



# Heck coupling reactions catalysed by Pd particles generated in silica in the presence of an ionic liquid

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**Abstract** Silica-supported Pd catalysts were synthesized in the presence of the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate. Two samples with extremely low Pd loadings, 0.35Pd and 0.08Pd, with Pd contents 0.35 and 0.08%, respectively, were subjected to further investigations. Structural characterization was performed by ICP-AES and Raman measurements. Raman spectra indicated the presence of the ionic liquid in the Pd-silica samples. The samples were tested as catalysts in the Heck coupling reactions of methyl acrylate and styrene, with substituted bromoarenes and chloroarenes. Both samples proved to be highly efficient catalysts and displayed excellent activities and selectivities for the reactions of activated haloarenes including chloroarenes, which could be efficiently transformed without applying harsh reaction conditions. As expected, the presence of an electron withdrawing group (EWG) on the aromatic ring of the haloarene was found to increase both the conversion and the selectivity to an appreciable extent. For the transformations of bromoarenes, the sample with the lowest Pd loading proved to be a more efficient catalyst. Upon recycling of the catalysts, a considerable activity loss was detected, which was attributed to an extensive leaching of Pd into the solution, as confirmed by hot filtration measurements.

**Keywords** Palladium · Ionic liquid · Heck coupling · Bromoarene · Chloroarene · Pd leaching

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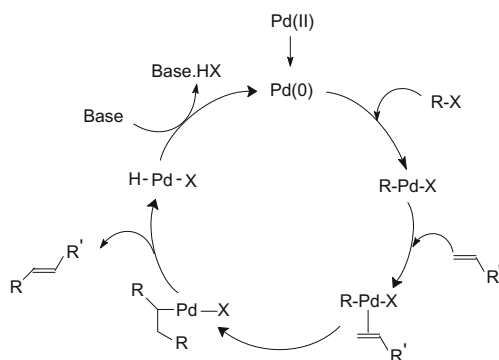
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## Introduction

The Heck coupling reaction has been considered as one of the most efficient and widely used procedures for the formation of C–C bonds. Such reactions have been frequently applied for the synthesis of complex organic molecules, suitable for a wide range of applications in the chemical and pharmaceutical industry [1–7]. The Heck coupling reactions have been generally carried out under homogeneous conditions. For these reactions, Pd-based systems are considered as the most efficient catalysts, as they ensure enhanced reaction rates, high turnover frequencies and improved selectivities [1–4]. The conventional procedure of the Heck coupling reaction involves the application of Pd(II) or Pd(0) complexes as homogeneous catalysts working in solution [4–9]. The generally accepted mechanism of the homogeneous Heck reaction is shown in Fig. 1.

In the first reaction step, the organic halide forms an organopalladium halide complex with the Pd catalyst via oxidative addition. Then, the reactant alkene is coordinated to Pd and an alkene complex is formed, followed by insertion of the alkene group into the Pd–R bond. The resulting Pd complex is decomposed through  $\beta$ -elimination, and the product is formed, a substituted alkene, in which the vinylic position is substituted by the organic moiety of the reactant halide. Meanwhile, a hydrido-palladium halide is obtained, which undergoes reductive elimination; hence, the active Pd species is regenerated [2, 10, 11].

The ligands of the Pd complexes are of particular importance, as they affect the catalytic activity and selectivity by sterically preventing interaction between the Pd atoms, thereby stabilizing the homogeneous Pd catalyst [2, 3, 12]. However, there are several drawbacks associated with homogeneous catalysis, which remain a challenge for pharmaceutical applications, as related to catalyst deactivation, difficult



**Fig. 1** Proposed mechanism of the Heck coupling reaction

separation of the Pd complex from the solution, the lack of recycling and the potential contamination of the products by residual metal species [4, 5, 13, 14]. A possible reason of deactivation is the aggregation of Pd nanoparticles formed in situ during the reaction [2, 5, 6, 15]. The initial aggregation should be prevented, as it was found to accelerate the formation of inactive Pd(0) species during the reaction [12]. This was also observed for simple ligand-free Pd catalysts, such as Pd(OAc)<sub>2</sub> and PdCl<sub>2</sub>, which exhibited excellent activities, but underwent deactivation through precipitation of the inactive Pd(0) particles [16–18].

The application of heterogeneous Pd catalysts proved to be particularly promising for several reasons including easy handling, simple recovery and efficient recycling. Therefore, the development of highly active and recyclable heterogeneous Pd catalysts has become an important issue for the research of nanomaterials to be employed for a large number of synthetic procedures [1–3]. Recent attempts to develop highly efficient and recyclable Pd catalysts for the Heck coupling reaction have been mainly focused on the utilization of graphite, carbon and silica-based support materials [2, 3, 16, 19, 20].

The Heck reaction performed by using heterogeneous Pd catalysts takes place in solution. In the first step, the catalytically active species are formed as soluble Pd complexes, via coordination with the solvent (e.g. N-methyl-pyrrolidone, NMP) and the base (e.g. triethylamine). Oxidative addition of the haloarene occurs to these Pd complexes and the reaction proceeds in the solvent, according to the general mechanism of the Heck reaction (Fig. 1). When the reactant is completely consumed, the complexes decompose and the Pd particles are redeposited on the surface of the support material. Since not all Pd species leach out into the solvent, the dissolved Pd species redeposit either on the bare surface of the support or on the surface of the Pd particles remaining on the support. It was found that redeposition occurred preferentially on the surface of the residual Pd particles, rather than on the bare surface of the support. Other factors, such as the nature of the support, the number and size of the residual metal particles and the surface functional groups of the support material may also affect the redeposition process [19]. It has also been reported that, for

phosphane or ligand-free Pd catalyst systems based on simple Pd salts, in situ formed colloidal Pd nanoparticles acted as catalysts in the Heck reaction [21]. Nevertheless, it is still a matter of debate and not yet clarified whether the Heck reaction catalysed by supported Pd catalysts is due to homogeneous or heterogeneous processes [22].

The majority of novel heterogeneous catalysts are based on silica supports, given that silica has an excellent chemical and thermal stability and provides good access for the reactants. Further, a variety of organic groups can be anchored on its surface to form active centres [19, 23, 24]. Ordered mesoporous silica materials prepared by micelle-templated syntheses have been employed as catalysts [25–27], and the surface modification of silica has also been performed to produce catalytically active materials. The functional groups of hybrid organic–inorganic materials may work either as active surface sites or as anchoring sites available for metal complexes [16, 28–30]. The incorporation of metallic Pd into amorphous silica and ordered mesoporous materials, including MCM-41, HMS and SBA-15, resulted in the formation of heterogeneous systems, which could be effectively used as catalysts in the Heck coupling reactions [31, 32].

Ionic liquids (ILs) have also attracted considerable attention in recent years, as solvents, which may replace conventional organic solvents in a variety of reactions. Imidazolium-based ILs, working as in situ formed imidazole carbene ligands of the transition metal complexes, have been extensively utilized as reaction media for Pd-catalysed coupling reactions [16, 33, 34].

Immobilization of a Pd catalyst on silica in the presence of an ionic liquid has been reported to be a beneficial method, as it is inexpensive, stabilizes the catalyst and facilitates the deposition of Pd particles on the surface of the support material [19, 35].

Yokoyama et al. reported high conversions for the Heck reactions in the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF<sub>6</sub>), by using a Pd/SiO<sub>2</sub> catalyst under ligand-free conditions [10, 36]. Further, Shi et al. introduced a new concept of designing and synthesizing highly dispersed ionic liquid catalysts developed through physical confinement or encapsulation of ILs, with or without metal complexes, in a silica-gel matrix through a sol–gel process and the catalysts obtained were reported to be effective for several organic reactions [37].

In the present study, the catalytic performances of novel silica-supported Pd catalysts, synthesized in the presence of the ionic liquid [bmim]PF<sub>6</sub>, were investigated for the Heck coupling reactions of methyl acrylate and styrene with bromoarenes. The same reactions were studied by using less reactive chloroarenes, considering that they are cheap and readily available, and may be suitable for industrial applications [16, 38]. The substituent effect on the transformation of the halogenated reactant was investigated, and the leaching of Pd was also studied.

## Experimental

### Materials

Bromobenzene (BrB, 98%), 4-bromoacetophenone (4BrAc, 98%), 4-bromobenzonitrile (4BrBn, 98%), 4-bromoanisole (4BrA, 98%), chlorobenzene (ClB, 98%), 4-chloroacetophenone (4ClAc, 98%), 4-chlorobenzonitrile (4ClBn, 98%), 4-chloroanisole (4ClA, 98%), methyl acrylate (MA, 99%), styrene (S, 99%), bis(triphenylphosphine)palladium(II) dichloride (>99.9%) and bis(benzonitrile)palladium(II) chloride (95%), all purchased from Sigma Aldrich, were used as received, whereas 4-bromonitrobenzene (4BrNB) and 4-chloronitrobenzene (4ClNB), both Reanal products, were purified by distillation or crystallization.

*N*-methyl-2-pyrrolidone (NMP, 99.5%, Aldrich) was used as a solvent, sodium acetate (Aldrich) was used as a base and decane (>99%, Aldrich) was applied as an internal standard for the GC analysis.

### Catalyst preparation

The catalysts were synthesized by the procedure described by Shi et al. [37]. First, the solution of the ionic liquid was prepared by dissolving 1.8 g of 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF<sub>6</sub>) in 10 ml of THF. This solution was added to a mixture of 20 ml of tetraethoxy orthosilicate (TEOS) and 15 ml of ethanol under efficient stirring at 333 K, in the presence of the Pd precursor. Then, 10 ml of 18% HCl was added, and stirring was maintained for 15 h. The solvents were subsequently removed by a rotary evaporator. The excess of the Pd precursor was eliminated from the surface of the solid by suspending it in toluene and keeping at reflux temperature for 1 h. Finally, the solids were filtered, dried at 343 K overnight and stored in a desiccator until further applications. The Pd loadings of the samples, determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES), were 1.43 and 1.46% for the two samples before solvent extraction. The latter procedure not only removed the excess precursor but also decreased the Pd contents of the samples to an appreciable extent. The samples employed for further investigations were 0.35 wt% Pd/IL/SiO<sub>2</sub> and 0.08 wt% Pd/IL/SiO<sub>2</sub>, denoted as 0.35 and 0.08 Pd, prepared from the precursors PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> and PdCl<sub>2</sub>(PhCN)<sub>2</sub>, respectively. For the sake of comparison, a reference Pd-silica sample (RPd) was prepared by omitting the ionic liquid from the synthetic procedure.

### Catalyst characterization

ICP-AES measurements were performed by using a Jobin Yvon 24 equipment. Raman spectra were acquired in a Thermo Scientific DXR Raman microscope equipped with a

532-nm excitation laser operated at 5 mW. Spectra were collected for 3 min at 4 cm<sup>-1</sup> resolution and then corrected for background effects.

### General reaction procedure

The reactions were implemented in 5-ml glass pressure tubes. The reaction mixture consisted of 10<sup>-3</sup> mol of aromatic halide, 1.2·10<sup>-3</sup> mol of alkene, 1.4·10<sup>-3</sup> mol of Na<sub>2</sub>CO<sub>3</sub> as a base and 2·10<sup>-4</sup> mol of tetrabutyl ammonium bromide (TBAB) as a modifier. The mass of catalyst was 10.4 mg, corresponding to Pd contents of 3.42·10<sup>-4</sup> mol% and 7.8·10<sup>-5</sup> mol% for 0.35 and 0.08 Pd, respectively. After addition of the solvent (1 ml of NMP), the mixture was subjected to magnetic stirring at 423 K. The reaction temperature was 423 K for all the reactions, and the reaction time was varied between 0.5 and 6 h. Afterwards, the reaction mixture was cooled down to room temperature, diluted by 5 ml of diethyl ether and filtered on a layer of alumina. The clean filtrate was analysed by a Hewlett Packard 5890 gas chromatograph, equipped by a HP-1 capillary column and FID. The product analysis was completed by GC-MS measurements, by using an Agilent 6890 N GC and an Agilent 5973 mass selective detector (MSD), operated under the same conditions. For a typical run, the initial temperature was 373 K, the heating rate was 283 K/min and the final temperature was 593 K, maintained for 10 min.

## Results and discussion

### Catalyst characterization

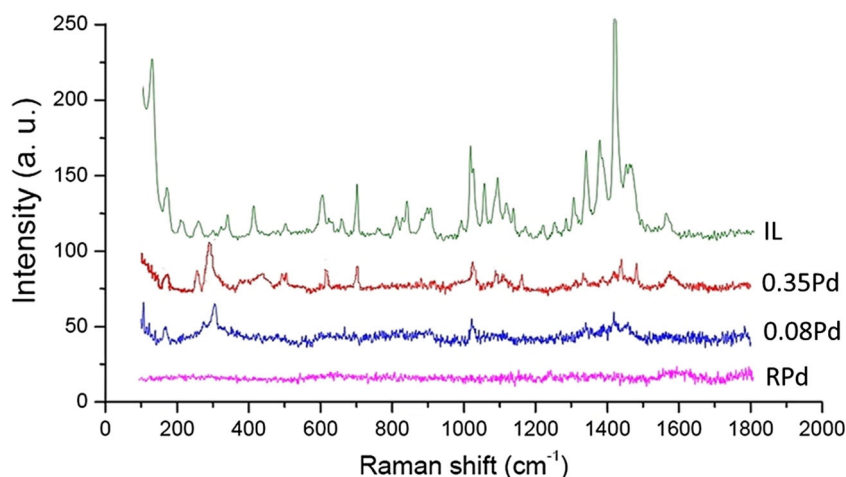
Figure 2 displays the Raman spectra of the 0.35Pd, 0.08Pd, the reference sample, RPd and the ionic liquid [bmim]PF<sub>6</sub>.

The characteristic bands of [bmim]PF<sub>6</sub> can be clearly distinguished for both 0.35 and 0.08Pd, indicating that the ionic liquid was confined in the silica gel matrix. The strongest band scan can be observed in the ranges 1300–1480 cm<sup>-1</sup> and 1010–1150 cm<sup>-1</sup>, and may be attributed to different skeletal modes of the imidazolium ring [37]. The Pd loading was found to have no appreciable effect on the Raman spectra of the IL-containing solids, which proved to be very similar. For RPd, the complete absence of the characteristic bands of the ionic liquid can be observed, which complies with our expectations.

### Catalytic test reactions

In the present study, the Heck coupling reactions were investigated in the presence of TBAB as a modifier. As shown previously, tetraalkyl ammonium compounds work as phase transfer catalysts and exert a beneficial effect on the performance of Pd catalysts applied in the Heck reaction [39, 40].

**Fig. 2** Raman spectra of 0.35Pd, 0.08Pd, RPd and [bmim]PF<sub>6</sub>



The accelerating effect of tetraalkyl ammonium salts on the reaction rate was found to depend on the counterion. Jeffery suggested that the most important influence of tetraalkyl ammonium compounds was related to their assistance in the regeneration of zerovalent palladium. Accordingly, such modifiers tend to prevent aggregation of the active Pd(0) species, which results in irreversible deactivation of the catalysts [39].

The first model reaction was the Heck arylation of methyl acrylate with halogenated aromatic compounds, including substituted bromoarenes and chloroarenes. The main reaction product was the thermodynamically most stable E stereoisomer **3** formed through  $\beta$ -coupling of the reactants (Fig. 3). The results are summarized in Table 1.

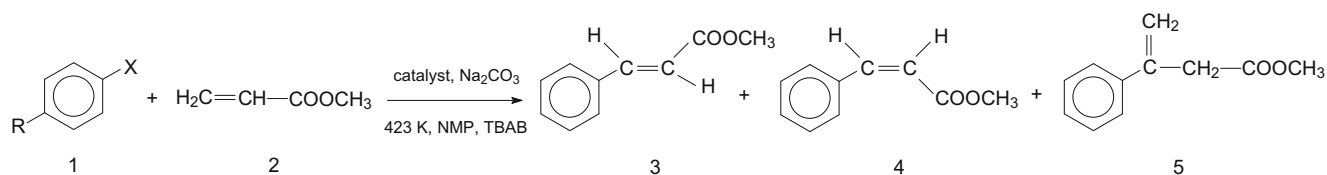
Electron withdrawing groups (EWGs) tend to increase the rate of the Heck coupling reaction by decreasing the electron density of the aromatic ring of the halogenated species and thus may be considered as activating groups. In contrast, electron donating groups (EDGs) increase the electron density of the aromatic ring and work as deactivating groups; this corresponds to the substituent effect observed for the nucleophilic substitution reactions of aromatic compounds.

It may be seen from Table 1 that despite its extremely low Pd loading, 0.35 Pd was a highly active catalyst for the reaction of bromobenzene and methyl acrylate, as the conversion was 43% after 30 min of reaction time and almost complete conversion was achieved after 3 h. The activating effect of the EWG groups of the substituted bromoarenes can be clearly observed by considering the conversions obtained after 30 min. In this respect, the least efficient activating group was the nitro group, whereas the effects of the acetyl and the

nitrile groups were exactly the same. It may be established that the application of 4-bromoacetophenone and 4-bromobenzonitrile proved to be highly beneficial as both afforded nearly complete conversions after only 30 min of reaction time. On the other hand, the presence of the electron donating methoxy group in 4-bromoanisole was found to decrease the conversion considerably, which was in line with our expectations.

Chloroarenes are much less active in the Heck coupling than bromoarenes and may require drastic reaction conditions (high temperature, no solvent or reacting solvent, e.g. methanol) [16, 22]. Hence, it was not surprising that the conversions obtained for chlorobenzene were very low, even after 3 h. However, the activating effects of EWGs could also be demonstrated, similarly as for bromoarenes. The conversions for activated chloroarenes proved to be considerably higher, even after 30 min, and conversions of 99% were obtained after 3 h. By this time, no difference in the activities of EWG-containing chloroarenes could be observed, whereas a significant variation was obtained after 30 min. The reactivity order of activated chloroarenes was 4-chlorobenzonitrile > 4-chloroacetophenone > 4-chloronitrobenzene, which was in accordance with the results obtained for bromoarenes. The deactivating effect of EDG was also confirmed by the low conversions obtained for the reactions of 4-chloroanisole.

The selectivities for the formation of the main product were found to vary between 94 and 100%, irrespective of the reaction time (Table 1). The highest selectivities were obtained for the activated reactants, including both bromoarenes and chloroarenes.



**Fig. 3** The Heck reaction of methyl acrylate with haloarenes

**Table 1** Heck reaction of methyl acrylate with halogenated aromatic reactants on 0.35 Pd

Reactant <sup>a</sup>	Conversion [%]		Selectivity [%] <sup>b</sup>
	<i>t</i> = 0.5 h	<i>t</i> = 3 h	
Bromobenzene	43	99	97
4-Bromoacetophenone	99	99	100
4-Bromobenzonitrile	99	99	98
4-Bromonitrobenzene	76	94	98
4-Bromoanisole	22	47	95
Chlorobenzene	3	6	94
4-Chloroacetophenone	75	99	99
4-Chlorobenzonitrile	82	99	100
4-Chloronitrobenzene	54	99	97
4-Chloroanisole	1	2	96

<sup>a</sup> *t* = 423 K, solvent: NMP, base: Na<sub>2</sub>CO<sub>3</sub>, additive: TBAB, catalyst: 3.42 · 10<sup>-4</sup> mol% Pd

<sup>b</sup> Selectivity for the formation of the main product, *t* = 3 h

The same reaction was investigated by using 0.08 Pd as a catalyst, and the results are listed in Table 2.

It may be observed from Table 2 that the catalytic performance of 0.08 Pd was very similar to that of 0.35 Pd. The catalytic activity obtained for the reaction of bromobenzene was significantly enhanced by applying reactants with EWGs, and no difference in their activating effect could be pointed out. The same observation can be made for the transformations of chloroarenes, for which nearly the same conversions were obtained at 3 h as those for 0.35 Pd (Table 1). Likewise, when deactivated reactants were employed, the conversions were decreased to similar extents for both catalysts (Table 1). The selectivities for the formation of the main product varied between 94 and 100%, similarly as those for 0.35 Pd.

The catalytic behaviour of the samples was also studied for the Heck arylation of styrene (Fig. 4), which was performed with the same haloarenes as those listed above. The results obtained for 0.35 Pd are summarized in Table 3.

For the reaction of styrene, the catalytic activities were significantly lower than those for the reaction of methyl acrylate (Table 1). The conversions at 0.5 h were very moderate, and considerable transformation was only obtained after 3 h. The catalytic activity of 0.35 Pd was found to depend strongly on the reaction time. Interestingly, no substituent effect could be demonstrated at 0.5 h, whereas at 3 h, a more significant variation in the conversions was observed. For the transformation of bromobenzene, 0.35 Pd displayed a pronounced catalytic activity, as the conversion was 94%, together with a selectivity of 96%. However, the presence of EWG on the bromoarene was found to decrease the conversion, which was an unusual experience. The deactivating effect of the EDG of 4-bromoanisole was also observed. Chlorobenzene proved to be completely inactive as a reactant, irrespective of the reaction time; hence, no deactivating effect of the EDG in 4-chloroanisole could be pointed out. On the other hand, the presence of EWG on the chloroarene resulted in nearly complete conversion. It may also be noted that no transformation was detected for 4-bromonitrobenzene and 4-chloronitrobenzene, although both reactants possess EWGs working as activating substituents. For these reactions, the reaction mixtures were found to turn black, which suggested that irreversible deactivation of the catalyst took place. It may be assumed that under the experimental conditions, part of the reactant styrene underwent polymerization and the polymer was adsorbed on the Pd(0) species, which resulted in deactivation of the catalyst via aggregation of the active Pd particles.

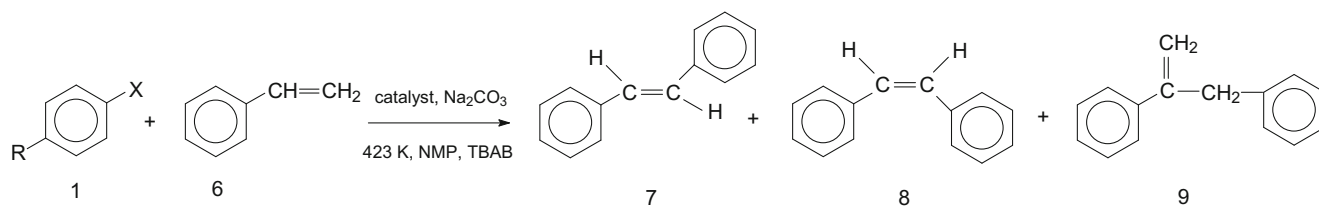
Figure 5 displays the reaction time dependence of the conversions, for the reactions of methyl acrylate and styrene with 4-bromoacetophenone, by using 0.35 Pd as a catalyst. It may be readily observed that the catalytic activity was considerably

**Table 2** Heck reaction of methyl acrylate with halogenated aromatic reactants on 0.08Pd

Reactant <sup>a</sup>	Reaction time [h]	Conversion [%]	Selectivity [%] <sup>b</sup>
Bromobenzene	0.5	76	96
4-Bromoacetophenone	0.5	99	98
4-Bromobenzonitrile	0.5	99	99
4-Bromonitrobenzene	0.5	99	97
4-Bromoanisole	0.5	31	94
Chlorobenzene	3	5	96
4-Chloroacetophenone	3	97	100
4-Chlorobenzonitrile	3	99	98
4-Chloronitrobenzene	3	97	98
4-Chloroanisole	3	3	95

<sup>a</sup> *t* = 423 K, solvent: NMP, base: Na<sub>2</sub>CO<sub>3</sub>, additive: TBAB, catalyst: 7.8 · 10<sup>-5</sup> mol% Pd

<sup>b</sup> Selectivity for the formation of the main product, *t* = 3 h



**Fig. 4** The Heck reaction of styrene with haloarenes

higher for the transformation of methyl acrylate than that for styrene. This may be due to steric restrictions, as related to the presence of the aromatic ring. For the reaction of styrene, the conversion was found to increase gradually until 3 h, and its highest value was 41%. On the other hand, the conversion for methyl acrylate displayed a saturation curve, and 97% was achieved at only 1 h.

0.08 Pd was also tested as a catalyst for the Heck coupling of styrene with different haloarenes, and the results are listed in Table 4.

By applying bromobenzene as a reactant, almost complete conversion was obtained at 3 h. Substitution of the aromatic ring of bromobenzene was found to exert a deactivating effect on the reactant, even when the substituent was an EWG.

As related to the moderate activities of chloroarenes, a prolonged reaction time of 6 h was employed for their reactions. Chlorobenzene proved to be inactive as a reactant, which was foreseen [16], but the presence of EWG was found to increase the conversion dramatically and resulted in almost complete transformation, which was the same experience as that obtained for 0.35 Pd (Table 3). It may therefore be ascertained that the catalytic performances of 0.35 and 0.08 Pd in the reactions of styrene with haloarenes were very similar. For the reactions of 4-substituted bromoarenes, the

substituent displayed a deactivating effect, whether it was an EWG or an EDG, but no such effect was observed for chloroarenes.

For a more meaningful comparison, the results are also presented in Figs. 6 and 7, which display the conversions determined on both catalysts, for the transformations of methyl acrylate and styrene with bromoarenes and chloroarenes, respectively. It may be observed in Fig. 6 that 0.08 Pd was a more efficient catalyst for the reactions of bromoarenes. The most significant difference can be ascertained for the reactions of methyl acrylate with bromobenzene and 4-bromonitrobenzene. On the other hand, no such difference can be pointed out for the reactions of chloroarenes (Fig. 7), for which the catalytic activities proved to be very similar.

### Catalyst recycling

The catalysts were tested for recycling for the Heck coupling of methyl acrylate with 4-bromoacetophenone, and the results are presented in Fig. 8.

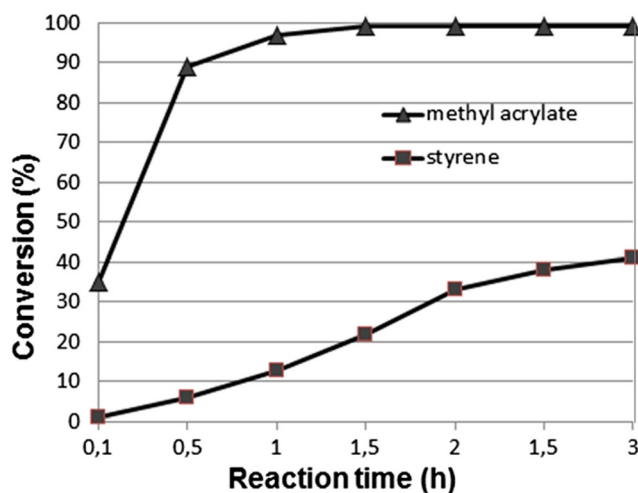
It was found that 0.35 Pd could be reused three times. In the second cycle, only a small decrease in the catalytic activity was observed, but then a significant activity drop occurred. A similar observation was made for 0.08 Pd, for which a more pronounced activity loss took place; hence, this sample could only be recycled two times.

**Table 3** Heck reaction of styrene with halogenated aromatic reactants on 0.35Pd

Reactant <sup>a</sup>	Conversion [%]		Selectivity [%] <sup>b</sup>
	<i>t</i> = 0.5 h	<i>t</i> = 3 h	
Bromobenzene	5	94	96
4-Bromoacetophenone	0	41	98
4-Bromobenzonitrile	1	35	100
4-Bromonitrobenzene	0	0	–
4-Bromoanisole	2	21	100
Chlorobenzene	0	0	–
4-Chloroacetophenone	5	98	97
4-Chlorobenzonitrile	7	96	98
4-Chloronitrobenzene	0	2	100
4-chloroanisole	0	0	–

<sup>a</sup> *t* = 423 K, solvent: NMP, base: Na<sub>2</sub>CO<sub>3</sub>, additive: TBAB, catalyst: 3.42 · 10<sup>-4</sup> mol% Pd

<sup>b</sup> Selectivity for the formation of the main product, *t* = 3 h



**Fig. 5** Conversion as a function of reaction time, for the Heck coupling reactions of methyl acrylate-4-bromoacetophenone and styrene-4-bromoacetophenone, by using 0.35 Pd as a catalyst

**Table 4** Heck reaction of styrene with halogenated aromatic reactants on 0.08 Pd

Reactant <sup>a</sup>	Reaction time [h]	Conversion [%]	Selectivity [%] <sup>b</sup>
Bromobenzene	3	99	97
4-Bromoacetophenone	3	49	98
4-Bromobenzonitrile	3	46	97
4-Bromonitrobenzene	3	0	–
4-Bromoanisole	3	35	95
Chlorobenzene	6	0	–
4-Chloroacetophenone	6	99	98
4-Chlorobenzonitrile	6	94	99
4-Chloronitrobenzene	6	1	100
4-Chloroanisole	6	0	–

<sup>a</sup>  $t = 423$  K, solvent: NMP, base:  $\text{Na}_2\text{CO}_3$ , additive: TBAB, catalyst:  $7.8 \cdot 10^{-5}$  mol% Pd

<sup>b</sup> Selectivity for the formation of the main product,  $t = 3$  h

### Hot filtration test

The development of reusable heterogeneous catalysts has been found to be of particular importance for the Heck coupling reactions, considering that the leaching of Pd has been observed under certain reaction conditions [41–43]. Köhler et al. reported that a large amount of Pd was dissolved into the solvent during the Heck coupling of chloroarenes and then the Pd species were redeposited on the surface of the support material. It has been confirmed that the dissolved Pd species tend to readsorb onto the support after the reaction has been completed [44]. In the present study, Pd leaching was investigated as follows: the reaction was interrupted at 30 min and the filtrate was collected from the hot reaction mixture. The reaction was then conducted for an additional 60 min, by using the filtrate, instead of the solid catalyst. This method, the so-called split technique, has been reported to supply reliable information on the active Pd species in solution [16, 21, 45]. Data were collected for the Heck coupling of methyl acrylate with 4-bromoacetophenone, and the results are listed in Table 5.

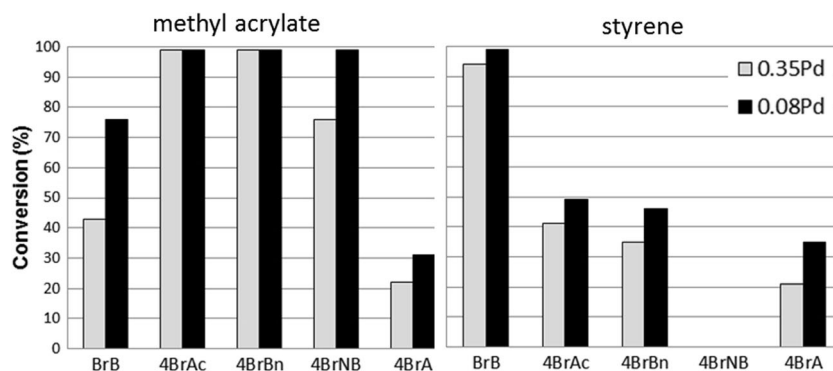
The conversions at 30 min were very similar. After hot filtration, enhanced conversions were obtained, which confirmed that a significant Pd leaching took place for both

samples. This proved to be more pronounced for 0.35 Pd, for which complete conversion was achieved at 90 min. The extent of leaching was found to depend on the Pd loading of the samples.

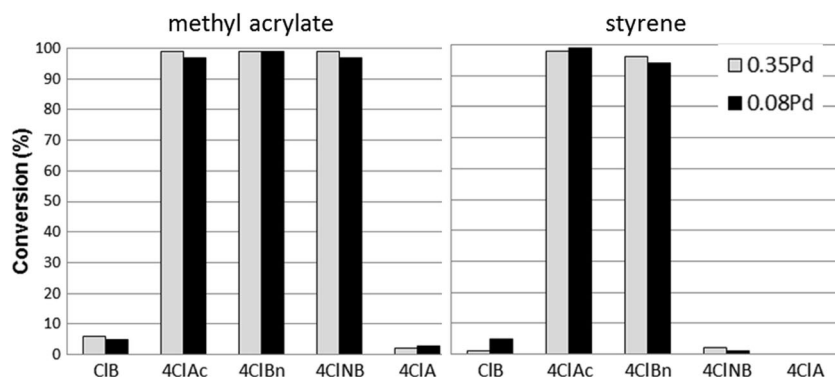
A similar observation was made for ionic liquids confined in silica gel. Shi et al. [37] reported that following a reflux in acetone for 3 h, the ionic liquid [bmim]PF<sub>6</sub> was completely leached out of the silica gel, as revealed by Raman measurements.

In the present study, it was found that after removal of the solid catalyst, the reaction mixture retained its activity. This may be related to the presence of active Pd species, either dissolved or as heterogeneous particles. ICP-AES measurements indicated that the amount of Pd in solution was 39 and 19 ppm, for 0.35 and 0.08 Pd, respectively. This confirmed that a substantial leaching occurred, which was of a similar extent as that reported for Pd/SiO<sub>2</sub> catalysts by Zhao et al. [42].

It may be established that the results of the hot filtration test were in accordance with those of the recycling experiments (Fig. 8). Under the current experimental conditions, an extensive Pd leaching took place, which may be held responsible for the loss of activity experienced in repeated applications of the catalysts. In fact, such phenomena are well-documented [46, 47], as Pd catalysts—both homogeneous complexes and

**Fig. 6** Conversions of methyl acrylate and styrene with bromoarenes

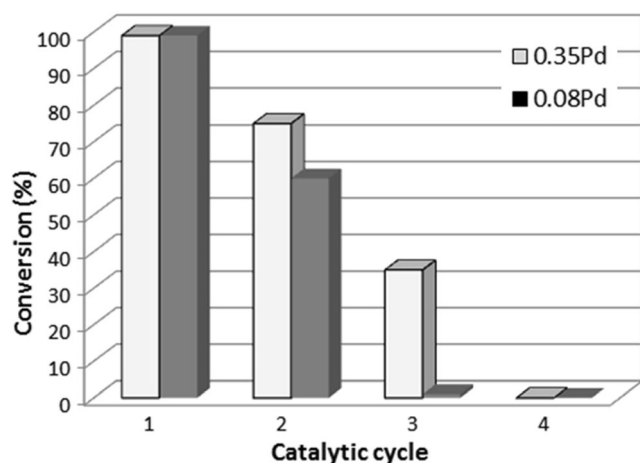
**Fig. 7** Conversions of methyl acrylate and styrene with chloroarenes



heterogeneous samples—may undergo significant changes upon use. Palladium in heterogenized samples can dissolve and then redeposit on the surface of the support material. As a result, the original catalyst is transformed into a sample containing supported Pd particles; that is, the catalyst works in a truly heterogeneous way, which implies Pd dissolution/redeposition. However, as it is clear from the results of the recycling experiments and ICP measurements, this is not the case with our catalysts. Obviously, the main reason for diminishing activities is the dissolution of Pd from the silica matrix. Dissolved Pd remains in solution and is lost in repeated applications. Pd dissolution/redeposition and the formation of large aggregated Pd particles with decreased activities may only have a minor effect. The role of the ionic liquid may also be taken into consideration, as under the present reaction conditions, the ionic liquid may form a cluster with the TBAB modifier and such an interaction tends to contribute to catalyst deactivation.

## Conclusions

Low-loaded Pd-silica catalysts were synthesized in the presence of the ionic liquid [bmim]PF<sub>6</sub>. Raman spectra



**Fig. 8** Recycling of the catalysts for the Heck coupling reaction of methyl acrylate with 4-bromoacetophenone

confirmed that the ionic liquid was confined in the silica gel matrix. The catalytic performances of 0.35 and 0.08 Pd were investigated in the Heck coupling reactions, by using methyl acrylate and styrene as alkenes and substituted bromoarenes and chloroarenes as halogenated reactants. For the reactions of methyl acrylate with bromoarenes, both samples proved to be highly active and stereoselective catalysts. The best performances were obtained for activated bromoarenes, for which complete conversion took place and the selectivity for the formation of the main product exceeded 97%. Although the catalysts displayed low activities for the transformation of chlorobenzene, the presence of EWG on the aromatic ring of the reactant proved to be highly activating and supplied similar results as those obtained for the reactions of bromoarenes. Despite the extremely low Pd loadings, the Pd-silica samples proved to be highly efficient catalysts, as confirmed by the excellent activities and high selectivities obtained for most EWG-containing haloarenes including chloroarenes. It is important to stress that the transformations of chloroarenes required no drastic reaction conditions. The same observation was made for the Heck coupling of styrene with haloarenes. The presence of EWG on the aromatic ring of the haloarene was found to have a beneficial effect on both the conversion and the selectivity. For the transformations of bromoarenes, 0.08 Pd proved to be a more efficient catalyst. The results of the hot filtration test indicated that under the current experimental conditions, a substantial Pd leaching took place. The main reason for diminishing activities is the dissolution of Pd from the silica matrix. Dissolved Pd remains in solution and is lost in repeated applications.

**Table 5** Hot filtration test

Sample	Conversion <sup>a</sup>	Conversion <sup>b</sup>
0.35 Pd	59	100
0.08 Pd	60	91

<sup>a</sup> Conversion at 30 min of reaction time

<sup>b</sup> Conversion after hot filtration, at an additional 60 min of reaction time



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