Pd nanoparticles immobilized in [bmim][PF₆] supported on laponite clay as highly recyclable catalysts for the Mizoroki–Heck reaction

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ABSTRACT

Mizoroki–Heck cross-couplings of aryl halides catalyzed by highly active palladium nanoparticles, immobilized on [bmim][PF₆] films supported on laponite clay, have been investigated. The reactions are performed at 100 °C in solventless conditions to afford the corresponding coupling products in good to excellent yields under non-anhydrous and non-degassed conditions. Highly recoverable catalytic systems have been prepared, allowing up to 17 catalytic cycles with good yields and excellent selectivities. A positive support effect seems to contribute to the long duration of these catalysts.

1. Introduction

Immobilization of heterogeneous catalysts is an area of continuous interest due to the advantages of heterogeneous catalysts regarding stability and reuse. In most cases, immobilization is carried out using solid supports, although the use of liquid supports has the advantage of the easier extrapolation of the knowledge of the homogeneous reaction. Among the different liquid supports described, ionic liquids constitute suitable and versatile alternatives due to their immiscibility in both water and some common organic solvents [1,2].

Imidazolium ionic liquids display a high degree of structural organization that has been used for the preparation of nanoscale structures. In particular, they have been applied to the synthesis and immobilization of transition metal nanoparticles. During the last years several catalytic systems based on ionic liquid-immobilized nanoparticles have proven to be efficient in several reactions, and some reviews have been published dealing with the preparation, characterization and use of metal nanoparticles in ionic liquids [3–6].

Ionic liquids are suitable and recyclable solvents for the Mizoroki–Heck reaction [7–9]. In this regard, palladium nanoparticles prepared in ionic liquids have proven to be outstanding catalysts for this reaction. As imidazolium ionic liquids are excellent solvents for the stabilization of transition metal nanoparticles [10], they have been tested in this reaction. 1,3-Dibutylimidazolium ionic liquids were excellent reaction media for the coupling reaction of iodobenzenes with olefins promoted by palladium nanoparticles under ultrasonic activation [11]. Moreover insights into the mechanism and role of Pd-nanoparticles dispersed in imidazolium ionic liquids in this reaction have been described [12]. Tetraalkylammonium salts have also been used as stabilizing agents for metal nanoparticles, and palladium nanoparticles

immobilized on tetrabutylammonium bromide (TBAB) have been successfully used in the Mizoroki–Heck reaction [13,14].

Supported liquid phases constitute a versatile strategy for the non-covalent immobilization of homogeneous catalysts [15–17]. In particular, the use of supported ionic liquids improves the handling and allows reducing the amount of these expensive solvents [18]. In this regard, metal nanoparticles dispersed onto supported ionic liquids have been used as alternative catalysts for the Mizoroki–Heck coupling. Thus, Pd-nanocolloids supported in chitosan behave as very efficient and recyclable heterogeneous catalyst in TBAB [19]. It is noteworthy that the same system is not active in imidazolium ionic liquids.

Numerous reports have been published dealing with the good properties, including recyclability, of commercial Pd/C catalysts [20]. A modification of these systems has been described consisting in the use of a commercial Pd/C catalyst in [bmim][PF₆] [21]. The catalyst thus prepared was recyclable after extraction with hexane or ethyl acetate, yield decreasing from 92% in the first run to 80% in the fifth, which was ascribed to the accumulation of Et₃NH⁺ I[−] in the ionic liquid phase. Corroborating this hypothesis, the activity of the catalytic phase was restored after washing with water. Solutions of catalysts in ionic liquids have been confined into the pores of amorphous silica and used in several reactions [18]. Some studies suggest that imidazolium ionic liquids are attached to silica mainly by hydrogen bonding between the imidazolium cation and the silanols [22,23]. Pd(OAc)₂ immobilized in [bmim][PF₆] supported in amorphous silica has been used in the Mizoroki–Heck reaction, in the presence of Bu₃N and dodecane, without any additional ligand [24]. The stability of this catalyst is high, although washing with aqueous Na₂CO₃ was necessary to eliminate the resulting Bu₃NH⁺ I[−]. The use of a reversed-phase silica-gel allowed the recycling of palladium-[bmim][PF₆] in Mizoroki–Heck reactions carried out in water [25]. Many other solids have been used to prepare supported ionic-liquid phases, such as molecular sieves [26], diatomaceous earth [27], and mesoporous silica [28]. Very recently, a palladium complex grafted on SBA-15 and confined in an ionic liquid has led to good results in aqueous phase Suzuki–Miyaura reactions [29].

Surprisingly clays have been scarcely used to support ionic liquids in spite to the fact that their charged sheets may establish strong interactions with the ionic liquid cations, imposing a particular order and allowing using small amounts of solvent. The high surface area and the possible interaction of the catalyst with the clay surface makes this system attractive for catalysis [30]. It may be speculated that these characteristics may also help to stabilize transition metal nanoparticles. In this paper we describe the easy preparation of palladium nanoparticles in [bmim][PF₆] supported on laponite clay, and we show the resulting solids are efficient and highly recyclable catalysts for the Mizoroki–Heck reaction [31–33].

2. Experimental

2.1. General

All reagents were purchased from commercial sources (Sigma–Aldrich) and used without further purification, unless otherwise indicated. Deuterated solvents were purchased from Aldrich. All analytical pure reagents were used as solvents. Laponite clay was obtained from Rockwood Additives Ltd. Compounds were characterized by ¹H NMR on a Bruker Advance 400 MHz spectrometer. High-resolution TEM micrographs were obtained with a JEOL-2000 FXII microscope. Field Emission SEM (FESEM) micrographs were obtained with a Carl Zeiss MERLIN™ microscope. Thermogravimetric analyses were carried out in an SDT-2960 Simultaneous TDA-TGA. The surface areas of the solid catalysts prepared were measured via

physical nitrogen adsorption at $-196\text{ }^{\circ}\text{C}$ using an ASAP 2010 (Micrometrics). The specific surface area was analyzed using the Brunauer–Emmett–Teller (BET) model. Prior to measurements, samples of the catalysts were degassed at $300\text{ }^{\circ}\text{C}$ for 2 h.

2.2. Preparation of palladium nanoparticles stabilized with polyvinylpyrrolidone (Pd-PVP NPs)

This nanoparticles synthesis method is based on the reduction of a palladium (II) complex with ethanol [34,35]. In a 100 ml flask, a 2 mM H_2PdCl_4 solution was prepared by mixing 35.4 mg of PdCl_2 (0.2 mmol), 2 ml of 0.2 M HCl, and 98 ml of H_2O . A mixture of 140 ml of H_2O , 94 ml of ethanol, 444.6 mg of PVP and 100 ml of the 0.02 mM H_2PdCl_4 solution was refluxed in a 500 ml flask during 3 h under air to synthesize the palladium nanoparticles protected by PVP. The black solution was evaporated at reduced pressure, and the remaining black solid was dissolved in 66 ml of ethanol. The result was a black stable colloidal suspension of Pd-PVP NPs (3 mM) in ethanol. The size distribution was determined by analysis of the TEM images (Fig. 1). The size range is 0.5–3.5 nm, with a typical value of 1.8 ± 0.6 nm.

Fig 1. TEM image and size distribution of the Pd-PVP nanoparticles.

2.3. Preparation of palladium nanoparticles stabilized with hexadecylamine (Pd-HDA NPs)

This synthetic method is based in the decomposition of a dinuclear palladium (0) complex by hydrogenation to give the palladium nanoparticles [36]. 150 mg (0.16 mmol) of $\text{Pd}_2(\text{dba})_3$, 78 mg (0.31 mmol) of HDA and 20 ml of anhydrous and degassed THF were added in a 15 ml pressure reactor under argon atmosphere. Then, argon was removed under vacuum and H_2 was introduced until reaching a pressure of 3 bar. The reaction was carried out in 20 hours under magnetic agitation at room temperature. After this period of time some precipitate was formed. The reaction mixture and the precipitate were transferred to four centrifugation tubes. Then, 15 ml of hexane were added to each tube and the mixture was centrifuged during 20 min at 6000 rpm. After the centrifugation, the liquid supernatant was removed. This operation was repeated three times, after which the sediment was collected and the remaining solvent evaporated. The result is 40 mg of a black solid composed of extra pure Pd-HDA NPs. The size distribution was determined by analysis of the TEM images (Fig. 2). The size range is 1–6 nm, with a typical value of 2.8 ± 0.7 nm.

Fig 2. TEM image and size distribution of the Pd-HDA nanoparticles.

2.4. Preparation of supported nanoparticles Pd-PVP@[bmim][PF₆]-laponite

In a 20 ml Schlenk flask, 3 g of laponite, 0.3 ml of [bmim][PF₆], 3 ml of the ethanol colloidal suspension of NPs Pd-PVP (3 mM) and 9 ml of dichloromethane (DCM) were mixed, and the mixture stirred by magnetic agitation during 20 min. After that, ethanol and DCM were removed under reduced pressure. The result was a dusty grey solid consisting of the Pd NPs supported onto the laponite-IL system. The size distribution was determined by analysis of the TEM images (Fig. 3). The size range is 1–17 nm, with an average value of 4.7 ± 3.6 nm (median value 3.5 nm, mode value 2.5 nm).

Fig 3. TEM image and size distribution of the Pd-PVP@[bmim][PF₆]-laponite nanoparticles.

2.5. Preparation of supported nanoparticles Pd-HDA@[bmim][PF₆]-laponite

In a glovebox, 16 mg of Pd-HDA NPs were dispersed in 6 ml of [bmim][PF₆] under argon atmosphere. Then, 0.3 ml of the resulting mixture were placed in a 20 ml Schlenck flask and dispersed in 3 g of laponite by magnetic agitation during 20 min, using DCM as dispersant agent. After that DCM was removed under reduced pressure, and the supported NPs were

isolated as a dusty grey solid. The size distribution was determined by analysis of the TEM images (Fig. 4). The size range is 1–5.4 nm, with an average value of 2.4 ± 0.8 nm.

Fig 4. TEM image and size distribution of the Pd-HDA@[bmim][PF₆]-laponite nanoparticles.

2.7. General procedure for Heck coupling reactions

In a 5 ml flask, 0.9 mmol of the corresponding aryl halide, 1.41 mmol of the olefin and 2.15 mmol of triethylamine were mixed. Then, the reagents mixture was transferred through a syringe to a 20 ml Schlenck flask containing 3.41 g of the catalytic system previously prepared. The reaction mixture got completely adsorbed onto the solid. The reaction was carried out in 20 hours at 100 °C. After this period of time, the solid was cooled to 65 °C, and washed with hexane (3 x 10 ml). The solid was then dried under reduced pressure to be reused, and the combined extracts containing the reaction products were analyzed by gas chromatography and ¹H-RMN.

3. Results and discussion

3.1. Catalytic tests with Pd-PVP@[bmim][PF₆]-laponite

Pd-PVP NPs were prepared in ethanol as described in the Experimental Section and added to 0.1 ml of [bmim][PF₆] (0.48 mmol) previously dispersed on laponite (1 g). The ethanol was evaporated under vacuum, giving rise to a free-flowing powder. The surface area of the resulting solid was determined by N₂ adsorption by applying the BET theory, and compared with those of the support and the supported ionic liquid (Table 1).

Table 1
BET surface areas and pore volumes of laponite and modified laponites used in this work.^a

Entry	[bmim][PF ₆] (mmol)	Pd (mmol)	Stabilizing agent	Surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)
1	—	—	—	348.2	0.268
2	0.48	—	—	235.1	0.176
3	1.46	—	—	173.3	0.139
4	0.48	0.003	PVP	250.1	0.187
5	0.48	0.003	HDA	143.2	0.145

^a All amounts referred to 1 g of laponite.

As can be seen from the results in Table 1, the formation of the [bmim][PF₆] ionic liquid film on the laponite results in a decrease of the surface area of the solid, which is more marked when a higher amount of ionic liquid is used (Table 1, entries 1–3). On the other hand, the deposition of the Pd-PVP NPs does not result in a further change of the surface area of the solids (Table 1, entries 2 and 4).

The supported Pd-PVP NPs, coded as Pd-PVP@[bmim][PF₆]-laponite, were tested in the benchmark reaction of iodobenzene with butyl acrylate, in the presence of NEt₃ and without the use of any additional solvent. After 20 h the solid was thoroughly washed with hexane (3 x 10 ml) and the organic extract analyzed by gas chromatography using decane as an internal standard. The results obtained (Table 2) depend on several factors, including the amount of Pd dispersed on the clay and the % mol of catalyst used.

Table 2

Results obtained in the reaction of iodobenzene with butyl acrylate.^a

Pd (mmol)	Pd (mol %)	laponite (g)	Cycle	Yield (%) ^b
0.003	0.09	1	1	92
			2	25
0.009	0.09	3	1	99
			2	52
			3	7
0.003	0.33	3	1	100
			2	16
0.009	1	3	1	100
			12 ^c	100
			13	95
			14	96
			15	43

^a All reactions were carried out on a 0.9 mmol scale of iodobenzene, 1.41 equiv. of butyl acrylate and 2.15 mmol of NEt₃, in 20 h at 100 °C in solventless conditions.

^b Determined by GC. Selectivity to butyl (*E*)-cinnamate was 100% in all cases.

^c Full recycling results are available as Supplementary Data.

All the conditions used led to high yields and complete selectivities, but the results after recovery were worse in most cases, and only by using 1% Pd it is possible to use the catalyst during 14 cycles keeping high yields and complete selectivity (complete results of all reaction cycles are available in the Supplementary Data).

TGA analysis of the fresh catalyst, together with elemental analysis, agrees with the presence of ca. 0.5 mmol of ionic liquid and about 0.1 g of PVP (Fig. 5).

Fig. 5. Thermogravimetric analyses of the fresh (left) and exhaust (right) Pd-PVP@[bmim][PF₆]-laponite catalysts.

TGA shows the main weight loss near 420 °C, which may correspond to the ionic liquid phase. The recovered catalyst shows a completely different pattern, whereas the original catalyst loses ca. 20% weight when heated under air up to 600°C, the loss in the case of the catalyst recovered from the 15th cycle is 66.5% at 650°C. Furthermore the main weight loss takes place around 270 °C (ca. 50% weight). Of course these changes are accompanied from changes in the composition, as established by elemental analysis, with a noticeable increase in the C and N percentages. These changes in TGA suggest a change in the structure of the ionic liquid because of the formation of the ammonium salt as a concomitant byproduct that is not eliminated during the extraction of the reaction products.

The amount of Pd, determined by ICP-MS, experiences a noticeable decrease, however conclusions about Pd leaching cannot be easily reached due to the deposition of a large amount of organic materials over the clay. To have a more reliable estimation of the amount of Pd remaining on the clay after 15 uses, we first eliminated all the organic materials by calcination

at 550 °C under air stream. We carry out the same operation on the fresh catalysts (to avoid any perturbation due to the presence of the ionic liquid and the stabilizing agent). The Pd content goes from 0.243 mg/g in the fresh catalyst (theoretical value 0.279) to 0.020 mg/g in the used one. A best estimate can be obtained by comparing the Pd/Mg ratio obtained from the ICP-MS analyses, given that the amount of Mg should remain constant. The results of these experiments are shown in Table 3, and point to a Pd leaching of ca. 90% (92% using the total Pd content and 88% using the Pd/Mg ratio). This important leaching of Pd could be at the origin of the poor recyclability of catalysts with low Pd load, as previously shown in Table 2.

Table 3

ICP-MS analyses of fresh and used Pd-PVP@[bmim][PF₆]-laponite catalysts, previously calcined at 550 °C under air stream.

Reaction	Pd (mg/g)	Mg(mg/g)	Pd/Mg	Leaching (%) ^d
Freshly prepared ^a	0.2428	168.30	1.44×10^{-3}	—
iodobenzene+acrylate ^b	0.0195	112.60	1.73×10^{-4}	92/88
iodobenzene+styrene ^c	0.1411	209.90	6.72×10^{-4}	42/47

^a The %wt. palladium content in the freshly prepared catalyst is 0.021%

^b After 15 uses.

^c After 12 uses.

^d Left value, estimated using the Pd content, right value, estimated using the Pd/Mg ratio.

The leaching of Pd in the first reaction was also determined by analyzing the hexane extraction phase. The amount of Pd in this extract, determined by ICP-MS, was 0.133 mg/g in a total mass of 170 mg. This represents a loss of 0.0226 mg of Pd, i.e. ca. 3% of the initial amount present in the solid (Table 3). This result, together the analyses of the exhaust catalyst, points to a continuous Pd leaching along the recycling uses. The presence of Pd in the reaction extract also raises the question of the true heterogeneous character of the catalyst. To test this point, we carried out two different hot filtration tests, by extracting two reactions after 1.5 and 3 h. Then, the hexane was evaporated, and DMF (a solvent commonly used in homogeneous catalysis of Heck reactions) was added. The composition of these solutions was analyzed during six days, and they did not change with regard to those found just after the filtration (Fig. 6). These experiments seem to indicate that the Pd species responsible for the leaching are not active for the catalysis of the reaction.

Fig. 6. Hot filtration experiments of the reaction of iodobenzene with butyl acrylate, catalyzed by Pd-PVP@[bmim][PF₆]-laponite.

TEM and SEM micrographs are consistent with TGA and elemental analyses. The comparison between the FESEM micrographs of the freshly prepared and exhaust catalysts reveals that the clay particles tend to disintegrate during use, probably by delamination of their structure (Fig. 7a). Furthermore, a large amount of Et₃NH⁺I⁻ is observed, both as independent particles, and also partially covering the laponite particles (Fig. 7b). Furthermore, flexible strands appear in some micrographs, which have been assigned to polymers formed during the reaction. In situ X-ray fluorescence elemental analyses corroborate these observations.

Fig. 7. FESEM micrographs of freshly prepared (left) and exhaust (right) Pd-PVP@[bmim][PF₆]-laponite catalysts at different magnifications: a) 200X, b) 5000X.

The comparison of the TEM images illustrates the loss of a large part of the palladium, since in the exhaust catalysts the presence of recognizable nanoparticles is scarce, and most of laponite particles lack Pd NPs (Fig. 8).

Fig. 8. TEM micrographs of freshly prepared (a) and exhaust (b) Pd-PVP@[bmim][PF₆]-laponite catalysts.

In the reactions between iodobenzene and styrene (Table 4) the amount of catalyst is again the most important factor influencing recovery. In this case catalyst recovered after the 12th cycle loses 55% weight until 660 °C with a pattern closely similar to the catalyst recovered from the reaction of butyl acrylate. In this case, a lower Pd leaching, ca. 45% was calculated from the ICP-MS analyses after calcination of the catalyst samples (Table 3).

Table 4

Results obtained in the reaction of iodobenzene with styrene catalyzed by Pd-PVP@[bmim][PF₆]-laponite.^a

Pd (mmol)	Pd (mol %)	laponite (g)	Cycle	Yield (%) ^b	Selectivity (%)	
0.003	0.33	3	1	87	94	
			2	17	94	
0.009	1	3	1	100	92	
			10 ^c	100	94	
			11	96	98	
			12	40	94	

^a All reactions were carried out on a 0.9 mmol scale of iodobenzene, 1.41 equiv. of butyl acrylate and 2.15 mmol of NEt₃, in 20 h at 100 °C in solventless conditions.

^b Determined by GC. Selectivity refers to the proportion of (*E*)-stilbene (regioselectivity).

^c Full recycling results are available as Supporting Data.

We tried to optimize the reaction time, and after some tests we found that in the reaction of iodobenzene with butyl acrylate, a reaction time of 4 h is enough to reach the total conversion of the limiting reagent. In these conditions, the catalyst could be used 16 times with almost 100% product yield, and still with 89% yield in the 17th run (Table 5) (complete results gathered in the Supplementary Data).

Table 5

Results obtained in the reaction of iodobenzene with butyl acrylate catalyzed by Pd-PVP@[bmim][PF₆]-laponite.^a

Pd (mmol)	Pd (mol %)	laponite (g)	Cycle	Yield (%) ^b
0.009	1	3	1	100
			15 ^b	98
			16	100
			17	89
			18	55

^a All reactions were carried out on a 0.9 mmol scale of iodobenzene, 1.41 equiv. of butyl acrylate and 2.15 mmol of NEt₃, in 4 h at 100 °C in solventless conditions.

^b Full recycling results are available as Supporting Data.

Similarly, in the case of the reaction with styrene, the optimal reaction time resulted to be 8 h. In this case, the recoverability was similar to that observed with 20 h reaction time, i.e. 11 uses with total conversion, falling to ca. 50% yield in the 12th use (complete results gathered in the Supplementary Data).

We also explored the applicability of this catalytic system to other related substrates, such as substituted styrenes and aryl halides. The results of this study are summarized in Table 6. As can be seen the use of the less reactive aryl bromides requires higher amounts of catalyst and higher reaction temperatures. In spite of this, the catalysts could only be used four times before deactivation, and the yields never reached 100%. No reaction at all was observed when aryl chlorides were used. In the case of the substituted styrenes the results were better, allowing 8-9 uses keeping good yields and selectivities.

Table 6

Results obtained in the reaction of aryl halides with different olefins, catalysed by Pd-PVP@[bmim][PF₆]-laponite.^a

Ar-X	R	Pd (mol %)	T (°C)	Cycle	Yield (%) ^b	Select. (%) ^b
PhCl	COO ⁿ Bu	2 ^c	120	1	0	—
4-MeOC ₆ H ₄ Cl	COO ⁿ Bu	2 ^c	120	1	0	—
PhBr	COO ⁿ Bu	2 ^c	120	1	63	100 ^d
				2	73	100 ^d
				3	79	100 ^d
				4	44	100 ^d
4-MeOC ₆ H ₄ Br	COO ⁿ Bu	2 ^c	120	1	98 ^h	100 ^d
				2	85 ^h	100 ^d
				3	79 ^h	100 ^d
				4	52 ^h	100 ^d
PhI	4-MeOC ₆ H ₄	1 ^e	100	1	96	78 ^f
				2	100	86 ^f

				8 ^g	99	89 ^f
				9	20	94 ^f
PhI	4-ClC ₆ H ₄	1 ^c	100	1	85	93 ^f
				2	100	92 ^f
				9 ^g	98	95 ^f
				10	83	96 ^f

^a All reactions were carried out on a 0.9 mmol scale of aryl halide, 1.41 equiv. of olefin and 2.15 mmol of NEt₃, in 20 h in solventless conditions.

^b Determined by GC.

^c 0.09 mmol Pd in 3 g of laponite with 0.3 ml of [bmim][PF₆].

^d Selectivity refers to the proportion of the corresponding butyl (*E*)-cinnamate (stereoselectivity).

^e 0.03 mmol Pd in 3 g laponite with 0.3 ml of [bmim][PF₆].

^f Selectivity refers to the proportion of (*E*)-stilbene (regioselectivity).

^g Full recycling results are available as Supplementary Data.

^h Results are referred to conversion of 4-bromoanisole.

3.2. Catalytic tests with Pd-HDA@[bmim][PF₆]-laponite

Trying to improve the results we tested a different strategy for the preparation of nanoparticles using a lower amount of a weaker stabilizing agent. In this method Pd nanoparticles were directly prepared by hydrogenation of a dinuclear Pd(0) complex, Pd₂[dba₃], in the presence of laponite, [bmim][PF₆], and hexadecylamine (HDA) as a dispersant, size controller and stabilizing agent of the Pd nanoparticles. After that, the resulting solid was thoroughly washed with hexane to eliminate the byproducts. The surface area of this solid was determined by N₂ adsorption by applying the BET theory (Table 1, entry 5). Differently to what happened in the case of the Pd-PVP NPS, in this case the deposition of the Pd-HDA NPs results in a further decrease of the surface area of the solid (Table 1, entries 2 and 5).

The solid catalyst was first tested in the coupling reaction of iodobenzene with butyl acrylate (Table 7).

Table 7

Results obtained in the reaction of iodobenzene with butyl acrylate catalyzed by Pd-HDA@[bmim][PF₆]-laponite.^a

Pd (mmol)	Pd (mol %)	laponite (g)	Cycle	Yield (%) ^b
0.009	1	3	1	100
			14 ^c	100
			15	94
			16	58
			17	21

^a All reactions were carried out on a 0.9 mmol scale of iodobenzene, 1.41 equiv. of butyl acrylate and 2.15 mmol of NEt₃, in 20 h at 100 °C in solventless conditions.

^b Determined by GC. Selectivity to butyl (*E*)-cinnamate was 100% in all cases.

^c Full recycling results are available as Supplementary Data.

It is worth noting that, although the Pd nanoparticles must be prepared in a glovebox under inert atmosphere when HDA is used as the stabilizing agent, due to its weaker coordinative ability, the supported nanoparticles exhibit a high stability in working conditions, since all the

reactions and subsequent work-ups are carried out in the open air, with no indication of catalytic activity loss by surface oxidation of the Pd nanoparticles. It seems then that the support (the ionic liquid film, the laponite or both) plays an additional stabilizing role.

TGA analysis of the fresh catalyst, together with the elemental analysis, agrees with the presence of 0.5 mmol of ionic with the main weight loss near from 420 °C, which may correspond to the ionic liquid phase. The experimental C/N ratio, 3.9, is close to 4, the theoretical value for [bmim][PF₆]. As in the Pd-PVP@[bmim][PF₆]-laponite case, the recovered catalyst shows a completely a different pattern in the TGA. Whereas the original catalyst loses 14% weight when heated under air until 600 °C, the recovered catalyst after the 17th cycle loses 70% until 630 °C. Furthermore the pattern is similar to the previously commented for the Pd-PVP@[bmim][PF₆]-laponite catalyst, and again these changes are accompanied from changes in the elemental analysis, with a noticeable increase in the C and N percentages. In this case the C/N ratio increases to 6, which is the value corresponding to the triethylammonium iodide. The Pd content goes from 0.232 mg/g (theoretical value 0.280) to 0.06 mg/g. However, as mentioned before, the gain of weight in the used catalyst due to the deposition of organic material does not allow a reliable estimation of the Pd leaching with these analyses. We therefore compared the ICP-MS analyses of samples previously calcined at 550 °C under air stream. The corresponding results are shown in Table 8.

Table 8

ICP-MS analyses of fresh and used Pd-HDA@[bmim][PF₆]-laponite catalysts, previously calcined at 550 °C under air stream.

Reaction	Pd (mg/g)	Mg(mg/g)	Pd/Mg	Leaching (%) ^d
Freshly prepared ^a	0.2316	172.80	1.34×10^{-3}	—
iodobenzene+acrylate ^b	0.0568	143.30	3.96×10^{-4}	75/70
iodobenzene+styrene ^c	0.0779	170.50	4.57×10^{-4}	66/66

^a The %wt. palladium content in the freshly prepared catalyst is 0.020%

^b After 17 uses.

^c After 9 uses.

^d Left value, estimated using the Pd content, right value, estimated using the Pd/Mg ratio.

In this case, the estimated total Pd leaching is about 70–75%, slightly lower than that observed in the precedent case (ca. 90%), above all if we consider the higher number of cycles reached with the Pd-HDA@[bmim][PF₆]-laponite catalyst (17 vs. 15 with Pd-PVP@[bmim][PF₆]-laponite).

The use of other aryl halides, namely bromobenzene and 4-methoxybromobenzene, was also tested for the cross coupling reaction with butyl acrylate. Unfortunately, yields were low and erratic for the first substrate during five reaction cycles (between 1% and 20%), and no reaction at all was noticed with the second substrate. Therefore, we did not further explore the use of aryl halides other than iodobenzene with this catalyst.

In the reactions between iodobenzene and styrene (Table 9) the amount of catalyst is again the most important factor influencing recovery. In this case catalyst recovered after the 9th cycle loses ca. 45% weight until 650 °C with a pattern closely similar to that found in the previous cases. In spite of the lower weight increase because of organic materials, as reveal the TGA, the total Pd content decreases to 0.065 mg/g, far from the initial value of 0.232 mg/g. The analyses of the calcined samples (Table 6) allow estimating a total Pd leaching of 66% in the nine runs.

Table 9

Results obtained in the reaction of iodobenzene with styrene catalyzed by Pd-HDA@[bmim][PF₆]-laponite.^a

Pd (mmol)	Pd (mol %)	laponite (g)	Cycle	Yield (%) ^b	Selectivity (%)
0.003	0.33	3	1	100	95
			6 ^c	100	97
			7	83	95
			8	46	95
			9	15	93

^a All reactions were carried out on a 0.9 mmol scale of iodobenzene, 1.41 equiv. of butyl acrylate and 2.15 mmol of NEt₃, in 20 h at 100 °C in solventless conditions.

^b Determined by GC. Selectivity refers to the proportion of (*E*)-stilbene (regioselectivity).

^c Full recycling results are available as Supplementary Data.

The use of this new strategy improves catalyst recovery carrying out the reactions under air and without any additional solvent.

4. Conclusions

To sum up, we have described a straightforward protocol to prepare supported palladium nanoparticles showing a high stability, which allows easy recovery and recycling in Mizoroki–Heck coupling reactions. Ionic liquid films on laponite clay have proved to be interesting candidates for the immobilization of this kind of nanoparticles by impregnation. Furthermore, the solid support has demonstrated to play an additional role, allowing the use of these catalysts under air and in solventless conditions with an improved reuse. In the best case, up to 17 reaction cycles have been carried out keeping total conversion, and excellent yields and selectivities. Work is in progress to exploit these kinds of supported catalysts, by optimizing the reaction conditions and recoverability, as well to apply them to other reactions.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcata.2013.12.010>.

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SUPPLEMENTARY DATA

Pd-nanoparticles immobilized in [bmim][PF₆] supported on laponite clay as highly recyclable catalysts for the Mizoroki–Heck reaction

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1. Gas chromatography analyses of the Heck coupling reactions

1.1 Heck coupling reaction of iodobenzene with *n*-butyl acrylate

FID from Hewlett–Packard 5890-II, Agilent J&W GC Columns HP-5:30 m × 0.25 mm × 0.25 μm; helium as carrier gas. 20 psi; injector temperature: 230 °C; detector temperature: 250 °C; oven program: 70 °C (1 min), 20 °C min⁻¹ to 250 °C (7,5 min); retention times: *n*-butyl acrylate: 2.6 min, *n*-decane: 3.4 min, iodobenzene: 3.7 min, (*E*)-butyl cinnamate: 8.7 min.

Fig. S1. Typical CG chromatogram for the Heck coupling reaction of iodobenzene with *n*-butyl acrylate.

In order to determine the Heck coupling yield *n*-decane is used as internal standard. The following equation was used to calculate the reaction yield, obtained from previous calibration experiments:

$$\text{Yield}(\%) = 1.208 \cdot \frac{\text{decane mmol} \cdot \text{cinnamate area}}{\text{iodobenzene mmol} \cdot \text{decane area}} \cdot 100$$

1.2 Heck coupling reaction of bromobenzene with *n*-butyl acrylate

FID from Hewlett–Packard 5890-II, Agilent J&W GC Columns HP-5: 30 m × 0.25 mm × 0.25 μm; helium as carrier gas. 20 psi; injector temperature: 230 °C; detector temperature: 250 °C; oven program: 70 °C (1 min), 20 °C min⁻¹ to 250 °C (7.5 min); retention times: *n*-butyl acrylate: 2.9 min, bromobenzene: 3.3 min, *n*-decane: 3.8 min, (*E*)-butyl cinnamate: 9.1 min.

Fig. S2. Typical CG chromatogram for the Heck coupling reaction of bromobenzene with *n*-butyl acrylate. In order to determine the Heck coupling yield *n*-decane is used as internal standard. The following equation was used to calculate the reaction yield, obtained from previous calibration experiments:

$$\text{Yield}(\%) = 1.208 \cdot \frac{\text{decane mmol} \cdot \text{cinnamate area}}{\text{bromobenzene mmol} \cdot \text{decane area}} \cdot 100$$

1.3 Heck coupling reaction of 4-bromoanisole with *n*-butyl acrylate

FID from Hewlett–Packard 5890-II, Agilent J&W GC Columns HP-5: 30 m × 0.25 mm × 0.25 μm; helium as carrier gas. 20 psi; injector temperature: 230 °C; detector temperature: 250 °C; oven program: 70 °C (1 min), 20 °C min⁻¹ to 250 °C (7.5 min); retention times: *n*-butyl acrylate: 2.6 min, 4-bromoanisole: 3.2 min, *n*-decane: 3.4 min, (*E*)-butyl 3-(4-methoxyphenyl)acrylate: 10.8 min.

Fig. S3. Typical CG chromatogram for the Heck coupling reaction of 4-bromoanisole with *n*-butyl acrylate. In order to determine the Heck coupling yield *n*-decane is used as internal standard. The following equation was used to calculate the reaction yield, obtained from previous calibration experiments:

$$\text{Conversion}(\%) = 1 - 0,5902 \cdot \frac{\text{decane mmol} \cdot 4\text{-bromoanisole area}}{4\text{-bromoanisole mmol} \cdot \text{decane area}} \cdot 100$$

1.4 Heck coupling reaction of iodobenzene with styrene

FID from Hewlett–Packard 5890-II, Agilent J&W GC Columns HP-5: 30 m × 0.25 mm × 0.25 μm; helium as carrier gas. 20 psi; injector temperature: 230 °C; detector temperature: 250 °C; oven program: 70 °C (1 min), 20 °C min⁻¹ to 250 °C (7.5 min); retention times: styrene: 2.6 min, n-decane: 3.4 min, iodobenzene: 3.7 min, 1,1-diphenylethene: 7.8 min, (*E*)-stilbene: 9.1 min.

Fig. S4. Typical CG chromatogram for the Heck coupling reaction of iodobenzene with styrene. In order to determine the Heck coupling yield n-decane is used as internal standard. The following equation was used to calculate the reaction yield, obtained from previous calibration experiments:

$$\text{Yield}(\%) = 1.4401 \cdot \frac{(\text{decane mmol} \cdot \text{stilbene area}) + (\text{decane mmol} \cdot 1,1 - \text{diphenylethene area})}{\text{iodobenzene mmol} \cdot \text{decane area}} \cdot 100$$

1.5 Heck coupling reaction of iodobenzene with 1-methoxy-4-vinylbenzene

FID from Hewlett–Packard 5890-II, Agilent J&W GC Columns HP-5: 30 m × 0.25 mm × 0.25 μm; helium as carrier gas. 20 psi; injector temperature: 230 °C; detector temperature: 250 °C; oven program: 70 °C (1 min), 20 °C min⁻¹ to 250 °C (7.5 min); retention times: n-decane: 3.4 min, iodobenzene: 3.7 min, 1-methoxy-4-vinylbenzene: 4.8 min, 1-methoxy-4-(1-phenylvinyl)benzene: 9.4 min, (E)-1-methoxy-4-styrylbenzene: 10.7 min.

Fig. S5. Typical CG chromatogram for the Heck coupling reaction of iodobenzene with 1-methoxy-4-vinylbenzene.

In order to determine the Heck coupling yield n-decane is used as internal standard. The following equation was used to calculate the reaction yield, obtained from previous calibration experiments:

$$\text{Yield(\%)} = 0.9305 \cdot \frac{((E)\text{-}1\text{-methoxy-}4\text{-styrylbenzene } A + 1\text{-methoxy-}4\text{-(1-phenylvinyl)benzene } A) \cdot \text{decane mmol}}{\text{iodobenzene mmol} \cdot \text{decane Area}} \cdot 100$$

1.6 Heck coupling reaction of iodobenzene with 1-chloro-4-vinylbenzene

FID from Hewlett–Packard 5890-II, Agilent J&W GC Columns HP-5: 30 m × 0.25 mm × 0.25 μm; helium as carrier gas. 20 psi; injector temperature: 230 °C; detector temperature: 250 °C; oven program: 70 °C (1 min), 20 °C min⁻¹ to 250 °C (7.5 min); retention times: n-decane: 3.4 min, iodobenzene: 3.7 min, 1-chloro-4-vinylbenzene: 4.2 min, 1-chloro-4-(1-phenylvinyl)benzene: 8.9 min, (E)-1-chloro-4-styrylbenzene: 10.2 min.

Fig. S6. Typical CG chromatogram for the Heck coupling reaction of iodobenzene with 1-chloro-4-vinylbenzene.

In order to determine the Heck coupling yield n-decane is used as internal standard. The following equation was used to calculate the reaction yield, obtained from previous calibration experiments:

$$\text{Yield}(\%) = 1.1834 \cdot \frac{(\text{1-chloro-4-(1-phenylvinyl)benzene} + \text{(E)-1-chloro-4-styrylbenzene}) \cdot \text{decane mmol}}{\text{iodobenzene mmol} \cdot \text{decane Area}} \cdot 100$$

2. Thermogravimetric analyses of freshly prepared and exhausted catalytic systems

2.1 Laponite

2.2 Freshly prepared Pd-PVP@[bmim][PF₆]-laponite catalyst

2.3 Exhaust Pd-PVP@[bmim][PF₆]-laponite catalyst applied to the reaction of iodobenzene with *n*-butyl acrylate

2.4 Exhaust Pd-PVP@[bmim][PF₆]-laponite catalyst applied to the reaction of iodobenzene with styrene

2.5 Freshly prepared Pd-HDA@[bmim][PF₆]-laponite catalyst

2.6 Exhaust Pd-HDA@[bmim][PF₆]-laponite catalyst applied to the reaction of iodobenzene with *n*-butyl acrylate

2.7 Exhaust Pd-HDA@[bmim][PF₆]-laponite catalyst applied to the reaction of iodobenzene with styrene

3. Complete results of recycling experiments

3.1 Heck coupling reaction of iodobenzene with *n*-butyl acrylate, catalyzed by Pd-PVP@[bmim][PF₆]-laponite

Run	% Yield ^a	% Isolated Yield	% Regioselectivity	Accumulated TON
1	100	93	100	99
2	97	92	100	196
3	100	91	100	295
4	100	98	100	394
5	100	93	100	493
6	100	77	100	593
7	100	83	100	692
8	100	94	100	791
9	100	93	100	891
10	100	87	100	990
11	100	89	100	1089
12	100	92	100	1188
13	95	91	100	1282
14	96	96	100	1378
15	43	n.d.	100	1421

^a Determined by gas chromatography

3.2 Heck coupling reaction of iodobenzene with *n*-butyl acrylate. Time optimization catalyzed by Pd-PVP@[bmim][PF₆]-laponite

Run	% Yield ^a	% Isolated Yield	AccumulatedTON
1	100	95	99
2	100	n.d.	199
3	100	n.d.	298
4	100	n.d.	397
5	100	n.d.	496
6	100	83	596
7	100	91	695
8	100	99	794
9	100	78	894
10	99	n.d.	991
11	100	n.d.	1091
12	100	94	1190
13	99	n.d.	1288
14	94	n.d.	1381
15	98	n.d.	1479
16	100	n.d.	1578
17	89	n.d.	1666
18	55	n.d.	1720

^a Determined by gas chromatography; butyl (*E*)-cinnamate is the only reaction product.

3.3 Heck coupling reaction of iodobenzene with *n*-butyl acrylate, catalyzed by Pd-HDA@[bmim][PF₆]-laponite

Run	% Yield ^a	AccumulatedTON
1	100	99
2	100	199
3	100	297
4	100	396
5	100	495
6	100	594
7	100	693
8	100	792
9	100	891
10	100	990
11	100	1089
12	100	1188
13	100	1287
14	100	1386
15	94	1480
16	58	1538
17	21	1559

^a Determined by gas chromatography; butyl (*E*)-cinnamate is the only reaction product.

3.4 Heck coupling reaction of bromobenzene with n-butyl acrylate catalyzed by Pd-PVP@[bmim][PF₆]-laponite

Run	% Yield ^a	Accumulated TON
1	63	31
2	73	67
3	79	107
4	44	129

^a Determined by gas chromatography; butyl (*E*)-cinnamate is the only reaction product.

3.5 Heck coupling reaction of 4-bromoanisole with n-butyl acrylate catalyzed by Pd-PVP@[bmim][PF₆]-laponite

Run	% Conversion ^a	Accumulated TON
1	98	49
2	85	97
3	79	136
4	52	162

^a Determined by gas chromatography; butyl (*E*)-4-methoxycinnamate is the only reaction product.

3.6 Heck coupling reaction of iodobenzene with styrene catalyzed by Pd-PVP@[bmim][PF₆]-laponite

Run	% Yield ^a	% Isolated Yield	% Regioselectivity	Accumulated TON
1	100	89	92	98
2	100	91	91	196
3	100	70	93	294
4	98	82	92	393
5	100	85	94	491
6	100	68	93	590
7	100	85	93	688
8	100	83	93	787
9	100	80	92	885
10	100	83	94	982
11	96	82	98	1077
12	40	n.d.	94	1114

^a Determined by gas chromatography

3.7 Heck coupling reaction of iodobenzene with styrene catalyzed by Pd-HDA@[bmim][PF₆]-laponite

Run	% Yield ^a	% Regioselectivity	Accumulated TON
1	100	95	99
2	100	95	198
3	100	95	297
4	100	98	396
5	100	95	495
6	100	97	594
7	83	95	677
8	46	95	723
9	15	93	738

^a Determined by gas chromatography

3.8 Heck coupling reaction of iodobenzene with 1-methoxy-4-vinylbenzene catalyzed by Pd-PVP@[bmim][PF₆]-laponite

Run	% Yield ^a	% Isolated Yield	% Regioselectivity	Accumulated TON
1	96	90	78	95
2	100	87	86	194
3	100	72	87	294
4	97	84	87	390
5	92	63	92	481
6	95	95	89	576
7	99	86	88	675
8	99	71	89	773
9	20	n.d.	94	792

^a Determined by gas chromatography

3.9 Heck coupling reaction of iodobenzene with 1-chloro-4-vinylbenzene catalyzed by Pd-PVP@[bmim][PF₆]-laponite

Run	% Yield ^a	% Isolated Yield	% Regioselectivity	Accumulated TON
1	85	88	93	85
2	100	98	92	184
3	100	81	92	283
4	100	82	94	383
5	100	61	94	482
6	100	80	95	581
7	100	89	95	680
8	100	65	95	780
9	98	78	96	877
10	83	76	95	959
11	10	n.d.	96	969

^a Determined by gas chromatography