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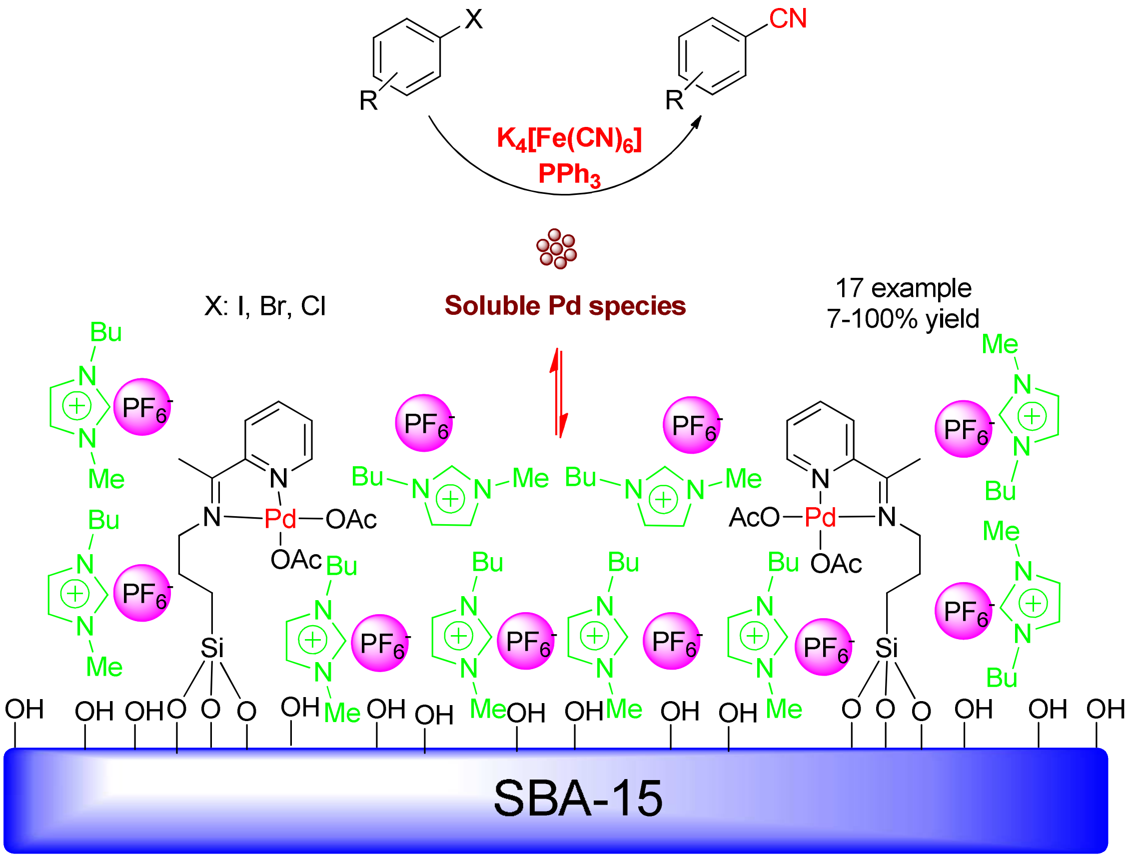
Graphical Abstract



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ARTICLE TYPE

Activity enhancement in cyanation of aryl halides through confinement of ionic liquid in the nanospaces of SBA-15-supported Pd complex

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A novel and practical ionic-liquid mediated route for the synthesis of various aromatic nitriles has been developed via the cyanation of aryl halides with $K_4[Fe(CN)_6]$ as a low cost, non-toxic and easily handled cyanating reagent in the presence of SBA-15 functionalized palladium complex partially confined with ionic liquids (**IL@SBA-15-Pd**) as the catalyst. Among the various ionic liquid tested in the cyanation reaction, 1-butyl-3-methylimidazolium hexafluorophosphate was found to provide the best medium for Pd-catalyzed cyanation of aryl halides. A variety of electron-rich and electron-poor aryl iodides and bromides gave the corresponding benzonitrile derivatives in good yield. Moreover, the catalyst was reused in four consecutive cycles with consistent catalytic activity. It was found that the presence of ionic liquid in the mesochannels of mesoporous support not only provides a means of stabilizing Pd nanoparticles during the reaction but also the salient phase transfer feature of imidazolium moieties may also serve as handles for faster penetration of $Fe(CN)_6^{3-}$ into the system pores to achieve highly concentrated reaction site in close proximity of the catalytic (Pd NPs) centers, which resulted in an enhancement of the catalyst activity performance.

Introduction

Synthesis of aromatic nitriles is one of the important organic transformations because of the wide-spread application of cyano containing structures as important building blocks of natural products, agrochemicals, pharmaceuticals, dyes and electronic materials.[1] In addition, cyano group is a highly useful intermediate in organic synthesis and can be converted to various functionalities such as amines, amidines, tetrazoles, aldehydes, amides, or other carboxy derivatives.[2] Conventional routes for the preparation of aromatic nitriles are the Sandmeyer reaction of aryl diazonium compounds and the Rosenmund-von Braun reaction of haloarenes[3] in which CuCN is used as the cyanating agent in super stoichiometric amounts under harsh reaction conditions (typically 150–250 °C). As a consequence, a substantial amount of research has been directed toward the development of various transition-metal catalysts such as Cu, Ni, Ga and Pd as well as a variety of organic or inorganic cyanide sources [KCN, NaCN, $Zn(CN)_2$, CuSCN, $(CH_3)_2C(OH)CN$ and $(CH_3)_3SiCN$] to synthesize diverse arrays of aromatic nitriles under milder reaction conditions.[4] Despite the fact that these catalytic protocols have shown significant improvement as compare with their earlier stoichiometric counterparts, there are still many limitations associated with these systems such as employing toxic and/or expensive cyanating agents at elevated temperatures particularly when using Ni or Cu based catalysts. To overcome these limitations, many attempts have been made to develop palladium-catalyzed cyanation of aryl halides with $K_4[Fe(CN)_6]$ as a low cost, non-toxic and easily handled cyanating reagent since its introduction by Beller and co-workers.[5] However, the main issue of palladium catalyzed cyanation of aryl halides is the existing compromise between the reaction efficiency (catalyst performance) and the strong catalyst poisoning effect of cyanide anion. At high cyanide ion concentration the poisoning effect of employed CN sources often becomes dominant providing a means of gradual deactivating the catalytically active intermediates through *in-situ* forming CN_3Pd-Ar which in turn results in a decline of the catalytic cycle.[6] Although, the poisoning issue of the catalyst could be partly circumvented by employing both/either less soluble cyanide sources (like $K_4[Fe(CN)_6]$) and/or various ligands such as phosphines[7] and amine ligands[8] as well as using of palladacycle complexes[9], the catalytic systems based on these approaches are still operating under homogeneous conditions and thus potentially suffering from some limitations such as catalyst separation and recovery, and high catalyst loading (up to 10mol%). On the other hand, while using low-soluble cyanide sources allows overcoming the problem of catalyst deactivation to some extent, this would concomitantly prohibit the cyanide ions to reach the reaction sites, a problem known as "slow cyanide delivery",[10] thus strongly suppressing the cyanation of aryl halides. Therefore, the possibility to control (or adjust) the concentration of cyanide ion could significantly influence the catalytic performance, and durability of catalyst in many of Pd-catalyzed cyanation reactions. To address these issues a few alternative methods of operation including use of 1:1 organic/aqueous solvent mixtures,[11,12] and phase transfer catalysis[13] accompanied with $K_4[Fe(CN)_6]$ as cyanide source have been proposed to replace

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conventional homogeneous catalysis, combining the benefits of an easy (fast) cyanide ion delivery through phase transfer mechanism with the low solubility strategy as an prerequisite for suppressing catalyst poisoning. Nevertheless, toxic traces of palladium contaminations in the final products coupled with the clear economic and environmental concerns, non-reusability and deactivation of the catalysts associated with the use of homogeneous system are still unwelcoming. Recycling of the catalysts is a task of great practical, economic and environmental importance. In this context, heterogeneous catalysts are favored because of easy separation, recycling, and the use of small amount in the production. As a matter of fact, the search for new efficient and recyclable heterogeneous catalysts has, therefore, received more and more attention. However, there are limited reports on the using of heterogeneous Pd catalysts for cyanation of aryl halides most likely because to requiring harsh reaction conditions and intrinsic difficulty of this reaction. In this regards, the application of Pd-supported polymers,[14] Pd/C,[15] Pd/CuO,[16] and Pd supported silica materials[17] have been reported to accelerate the synthesis of aromatic nitriles during the recent years. Although, considerable successes have been achieved using this supported catalytic systems, some limitations such as deactivation of catalyst through the leaching of Pd in subsequent runs and restricted substrate scope have remained as the main drawbacks of these protocols. Consequently, it seems that there is still much room to develop novel supported Pd-catalysts that have superior activity especially for less reactive aryl bromides and chlorides in cyanation of aryl halides. The concept of supported ionic liquid phase (SILP) catalysis in which an ionic liquid is either grafted[18] or impregnated[19] on a solid support has been shown to be an effective strategy that enable the easy handling of ionic liquids while creating a nano-liquid-like environment that greatly enhances the catalytic efficiency and concomitantly prevents the aggregation of metal nanoparticles.[20] In addition, it has been clearly shown by kinetic analyses that the active catalyst immobilized in the ionic liquid layer inside the nanospace of SILPs, are operating in a genuinely homogeneous manner,[21] despite their close proximity to the surface of support. Recently, we have been very interested in designing different kinds of recyclable solid catalysts based on the use of supported ionic liquid concept,[22] including the system comprising the confinement of ionic liquid salts in the interior of system pores of SBA-15-functionalized materials.[23] In particular, we showed that novel SBA-15 functionalized palladium complex partially confined with ionic liquid 1-butyl-3-methylimidazolium bromide ([BMIm] Br) efficiently catalyzes the Suzuki–Miyaura coupling of aryl halides.[24] In continuation of this study, we wish to report here the application of this reusable pd catalyst in the efficient cyanation of aryl halides with $K_4[Fe(CN)_6]$. We suspected here that the confinement of ionic liquid in the system pore of our catalyst could not only provide a nano-liquid environment to stabilize Pd nanoparticles inside the mesochannels of the catalyst, but the salient phase transfer feature of imidazolium moieties may also serve as handles to control (adjust) the rate of cyanide delivery into the reaction sites while enabling to minimize the catalyst poisoning. (More compelling information about the role of supported ionic liquid layer is provided later in the manuscript.)

Experimental

General information

All chemicals were purchased from commercial suppliers and all solvents were purified and dried using standard procedures. Liquid NMR was obtained on a 400 MHz Bruker Avance instrument using $CDCl_3$ as solvent and TMS as internal standard. Nitrogen sorption experiments were recorded using a Belsorp-BEL, Inc. analyzer at 77 K. Prior to the measurement, the materials was degassed at 373 K for 12 h. The surface areas were calculated by BET method and the pore size distributions were calculated from the adsorption branch of the isotherms using BJH method. TEM image was taken on a FEI Tecnai 12 BioTWIN microscope operated at 120 kV. Thermogravimetric analysis was conducted from room temperature to 800 °C in an air flow using a Pheometric Scientific analyzer.

Preparation of SBA-15

The synthesis of SBA-15 has been achieved using known procedure described by Stucky and his co-workers.[25] In a typical preparation procedure, 4.0 g of Pluronic P123 (Aldrich, average Mw =5800) was dissolved in 30 g of water and 120 g of 2 M HCl solution with stirring at 35 ºC. Then 8.50 g of tetraethoxysilane (TEOS) was added into that solution with stirring at 35 ºC for 20 h. The mixture was aged at 80 ºC overnight without stirring. The solid was filtered off and washed thoroughly with hot ethanol/water using a Soxhelet apparatus for 18 h to remove the surfactant molecules. Then, it was dried in air at 110 ºC overnight.

Preparation of aminopropyl functionalized SBA-15

Aminopropyl functionalized SBA-15 was obtained via the Refluxing of SBA-15 (10 g) with 3-aminopropyltrimethoxysilane (10 mmol) in dry toluene for 18 h. The solid materials were filtered off and washed with hot toluene for 12 h in a continuous extraction apparatus (Soxhelet) and then dried in oven at 90 ºC overnight to give aminopropyl functionalized SBA-15.

Preparation of iminopyridine functionalized SBA-15

2-acetylpyridine (0.97 g, 8 mmol) was added to a mixture of the oven dried aminopropyl functionalized SBA-15 (5 g) in super dry ethanol (150 mL) in a 250 mL round bottomed flask. The reaction mixture was stirred at 60 ºC for 24 h. The ligand-grafted silica was filtered at the reaction temperature and the resulting solid was washed thoroughly with hot toluene and ethanol to remove unreacted ketone. It was dried in air at 90 ºC overnight to furnish the corresponding iminopyridine functionalized SBA-15.

Preparation of SBA-15-Pd

iminopyridine functionalized SBA-15 (3 gr) was added to a solution of palladium acetate (0.035 gr Merck) in dry acetone (100 mL). The reaction mixture was stirred at room temperature for 24 h. After stirring, the solid was filtered, washed with acetone, ethanol and ether in order to remove any adsorbed palladium on the surface. It was then dried in an oven at 90 ºC overnight to furnish the corresponding SBA-15 supported complex (**SBA-15-Pd**).

Preparation of IL@SBA-15-Pd catalyst

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SBA-15-Pd (3 gr) was added to a solution of 1-butyl-3-methylimidazolium hexafluorophosphate (1.5 cc) in dry acetone (100 mL). The reaction mixture was stirred at room temperature for 24 h. After stirring, acetone was slowly removed under reduced pressure. The resulting powder was then dried in an oven at 90 ºC overnight to give final catalyst at a Pd loading *ca.*0.032 ± 0.001 mmol g^{-1} (atomic absorption spectroscopy (AA)).

General procedure for the cyanation reaction using IL@SBA-15-Pd

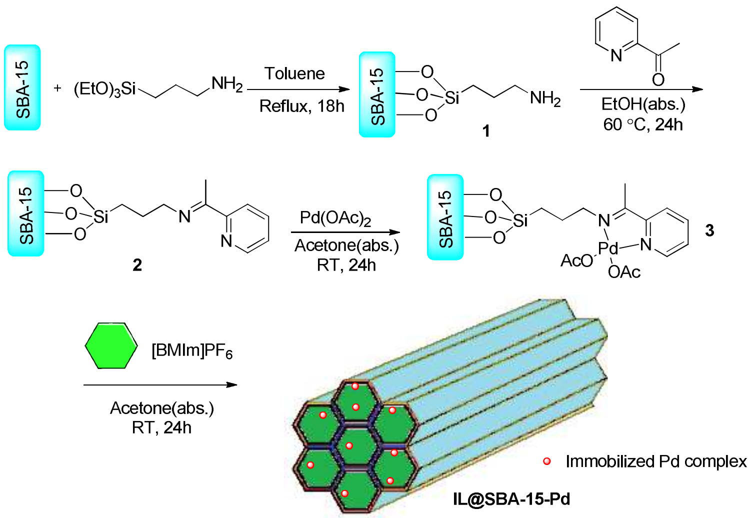
a mixture of 1.0 mmol aryl halide, 0.7 mmol $K_4[Fe(CN)_6]$ ($K_4[Fe(CN)_6].3H_2O$ is ground to a fine powder and dried in vacuum (ca. 2 mbar) at 80 ºC over night), 2 mmol K_2CO_3, 2-4 mol% phosphine ligand and 1-2 mol% catalyst in 2 mL DMF at 120 ºC was stirred vigorously under argon atmosphere. The 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 ethyl 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.

Result and discussion

The ordered mesoporous silica (SBA-15) was used as the support for immobilization of Pd complex because its regular porosity, high surface area and excellent thermal and hydrothermal stability.[26] The designed Pd catalyst denoted as **IL@SBA-15-Pd** were readily prepared via a 4-step procedure following to the our previously reported route (Scheme 1):[24] (1) functionalization of SBA-15 with 3-aminopropyltrimethoxy-silane; (2) condensation of aminopropyl functionalized SBA-15 with 2-acetylpyridine; (3) complextion of iminopyridine functionalized SBA-15 with $Pd(OAc)_2$ (**SBA-15-Pd**) and (4) mixing of **SBA-15-Pd** with acetone solution of 1-butyl-3-methylimidazolium hexafluorophosphate $[BMIm][PF_6]$ to obtain **IL@SBA-15-Pd**.

The as-prepared materials were fully characterized with various physio-chemical techniques such as nitrogen adsorption/desorption and thermo-gravimetric analyses. A typical nitrogen adsorption/desorption type IV profile with a sharp hysteresis loop, which is characteristic of the highly ordered mesoporous materials, was obtained for both **SBA-15-Pd** and **IL@SBA-15-Pd** catalyst. The calculated BET surface area, BJH average pore size distributions and primary mesoporous volume of **SBA-15-Pd** (**3** in scheme 1) were shown to be 599 m^2g^{-1}, 5.4 nm and 0.99 cm^3g^{-1}, respectively. On the other hand, **IL@SBA-15-Pd** display considerably lower BET surface area (119 m^2g^{-1}), and primary mesoporous volume (0.30 cm^3g^{-1}) in comparison to **SBA-15-Pd**. It is also worth nothing that the BJH average pore size of **IL@SBA-15-Pd** was also slightly decreased to 4.1 nm.[27] These results suggest that ionic liquid $[BMIm][PF_6]$ were successfully introduced into the inside of nanospaces of SBA-15, where covalently immobilized palladium complexes are located. As inferred from N_2 sorption analysis no measurable widening and/or tailing of desorption branch of hysteresis loop in **IL@SBA-15-Pd** isotherm was observed, suggesting that the surface modification, Pd immobilization as well as ionic liquid confinement stages, did not provide any appreciable constriction (or pore blocking) to the accessibility of the mesopores in the materials. In addition, comparing the TGA curves of **SBA-15-Pd** and **IL@SBA-15-Pd** in agreement with N_2 adsorption/desorption analysis well-identified the presence of considerable amount of ionic liquid in the channels of SBA-15 (Fig S2 vs. Fig S3). Also, on the basis of the AA analysis of a solution obtained by washing the catalyst with nitric acid, the amount of palladium loading on **IL@SBA-15-Pd** was found to be 0.032 ± 0.001 mmol g^{-1}.

To ascertain the validity of the proposed double role of confined ionic liquid to control the cyanide ion delivery while stabilizing the catalytic species in our catalyst system, the catalytic performance of **IL@SBA-15-Pd** was evaluated in the cyanation of iodobenzene using $K_4[Fe(CN)_6]$ in DMF as solvent. Firstly, the role of ionic liquid as well as its alkyl side chain and its counter ion in the overall efficiency of catalyst was investigated. The reaction was initially tested using phenyl



Scheme 1 General procedure for preparation of SBA-15-functionalized palladium complex partially confined with $[BMIm][PF_6]$ ionic liquid

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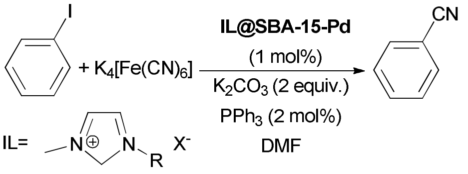
iodide, $K_4[Fe(CN)_6]$, PPh_3 and K_2CO_3 as base in DMF at 120 °C (Table 1).[28]

Table 1 Cyanation of iodobenzene with $K_4[Fe(CN)_6]$ using various type of IL confined SBA-15 functionalized palladium complex



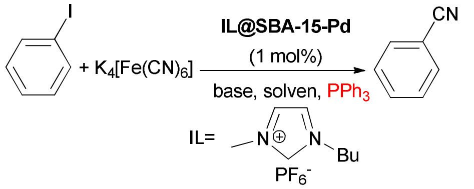
Entry	R	X	Loading of IL (g IL/g **SBA-15-Pd**)	Yield (%)[a]
1	**Bu^n**	**PF_6**	**0.5**	**91**
2	Oct^n	PF_6	0.5	24
3	Dodec^n	PF_6	0.5	9
4[b]	-	-	-	43
5	Bu^n	PF_6	1	24
6	Bu^n	Br	0.5	54

[a] Reaction condition: iodobenzene (1 mmol), $K_4[Fe(CN)_6]$ (0.7 mmol), K_2CO_3 (2 eq.), PPh_3 (2 mol%), IL@SBA-15-Pd, DMF (2 ml), 120 °C, 10h, under argon atmosphere.[b]**SBA-15-Pd** was used.

As shown in Table 1, **IL@SBA-15-Pd** is a certainly more efficient catalyst in comparison with the catalyst not containing IL (Table 1, entry 4) or catalyst having higher ratio of IL to **SBA-15-Pd** (**SBA-15-Pd** / IL = 1g / 1 g, Table 1, entry 5). This prominent catalytic performance of **IL@SBA-15-Pd** as compared with **SBA-15-Pd** might be attributed to a great extent to the crucial promoting effect of confined ionic liquid in obtaining high catalytic activity possibly through suppressing the catalyst deactivation and enabling easy CN^- delivery via a phase transfer mechanism. It should be noted that the promoting effect of ionic liquid on the catalyst performance is however closely dependent on its content inside the mesopores of catalyst (Table 1, entry 1 vs. 5). With an ionic liquid content higher than 0.5g/g SBA-15-Pd, diffusion of aryl halide substrate into the system pores and concomitant increase of CN^- ions in the near proximity of active sites become dominant resulting in a dramatic decrease of cyanation reaction to the benefit of catalyst poisoning. Additionally, when $[BMIm][PF_6]$ was replaced with the same weight of n-octyl, n-dodecyl-3-methyl imidazolium hexafluorophosphate or [BMIm][Br], the yield of cyanation product dramatically dropped to 24%, 9%, and 54%, respectively (Table 1, entries 2, 3 and 6), suggesting that both counter ion and hydrophobic-hydrophilic balance in ionic liquid are important factor to ensure high catalytic activity in our system.

In the next stage, we focused on the effect of various base and solvent on the cyanation of iodobenzene using $[BMIm][PF_6]$ confined SBA-15-Pd catalyst (Table 2). Our investigations revealed that among the various organic and inorganic bases used in the reaction, K_2CO_3 had resulted in the highest product yield (Table 2, entries 1-6). It is important to note that when DMF was replaced with other solvents such as NMP, toluene, dioxane, THF, and DMSO the yield of cyanation product was also decreased, highlighting the notion that the type of solvent needs to be respected in order of achieving acceptable product yields. Thus, the use of K_2CO_3 as base, DMF as reaction medium and $[BMIm][PF_6]$ as the best effective ionic liquid were selected as the optimized reaction conditions for cyanation of aryl halides.

Table 2 Optimizing the base and solvent in the Cyanation of iodobenzene with $K_4[Fe(CN)_6]$ in the presence of **IL@SBA-15-Pd** catalyst



Entry	base	solvent	Yield (%)[a]
1	**K_2CO_3**	**DMF**	**91**
2	K_3PO_4	DMF	88
3	NaOAc	DMF	51
4	NEt_3	DMF	55
5	NBu_3	DMF	69
6	KOtBu	DMF	38
7	K_2CO_3	NMP	73
8	K_2CO_3	DMSO	33
9[b]	K_2CO_3	THF	-
10[b]	K_2CO_3	Toluene	-
11[b]	K_2CO_3	Dioxane	-
12[c]	K_2CO_3	DMF	19

[a] Reaction condition: iodobenzene (1 mmol), $K_4[Fe(CN)_6]$ (0.7 mmol), base (2 eq.), PPh_3 (2 mol%), IL@SBA-15-Pd (1 mol%), solvent (2 ml), 120 °C, 24h, under argon atmosphere; GC yield; [b] 10h, under reflux; [c]Reaction without PPh_3.

Having the optimized reaction conditions in hand, **IL@SBA-15-Pd** was then tested in the cyanation of various types of aryl halides with $K_4[Fe(CN)_6]$. The reactions were conveniently carried out in a batch reactor at 120 °C. As shown in Table 3, the coupling of aryl iodides bearing both electron withdrawing and electron donating groups at *para* position with $K_4[Fe(CN)_6]$ in the presence of **IL@SBA-15-Pd** (1 mol%), PPh_3 (2 mol%) and K_2CO_3 (2 mmol) in DMF at 120 ºC proceeded well to give the corresponding benzonitriles in excellent yields within 7-15 h (Table 3, entries 1-6). Interestingly, hindered *o*-substituted 2-iodobenzonitrile was reacted with $K_4[Fe(CN)_6]$ providing good yields of the cyanation product in the presence of $^tBu_3P$ as the phosphine ligand (Table 3, entries 7 and 8).

We then investigated the cyanation reaction of more challenging aryl bromides using the presented catalytic system. As shown in Table 3, the reactions of various aryl bromides including electron-rich (deactivated) and electron-deficient (activated) substrates proceeded readily using as low as 2 mol% catalyst loading in DMF, furnishing the corresponding coupled products in moderate to excellent yields (Table 3, entries 9–15).

Encouraged by these promising results, we next attempted to extend the ability of the present method for cyanation to even more challenging and less reactive aryl chlorides. *To the best of our knowledge there is no precedent study of employing supported Pd catalyst in cyanation of aryl chlorides*. However, our catalyst provides 29% and 7% of cyanation products using activated aryl chlorides and its activity was insufficient to drive the reaction of aryl chlorides to completion even after 24h (Table 3, entries 16 and 17).

The reusability and recovery of the catalyst are important issue, especially when the supported catalysts have employed in the reaction. Using the coupling reaction of phenyl iodide with $K_4[Fe(CN)_6]$ as a model reaction, it was found that our supported Pd catalyst could be recovered and reused up to 4 times without significant loss of its reactivity (1st reuse: 86%, 2nd reuse: 85%,

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3rd reuse: 80%, 4th reuse: 72%).

Table 3 Cyanation of aryl halides with $K_4[Fe(CN)_6]$ using **IL@SBA-15-Pd**

Entry	X	R	R'	**Cat.**/PR'$_3$ (mol %)	Time (h)	Yield (%)[a]
1	I	H	Ph	1/2	10	91
2	I	4-NO_2	Ph	1/2	7	100
3	I	4-CHO	Ph	1/2	10	92
4	I	4-Br	Ph	1/2	10	93
5	I	4-Me	Ph	1/2	13	88
6	I	4-MeO	Ph	1/2	15	91
7	I	2-CN	Ph	2/4	24	51
8	I	2-CN	*t*-Bu	2/4	24	75
9	Br	H	*t*-Bu	2/4	15	89
10	Br	4-CHO	*t*-Bu	2/4	12	98
11	Br	3-CHO	*t*-Bu	2/4	15	92
12	Br	4-Me	H	2/4	24	62
13	Br	4-MeO	*t*-Bu	2/4	24	59
14	Br	4-Cl	*t*-Bu	2/4	15	78
15	Br	3-Cl	*t*-Bu	2/4	17	69
16	Cl	4-NO_2	*t*-Bu	2/4	24	29
17	Cl	4-CHO	*t*-Bu	2/4	24	7

[a] Reaction condition: Aryl halide (1 mmol), $K_4[Fe(CN)_6]$ (0.7 mmol), K_2CO_3 (2 eq.), PR'$_3$ (2-4 mol%), IL@SBA-15-Pd (1-2 mol%), DMF (2 ml), 120 °C, under argon atmosphere; GC yield.

To further study the contribution of homogeneous catalysis, we conducted a hot-filtration test after the reaction of phenyl iodide with $K_4[Fe(CN)_6]$ was initiated and before the complete consuming of substrates. We found that a further 35% conversion of the coupling reaction was observed upon the heating of the catalyst-free solution for 24 h at 120 ºC. This observation reveals that the present **IL@SBA-15-Pd** catalyst acts as a *release-capture* mechanism for highly active and soluble Pd species that located inside the mesopores of SBA-15. In Addition, it is obvious that the ionic liquid medium elegantly provides the stabilization of Pd species and protects them from the aggregation thus allowed the successful recycling of the catalyst. In this regard, one plausible role of R_3P might be the stabilization of the above-mentioned released (soluble) Pd species against agglomeration during the catalysis until their recapturing by ionic liquid layer inside the nanospaces of parent functionalized SBA-15. It is also not surprising to speculate that coordinated R_3P ligands could also enhance the catalytic activity of soluble Pd species in the catalytic cycles.

To understand the changes in our catalyst system on a molecular level during the reaction conditions, the recovered catalyst was further subjected to N_2-adsorption/desorption analysis, transmission electron microscopy (TEM) and TG analysis. N_2-sorption studies and TEM analysis can be provide valuable information about the surface properties and ultrastructure of the recovered catalyst. It is noteworthy that even after the four reactions; the recovered catalyst exhibited a type IV isotherm with sharp condensation/evaporation stage, which indicates that the ordered mesostructures have mostly survived (Fig. S7). Notably, the materials also showed a total pore volume slightly lower than that of the fresh catalyst charged with ionic liquid. While this result indicates a partial loss of ionic liquid during the catalysis and work-up stages, it strongly points the fact that the total loss of ionic liquid [BMIm][PF_6] was still not significant in the recovered catalyst.[27] TEM image of the catalyst after the 4th reaction cycle is display in Fig. 1. This micrograph demonstrates that not only the 2D-hexagonal structure of the catalyst is largely survived but also a well-distribution of Pd nanoparticles throughout the regular channels of the parent SBA-15 is clear. This observation in agreement with successful recycling of the catalyst clearly demonstrated that the presence of ionic liquid in the channels of mesoporous support provides a means of stabilizing of Pd nanoparticles from the agglomeration inside the mesochannels of catalyst system during the reaction.

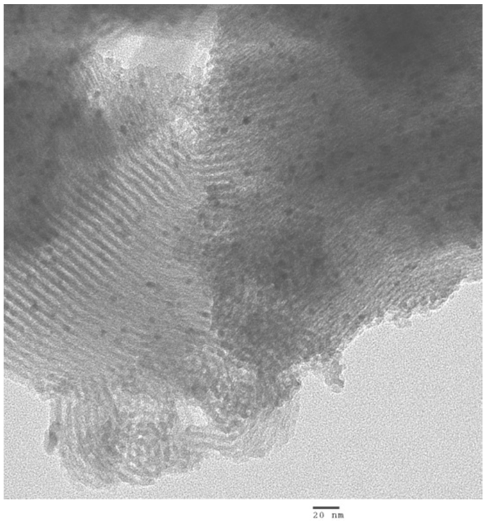

Fig. 1 TEM image of recovered **IL@SBA-15-Pd** material showing two-dimensional hexagonal symmetry with superior uniformity of the mesoporous channels and presence of Pd nanoparticles in the nanospaces of the materials where physically adsorbed ionic liquids are located

Conclusions

In summary, we have demonstrated that SBA-15 functionalized palladium complex partially confined with imidazolium type ionic liquids is a highly efficient and reusable catalyst for the cyanation reaction of aryl halides using $K_4[Fe(CN)_6]$ as the commercially available and safe cyanating agent. A variety of electron-rich and -poor aryl iodides and bromides gave the corresponding benzonitrile derivatives in good yield. Moreover the catalyst was reused for four consecutive cycles with consistent catalytic activity. Interestingly, it was found that while hot filtration tests showed the presence of soluble Pd species during the reaction process, recovering studies illustrated that no significant decrease has been occurred in the activity and metal content of recovered catalyst. Superior activity of the presented supported Pd catalyst for cyanation of aryl halides may be attributed to the presence of ionic liquid in the channels of mesoporous support that not only provides a means of stabilizing Pd nanoparticles during the reaction but also the salient phase transfer feature of imidazolium IL moieties may also serve as handles for faster penetration of $Fe(CN)_6^{3-}$ into the system pores to achieve highly concentrated reaction site in close proximity of the catalytic (Pd NPs) centers with the low solubility strategy as an prerequisite for suppressing catalyst poisoning, which resulted in an increase in the catalyst performance.

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Notes and references

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27 See Supporting Information for details

28 The optimum amounts of ionic liquid needed to partially fill nanospace of **SBA-15-Pd**, was optimized based upon the activity of catalyst via comprising different volume of [BMIm][PF_6] in a typical cyantion reaction of phenyl iodide with with $K_4[Fe(CN)_6]$ under the described reaction protocol in experimental.