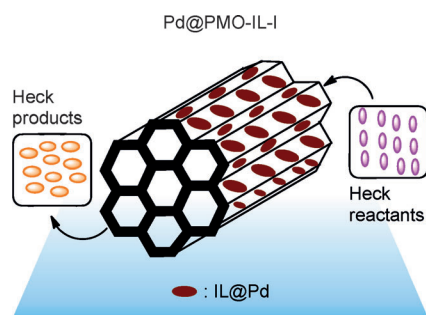


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**A Heck of a nanocatalyst!** The catalytic application of a novel palladium-containing ionic liquid-based periodic mesoporous organosilica (Pd@PMO-IL-I) in the Heck coupling of different aryl halides with alkyl acrylates has been described. This nanocatalyst demonstrated extremely high reactivity in the Heck reaction of aryl iodides, aryl bromides and aryl chlorides with electron-withdrawing groups. The catalyst could be recovered and reused several times with no decrease in activity.



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**Palladium-Containing Ionic Liquid-Based Ordered Mesoporous Organosilica: An Efficient and Reusable Catalyst for the Heck Reaction**



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# Palladium-Containing Ionic Liquid-Based Ordered Mesoporous Organosilica: An Efficient and Reusable Catalyst for the Heck Reaction

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The catalytic application of a novel palladium-containing periodic mesoporous organosilica with ionic liquid framework (Pd@PMO-IL-I) in the Heck cross-coupling reaction was described. This nanocatalyst was first synthesised and characterised by using diffuse reflectance infrared Fourier transform spectroscopy, thermogravimetric analysis, transmission electron microscopy and nitrogen sorption analysis. The efficiency of the Pd@PMO-IL-I catalyst was investigated in the Heck cross-coupling of various aryl halides with alkyl acrylates in the presence of *N*-methylpyrrolidone at 140 °C. The catalyst demonstrated excellent catalytic activity with various aryl iodides, aryl bro-

mides, and activated aryl chlorides, which gave the corresponding coupling products in good to excellent yields and with excellent E-selectivities. Moreover, the recoverability, reusability and the actual nature of the Pd@PMO-IL-I catalyst were investigated to show the effect of ionic liquid moieties on the stabilisation of palladium species during the reaction. Our study showed that the catalyst could be recovered and reused at least nine times without any appreciable decrease in activity and selectivity, which confirmed its high efficiency and high stability under the reaction conditions and during recycling stages.

## Introduction

The palladium-catalysed Heck cross-coupling of alkenes with aryl or vinyl halides is one of the most significant and efficient transformations in chemical processes<sup>[1]</sup> because of its key role in the synthesis of significant intermediates in asymmetric, pharmaceutical, polymer, herbicide and industrial chemistry.<sup>[1]</sup> The classical use of phosphine ligands in the Heck cross-coupling process is an efficient pathway for the preparation of substituted alkenes through the reaction of aryl halides with olefins under homogeneous conditions.<sup>[2]</sup> In this transformation, several ligand systems such as tertiary phosphines,<sup>[3]</sup> sulphides<sup>[4]</sup> and, in particular, *N*-heterocyclic carbenes<sup>[5]</sup> have been found to be valuable stabilisers for palladium species. Moreover, ionic liquids have been considered as potential stabilisers in this field.<sup>[6]</sup> However, homogeneous systems have some disadvantages, such as catalyst recycling and product separation.<sup>[7]</sup> Therefore, the development of heterogeneous transition-metal catalysts has attracted much attention to address these issues. Over the past few years, several strategies and materials have been used to immobilise the palladium catalyst

onto solid supports to combine the advantages of both homogeneous and heterogeneous catalysts in a number of cross-coupling reactions.<sup>[8]</sup> Of these, silica-based materials have attracted more attention because of their easy separation, low cost and high stability.<sup>[9]</sup> Nevertheless, in most reports, the catalytically active sites were inside the support; therefore, they were less accessible to the substrates, and so it is necessary to use a high loading of these palladium-based catalysts in a typical reaction. Hence, the development of the palladium-based heterogeneous catalysts in the Heck coupling reaction is still of paramount importance.

On the other hand, imidazolium-based ionic liquids are excellent molten salts that have attracted attention in the fields of chemistry and industrial processes because of their outstanding properties, such as low vapor pressure, high thermal and moisture stability, good dissolving capability of a broad range of either organic or inorganic compounds and, more especially, the possibility of tuning their hydrophilicity/hydrophobicity using an appropriate cation/anion.<sup>[10]</sup> These unique properties make ionic liquids more attractive as media for various applications in different chemical processes.<sup>[10]</sup> In the cross-coupling reactions, ionic liquids play a significant role in dissolving and stabilising transition-metal catalysts.<sup>[11]</sup> However, despite promising results, their widespread application in process chemistry is still limited because many of these catalysts are expensive and toxic.<sup>[12]</sup> Moreover, the high viscosity of ionic liquids induces mass transfer restrictions and causes the reaction to occur only in a narrow diffusion layer; hence, only a small fraction of ionic liquid-containing catalyst is used in a chemical transformation. Furthermore, the heterogeneous catalyst systems are still industrially and economically preferred

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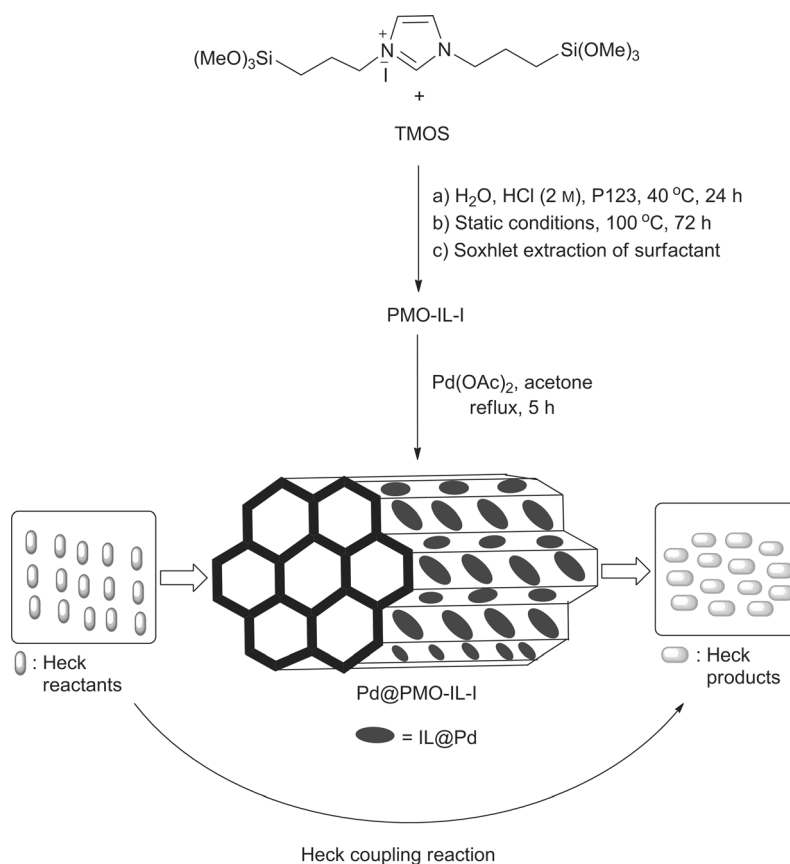
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because of their easy separation and the possibility of using a fixed-bed reaction. To address these issues, some valuable strategies for the physical and/or chemical immobilization of ionic liquids on solid surfaces have been developed to combine the inherent characteristics of ILs and solid supports.<sup>[13]</sup> These approaches were successful for the simple separation and reuse of ionic liquids in a typical reaction; however, for physically immobilised systems in which a solvent can dissolve an IL, the IL layer-containing metal catalyst can be more susceptible to leaching on the solid support.<sup>[13a,c]</sup> For chemically immobilised systems, some other disadvantages such as low stability and low loading of ionic liquid moieties as well as non-uniform distribution of ILs on the solid supports still remain unresolved.<sup>[14]</sup> To overcome these problems, we discovered an efficient and powerful route for the chemical immobilisation of the ionic liquid in the channel walls of a novel ordered mesoporous organosilica material.<sup>[15]</sup> The obtained ionic liquid-based periodic mesoporous organosilica (PMO-IL) material was then used in the immobilisation of palladium acetate (Pd@PMO-IL), which then applied as a novel nanocatalyst for the Suzuki coupling reaction and aerobic oxidation of alcohols.<sup>[15]</sup> For the Suzuki coupling, the PMO-IL material acted as a nanoscaffold to recapture and release the palladium nanoparticles into the mesochannels, which thus prevented the extensive agglomeration of palladium species.<sup>[15a]</sup> However, in the aerobic oxidation, the same Pd@PMO-IL catalyst system operated through a heterogeneous pathway. In the latter reaction, the catalyst could be recovered at least in nine consecutive reaction cycles with a small decrease in activity.<sup>[15b]</sup> This superior performance of the Pd@PMO-IL catalyst has been attributed to ionic liquid units incorporated into the mesochannels, which prevent the formation of agglomerated palladium nanoparticles whilst maintaining the catalytic activity of palladium species. Considering the importance of the Heck cross-coupling reaction as well as remarkable properties of ionic liquid-based nanomaterials in organic transformations, we prepared another novel ionic liquid-based ordered mesoporous organosilica (PMO-IL-I) material by using 1,3-bis(trimethoxysilylpropyl)imidazolium iodide and tetramethoxysilane as silica precursors.<sup>[15,16]</sup> The PMO-IL-I material was then used as an efficient support for the immobilisation of the palladium catalyst (Pd@PMO-IL-I) in the Heck coupling of various aryl halides with

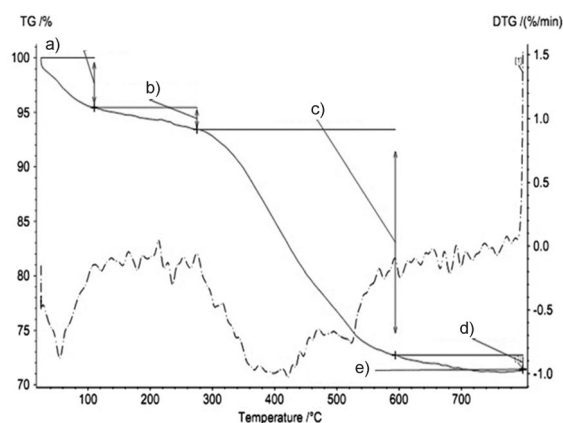
olefins. The recyclability, reusability and stability of the catalyst have also been investigated. Moreover, several compelling experiments such as hot filtration test, TEM and nitrogen sorption analysis of the recovered catalyst have been used to detect the actual nature of the catalyst in the reaction media.

## Results and Discussion

The PMO-IL-I material was prepared through hydrolysis and co-condensation of 1,3-bis(trimethoxysilylpropyl)imidazolium iodide and tetramethoxysilane with Pluronic P123 as a template under acidic conditions. The material was then reacted with a substoichiometric amount of palladium acetate under an argon atmosphere to yield the Pd@PMO-IL-I precatalyst (Scheme 1). Both pristine PMO-IL-I and Pd@PMO-IL-I materials were characterised by using a number of selected techniques. The presence of ionic liquid moieties inside the PMO-IL-I network was identified by using diffuse reflectance infrared Fourier transform spectroscopy (Figure S1). The asymmetric and symmetric stretching vibrations of Si–O–Si bonds were observed clearly at 1090 and 926  $\text{cm}^{-1}$ , respectively.<sup>[17]</sup> This spectrum also demonstrated other absorption peaks at 3126  $\text{cm}^{-1}$  (unsaturated C–H stretching), 3052 and 2919  $\text{cm}^{-1}$  (aliphatic C–H stretching), 1622  $\text{cm}^{-1}$  (C=N stretching of the imidazolium ring), 1562  $\text{cm}^{-1}$  (C=C stretching of the imidazolium ring), 1443  $\text{cm}^{-1}$  (C–H deformation vibrations), 700–792  $\text{cm}^{-1}$  (C–Si



**Scheme 1.** Synthesis of the Pd@PMO-IL-I precatalyst and its application to the Heck coupling reaction. TMOS = tetramethoxysilane.

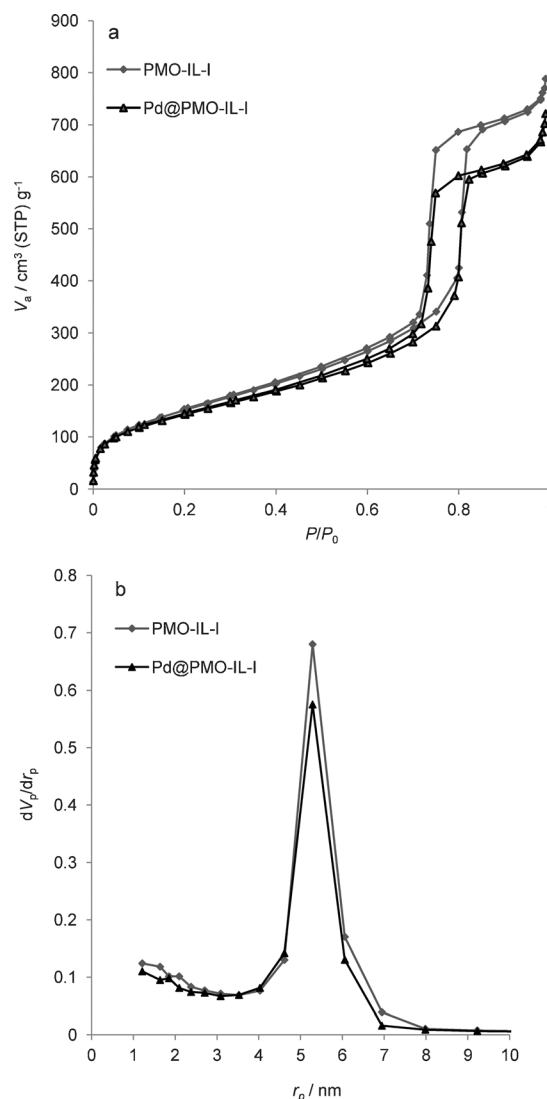


**Figure 1.** Thermogravimetric (TG) analysis with mass changes of a)  $-4.56$ , b)  $-2.00$ , c)  $-20.74$  and d)  $-1.29$ %, and e) residual mass  $71.40\%$  ( $789^\circ\text{C}$ ) and derivative thermogravimetric (DTG) analysis of the PMO-IL-I material.

stretching) and a broad peak located at approximately  $3300\text{ cm}^{-1}$  (O–H stretching).<sup>[17,18]</sup> To confirm the thermal stability of the PMO-IL-I material, the thermogravimetric analysis of this material was performed at temperatures ranging from room temperature to  $800^\circ\text{C}$  (Figure 1). This analysis showed three weight losses. The first one appearing below  $100^\circ\text{C}$  ( $4.6\%$ ) is attributed to the elimination of water and alcoholic solvents from the solid surface, whereas the second one appearing from  $110$  to  $290^\circ\text{C}$  ( $2\%$ ) corresponds to the surfactant template that remained after the extraction process. The main weight loss appearing between  $300$  and  $600^\circ\text{C}$  ( $20.7\%$ ) is related to organic functional groups located inside the solid network. These data are in good agreement with the results of IR analysis and confirmed the incorporation of ionic liquid groups into the material framework as well as their high stability during preparation and purification stages.

The nitrogen adsorption–desorption isotherm of PMO-IL-I typically showed a type IV isotherm with a sharp H1 hysteresis loop, which is characteristic of ordered mesostructures with high regularity (Figure 2). The BET surface area, BJH pore diameter and primary mesopore volume of PMO-IL-I were found to be  $563\text{ m}^2\text{ g}^{-1}$ ,  $11\text{ nm}$  and  $1.21\text{ cm}^3\text{ g}^{-1}$ , respectively. Moreover, the BJH pore size distribution of this mesostructure showed a narrow and sharp peak, which confirms the high regularity of the pore structures in the materials. The nitrogen sorption analysis of Pd@PMO-IL-I also confirms a regular and uniform mesostructure with a decrease in surface area, pore diameter and pore volume parameters in comparison with that of pristine PMO-IL-I (Figure 2 and Table 1).

This result confirms the successful incorporation of the palladium species into the PMO-IL-I mesochannels. The TEM image of the Pd@PMO-IL-I catalyst is in good agreement with the nitrogen sorption experiment and shows a uniform rodlike structure with high regularity, which is characteristic of the ordered mesoporous materials with a 2D hexagonal pore structure. The transmission electron microscopy (TEM) image also confirms the high stability of the material structure after the immobilisation of the palladium precursor inside the mesochannels (Figure 3). The catalytic activity of the resulting Pd@PMO-



**Figure 2.** a) Nitrogen adsorption–desorption isotherms and b) pore size distributions of the PMO-IL-I and Pd@PMO-IL-I materials.  $V_n$  = pore volume,  $V_p$  = total pore volume,  $r_p$  = mesopore radius.

IL-I catalyst was then examined in the Heck cross-coupling of aryl halides with alkyl acrylates. The effects of palladium loading, solvent, reaction temperature and base were investigated initially in the reaction of bromobenzene with ethyl acrylate as a test model.

The results showed that of the different inorganic bases such as potassium carbonate, sodium acetate, potassium phosphate and sodium carbonate, potassium carbonate gave the highest yield in the presence of as little as  $0.05\text{ mol}\%$  of the

**Table 1.** Structural parameters of PMO-IL-I and Pd@PMO-IL-I materials determined from nitrogen sorption experiments.

Sample	BET surface area [ $\text{m}^2\text{ g}^{-1}$ ]	Pore diameter [nm]	Pore volume [ $\text{cm}^3\text{ g}^{-1}$ ]
PMO-IL-I	563	11	1.21
Pd@PMO-IL-I	521	10.9	1.11

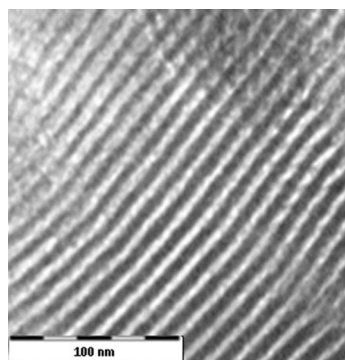


Figure 3. TEM image of the Pd@PMO-IL-I catalyst.

**Table 2.** Effect of solvent, base, palladium loading and temperature in the Heck coupling reaction using the Pd@PMO-IL-I catalyst.<sup>[a]</sup>

Entry	Solvent	Base	Catalyst [mol %]	T [°C]	Yield [%] <sup>[b]</sup>
1	NMP	NaOAc	0.05	140	58
2	NMP	Na <sub>2</sub> CO <sub>3</sub>	0.05	140	61
3	NMP	K <sub>3</sub> PO <sub>4</sub>	0.05	140	55
4	NMP	K <sub>2</sub> CO <sub>3</sub>	0.05	140	> 99
5	NMP	Et <sub>3</sub> N	0.05	140	> 99
6	DMF	K <sub>2</sub> CO <sub>3</sub>	0.05	140	45
7	NMP	K <sub>2</sub> CO <sub>3</sub>	0.03	140	50
8	NMP	K <sub>2</sub> CO <sub>3</sub>	0.1	140	> 99 <sup>[c]</sup>
9	NMP	K <sub>2</sub> CO <sub>3</sub>	0.05	120	50
10	NMP	K <sub>2</sub> CO <sub>3</sub>	0.05	100	< 5
11	NMP	K <sub>2</sub> CO <sub>3</sub>	0.05	140	35 <sup>[d]</sup>

[a] Reaction conditions: bromobenzene (1 mmol), ethyl acrylate (1.2 mmol), base (2 mmol), solvent (3 mL), 140 °C and 3.5 h; NMP = *N*-methylpyrrolidone; [b] GC yields; [c] Time = 2 h; [d] Pd@PMO-IL-Cl was used as the catalyst.

catalyst in *N*-methylpyrrolidone (NMP) at 140 °C (Table 2, entries 1–4). Although triethylamine (Table 2, entry 5) also furnished the corresponding coupling adduct in excellent yield, we preferred to use potassium carbonate for the subsequent studies because of its easy separation in the work-up process. When DMF was used as the reaction solvent instead of NMP, much inferior result was obtained with regard to the product yield under the same reaction conditions (Table 2, entry 6). Moreover, the results showed that both catalyst loading and reaction temperature have a significant effect on the reaction and the use of 0.05 mol% catalyst in the presence of NMP at 140 °C were the optimum conditions in this transformation (Table 2, entry 4 vs. entries 7–10). In another study, our previous catalyst, Pd@PMO-IL-Cl,<sup>[15]</sup> showed lower catalytic activity in the Heck coupling of bromobenzene with ethyl acrylate as a model under the same reaction conditions, which afforded the corresponding coupled product in 35% yield (Table 2, entry 11). This result confirmed the significant role of halide counterions in obtaining high activity of the catalyst. At the

moment, the precise explanation for this observation is unclear. However, a plausible explanation is that the iodide anion in Pd@PMO-IL-I may react initially with either aryl bromide or aryl chloride to afford the corresponding aryl iodides, which are certainly much more reactive substrates in the subsequent Heck olefination. Nevertheless, it is difficult at this stage to attribute the superior activity of Pd@PMO-IL-I solely to this proposed phenomenon and further investigations are necessary to clarify this subject. We are currently working on this issue, and the results will appear in due course.

By using the optimized reaction conditions, we extended the scope of the present catalyst system to the Heck cross-coupling of different kinds of alkyl acrylates with various activated and deactivated aryl halides (Table 3). As expected, the catalyst demonstrated excellent efficiency in the reaction of iodobenzene with either ethyl- or *n*-butyl acrylate, which afforded the corresponding coupled products in quantitative yield (Table 3, entries 1 and 2). Aryl bromides were similarly coupled with the same acrylates to produce the corresponding products in excellent yields. As shown in Table 3, bromobenzene itself (entries 3 and 4) and those aryl bromides bearing either electron-withdrawing or electron-donating substituents on the benzene ring afforded the corresponding Heck adducts in excellent yields and E-selectivities (Table 3, entries 5–11). Notably, aryl bromides bearing strong electron-donating groups, such as MeO substituents, that are relatively inactive substrates in the Heck coupling reaction also furnished the corresponding alkenylated products in high yields (Table 2, entries 9–11),

**Table 3.** Heck cross-coupling reaction of aryl halides with olefins in the presence of the Pd@PMO-IL-I catalyst.<sup>[a]</sup>

R: electron-donating or releasing groups  
R<sup>1</sup>: Me, Et, and *n*-Bu

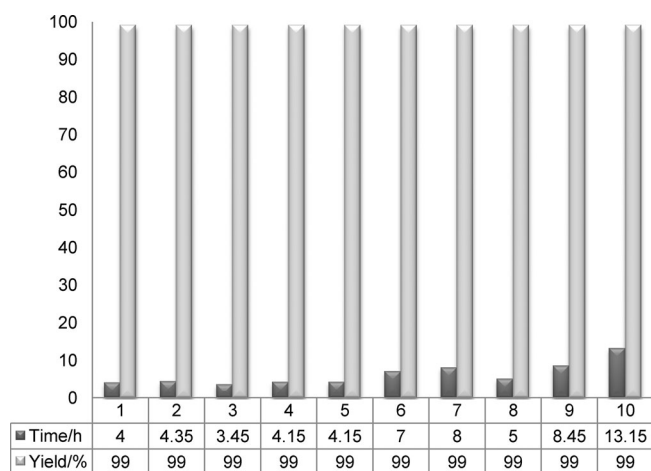
Entry	R	R <sup>1</sup>	X	Time [h]	Yield [%] <sup>[b]</sup>
1	H	Et	I	0.5	96
2	H	<i>n</i> Bu	I	0.5	95
3	H	Et	Br	3.5	96
4	H	<i>n</i> Bu	Br	3.5	96
5	4-CHO	Me	Br	2.5	95 <sup>[c]</sup>
6	4-CHO	Et	Br	2.5	92
7	4-CHO	<i>n</i> Bu	Br	2.5	90
8	3-CHO	Me	Br	3.5	92 <sup>[c]</sup>
9	4-MeO	Me	Br	20	90 <sup>[c]</sup>
10	3-MeO	Me	Br	20	88 <sup>[c]</sup>
11	4-Et	Me	Br	18	90 <sup>[c]</sup>
12	naphthyl	Et	Br	18	88
13	4-CHO	Me	Cl	24	88 <sup>[c]</sup>
14	4-CHO	Et	Cl	24	86
15	4-CHO	<i>n</i> Bu	Cl	24	85
16	3-CHO	Me	Cl	24	86 <sup>[c]</sup>
17	4-NO <sub>2</sub>	Me	Cl	18	90 <sup>[c]</sup>

[a] Reaction conditions: haloarene (1 mmol), Pd@PMO-IL-I (0.05 mol%), alkylacrylate (1.2 mmol), K<sub>2</sub>CO<sub>3</sub> (2 mmol), *N*-methylpyrrolidone (3 mL), 140 °C; [b] Isolated yields; [c] 2 equiv. of methyl acrylate was used.



though with longer reaction times. In addition, 2-naphthyl bromide produced the corresponding product in high yield upon reacting with ethyl acrylate under the same reaction conditions (Table 3, entry 12). Notably, the successful application of aryl chlorides in the Heck reaction is limited.<sup>[9c,19]</sup> As an example, recently Nacci et al. reported the efficiency of palladium nanoparticles in the Heck reaction of aryl chlorides in tetraalkylammonium ionic liquids.<sup>[19g]</sup> The present catalyst system also demonstrated excellent activity in the coupling of aryl chlorides bearing electron-withdrawing groups, such as 4-chlorobenzaldehyde (Table 3, entries 13–15), 3-chlorobenzaldehyde (Table 3, entry 16) and 4-chloronitrobenzene (Table 3, entry 17), with various acrylates and gave high yields of the corresponding Heck adducts under similar reaction conditions. These results showed high efficiency and reactivity of the designed catalyst compared to other reported catalytic systems used in this field.<sup>[14]</sup> Because the recoverability and recycling of the catalyst are important issues from both practical and economical viewpoints, we next investigated the reusability of the Pd@PMO-IL-I catalyst in the reaction of bromobenzene with methyl acrylate under the optimised reaction conditions. The result showed that the catalyst can be recovered and reused in nine reaction cycles, although longer reaction times were needed after the fifth run to ensure complete conversion (Figure 4). All recycling runs furnished the corresponding Heck product in more than 99% purity by using GC analysis.

The mechanism of the palladium-catalysed Heck coupling reaction has been studied by several researchers.<sup>[8c,20]</sup> The results showed that in some cases the catalysts operated in a heterogeneous mode<sup>[4,9a,21]</sup> but in others the support acted as a reservoir for the soluble palladium species.<sup>[8e,22]</sup> To demonstrate the behaviour of our catalyst during the reaction process, a hot filtration test was performed in the Heck coupling of bromobenzene with ethyl acrylate.<sup>[22a,23]</sup> After 45 min, the reaction was stopped and filtered while it was hot. Then, the solid-free filtrate was reacted under normal reaction conditions (140 °C, K<sub>2</sub>CO<sub>3</sub>). After 6 h, an additional conversion of only 5% was observed in the coupling reaction. Furthermore, atomic adsorp-



**Figure 4.** Reusability of the Pd@PMO-IL-I catalyst in the Heck coupling of bromobenzene with ethyl acrylate over 10 runs.

tion spectroscopy (AAS) performed for the filtrate demonstrated that the amount of leached palladium is less than 1 ppm. However, the negative hot filtration test and the near absence of leaching (as demonstrated by AAS) can sometimes result in erroneous conclusion regarding the heterogeneous nature of the catalyst<sup>[23e,f]</sup> because the amount of leached palladium species can be lower than the detection limit of AAS (parts per billion level); however, the leached palladium species still demonstrate extremely high catalytic activity.<sup>[24]</sup> In many instances the leached palladium species are responsible for the observed catalysis. In addition, these solubilised palladium species redeposit on the support after catalysis. Therefore, it is often necessary to provide enough compelling evidences to verify whether a solid catalyst operates through a heterogeneous pathway.<sup>[24]</sup> To verify whether the present catalyst system operates through a heterogeneous pathway or whether it merely generates more active soluble palladium species, a series of control experiments have been established. First, in a separate coupling reaction of bromobenzene with ethyl acrylate under our optimal reaction conditions, a large excess of Hg<sup>0</sup> (Hg/Pd = 400:1) was added under vigorous stirring. The kinetic profile of this reaction was then compared with that of the reaction in the absence of Hg<sup>0</sup>. Then, in another separate experiment, an excess amount of poly(4-vinylpyridine) (N/Pd = 400:1) was used in the same Heck coupling reaction under otherwise similar reaction conditions. As can be clearly seen from the reaction profile (Figure S2), in both the poisoning experiments a gradual (but not remarkable) decrease in catalytic activity was observed upon the addition of poisons. These results clearly indicate that the Pd@PMO-IL-I catalyst operates through at least a partial homogeneous pathway.

The nitrogen sorption experiment and TEM micrograph of the recovered catalyst were investigated to shed further light on the catalyst evolution during catalysis and recycling stages. The nitrogen adsorption–desorption isotherm of the recovered palladium catalyst (RPd@PMO-IL-I) showed a type IV isotherm with a sharp H1 hysteresis loop, which is observed typically in the mesoporous materials with a regular rodlike structure (Figure S3). The BET surface area, pore volume and average pore size of the RPd@PMO-IL-I catalyst decreased to 345 m<sup>2</sup>g<sup>-1</sup>, 0.63 cm<sup>3</sup>g<sup>-1</sup> and 9.2 nm, respectively, which confirms the generation of palladium nanoparticles inside the mesopores of the PMO-IL-I material.<sup>[25]</sup> Furthermore, the TEM image of the recovered catalyst after five reaction cycles showed the high stability of the mesochannels under the applied conditions, which is in good agreement with the data obtained from the nitrogen sorption experiments (Figure S4). This micrograph also showed that the palladium nanoparticles are well dispersed inside the mesochannels without any detectable aggregation and large particle formation. In another study, the recyclability of an ionic liquid-free Pd@SBA-15<sup>[26]</sup> catalyst with the same loading of palladium in the Heck coupling reaction of bromobenzene with ethyl acrylate was investigated. By using the same reaction time as used in the case of the Pd@PMO-IL-I catalyst (Table 3, entry 3), the product yields decreased rapidly from 98 to 48 to 17% upon three successive reaction cycles. This result confirmed the higher efficiency of PMO-IL-I compared to SBA-

**Table 4.** Comparison study of the efficiency of the Pd@PMO-IL-I catalyst with that of previous catalytic systems.<sup>[a]</sup>

Catalyst	Conditions	Ar-X	Cycle times	Reference
SBA-15-IL/Pd	solvent-free, Et <sub>3</sub> N, 140 °C	Ar-I, Ar-Br	7	[9g]
NHC-Pd/IL@SiO <sub>2</sub>	NMP, NaOAc, 140 °C	Ar-I, Ar-Br	4	[14g]
Pd-NHC/organosilica	DMF, Et <sub>3</sub> N, MW, 120 °C	Ar-I, Ar-Br	5	[14h]
NHC-Pd/SBA-16-IL	NMP, NaOAc, 130–140 °C	Ar-Br	8	[27]
Pd@PMO-IL-I	NMP, K <sub>2</sub> CO <sub>3</sub> , 140 °C	Ar-I, Ar-Br, Ar-Cl	10	this work

[a] NHC = *N*-heterocyclic carbene; NMP = *N*-methylpyrrolidone.

15 in immobilising and stabilising palladium species under the same reaction conditions. In this last study, the Pd@PMO-IL-I catalyst was compared with a number of reported silica-supported palladium catalysts in the Heck reaction (Table 4).<sup>[9g, 14g, h, 27]</sup> This investigation showed that although the previous catalytic systems have good activity and selectivity under approximately the same reaction conditions as for Pd@PMO-IL-I, the recyclability and stability of the present catalyst are much better. This comparison also demonstrated that only our catalyst can convert aryl chlorides to the corresponding Heck coupling products, which indicates better activity of this catalytic system. These findings may be attributed to the imidazolium moieties incorporated into the mesochannels of PMO-IL-I, which stabilise palladium species by preventing their agglomeration.

## Conclusions

In summary, the design and preparation of a novel palladium-containing ionic liquid-based ordered mesoporous organosilica (Pd@PMO-IL-I) and its catalytic application in the Heck coupling reaction have been described. The reaction system was significantly affected by catalyst loading, reaction temperature, solvent and the type of base. The Pd@PMO-IL-I catalyst demonstrated extremely high reactivity in the Heck reaction of aryl iodides, aryl bromides and, most importantly, activated aryl chlorides bearing electron-withdrawing groups, along with the advantages of easy product separation and no dehalogenation reaction. In addition, the catalyst could be recovered and reused at least nine times with no decrease in its activity and selectivity. However, it was found that in contrast to highly recyclable properties of our catalyst under the described reaction conditions, controlled poisoning experiments revealed that Pd@PMO-IL-I could be the source of production of active soluble palladium species, most likely in the form of soluble palladium nanoparticles. We attributed the high recyclability and durability of the present catalyst system to the high surface area and uniformly incorporated ionic liquids into the material network, which protected palladium species against agglomeration and palladium black formation. Further investigations of the scope and mechanism as well as some applications of the

catalyst in other organic transformations are currently underway in our laboratories.

## Experimental Section

### Synthesis of PMO-IL-I

General procedure: The synthesis of PMO-IL-I was accomplished according to our previous method with a little modification.<sup>[15]</sup> Typically, potassium chloride (8.5 g) was added to a solution of deionised water (10.10 g) and HCl (2 M, 44.3 g) and stirred at RT. Then, Pluronic P123 (1.6 g) was added and the mixture was stirred vigorously at 40 °C for 3 h. After obtaining a clear homogeneous solution, a mixture of tetramethoxysilane (17.10 mmol) and 1,3-bis(trimethoxysilylpropyl) imidazolium iodide ionic liquid (1.90 mmol) was added to the reaction vessel and stirred at the same temperature for 24 h. The obtained mixture was then transferred to a Teflon-lined autoclave and heated statically at 100 °C for 72 h. Next, the obtained solid material was filtered, washed completely with deionised water and dried at RT. The surfactant was removed with a Soxhlet apparatus by using a mixture of ethanol and conc. HCl (EtOH/HCl 100:3 v/v). The final periodic mesoporous organosilica material was dried at 70 °C and labelled as PMO-IL-I.

### Preparation of Pd@PMO-IL-I catalyst

In a typical synthesis, palladium acetate (0.14 mmol) was added to a uniform solution of ionic liquid-based periodic mesoporous organosilica (PMO-IL-I, 1 g) in acetone (5 mL) under an argon atmosphere. The reaction mixture was stirred vigorously and heated to reflux for 5 h, and then it was cooled to RT. The obtained mixture was then washed completely with CH<sub>2</sub>Cl<sub>2</sub> to eliminate non-adsorbed Pd(OAc)<sub>2</sub>. Finally, the Pd@PMO-IL-I material was obtained after drying by evacuation at 50 °C for 12 h. The elemental analysis showed that the loading of palladium on the solid surface was 0.11 mmol g<sup>-1</sup>.

### Heck coupling reaction with the Pd@PMO-IL-I catalyst

General procedure: Alkyl acrylate (1.2 mmol), aryl halide (1.0 mmol), a base (2 mmol) and the catalyst (0.0005 equiv. to aryl halide) were mixed in a solvent (NMP or DMF) and stirred vigorously at 140 °C under an argon atmosphere. The reaction progress was monitored by using TLC and GC after the completion of the reaction; the mixture was cooled to RT and then filtered and washed with ethyl acetate and water. The organic phase was first separated and dried over MgSO<sub>4</sub>, and then the solvent was removed under reduced pressure. Finally, pure products were obtained after the recrystallisation or isolation of the residue by using column chromatography on silica.

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