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Ordered Mesoporous Organosilica with Ionic-Liquid Framework: An Efficient and Reusable Support for the Palladium-Catalyzed Suzuki–Miyaura Coupling Reaction in Water

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Abstract: The preparation of a novel palladium-supported periodic mesoporous organosilica based on alkylimidazolium ionic liquid (Pd@PMO-IL) in which imidazoilium ionic liquid is uniformly distributed in the silica mesoporous framework is described. Both Pd@PMO-IL and the parent PMO-IL were characterized by N_2-adsorption–desorption, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), TEM, and solid-state NMR spectroscopy. We have demonstrated that Pd@PMO-IL is an efficient and reusable catalyst for the Suzuki–Miyaura coupling reaction of various types of iodo-, bromo-, and even deactivated aryl chlorides in water. It was also found that although the PMO-IL nanostructure acts as reservoir for soluble Pd species, it can also operate as a nanoscaffold to recapture the Pd nanoparticles into the mesochannels thus preventing extensive agglomeration of Pd. This observation might be attributed to the isolated ionic liquid units that effectively control the reaction mechanism by preventing Pd agglomeration and releasing and recapturing Pd nanoparticles during the reaction process. The catalyst can be recovered and reused for at least four reaction cycles without significant loss of activity.

Keywords: ionic liquids • nanoparticles • palladium • organosilica • Suzuki–Miyaura coupling • water chemistry

Introduction

The palladium-catalyzed Suzuki coupling reaction of haloarenes and triflates with arylboronic acids is one of the most important transformations in biaryl synthesis from both academic and industrial points of view.[1,2] This is because the resulting biaryls are versatile building blocks in the field of liquid crystals, pharmaceuticals, conducting polymers, herbicides, and natural products.[3] Whereas the Suzuki reaction has been traditionally carried out by using homogeneous systems in the presence of trivalent phosphine ligands,[3] more recently, N-heterocyclic carbenes (NHCs) have attracted considerable attention as valuable ligands for this transformation.[4,5] However, separation of the catalyst from the product can often be problematic in the homogeneous systems. Moreover, for economic reasons, catalyst recovery is highly desirable, in particular, if precious metal catalysts are used with high loading.

On the other hand, the use of ionic liquids (ILs) as reaction media for palladium-catalyzed coupling reactions shows clear advantages over commonly used organic solvents, especially if less reactive bromo- and chloroarenes are used as starting materials. In this regard, the in situ formation of palladium–NHC complexes in imidazolium-based ionic liquids was found to be responsible for superior catalytic reactivities.[6–8] However, despite the remarkable utility of ionic liquids, these systems often require large amounts of relatively expensive ionic liquids, which may hinder their widespread practical implementation. Furthermore, depending on the relatively high viscosity of the ionic liquids, the bulk ionic liquid may suffer from slow diffusion, causing the main part of the reaction to proceed in a small fraction of ILs called the "diffusion layer". Therefore, from both economical and technical points of view, the productivity of the reaction based on bulk ILs is hampered since a large part of IL (and the associated catalyst) is not contributing in the overall process. To address these inherent limitations, immobilized ionic liquids offer many advantages over homogeneous

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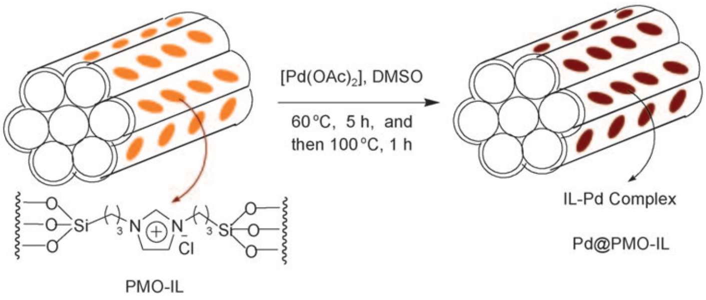
IL systems, such as easy handling and recyclability.[9] Although, these approaches decrease the amount of IL utilized in a typical process relative to homogeneous systems; leaching of IL from the heterogeneous support is fairly commonplace. This problem can be partly impeded by using a variety of chemically bounded ionic liquids,[10] but one of the major difficulties concerned that still remains unresolved is the low loading of the immobilized ionic liquid. We have overcome this difficulty by designing a novel periodic mesoporous organosilica comprising imidazolium ionic liquid (PMO-IL).[11] The periodic mesoporous organosilica is built from bridge organosilanes of type $(R'O)_3Si{-}R{-}Si(OR')_3$ wherein organic groups R are homogeneously distributed throughout the stable inorganic framework.[12–16] In fact, this innovative area has provided a new opportunity for the design of novel nanostructured materials in which the chemical functionalities can be precisely tuned by changing the structure and composition of the organic groups in the framework of nanopores. An important and unique aspect of the PMO materials is that the organic groups R are located in the channel wall, thus allowing higher organic loading without significant channel blockage.[15,16]

We have found that palladium catalyst in the ionic liquid environment of our new designed imidazolium-based periodic mesoporous organosilica shows extremely high catalytic activity for the Suzuki–Miyaura coupling of aryl halides in water. The preparation of our Pd@PMO-IL catalyst was achieved by treatment of a substoichiometric amount of $Pd(OAc)_2$ with an excess amount of PMO-IL under an argon atmosphere in dimethylsulfoxide (DMSO) solvent (Scheme 1).[11,17]



Scheme 1. Preparation of the Pd@PMO-IL catalyst.

Results and Discussion

The parent ordered mesoporous organosilica with ionic liquid framework (PMO-IL) was synthesized by hydrolysis and co-condensation of 1,3-bis(3-trimethoxysilylpropyl)imidazolium chloride[18] and tetramethoxysilane in the presence of Pluronic P123 as a template under acidic conditions.[19] This organosilica material showed typically type IV N_2-sorption isotherms with a sharp H1 hysteresis loop, according to the IUPAC classification, which is characteristic of ordered mesoporous materials (Figure 1).

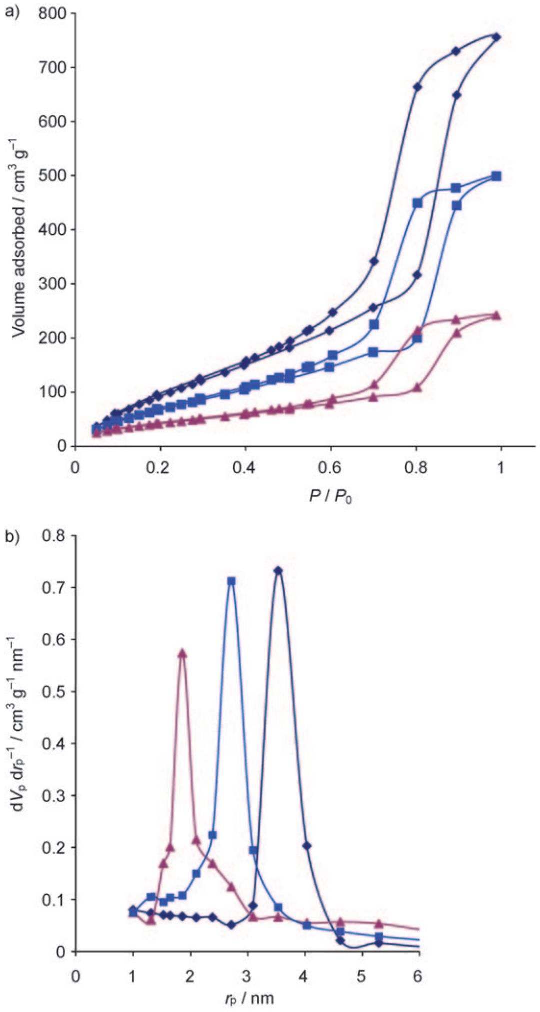


Figure 1. Nitrogen adsorption–desorption isotherms (a) and pore size distributions (b) of the PMO-IL (black diamond), Pd@PMO-IL (blue square), and recovered Pd@PMO-IL (RPd@PMO-IL, pink triangle) materials.

The TEM image of solvent extracted PMO-IL material also illustrates a uniform rodlike structure with two-dimensional hexagonal symmetry in the mesoporous channels that is characteristic of high-ordered SBA-15[20]-type materials (Figure 2).

The ^{13}C CP/MAS NMR spectrum of the PMO-IL sample was also carried out to confirm the presence of IL in the mesoporous framework. The ^{13}C CP/MAS NMR spectrum of the PMO-IL material strongly reveals the characteristic signals of the IL bridging moiety. Figure 3 shows solid-state ^{13}C NMR spectra of PMO-IL that can be assigned to the C species as follows: $\delta = 9.0$ ($SiCH_2$), 24.0 ($CH_2CH_2CH_2$), 52.1 (CH_2N), 122.7 (CHCH), and 135.4 ppm (NCHN). This analysis indicates successful incorporation of ionic liquid in the mesoporous framework. Moreover, the absence of any further carbon resonance in the ^{13}C NMR spectrum clearly confirms that all Si−C bonds survived intact during the synthesis and extraction processes.

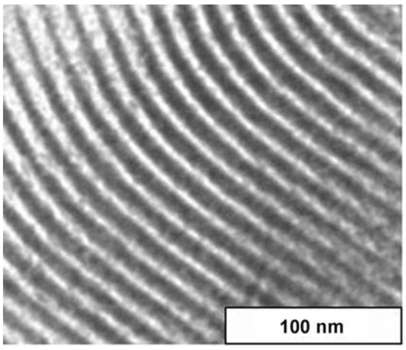


Figure 2. TEM image of PMO-IL material.

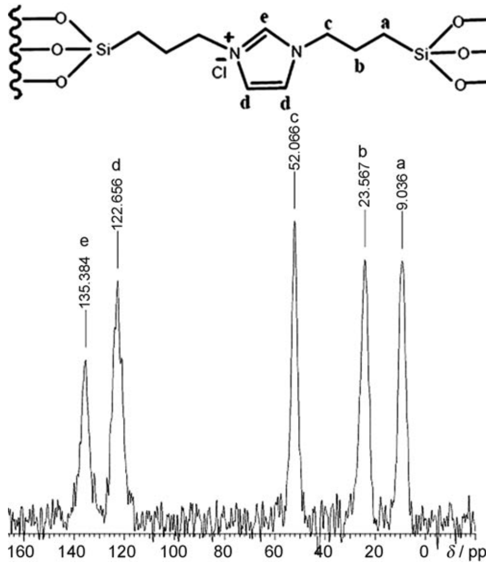


Figure 3. Solid-state ^{13}C NMR spectra of the PMO-IL material.

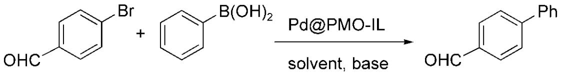
Thermal gravimetric analysis (TGA) of PMO-IL was also conducted to prove the thermal stability of the mesoporous framework (see Figure 2S in the Supporting Information). The first weight loss that appeared below 100 °C corresponded to omission of water and alcoholic solvents remaining from the solvent extraction process. The main weight loss observed around 350 to 450 °C is attributed to thermal dissociation of the ionic liquid groups. This data clearly demonstrates the high thermal stability of nanostructured PMO material. Furthermore, solid-state ^{29}Si NMR spectra (see Figure 6S in the Supporting Information,) and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS, see Figure 7S in the Supporting Information) data of the synthesized PMO-IL material nicely confirm the presence and stability of ionic liquid moieties in the mesoporous framework.

This novel nanostructured PMO-IL material was then reacted with a substoichiometric amount of Pd(OAc)$_2$ to afford the corresponding palladium-containing periodic mesoporous organosilica (Pd@PMO-IL) catalyst for the Suzuki reaction. To elucidate successful incorporation of palladium into the mesoporous framework, the textural properties of the final nanostructure were evaluated by nitrogen-sorption experiments. The N$_2$-adsorption–desorption isotherm of Pd@PMO-IL catalyst, the same as parent PMO-IL, illustrated a type IV isotherm with a H1 hysteresis loop that is characteristic of SBA-15-type materials with two-dimensional structure (Figure 1). The nitrogen-sorption experiment also showed that the original PMO-IL has a BET surface area of 671 m^{2}g^{-1} and a primary mesopore volume of 1.21 cm^{3}g^{-1}. The average pore diameter is also calculated from the adsorption branch of the isotherm to be 7.0 nm for PMO-IL by using the BJH method (see Table 1S in the Supporting Information). The N$_2$-adsorption isotherm and pore size distribution of the Pd@PMO-IL were significantly different from that of the original PMO-IL. The BET surface area of Pd@PMO-IL was 458 m^{2}g^{-1}, whereas the mesopore volume was 0.88 cm^{3}g^{-1}. The BJH pore size distribution also illustrated a narrow peak pronounced at around 5.3 nm for this material, which displays a considerably lower pore diameter in comparison to the original PMO-IL. These results clearly demonstrate that the immobilization of palladium has been successfully achieved inside the nanosized pores of the PMO-IL.

The resulting Pd@PMO-IL catalyst was then tested in the Suzuki cross-coupling reaction of arylboronic acids with various types of aryl halide in the presence of different bases and solvents. To optimize the overall process, the reaction of 4-bromobenzaldehyde with phenylboronic acid was chosen as a model reaction. The reactions were conveniently carried out in a batch reactor in the temperature range 60–90 °C. The efficiency of Pd@PMO-IL is considerably affected by the type of solvent and base used in the reactions (Table 1).

Although in EtOH and MeOH, the catalyst system afforded the corresponding coupling product in moderate yields (Table 1, entries 1 and 2), acetone, THF, and DMF

Table 1. The effect of solvent and base in the Suzuki coupling of 4-bromobenzaldehyde with phenylboronic acid by using Pd@PMO-IL as the catalyst.[a]



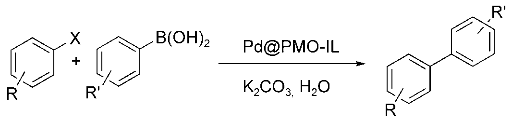
Entry	Solvent	Base	Yield [%][b]
1	EtOH	K_2CO_3	49
2	MeOH	K_2CO_3	56
3	acetone	K_2CO_3	8
4	THF	K_2CO_3	5
5	DMF	K_2CO_3	10
6	EtOH/H_2O 1:1	K_2CO_3	61
7	DMF/H_2O 1:1	K_2CO_3	35
8	**H_2O**	**K_2CO_3**	**>99**
9	H_2O	Na_2CO_3	30
10	H_2O	NaOAc	21
11	H_2O	*t*BuOK	28
12	H_2O	K_3PO_4	24
13	H_2O	Cs_2CO_3	85

[a] Reaction conditions: 4-bromobenzaldeyde (1 mmol), phenylboronic acid (1.1 mmol), base (3 mmol), catalyst (0.2 mol %), solvent (3 mL), 60 °C, 2.5 h. [b] GC yields [%].

were proven to be poor solvents for the same process (entries 3–5). On the other hand, remarkably high activity was reproducibly found in water (entry 8), whereas mixtures of either EtOH/H_2O or DMF/H_2O in a ratio 1:1 were not suitable for the present system (entries 6 and 7). The ability to use water as the reaction medium greatly increases the green credentials of the method. Among the various bases screened in water, K_2CO_3 provided the highest cross-coupling yield of >99 % in 2.5 h (entry 8).

With the optimized reaction conditions in hand, we next managed to examine the scope and limitation of this palladium cross-coupling reaction with various types of iodo-, bromo-, and chloroaryl derivatives and arylboronic acids (Table 2).

Table 2. Suzuki cross-coupling of various arylhalides with $ArB(OH)_2$ in the presence of Pd@PMO-IL catalyst in water.[a]



Entry	R	R′	X	cat. [mol %]	T [°C]	t [h]	Yield [%][b]
1	4-MeO	H	I	0.1	60	2.5	>99
2	4-MeO	4-Me	I	0.1	60	2	>99
3	4-CHO	H	Br	0.2	60	2.5	>99
4	4-CHO	4-Me	Br	0.2	60	2	>99
5	3-CHO	H	Br	0.2	60	4	94
6	3-CHO	4-Me	Br	0.2	60	4	96
7	2-CHO	H	Br	0.2	60	8	80
8	2-CHO	4-Me	Br	0.2	60	8	83
9	3-Ac	H	Br	0.2	60	5	93
10	4-CN	4-Me	Br	0.2	60	2.5	98
11	4-MeO	H	Br	0.2	75	5	95
12	4-MeO	4-Me	Br	0.2	75	4.5	95
13	4-Et	H	Br	0.2	75	5	94
14	4-Me	H	Br	0.2	75	4.5	94
15	4-Me	4-Me	Br	0.2	75	4.5	95
16	3-py.[c]	H	Br	0.5	70	6	85
17	3-py.[c]	4-Me	Br	0.5	70	5.5	92
18	4-CHO	H	Cl	0.8	90	15	78
19	4-CHO	4-Me	Cl	0.8	90	15	85
20	4-CN	4-Me	Cl	0.8	90	15	83
21	3-Ac	H	Cl	0.8	90	20	73
22	3-CHO	H	Cl	0.8	90	20	75
23	3-CHO	4-Me	Cl	0.8	90	20	77
24	H	H	Cl	0.8	90	20	75[d]
25	H	4-Me	Cl	0.8	90	20	72[d]
26	4-Me	H	Cl	1	90	20	72[d]
27	4-Me	4-Me	Cl	1	90	20	73[d]
28	4-MeO	H	Cl	1	90	20	55[d]
29	4-MeO	4-Me	Cl	1	90	20	60[d]

[a] Reaction conditions: arylhalide (1 mmol), arylboronic acid (1.1 mmol), K_2CO_3 (3 mmol), H_2O (3 mL). [b] Isolated yields (%) after recrystallization or column chromatography unless otherwise stated. [c] 3-Pyridine. [d] 0.5 equiv $n$$Bu_4NBr$ was added.

In general, all the reactions were very clean and the corresponding bis(aryl) products were isolated in good to excellent yields. As demonstrated in Table 2, as expected, aryl iodides were rapidly converted to the corresponding bis(aryl) products with excellent yields (Table 2, entries 1 and 2).[21] This coupling reaction was also equally effective with both electron-rich and -poor aromatic bromoarene derivatives,[21] and the reactions proceeded smoothly to furnish the Suzuki product with good to excellent yields in relatively short reaction times (entries 3–17).

Worthy of note is that heteroaromatic substrates, such as highly deactivated 4-bromoanisole and 3-bromopyridine led to the corresponding bis(aryl) products in excellent yields (Table 2, entries 11, 12, 16 and 17). Although, a few solid catalysts have been shown to promote the Suzuki–Miyaura reaction with chloroarenes,[22] most of them use organic solvent and are not capable of catalyzing this transformation with water as the solvent.[23] However, we found that Pd@PMO-IL is also capable of activating chlorobenzene to produce a significant yield of the desired products under the desired reaction conditions (entries 24 and 25). Moreover, various functional groups, such as cyano, acyl, CHO, methyl, and methoxy were tolerated and the corresponding coupled products were obtained in good to excellent isolated yields (entries 18—23 and 26–29). It is also worth noting that more sterically demanding substrates were also smoothly converted to the corresponding products as exemplified by entries 7 and 8.

The reusability and recovery of the catalyst are important issues, especially when the reactions use solid catalysts. By using the coupling reaction of phenylboronic acid and 4-bromobenzaldehyde as a test model, it was found that recovery can be successfully achieved in four reaction runs without significant loss of catalytic activity (Figure 4).

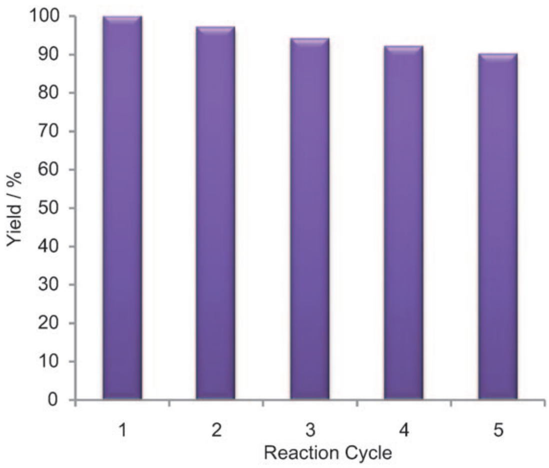


Figure 4. Reusability of the Pd@PMO-IL catalyst in the Suzuki coupling.

Although, no significant reduction in the activity of the catalyst was observed, to test if any palladium is leached from the solid catalyst during the process, a hot filtration test was performed for the reaction of 4-bromobenzaldehyde with phenylboronic acid after ~40 % of the coupling reaction is completed. Interestingly, we found that whereas no palladium species was detected by using atomic absorption spectroscopy in the filtrate, a further 14 % conversion of the coupling reaction was observed upon the heating of the catalyst-free solution for 20 h at 60 °C. According to this observation it appears that Pd-containing PMO-IL operates at least partially through a homogeneous mechanism. To further ascertain whether the catalyst was operating by a homogeneous or heterogeneous mechanism, a set of three independent experiments including a Hg^0 and two three-phase poisoning tests were designed for the coupling reaction of 3-bromoacetophenone with phenylboronic acid under the standard reaction conditions. To conduct the test, three different flasks were charged with 3-bromoacetophenone (1 mmol), phenyl boronic acid (1.1 mmol), Pd@PMO-IL (0.2 mol%), and K_2CO_3 (3 mmol) in water (3 mL) as the solvent. The mixture of three flasks were then heated to 60 °C, while mercury was added to the first flask, SBA-15-propyl-SH to the second one, and poly-(4-vinylpyridine) (PVP) to the third flask in a ratio of 400 equivalents to the initial palladium content of the catalyst.[11] These control experiments showed that the reactions were quenched completely over all three flasks upon addition of the poison (Figure 5).

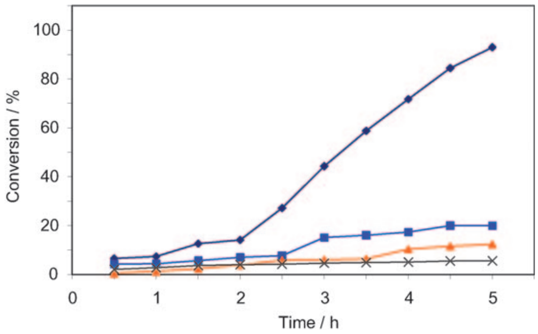


Figure 5. Reaction progress as a function of time on the Suzuki coupling of 3-bromoacetophenone with phenylboronic acid by using Pd@PMO-IL catalyst in water under: a) normal conditions (black diamond), b) in the presence of 400 equiv Hg^0 (blue square), c) in the presence of 400 equiv PVP (orange triangle), and d) in the presence of 400 equiv SBA-propyl-SH (black cross).

These results suggest that for the present reaction, supported palladium catalyst serves as a reservoir for active Pd species that are dissolved from the solid catalyst under the described reaction conditions. A relatively similar observation about the nature of Pd species in the so-called heterogeneous C–C coupling reaction has been made through the elegant work of Finke, Jones, and others.[24–27] Although, it appears that the reactions are performed by a partially homogeneous mechanism, we surprisingly found that no significant change had occurred in both the activity and the metal content the recovered Pd@PMO-IL (RPd@PMO-IL).

To further shed light on whether our system works on a molecular level, the recovered catalyst was also studied by means of TEM and N_2-adsorption–desorption analyses. The N_2 sorption diagram of the recovered catalyst RPd@PMO-IL interestingly showed a type IV isotherm with relatively sharp hysteresis loop, which indicates that the high-ordered mesostructures have survived (Figure 1). On the other hand, BJH calculations demonstrated that the mesochannels were shifted to a lower pore size (3.7 nm) relative to the parent PMO-IL (7.0 nm) and fresh Pd@PMO-IL (5.3 nm). Moreover, the BET surface area and mesoporous volume of the recovered catalyst were also reduced from 458 and 0.88 to 313 $m^2 g^{-1}$ and 0.60 $cm^3 g^{-1}$, respectively (Table 3).

Table 3. Structural parameters of PMO-IL, Pd@PMO-IL, and recovered Pd@PMO-IL catalyst (RPd@PMO-IL) determined from nitrogen-sorption experiments.

Sample	BET surface area [$m^2 g^{-1}$]	Pore diameter [nm]	Pore volume [$cm^{-3} g^{-1}$]
PMO-IL	671	7.0	1.21
Pd@PMO-IL	458	5.3	0.88
RPd@PMO-IL	313	3.7	0.60

A TEM micrograph of the recovered catalyst after the fifth reaction cycle viewed along the channels also revealed that most of the nanoscale channels remained unchanged during both the reaction and the recovery process (Figure 6).

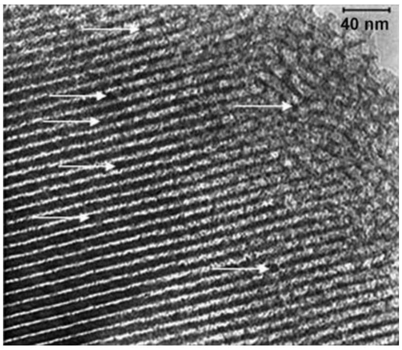


Figure 6. TEM image of Pd@PMO-IL catalyst after the fifth reaction cycle. The arrows show the presence of Pd nanoparticles inside PMO-IL mesochannels.

Further inspection of the TEM micrograph of the recovered catalyst demonstrates that the Pd nanoparticles throughout the regular mesochannels of the parent PMO-IL are well-distributed. This observation shows, interestingly, that while Pd@PMO-IL acts as a reservoir for highly active and soluble Pd species, it may also operate as a nanoscaffold to recapture the palladium nanoparticles inside the mesochannels, thus preventing Pd agglomeration. We believe that the ionic liquid nature of the walls in the parent PMO-IL has a crucial role in this release and capture mechanism because the same phenomena has not been observed for a similar nonfunctionalized Pd@SBA-15 catalyst with the same loading. In this case, the catalyst Pd@SBA-15 was extensively deactivated after the first reaction cycle.

Conclusion

We have demonstrated for the first time that an ionic liquid based periodic mesoporous organosilica is an effective and powerful support for the immobilization and stabilization of Pd nanoparticles on the Suzuki-coupling reaction in water. Our study showed that this innovative system could be successfully applied as an effective and reusable catalyst for the Suzuki coupling of a variety of activated and deactivated haloarenes with arylboronic acids. Interestingly, it was found that while hot filtration tests and selective catalyst poisons showed the presence of soluble Pd species during the reaction process, atomic spectroscopy and catalyst recovery studies illustrated that no significant decrease has been seen in the activity and metal content of recovered Pd@PMO-IL. Furthermore, the TEM image of the recovered catalyst showed the presence of well-distributed Pd nanoparticles in the mesochennels of the PMO-IL material. Based on these results, we conclude that although the PMO-IL nanostructure acts as reservoir for the soluble Pd species, it can also operate as a nanoscaffold to recapture the Pd nanoparticles into the mesochannels, thus preventing extensive agglomeration of Pd nanoparticles. This remarkable ability of the PMO-IL mesostructure may be attributed to ionic liquid units that effectively manage the reaction through preventing Pd agglomeration and releasing and recapturing Pd nanoparticles during reaction process. Since the supported ionic liquid catalysis systems have many advantages over traditional catalysts, we therefore speculate that this innovative system would open a new gate for the design and synthesis of new types of supported metal catalysts based on PMO-IL with high and yet tunable loading of ionic liquid moieties.

Experimental Section

General procedure for the synthesis of 1,3-bis(trimethoxysilylpropyl)imidazolium chloride:[18] The alkyl imidazolium based ionic liquid was synthesized by a modification of a literature procedure. In a typical experiment, sodium imidazolide (3.002 g, 30 mmol) and 3-chloropropyl-trimethoxysilane (6.082 g, 30 mmol) were added to a well-dried flask containing super dry THF (100 mL) and stirred at 65 °C for 24 h under an argon atmosphere. After cooling the reaction mixture to room temperature, the solvent was removed under reduced pressure and the oil obtained was transferred to another flask containing 3-chloropropyl-trimethoxysilane (30 mmol) in absolute toluene (100 mL) and refluxed for 48 h in the absence of light. After cooling the solution to room temperature, the reaction mixture was first washed thoroughly with toluene (5×50 mL) and then super dry CH_2Cl_2 was added to precipitate NaCl. The supernatant dichloromethane solution was transferred into another well-dried flask. A yellow viscous ionic liquid (**1**) was obtained after removal of the solvent and drying under vacuum. The spectral data for IL **1** is as follows. ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C, TMS): $\delta=10.00$ (s, 1H; NCHN), 7.46 (d, 2H, $J=1.7$ Hz; CHCH), 4.32 (t, 4H, $J=7.1$ Hz; NCH_2), 3.60 (s, 18H; $6OCH_3$), 2.00 (m, 4H; $CH_2CH_2CH_2$), 0.62 ppm (t, 4H, $J=8.1$ Hz; $SiCH_2$); ^{13}C NMR (63 MHz, $CDCl_3$, 25 °C, TMS): $\delta=136.08$ (NCHN), 122.20 (CHCH), 51.76 (NCH_2), 50.77 (OMe), 24.12 ($CH_2CH_2CH_2$), 5.81 ppm ($SiCH_2$).

General procedure for the synthesis of ionic liquid based periodic mesoporous organosilica (PMO-IL): PMO-IL was prepared according to a previous reported procedure.[19] In a typical synthesis, Pluronic P123 (1.67 g) and KCl (8.8 g) were added to a solution of distilled water (10.5 g) and HCl (2 M, 46.14 g) with stirring at 40 °C. After a clear homogeneous solution had been produced, a pre-prepared mixture of ionic liquid (0.86 g) and tetramethoxysilane (2.74 g), in absolute methanol was rapidly added and stirred at the same temperature for 24 h. The resulting mixture was then transmitted into a Teflon-lined autoclave and statically heated at 100 °C for 72 h. The obtained solid material was filtered, washed completely with deionized water, and dried at room temperature. The extraction of surfactant was accomplished four times by a Soxhlet apparatus by using ethanol (100 mL) and concentrated HCl (3 mL, for each time) for 1 g of sample over 12 h. The final PMO material was denoted as PMO-IL.

Preparation of Pd@PMO-IL catalyst: Pd@PMO-IL was also prepared based on a literature procedure with a slight modification.[17] Palladium acetate (27 mg, 0.12 mmol) was added to a well-dispersed solution of ionic liquid based periodic mesoporous ionic liquid (PMO-IL) (1 g, 1.0 mmol IL g^{-1}) in DMSO (4.5 mL) under an argon flow. The system was stirred at 60 °C for 5 h and then at 100 °C for 1 h. After cooling the reaction solution to room temperature, the resulting mixture was washed with CH_2Cl_2 (3×10 mL) to remove unreacted $Pd(OAc)_2$. The final material was obtained after drying by evacuation at 50 °C for 12 h. Elemental analysis showed that the loading of Pd was 0.1 mmol Pd/g solid.

General procedure for the Suzuki coupling reaction by using Pd@PMO-IL as the catalyst: The Suzuki reaction was performed by using arylboronic acid (1.1 mmol), aryl halide (1.0 mmol), K_2CO_3 (3 mmol), and catalyst (0.002–0.01 equiv to aryl halide) in distilled water at 60–90 °C. The reaction progress was monitored by GC analysis after completion of the reaction; the mixture was allowed to cool to room temperature and was then filtered and washed with H_2O and diethyl acetate. The organic phase was separated and dried over $MgSO_4$ and the solvent was then removed under reduced pressure. Pure products were obtained after recrystallization or by isolation of the residue by column chromatography on silica.

Acknowledgements

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