Applications of pore-expanded mesoporous silica
6. Novel synthesis of monodispersed supported palladium nanoparticles and their catalytic activity for Suzuki reaction

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Abstract

MCM-41 silica, whose pores have been expanded by post-synthesis treatment with N,N-dimethyldecylamine, was used as an inexpensive high-surface area, large-pore support for rapid preparation of monodispersed palladium nanoparticles. The nanoparticles, initially prepared at room temperature, showed remarkable thermal stability as their size increased from 2.8 ± 0.8 to only 3.4 ± 0.8 nm after calcination at $500\,^\circ$C in air followed by reduction in H_2 at the same temperature. These materials were found to be highly active and stable catalysts for the Suzuki coupling reaction with virtually no leaching.

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Keywords: PE-MCM-41; Pd-nanoparticle; Thermal stability; Suzuki coupling; Leaching

1. Introduction

Catalysis over metallic particles involves only surface atoms, the relative amount of which is directly related to the particle size. Thus controlling particle size is of paramount importance for catalytic applications. As the particle size decreases, the relative number of surface atoms increases, and the activity (per weight) increases. In addition, due to quantum size effects, nanometer-sized particles may exhibit unique electronic, magnetic, optical, mechanical, or thermal properties suitable for a wide range of applications [1–4]. In many instances, the turnover frequency (TOF; activity per surface atom) increases as the particle size decreases due to favorable changes in the electronic properties of surface atoms, which are located mainly on edges and corners in small particles and mostly on flat surfaces in large particles. To take advantage of this compounded beneficial effect in catalysis, researchers have been very active in the synthesis, characterization, and application of metallic nanoparticles. The key challenges in this area are in preparing metallic nanoparticles with controlled sizes and stabilizing them against both sintering into larger particles and leaching into the solution during liquid-phase catalysis. Many "stabilizers," both electrostatic [5,6] and steric [5,7–9] in nature, have been developed. Polymerized materials bearing amine and/or amide groups, such as amine terminated hyperbranched polymers [10] and poly(amidoamine) (PAMAM) dendrimers [11–14], were used to synthesize occluded metallic nanoparticles with controlled sizes through cation complexation followed by gentle reduction. Likewise, the alcohol reduction method in the presence of poly(vinylpyrrolidone) (PVP) affords polymer-stabilized metallic nanoparticles with a narrow size distribution [15,16]. However, not only are all of these supports fragile and cannot withstand any thermal activation or regeneration, but also some of them (e.g., PAMAM dendrimers) are prohibitively expensive or their preparation is quite tedious. Moreover, these materials are not particularly porous, which may adversely affect the rate of catalytic reactions. There are several literature reports dealing with the development of supported metal nanoclusters/nanoparticles on solid supports using such strategies as adsorption/impregnation [17–21], immobilization on surfaces functionalized with appropriate ligands [22–24], co-precipitation [17,25], sol–gel [17,26], vapor-phase deposition

of organometallic complexes [27], microemulsion [28], electrochemical treatment [29], diffusion of preformed nanoparticles into the pores via sonication [16], and fabrication of nanoparticles via electron beam lithography [30,31]. However, many of the above methodologies are tedious, and some of them (e.g., such as the impregnation method) allow hardly any control of nanoparticle size. Because of their high surface areas, regular pore channels, and large pore diameters (2–20 nm), ordered mesoporous materials, such as SBA-15 and MCM-41, have been used as suitable scaffolds for the dispersion of small metal nanoparticles [32–35]. Moreover, because most of the nanoparticles are formed inside the pore channels, the support prevents the agglomeration of small nanoparticles to larger ones. Here we used pore-expanded MCM-41 silica (PE-MCM-41) as a suitable support for the rapid synthesis of monodispersed, highly active Pd nanoparticles inside its channels. The amine functionality of N,N-dimethyldecylamine (DMDA), introduced within the pore system during the post-synthesis pore expansion process (vide infra), drives the metallic cations inside the pores before their reduction. Moreover, because the amine is weakly supported as opposed to grafted, it is easily eliminated during washing of the catalyst with ethanol. The Pd nanoparticles thus obtained were found to be highly active, recyclable, and stable catalysts for the Suzuki coupling reaction in both organic and aqueous media.

2. Experimental

2.1. Material synthesis

MCM-41 silica was synthesized using Cab-O-Sil M5 fumed silica, cetyltrimethylammonium bromide (CTAB), and tetramethylammonium hydroxide (TMAOH) in the following relative molar amounts: SiO_2:TMAOH:CTAB:H_2O = 1:0.32:0.45: 67. The pore-expanded MCM-41 silica (PE-MCM-41) was prepared by enlarging the pores of as-synthesized MCM-41 via a postsynthesis hydrothermal treatment in the presence of DMDA (1.25 g/g of as-synthesized MCM-41). Details on the preparation of MCM-41 and PE-MCM-41 silicas have been given elsewhere [36–38]. For the synthesis of Pd nanoparticles inside the pore channels, 1 g of PE-MCM-41 was added to 25 mL of 0.002 molar aqueous solution of $PdCl_2$, and the mixture was stirred for 1 h. The solid was separated by filtration, washed copiously with distilled water, and dried at 45 °C overnight. This light-yellow solid was reduced by excess $NaBH_4$ in aqueous suspension (0.25 molar aqueous solution, 10 mol per mol of Pd) at room temperature, washed several times with water followed by ethanol (three times), and dried at 110 °C for 10 h under N_2 flow. The Pd loading in this solid was 1 wt%. Another catalyst with 2 wt% palladium loading was prepared using the same procedure, except for the addition of 50 mL of $PdCl_2$ solution instead of 25 mL. As shown schematically in Fig. 1, the DMDA was selectively removed during washing with ethanol [39]. The Pd content in the final materials was determined by inductively coupled plasma (ICP) analysis of the solution after removing the silica via HF treatment and dissolving Pd by treating in freshly prepared aqua regia and concentrated HCl. Furthermore,
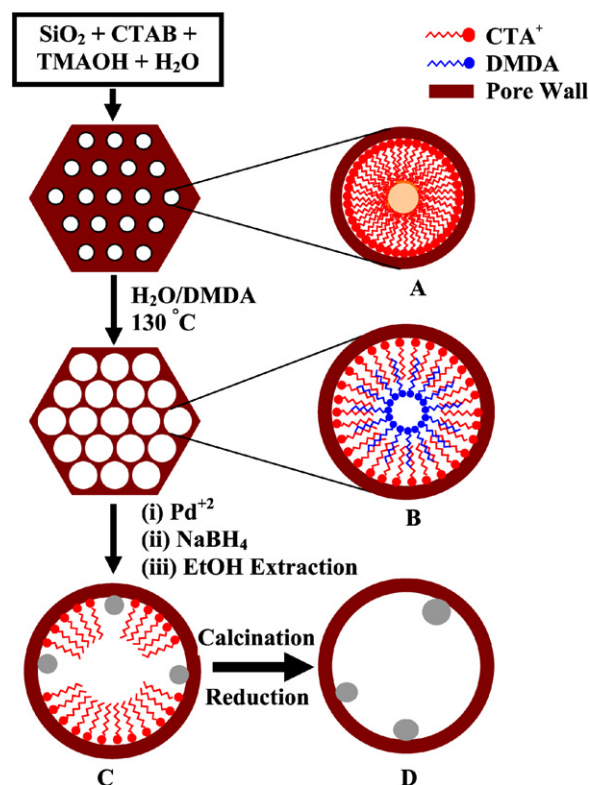

Fig. 1. Schematic of synthesis of pore-expanded MCM-41 and supported monodispersed Pd nanoparticles.

the Pd content in the liquid phase collected during filtration and washing before and after reduction was also measured. To do this, all of the liquid was evaporated, and the residue was treated with 3 mL of freshly prepared aqua regia, followed by evaporating to dryness. This dissolution–evaporation process was repeated twice more with aqua regia and three times with concentrated HCl. Finally, about 25 mL of double-distilled water was added, the content was filtered, and the filtrate was diluted to 100 mL with 1% HNO_3 solution before ICP measurement.

2.2. Suzuki coupling reaction

A 50-mL two-necked round bottomed flask, equipped with a condenser and magnetic stirrer, was charged with aryl halide (2 mmol), phenylboronic acid (PBA; 2.4 mmol), base (K_3PO_4 or Na_2CO_3; 6 mmol), and 5 mL of solvent (ethanol or water) and heated in an oil bath maintained at the desired temperature. After completion of the reaction, the liquid products were separated by filtration and analyzed by gas chromatography, using an HP 5890 instrument fitted with a 50-m-long HP-1 capillary column and a flame ionization detector. For the reaction in water, the catalyst was separated by filtration. Then the reaction products were extracted with ethyl acetate, dried over Na_2SO_4, and analyzed by gas chromatography.

2.3. Three-phase test

The three-phase test developed by Rebek and Gavina [40] is considered a definitive test for answering the homogeneity/ heterogeneity question. In this test, one of the reactants (aryl

halide, i.e., *p*-bromobenzoylamide in the current case) is anchored on a support surface. This supported reactant and another reactant in the liquid phase (*p*-bromoacetophenone in this case) are subjected to reaction in the presence of catalyst, which is present in the third phase (solid, Pd/PE-MCM-41 in this case). If leaching of active Pd species occurs, then the supported reactant will undergo the same chemical reaction as the reactant present in the liquid medium. However, in the case of heterogeneous reaction, the supported substrate would remain unreacted, and the soluble reactant would form the product.

The three-phase test was carried out as follows. A solution of 0.25 mmol *p*-bromoacetophenone, 0.37 mmol PBA, and 0.5 mmol K_2CO_3 in 5 mL of H_2O was subjected to reaction in the presence of Pd/PE-MCM-41 (1 mol% Pd with respect to substrate) and 250 mg of *p*-bromobenzoylamide-supported PE-MCM-41 (BrPhCONH-PE-MCM-41) at 100 °C for 24 h. Subsequently, the mixture was filtered, extracted with ethyl acetate, and analyzed as discussed above. The solid was then hydrolyzed with 2 molar ethanolic KOH solution (1.68 g KOH in 10 mL of ethanol and 5 mL of water) for 3 days at 90 °C. The resulting solution was neutralized with 10% HCl (v/v; 9.1 mL) extracted with dichloromethane, concentrated, and analyzed by ^{1}H NMR and mass spectrometry.

3. Results and discussion

The postsynthesis pore expansion procedure for MCM-41 silica has been described in detail elsewhere [36–38]. This two-step strategy involves synthesizing MCM-41 in the presence of cetyltrimethylammonium cations (CTA$^+$), followed by further hydrothermal treatment in the presence of an aqueous suspension of DMDA. It is believed that DMDA and CTA$^+$ self-organize within the pore channels, as shown in Fig. 1, due to favorable hydrophobic interactions between the two carbon chains (Fig. 1B) [41]. The DMDA molecules form an inverted cylindrical micelle, with the amine head groups pointing toward the pore center; thus creating a hydrophilic channel within the pores. This would facilitate the transfer of species dissolved in water, such as Pd^{2+} cations, within the channels of PE-MCM-41 and their complexation by the readily accessible amine groups. Reduction of such ions by excess NaBH$_4$ at room temperature affords small Pd nanoparticles inside the channels, referred to as Pd/PE-MCM-41 (Fig. 1C). This mechanism is reminiscent of the genesis of metallic nanoparticles in amine-terminated hyperbranched polymers [10] and PAMAM dendrimers [11–14]. To conclusively prove the role of DMDA in entrapping Pd inside the pores from the solution, a similar synthesis protocol to that of Pd/PE-MCM-41 was applied to calcined PE-MCM-41 (containing no CTA$^+$ or DMDA inside the pores) and ethanol-extracted PE-MCM-41 (containing no DMDA). Only 3.3% of the total Pd was absorbed/adsorbed on the silica surface, vs >99% for as-synthesized PE-MCM-41. Moreover, no Pd nanoparticles could be detected by TEM imaging of the final material after reduction. Furthermore, the same synthesis experiment with ethanol-washed PE-MCM-41 (which contained only CTA$^+$ inside the pores) showed similar results to the calcined sample. However, noncalcined PE-MCM-41,

which contained both CTA$^+$ and DMDA inside the pores, was found to be an excellent scavenger for Pd^{2+} cations. Indeed, ICP analysis showed that the filtrates and washings contained only 0.78% of Pd with respect to the total amount of Pd used during synthesis, thus confirming the role of Pd complexation by DMDA as the driving force for Pd loading. This finding indicates that (i) the Pd uptake is almost quantitative, and (ii) no loss of Pd occurs during washing with water (before reduction) or ethanol (after reduction).

Elemental analysis of Pd/PE-MCM-41 (expected Pd loading of 2 wt% during synthesis) by ICP revealed a Pd content of 1.92 wt%. For the 1 wt% Pd/PE-MCM-41 sample the Pd content was found to be 1.03 wt%. Because these final loadings were close to the amounts of Pd used in the synthesis, they were considered to be 2 and 1 wt%, respectively. The Pd/PE-MCM-41 (Fig. 1C) exhibited a surface area of 731 m^2/g, pore volume of 1.5 cc/g, and pore diameter of 8 nm. A similar material without Pd, obtained by selectively removing DMDA from the pore channels of as-synthesized PE-MCM-41 via ethanol extraction, showed a surface area of 509 m^2/g, pore volume of 1.5 cc/g, and pore diameter of 8 nm, indicating that the structural properties of the PE-MCM-41 support were not affected by Pd loading and further chemical reduction.

The TEM images of 1 wt% Pd/PE-MCM-41 (Figs. 2A and 2B) showed the occurrence of highly dispersed, uniformly sized Pd nanoparticles with an average size of 2.8 ± 0.8 nm. Increasing the Pd loading to 2 wt% provided a material with an average Pd particle size of 3.8 ± 1.5 nm (Figs. 2E and 2F). Although most of the Pd nanoparticles were in the range of average particle size, a few were relatively larger (6–9 nm) with a cylindrical morphology, providing further evidence that the Pd particles were formed inside the PE-MCM-41 channels. More interestingly, the Pd nanoparticles were found to be remarkably stable even under harsh calcination and reduction conditions. Indeed, the average particle size of 1 wt% Pd/PE-MCM-41 increased to only 3.4 ± 0.8 after calcination at 500 °C in air followed by reduction in H$_2$ at the same temperature (Figs. 2C and 2D).

The 2 wt% Pd/PE-MCM-41 catalyst showed high activity (Table 1) for the Suzuki coupling reaction of halobenzenes with phenylboronic acid (PBA) at room temperature (22 ± 2 °C) in air (entries 3–5). For coupling with iodobenzene, a reaction yield >99% was obtained at 78 °C after 5 h with a palladium-to-substrate ratio as low as 0.01 mol% (entry 2). The same catalyst was moderately active (61% yield after 20 h) for coupling with bromobenzene (entry 5). Literature data using unsupported hollow palladium spheres showed quantitative conversion after 3 h of reaction at 78 °C [41]. However, the Pd-to-substrate ratio used was 300 times higher than in the current investigation (entries 2 and 6). Furthermore, compared with a commercial Pd-carbon catalyst (10% Pd loading; Matheson, Coleman, and Bell), the current Pd/PE-MCM-41 catalyst proved much more active for the coupling of iodobenzene with PBA (entries 3 and 4).

The current catalyst also showed high activity for the coupling with other aryl bromo-derivative substrates, such as 4-bromobenzaldehyde and 4-bromotoluene (entries 7 and 8).
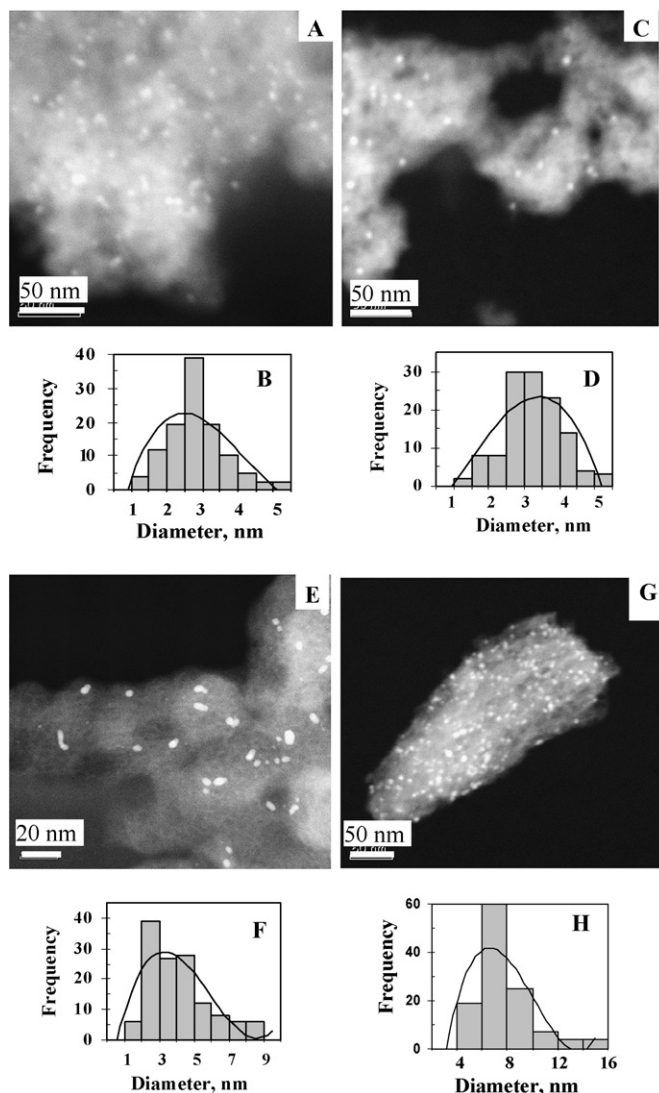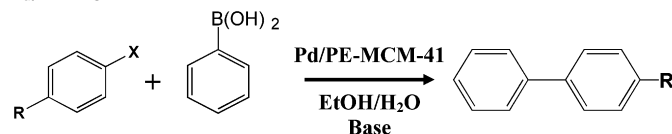
Fig. 2. STEM images and particle size distributions (from populations of >100 particles) of uncalcined (A, B) and calcined then reduced (C, D) 1 wt% Pd/PE-MCM-41, uncalcined (E, F) 2 wt% Pd/PE-MCM-41, and spent catalyst in Suzuki reaction (G, H) involving bromobenzene (after 4th cycle, see Table 2 for details), respectively.

Table 1
Suzuki coupling reaction[a] of halobenzenes with PBA in the presence of 2 wt% Pd/PE-MCM-41

Entry	Substrate	Catalyst (Pd, mol%)[b]	Temperature, °C (time, h)	Solvent	Yield, %
1	C_6H_5-I	Pd/PE-MCM-41 (0.1)	78 (5)	H_2O	93
2	C_6H_5-I	Pd/PE-MCM-41 (0.01)	78 (5)	Et–OH	99
3	C_6H_5-I	Pd/PE-MCM-41 (0.1)	22 (3)	Et–OH	60 (62)[c]
4	C_6H_5-I	Pd/Carbon (0.5)	22 (5)	Et–OH	55
5	C_6H_5-Br	Pd/PE-MCM-41 (0.1)	22 (20)	Et–OH	61
6	C_6H_5-I	Pd-Sphere (3)	78 (3)	Et–OH	99[d]
7	BBD[e]	Pd/PE-MCM-41 (1)	90 (15)	H_2O	100 (97)[g]
8	BT[f]	Pd/PE-MCM-41 (1)	90 (15)	D/W	55 (82)[g]
9	BT[f]	Pd/PE-MCM-41 (0)	90 (15)	D/W	0

[a] Reaction conditions: 2 mmol aryl halide, 2.4 mmol PBA, 6 mmol base (K_3PO_4); 5 mL solvent. D/W: DMF/H_2O (20:1).
[b] Pd mol% with respect to substrate.
[c] Yield of biphenyl in the filtrate after 24 h.
[d] Ref. [41].
[e] 4-Bromobenzaldehyde.
[f] 4-Bromotoluene. In entries 7, 8, and 9 substrate:PBA:Na_2CO_3 = 1:1:2.3 (molar ratio).
[g] The data in parenthesis are from Ref. [22] obtained using Pd supported on SBA-15 as catalyst.

Table 2
Reusability of 2 wt% Pd/PE-MCM-41 for Suzuki reaction with iodobenzene[a] and bromobenzene[b]

No. of cycle	Biphenyl yield[a], %	TON, h^{-1}	Biphenyl yield[b], %	TON, h^{-1}
Cycle-1	63 (99)[c]	713	56	160
Cycle-2	58 (99)[c]	655	50	143
Cycle-3	42 (93)[c]	475	33	95
Cycle-4	41	465	32	88

Note. TON: turnover number expressed in moles of product formed per moles of surface Pd per hour.
[a] Reaction conditions the same as entry 3 of Table 1.
[b] Reaction conditions the same as entry 5 of Table 1, except reaction time of 12 h instead of 20 h.
[c] Reaction conditions the same as entry 2 of Table 1 with Pd-to-substrate ratio of 0.1 mol%.

The activities were compared with those obtained by Crudden et al. [22] using a Pd supported on mercaptopropyl-modified SBA-15 catalyst under otherwise similar conditions. It showed the same activity as obtained by Crudden et al. [22] when 4-bromobenzaldehyde was used as the substrate (entry 7), however the activity was somewhat lower (55% yield vs 82% yield) for 4-bromotoluene as the substrate (entry 8). Replacing ethanol with water as solvent required 10 times more catalyst to achieve similar yield (entries 1 and 2). Despite this, however, water is a desirable medium because it is a readily available green solvent.

In a recent report, Arvela et al. [42] showed that unexpectedly low amounts of Pd (at ppb levels) present in Na_2CO_3 as impurities may catalyze the Suzuki coupling reaction. To verify this, we carried out the reaction in entry 8 of Table 1 in the absence of Pd/PE-MCM-41. It showed no conversion of 4-bromotoluene (entry 9 in Table 1), indicating that under our conditions, the activity in entry 8 was due solely to the catalyst used.

The reusability of solid catalysts in liquid-phase reactions often has been claimed based on a series of successive tests with quantitative conversions [22,41,43–46]. Such reaction conditions may not be appropriate, because the apparent stability of the catalyst at complete conversion may be due to favorable conditions, such as excessive temperature, excessive reaction time, and/or excessive catalyst-to-substrate ratio, rather than to the absence of catalyst deactivation. Here we addressed this issue by stopping the first reaction at ca. 60% conversion (Table 2) and carrying out three additional tests using the recycled catalyst under otherwise similar conditions. Table 2 shows a clear decrease in activity with the number of cycles for both reactants. Assuming that the Pd nanoparticles are spherical with

an average size of 3.8 nm and considering 1.27×10^{19} Pd atoms per square meter present in the surface as in the case of polycrystalline palladium [47], the average number of atoms present on the surface was determined and used to calculate the turnover numbers (TONs) in moles of product formed per mole of surface Pd per hour. This value decreased from 713 h^{-1} in the first cycle to 465 h^{-1} in the fourth cycle for reaction using iodobenzene as the substrate. Similarly, for the reaction involving bromobenzene, the TON decreased from 160 to 88 h^{-1}. Nonetheless, the activity seemed to stabilize after three reaction cycles (TONs of 475 and 465 h^{-1} for iodobenzene and 95 and 88 h^{-1} for bromobenzene in the third and fourth cycles, respectively). Just to prove the point that, as far as catalyst stability is concerned, running successive tests at close to 100% conversion may be misleading, we carried out three consecutive tests for the iodobenzene reaction under the conditions of entry 2 (Table 1) with a Pd-to-substrate ratio of 0.1%. The conversions obtained were 99, 99, and 93% (Table 2). Based on these data, the catalyst would seem to be recyclable without activity loss, which is an erroneous conclusion.

The nature of the active palladium species (homogeneous vs heterogeneous) in C–C coupling reactions has been a matter of much debate [48,49]. Most of the recent literature data point toward homogeneous Pd species being, at least partially, responsible for such coupling reactions [48,49]. Although few authors [43–45] have argued that their catalysts are truly heterogeneous, the claims were not as convincing. In the current case, the heterogeneity of the reaction was tested at room temperature by interrupting the iodobenzene conversion at ca. 60%, followed by separating the catalyst and monitoring the filtrate for an extended period. No appreciable change in conversion was noted (entry 3, Table 1); thus, leaching of Pd from the catalyst surface was ruled out. To confirm that this statement applies even for reactions at elevated temperature, another hot filtration test was carried out at 78 °C using the conditions specified in entry 2 of Table 1. The catalyst was separated by filtration at the same temperature; then fresh iodobenzene, PBA, and K_3PO_4 were added to the filtrate. The mixture was stirred for 5 h at 78 °C. No further conversion was observed, indicating the absence of any Pd species in the filtrate. Moreover, the current observation showed that the coupling reaction did not occur without the presence of the Pd catalyst even by using the iodobenzene as the substrate. Furthermore, ICP analysis of the filtrate after reaction was carried out to estimate the Pd leached out into the solution. For the reaction in entry 7 of Table 1, which was carried out at 90 °C, only 6 ppb of Pd was detected in the solution corresponding to 0.003% of the total Pd used in the reaction. The filtrate for the reaction in entry 3 of Table 1, in which the reaction was stopped at 60% conversion, showed the presence of <0.001% of the total Pd used in the reaction. A similar amount was also obtained for the reaction in entry 1 of Table 1. These results showed that the leaching of Pd species from the catalyst was extremely limited. A close look at the results in entry 3 of Table 1 reveals that the filtrate obtained after separating the catalyst at 60% iodobenzene conversion showed no further increase. Nonetheless, based solely on this observation, it would be difficult to claim that the reaction occurs in a truly heteroge-

neous medium, because the mobile active homogeneous species may redeposit onto the support surface during the filtration as a result of an unavoidable minor temperature decrease during the filtration workup [50,51].

To conclusively prove the heterogeneity of the reaction, we carried out the three-phase test using the procedure reported by Baleizao et al. [52]. Accordingly, one of the reactants (*p*-bromobenzoylamide in the current case) was immobilized onto calcined PE-MCM-41 surface (denoted as BrPhCONH-PE-MCM-41). This grafted material was added to the reaction medium along with *p*-bromoacetophenone and PBA in the presence of Pd/PE-MCM-41 using the conditions reported in Section 2. Analysis of the filtrate at the end of the reaction showed >99% conversion of *p*-bromoacetophenone. The supported compound was brought into solution by hydrolyzing in 2 M KOH, neutralized with HCl, and isolated as carboxylic acids. After the extraction workup and evaporation of the solvent under vacuum, the product was analyzed by ^{1}H NMR spectroscopy and mass spectrometry. The only compound detected was *p*-bromobenzoic acid, and no Suzuki reaction product (i.e., *p*-phenylbenzoic acid) was detected, confirming the heterogeneity of the reaction under the current catalyst conditions.

TEM images of the spent catalyst used in the aforementioned recycling experiments (Figs. 2G and 2H) showed an increase in Pd particle size from an average of 3.8 nm in the fresh catalyst to ca. 7 nm in the catalyst used for four cycles. Narayanan and El-Sayed [53] have reported similar observations; the size of PVP capped Pd nanoparticles supported on carbon increased during Suzuki coupling reaction from 1.9 nm before reaction to 3.1 nm at the end of the second cycle. Sintering is most likely the reason for catalyst deactivation in the current case. Although the surface mobility of solid Pd particles is the likely cause for the particle size increase, effects due to the redeposition of soluble Pd species, if any, cannot be ruled out.

In conclusion, we have shown that the pore-expanded MCM-41 silica can provide a suitable support for synthesizing highly dispersed palladium nanoparticles with narrow size distribution inside its pores. This gave rise to active and reusable catalysts for Suzuki reaction with virtually no leaching of Pd species. The synthesis methodology of PE-MCM-41-supported Pd nanoparticles can be easily extended to other metal and semiconductor particles.

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