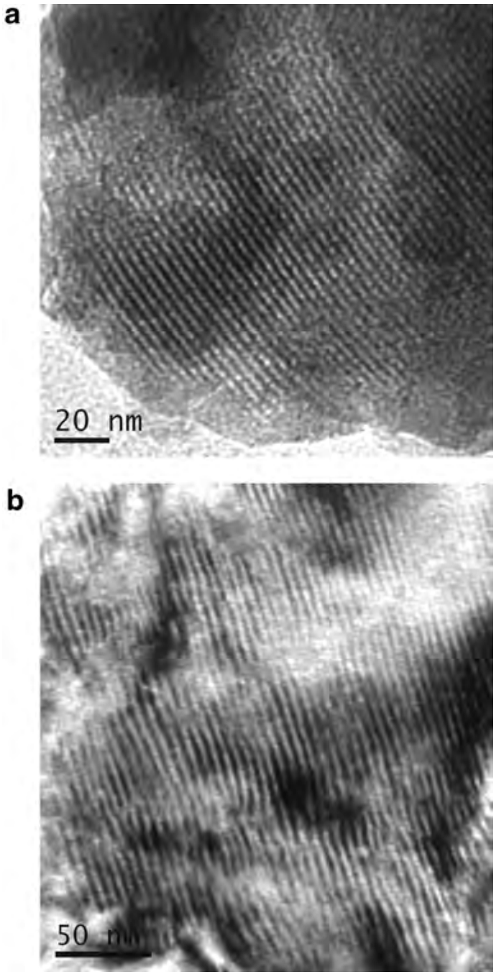

Figure 3. Transmission electron micrograph of (a) MCM-41 and (b) Pd(0)-MCM-41.

TEM Studies. Transmission electron micrographs of MCM-41 and Pd(0)-MCM-41 have been measured. Figures 3A and 3B show the representative TEM micrographs of Pd(0)-MCM-41 catalyst and MCM-41, respectively. Both Pd(0)-MCM-41 and MCM-41 feature an open-ended lamellar type arrangement of hexagonal porous tubules. When electron beam falls on MCM-41 type mesoporous materials perpendicular to the pore axis, the pores are seen to be arranged in patches composed of regular rows as has been interpreted by Chenite et al.[44,45] TEM micrograph of MCM-41 viewed along the pore axis reveals a hexagonal array

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(38) Dabadie, T.; Ayral, A.; Guizard, C.; Cot, L.; Lacan, P. *J. Mater. Chem.* **1996**, *6*, 1789.

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(40) Sonwane, C. G.; Bhatia, S. K.; Calos, N. *Ind. Eng. Chem. Res.* **1998**, *37*, 2271.

(41) Iler, R. K. *The Chemistry of Silica*; Wiley: New York, 1979.

(42) Alfredsson, V.; Keung, M.; Monnier, A.; Stucky, G. D.; Unger, K. K.; Schüth, F. *J. Chem. Soc., Chem. Commun.* **1994**, 921.

(43) Monnier, A.; Schüth, F.; Huo, Q.; Kumar, D.; Margolese, D.; Maxwell, R. S.; Stucky, G. D.; Krishnamurty, M.; Petroff, P.; Firouzi, A.; Janicke, M.; Chmelka, B. F. *Science* **1993**, *261*, 1299.

(44) Chenite, A.; Page, Y. Le; Sayari, A. *Chem. Mater.* **1995**, *7*, 1015.

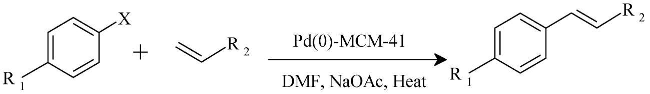
having channel dimension of ∼4 nm,which is consistent with the XRD results. Pd(0)-MCM-41 also exhibits a similar type of array of regular rows in TEM micrographs. Therefore, it can be concluded that both MCM-41 and Pd(0)-MCM-41 have a similar type of external morphology. In our case, the morphology of the tubules in MCM-41, as well as Pd(0)-MCM-41, are rectilinear, and they are 1200−1600 Å long. However, from a comparison of TEM micrographs of MCM-41 and Pd(0)-MCM-41, it appears that the channels are less ordered in Pd(0)-MCM-41 than those in MCM-41, which is indicative of amorphization of MCM-41 upon immobilization Pd(0). Palladium particles are not observed on the surface of the catalyst even at the highest resolution of the TEM micrographs measured for Pd(0)-MCM-41. It seems, therefore, that the agglomeration of Pd particles, if any occurs on the external surface of the catalyst, is negligibly small.

Coupling Reactions. At first the catalytic activity of Pd(0)-MCM-41 is tested for Heck coupling reaction using substituted and nonsubstituted aryl halides and styrene or *n*-butyl acrylate as the vinylic substrate. The reactions are conveniently carried out in batch reactors in air at the normal pressure in the temperature range of 80−100 °C (Table 1). The yield of the reaction products in the case of substituted aryl-halides with respect to reaction time shows that *n*-butyl acrylate is more reactive substrate than styrene. Among nonsubstituted aryl-halides, iodobenzene shows the highest conversion. Although bromo-benzene shows very poor activity, its para-substituted substrates ($R_1 = -NO_2$, $-COCH_3$) not only exhibit enhanced activity but also yields of 100% (Table 1). In all the coupling reactions, high trans-selectivity was observed. It is noteworthy that the catalyst is capable of activating chlorobenzene to give a significant yield of the desired products under the reaction conditions, those that are normally employed in Heck reactions. While the reaction of *n*-butyl acrylate with chlorobenzene showed an impressive 45% conversion, for styrene the conversion was ∼15%. As far as we know, only a few Pd(0)-based heterogeneous catalysts are capable of activating chlorobenzene in the Heck reaction (Table 2).[15,46]

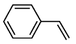
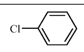
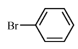
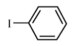
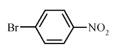
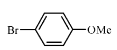
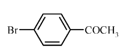
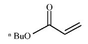
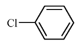
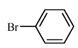
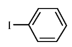
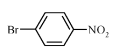
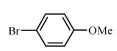
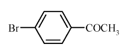
Catalytic efficacy of Pd(0)-MCM-41 has been tested in Sonogashira reaction also. Substituted and nonsubstituted aryl halides are coupled with terminal alkyne, namely, phenyl acetylene in DMF in the presence of CuI in air at 80−100° (Table 3). Tetra-*n*-butylammonium acetate is found to be more efficient base than NaOAc and Et_3N in this case. Iodobenzene showed the highest activity among the nonsubstituted aryl halides, followed by bromobenzene, while chlorobenzene exhibited a significant amount of conversion (∼30%). Chlorobenzene usually remained inactive in Sonogashira reaction toward this type of catalyst.

Hg(0) Poisoning Test.[47] To determine Pd(0) as the active site of the Pd(0)-MCM-41, Hg(0) poisoning test was done which was suggested by Crabtree and Anton.[47a] This test also indicates that the Pd(0)/Pd(II) cycle is operating to catalyze the cross coupling reactions.[47b,48] To perform the test, 1 mL (13.5 g) of mercury was added to 8 mL of DMF along with 0.05 g of Pd(0)-MCM-41, and the mixture was stirred for 12 h at room temperature. To this, 1 mmol of iodobenzene, 1.5 mmol of styrene, and 1.5 mmol of NaOAc

Table 1. Heck Olefination[a] of Aryl Halides Over Pd(0)-MCM-41 Catalyst

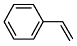
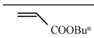


R_1 = H, NO_2, OCH_3, $COCH_3$
R_2 = Ph, ${}^nBuOC(O)$
X = I, Br

Vinyl	Aryl halide	*T* /°C	Time (h)	Conversion[b] (wt %)	Selectivity[c] (wt %)	TOF[d] (h^{-1})
		100	24	15	100	1493
		100	24	56	96	3995
		100	24	88	90	4831
		100	12	96	95	5323
		100	24	30	80	1797
		100	12	90	93	5064
		100	24	45	100	4470
		100	24	76	100	5421
		80	12	100	100	5490
		80	10	100	100	5545
		100	24	45	100	3294
		80	10	100	100	5627

[a] All the reactions are carried out in air using 1 mmol of aryl halide, 1.5 mmol of terminal alkene, 8 mL of DMF, 0.05g of Pd(0)-MCM-4,1 and 1.5 mmol of NaOAc. [b] Conversion of reactant is determined by gas chromatography. [c] In all the reactions, complete E selectivity was observed. Side products: transformation of styrene − the product of α coupling. [d] TOF (turn over frequency) = moles converted/mole of active site/time.

Table 2. Heck Reaction of Aryl Chloride over a Variety of Heterogeneous Pd-Catalysts

Vinyl	Catalyst	Reaction time (h)	Reaction temp. (°C)	Conversion (selectivity) (wt %)	TOF[a] (h^{-1})	Reference
	Pd(0)-MCM-41	24	120	15 (100)	1493	This study
	Pd-nanoparticle composite	24	110	< 5	-	46
	Pd(0)-MCM-41	24	100	45(100)	4470	This study
	Pd-TMS11	32	170	16 (40)	2	15

[a] TOF (turn over frequency) = moles converted/mole of active site/time.

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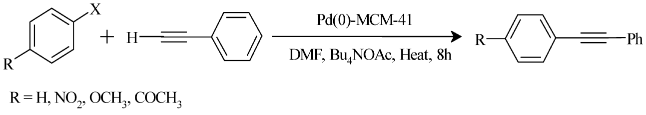
(45) Cheng, C.-F.; He, H.; Zhou, W.; Klinowski, J.; Sousa Gonciüalves, J. A.; Gladden, L. F. *J. Phys. Chem.* **1996**, *100*, 390.

(46) Ding, J. H.; Gin, D. L. *Chem. Mater.* **2000**, *12*, 22.

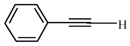
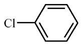
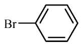
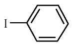
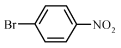
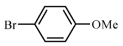
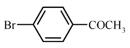
(47) (a) Anton, D. R.; Crabtree, R. H. *Organometallics* **1983**, *2*, 855. (b) Yu, K.; Sommer, W.; Richardson, J. M.; Weck, M.; Jones, C. W. *Adv. Synth. Catal.* **2005**, *347*, 161. (c) Widegren, J. A.; Finke, R. G. *J. Mol. Catal. A: Chem.* **2003**, *198*, 317.

(48) (a) Klingelhöfer, S.; Heitz, W.; Oestreich, S.; Förster, S.; Antonietti, M. *J. Am. Chem. Soc.* **1997**, *119*, 10116. (b) Richardson, J. M.; Jones, C. W. *Adv. Synth. Catal.* **2006**, *348*, 1207.

Table 3. Sonogashira Coupling[a] of Aryl Halides Over Pd(0)-MCM-41 Catalyst



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

Alkyne	Aryl halide	T /°C	Conversion[b] (wt %)	Selectivity[c] (wt %)	TOF[d] (h^{-1})
		100	30	29	8956
		100	88	80	18831
		80	100	82	16472
		80	97	>99	16135
		100	16	16	2874
		80	84	88	14180

[a] All the reactions are carried out in air using 1 mmol of aryl halide, 1.5 mmol of phenylacetylene, 1.5 mmol of TBAA, 0.05mmol of CuI, 6 mL of DMF, and 0.05g of Pd(0)-MCM-41 catalyst for 8 h. [b] Conversion of reactant is determined by gas chromatography. [c] Side product: homo-coupling product (Hay coupling).[53] [d] TOF (turn over frequency) = moles converted/ mole of active site/time.

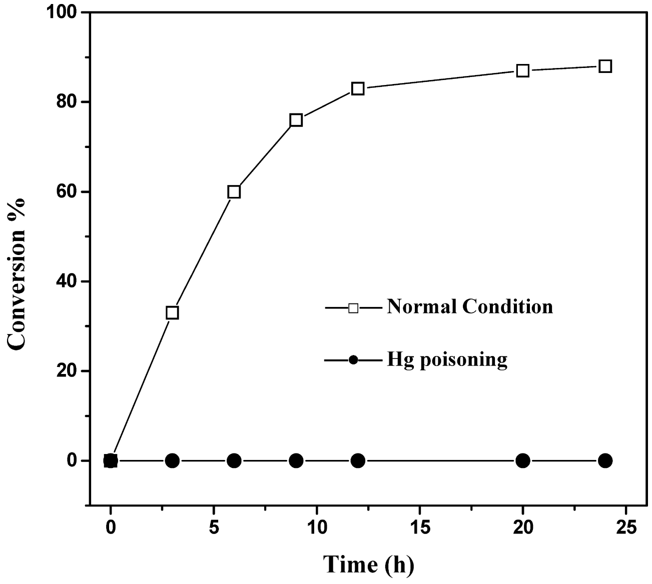


Figure 4. Plot of conversion of iodobenzene versus time for Heck catalysis with Pd(0)-MCM-41 under normal conditions (●) and in presence of excess Hg(0) (●).

were added. The mixture was then heated up to 100 °C in an oil bath. The progress of reaction is studied as per the protocol described in the Experimental Section. The catalyst is found to be totally inactive toward the coupling reaction in this condition (Figure 4). This shows that the metallic mercury amalgamates with Pd(0), thereby quenching the activity of the palladium(0) particles that catalyze the coupling reactions.

Heterogeneity Test. Recovery and reuse of the catalyst and leaching of Pd metal in solution are the important issues in coupling reactions, especially when the reactions undergo in heterogeneous conditions.[49] To address these issues, we have undertaken a series of tests as described below.

Hot Filtration Test.[50] To test if palladium is leaching from the solid catalyst during reaction, the liquid phase of the reaction mixture is collected by filtration at the reaction temperature after 30% of the coupling reaction is completed. Atomic absorption spectrometric analysis of the liquid phase of the reaction mixtures thus collected by filtration confirms that Pd is absent in the reaction mixture. It is noticed that after filtration of the Pd(0)-MCM-41 catalyst from batch reactor at the reaction temperature, coupling reactions do not proceed further. Pd is also not detected in the liquid phase of the reaction mixture after the completion of the reaction. It is noteworthy that the DMF remains completely colorless on addition of Pd(0)-MCM-41. These results suggest that the Pd is not being leached out from the catalyst during cross coupling reactions.

Three-Phase Test.[51] To ascertain if the reactions are truly heterogeneous we have performed the three-phase test for Heck and Sonogashira reactions using a designed aryl halide in usual condition. In this test, one of the reactants (aryl halide, namely, *p*-bromo-acetophenone in this case) is anchored on the modified surface of Si-MCM-41. MCM-41-anchored *p*-bromo-acetophenone, PBA-MCM-41, has been prepared according to the method given in Scheme 1. A solution of 1 mmol of *p*-nitrobromobenzene, 1.5 mmol of styrene, and 1.5 mmol of NaOAc in 8 mL of DMF was stirred in the presence of 0.05 g of Pd(0)-MCM-41 and 1 g of PBA-MCM-41 at 100° for 24 h. The reaction mixture was collected by filtration and washed with fresh DMF several times. The collected filtrate was then extracted with ethyl acetate and analyzed by GC and ^{1}H NMR, which showed about 95% of *p*-nitrobromobenzene converted to 4-nitrostilbene as expected for Heck reaction.

The residue obtained from reaction mixture was then hydrolyzed with 2 N aqueous HCl solution (1.7 mL HCl in 8.5 mL H_2O) for 3 h under refluxing condition. The resulting solution was neutralized, extracted with ethyl acetate, concentrated, and analyzed by GC and ^{1}H NMR. The only compound obtained in this process was *p*-bromoacetophenone. The expected Heck product for *p*-bromoacetophenone, that is, 4-acetylstilbene was not detected in extracted the liquid. This clearly shows that *p*-bromoacetophenone has not participated in the coupling reaction while anchored on the MCM-41.

The same test was also performed for Sonogashira reaction using 1.5 mmol of TBAA, 1.5 mmol of phenylacetylene, 1.0 mmol of *p*-nitrobromobenzene, and 0.05 mmol of CuI in presence of 0.05 g Pd(0)-MCM-41 and 1 g of PBA-MCM-41 at 80° C for 10 h. In this case, analysis of the filtrate also showed >99% conversion of *p*-nitrobromobenzene, while the compound recovered from residue after hydrolysis was solely *p*-bromoacetophenone. Should there be any leaching of palladium species from Pd(0)-MCM-41, the anchored

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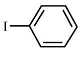
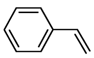
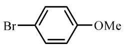
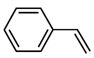
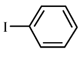
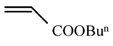
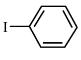
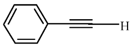
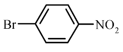
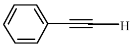
(49) Pröckl, S. S.; Kleist, W.; Köhler, K. *Inorg. Chem.* **2007**, *46*, 1876.
(50) Karimi, B.; Enders, D. *Org. Lett.* **2006**, *8*, 1237.
(51) (a) Baleizao, C.; Corma, A.; Garcia, H.; Leyva, A. *J. Org. Chem.* **2004**, *69*, 439. (b) Das, D. D.; Sayari, A. *J. Catal.* **2007**, *246*, 60.

Table 4. Performance of the Pd(0)-MCM-41 Catalyst in Solid-Phase Poisoning Test

Aryl halide	Vinyl / Alkyne	Coupling Reaction	Temp. /°C	SH-MCM-41 added	Conversion[c] (Selectivity) (wt %)	TOF[d] (h^{-1})
		Heck[a]	100	No	88 (90)	4831
				Yes	90 (95)	4941
			100	No	30 (80)	1797
				Yes	27 (80)	1617
			80	No	100 (100)	5490
				Yes	97 (100)	5325
		Sonogashira[b]	80	No	100 (82)	16472
				Yes	95 (80)	15648
			80	No	97 (99)	16135
				Yes	100 (100)	16634

[a] Reactions are carried out in air using 1 mmol of aryl halide, 1.5 mmol of terminal alkene, 8 mL DMF, 0.05g of Pd(0)-MCM-41, and 1.5 mmol of NaOAc. [b] Reactions are carried out in air using 1 mmol of aryl halide, 1.5 mmol of phenylacetylene, 1.5 mmol of TBAA, 0.05mmol of CuI, 6 mL of DMF, and 0.05g of Pd(0)-MCM-41 catalyst for 8 h. [c] Conversion of reactant is determined by gas chromatography. [d] TOF (turn over frequency) = moles converted/mole of active site/time.

p-bromoacetophenone would have also participated in the above-described Heck and Sonogashira reactions. However, this is not the case for the present catalyst.

Solid-Phase Poisoning Test.[33] Richardson and Jones suggested that the solid-phase poisoning test is the most definitive test available to date to ascertain the true heterogeneity of the Pd-based catalyst in C−C coupling reactions. In this test, metal-free mercaptopropyl-functionalized silica (in our case SH-MCM-41 and SH-SiO_2) was used as an effective palladium scavenger that selectively coordinates and deactivates the leached out palladium.[33,52] Thereby, cessation of the reaction is expected if catalysis of the coupling rection catalyzed by leached palladium species from the solid support. Richardson and Jones also observed that the poisoning is effective when the S/Pd (mole ratio) is greater than 5.3:1. We have performed solid-phase poisoning tests varying the S/Pd ratio from 5:1 to 1000:1 for Heck and Sonogashira coupling reactions using SH-MCM-41 and SH-SiO_2 as poisoning agent.

For Heck reactions, appropriate amounts of Pd(0)-MCM-41 and SH-MCM-41 were taken in the solution of different arylhalides (1 mmol), styrene/*n*-butyl acrylate (1.5 mmol), and NaOAc (1.5 mmol) in 15 mL of DMF. The mixture was stirred continuously maintaining the desired temperature. The progress of the reactions was monitored by the method described above. The poisoning test was performed for Sonogashira reaction also using 1 mmol of arylhalide, 1.5 mmol of phenylacetylene, 1.5 mmol of TBAA, and 0.05 mmol of CuI at desired temperature in presence of required amount of Pd(0)-MCM-41 and SH-MCM-41, maintaining the above-mentioned S/Pd ratio.

A comparison of percentage of conversion in C−C coupling reactions clearly shows that the catalytic efficacy of Pd(0)-MCM-41 is not affected when SH-MCM-41 is added to the reaction mixture. Results obtained in a typical test with sulfur to palladium ratio of 500:1, were collated in Table 4, showing the effect of mercaptopropyl-functionalized MCM-41 on catalytic action of Pd(0)-MCM-41. Clearly in both the coupling reactions catalyst remain active even in presence of large excess of SH-MCM-41.

In addition to the above solid-phase poisoning test with SH-MCM-41, we have also performed this test using commercially available (purchased from Sigma-Aldrich) 3-mercaptopropyl-functionalized silica (SH-SiO_2). In a typical Heck reaction, 1 mmol (0.2 g) iodobenzene, 1.5 mmol (0.2 g) *n*-butyl acrylate, and 1.5 mmol (0.123 g) NaOAc were mixed in 15 mL DMF and placed in a batch reactor. To this, 1 g of Pd(0)-MCM-41 was added and 0.0043 g of 3-mercaptopropyl-functionalized silica gel (SH-SiO_2) was added as a solid-phase poison (S/Pd molar ratio = 7:1). In this case, also we did not observe any appreciable change of the catalytic efficacy of Pd(0)-MCM-41 in presence of the poisoning agent SH-SiO_2. The kinetic profiles of the typical Heck reactions in presence of the poisoning agent SH-MCM-41 and SH-SiO_2 are shown in Figure 5. Notably there was no induction period in these reactions in presence or in absence of the poisoning agent.

Therefore, all the above tests convincingly demonstrate that there were no leaching of Pd species occurring in the Pd(0)-MCM-41 catalyzed C−C coupling reactions.

Recycling of the Catalyst. For recycling study, Heck reaction was performed with styrene and iodobenzene maintaining the same reaction conditions as described above using the recovered catalyst. Each time, after the completion of reaction the catalyst was recovered by centrifugation and then washed thoroughly with DMF followed by a 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 reaction up to four successive runs is summarized in Table

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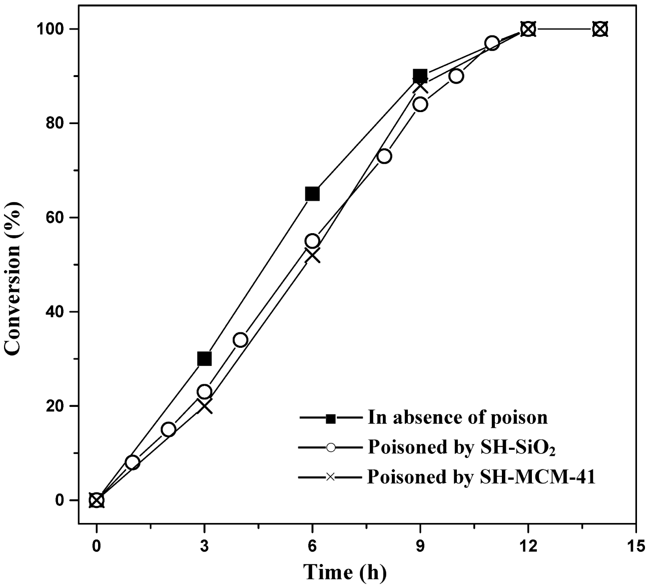

Figure 5. Kinetic profiles for the Heck coupling reaction of iodobenzene with *n*-butyl-acrylate in the absence of solid-phase poison (■), in the presence of $SH\text{-}SiO_2$ as the solid-phase poison (○), and in the presence of SH-MCM-41 as the solid-phase poison (×).

Table 5. Catalytic Efficacy of the Recovered Pd(0)-MCM-41 in Successive Runs[a]

cycles	conversion[b] (wt %)	selectivity (wt %)	TOF[c] (h^{-1})
	88	90	4831
first reuse	88	95	4831
second reuse	87	90	4798
third reuse	89	95	4850
fourth reuse	87	90	4798

[a] Reaction conditions: 1 mmol of iodobenzene, 1.5 mmol of styrene, 8 mL DMF, 0.05 g of Pd(0)-MCM-41, and 1.5 mmol of NaOAc. [b] Conversion of reactant is determined by gas chromatography. [c] TOF (turn over frequency) = moles converted/mole of active site/time.

5. The catalytic efficacy of recovered Pd(0)-MCM-41 remains almost the same for Heck coupling reaction of styrene and iodobenzene in every run.

Conclusions

In summary, we have succeeded in the preparation of an efficient Pd(0) immobilized mesoporous heterogeneous catalyst, Pd(0)-MCM-41, by simultaneous incorporation of palladium and self-assembly of mesoporous silica matrix via a simple and hassle free synthesis route. The prepared catalyst has shown high activity toward Heck and Sonogashira carbon−carbon coupling reactions. The catalyst can be reused several times without any loss of activity. In addition, the Pd(0)-MCM-41 acts as a true heterogeneous catalyst in cross coupling reactions. There are only a few catalysts that can catalyze C−C coupling reactions in truly heterogeneous catalytic conditions.[22,48] Notably, Pd(0)-MCM-41 is capable of activating arylchloride in both the Heck and Sonogashira reactions under mild conditions. Arylchlorides normally remain inactive toward this type of catalyst especially in heterogeneous condition. Because the reaction medium is heterogeneous, the prepared catalyst Pd(0)-MCM-41 might be useful for industrial applications.

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Supporting Information Available: Pore distribution plots of Pd(0)-MCM-41 and MCM-41 obtained from N_2 sorption measurement, IR spectrum of SH-MCM-41, purification procedures of the products obtained in C−C coupling reactions, and ^{1}H NMR data of the isolated products. This material is available free of charge via the Internet at http://pubs.acs.org.

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