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Encapsulation of $Pd(OAc)_2$ catalyst in an ionic liquid phase confined in silica gels. Application to Heck–Mizoroki reaction

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Ionogels encapsulating $Pd(OAc)_2$ were successfully used as catalysts in Heck–Mizoroki coupling reactions. Reaction rates were compared to homogeneous systems showing no significant difference. Leaching tests showed that catalysis actually took place in the ionic liquid phase confined within the silica matrix. The absence of leaching of palladium, the trapping of salt by-product in ionogels and the ability to produce convenient ready-to-use catalyst doses open interesting potential applications.

Introduction

The concept of confining catalysts on porous supports is far from new, but it is still the subject of numerous studies involving organic chemistry, materials chemistry, physicochemistry, calculations *etc.*[1,2] A supported liquid-phase catalyst (SLPC), which consists of a catalyst component dissolved in a liquid (PEG,[3] water,[4] ionic liquid[5] *etc.*) coated on the surface of a high-surface porous material, belongs to this common concept.

Ionic liquids have been claimed as green solvents, especially for sustainable metal catalyzed reactions, with high efficiency and recyclability.[6,7] However ionic liquids still are expensive, which is very restrictive for large scale uses. A second limitation arises from the high viscosity of ionic liquids, which implies highly energy-consuming stirring, not suitable for industrial applications. Moreover, in biphasic systems, mass transfer limitations mean that the sole catalyst involved in the process is that contained in the narrow diffusion layer at the liquid–liquid interface.

The immobilization of the ionic liquid phase containing the metal catalyst as a thin film adsorbed on an inorganic support has been recently developed to circumvent these limitations.[5,8–10] Typically silica support beads with 25 wt% of ionic liquid loading are easily obtained as free flowing powders. Actually, the supported ionic liquid film (SILF) approach provides major advantages: (i) a small amount of ionic liquid, (ii) an inexpensive immobilization of the metal catalyst without using coupling agents, (iii) a possible confinement effect in relation to the concentration of both metal catalyst and substrate in the ionic liquid film, (iv) a possible effect of the nature of the surface support on the selectivity of reactions.[11] Moreover it could be particularly suitable for continuous fixed-bed reactors. However, the main drawback is the risk of leaching of ionic liquid after a few cycles.

Another approach is the immobilization of ionic liquids in silica matrices by sol–gel processing, which has been recently reported.[12–17] It results in a more intimate biphasic system than the simple impregnation of oxide particles. The confined ionic liquid was shown to fill 3D-interconnected mesopores (mean pore diameters in the 7–20 nm range, depending on the ratio of ionic liquid to silica), which gives rise to percolating ionic conduction paths.[13] However, despite confinement the ionic liquid nanophase was shown to keep liquid-like dynamics.[12] Accordingly these ionogels gave ionic conductivity performances close to those of pure ionic liquids.[13] The interconnected pore structure of ionogels should facilitate the internal diffusion of reactants and products in catalyzed reactions. Nevertheless, whereas numerous applications of SILF have been reported, particularly in transition metal catalysis, such as Rh-catalyzed hydroformylations,[16] hydrogenations,[18] Pd-catalyzed Heck–Mizoroki[14,15] and Suzuki–Miyaura[19] reactions, and Rh-, Pd-, and Zn-catalyzed hydroaminations,[20–22] there are to date only a few papers on the use of ionogels in the same area. Actually Deng *et al.* reported the enhanced catalytic performance of the carbonylation of aniline into ureas and carbamates in the presence of ionogels loaded with $Rh(PPh_3)_3Cl$ and $Pd(PPh_3)_2Cl_2$.[23,24] Reactions were carried out *without additional solvent* in an autoclave at 135–180 °C under 5 MPa CO pressure. These promising results prompted us to evaluate the efficiency of this method of catalyst encapsulation *when operating in the presence of an organic solvent*, in the synthesis of *metal-free* organic compounds, especially in Heck–Mizoroki coupling reactions.

Actually, the palladium-catalyzed Heck–Mizoroki reaction is one of the most powerful tools for the coupling of olefins with aryl and vinyl halides. Usually it is performed in polar solvents (typically dimethylformamide and acetonitrile), in the presence of phosphine ligands, which are required to stabilize the palladium catalyst species, especially with less reactive bromide and chloride substrates. It has been shown that the reaction could be performed in room-temperature ionic liquids,[25–29] even without additive phosphine ligands.[25,30] The mechanism by which the phosphine stabilizes the

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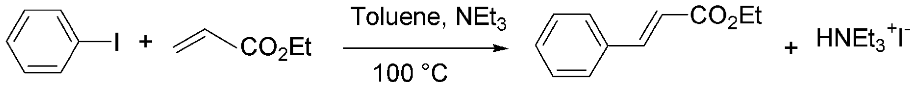


Scheme 1 Heck coupling of 4-iodobenzene and ethyl acrylate.

palladium is not completely clear to date.[31–34] However, the effect of the ionic liquid solvent on the activity of palladium catalysts has been reported.[28,35,36] For instance higher conversion and better selectivity to the *trans* isomer were found in 1-butyl-3-methylimidazolium bromide ([BMI][Br]) than in the analogous tetrafluoroborate salt ([BMI][BF_4]).[37]

In the first part, we tested the ability of $Pd(OAc)_2$ encapsulated in ionogels to act as a catalyst without leaching out into the bulk solution. The coupling of ethyl acrylate with iodobenzene was chosen as a model reaction (Scheme 1), as this typical arylation reaction has been widely studied in bulk ionic liquids[25,29,38] and supported ionic liquid systems as well.[15,39] In the second part, we applied the catalyst ionogels to the coupling of 4-vinyl pyridine with 4-iodo-*N*,*N*-dibutylaniline (Scheme 2). The coupling product is of interest as a labeling molecule in biology and it is important to be able to synthesize it without any metal traces.[40]

Experimental

Instrumentation

The Heck couplings of 4-vinyl pyridine were performed in parallel with a 24-tube semi-automated synthesis robot (Syncore from Büchi). Gas chromatography analyses were performed on a HP 6890 series gas chromatograph using a SE30 column, dihexyl ether as internal reference. NMR spectra were recorded on a Bruker DPX 300 (^{1}H 300 MHz) spectrometer at room temperature. ^{1}H chemical shifts (δ) are given in ppm and are referenced to residual solvent peaks ($CDCl_3$: δ 7.26 ppm ^{1}H; δ 77.0 ppm ^{13}C). Coupling constants (J) are reported in Hz. The elemental analysis of palladium was determined by ICP-MS and carried out by the Centre of Chemical Analyses of the Centre National de la Recherche Scientifique (Vernaison, France).

Chemicals

The following chemicals were purchased and used as received: iodobenzene 98%, tetramethoxysilane 98% and methyltrimethoxysilane 97% from Alfa Aesar; 1-bromobutane, $Pd(OAc)_2$ and formic acid 99% from Acros Organics; ethyl acrylate from Merck; PPh_3 99% from Lancaster. Toluene was distilled over sodium before use; triethylamine, dichloromethane and 1-methylimidazole 99% were distilled over CaH_2; 4-vinylpyridine was distilled before use.

1-Butyl-3-methylimidazolium bromide, referred to as [BMI][Br], was prepared according to the literature.[41] 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonylimide), [BMI][TFSI], and 1-butyl-3-methylimidazolium hexafluorophosphate, [BMI][PF_6], were synthesized by metathesis reaction using lithium bis(trifluoromethylsulfonylimide) and potassium hexafluorophosphate, respectively.[42]

After the metathesis reaction, the ionic liquids were washed several times with aliquots of water until no more halogen residues could be detected by the $AgNO_3$ test. The 4-iodo-*N*,*N*-dibutylaniline was synthesized according to the literature.[40]

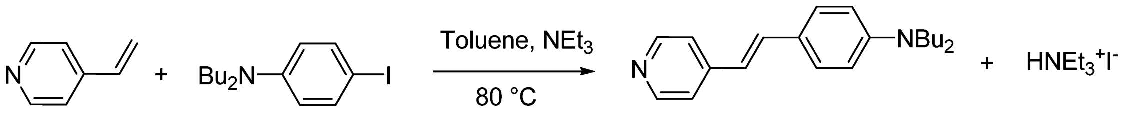
Synthesis

Synthesis of catalyst ionogels for the coupling reaction of ethyl acrylate with iodobenzene

Ionogel without phosphine. For the reaction without phosphine, a stock dichloromethane solution was prepared by dissolving $Pd(OAc)_2$ (22.4 mg; 0.1 mmol) into 2 ml of CH_2Cl_2. 0.2 mL of this solution was added to a mixture of [BMI][Br] (0.74 g, 0.5 eq.) and formic acid (2 mL, 2 eq.); the resulting solution was stirred at room temperature for 10 min. Finally, tetramethoxysilane (TMOS) (1 mL, 1 eq.) was added and the mixture was stirred for another 10 min. A yellow ionogel pellet (Fig. 1) was obtained after 1 h and was aged until no more volatiles evolved (constant weight was observed after about two weeks). The final concentration of Pd in ionic liquid was 1×10^{-2} mol L^{-1}.

Ionogel with phosphine. In this case the stock solution was obtained by dissolving $Pd(OAc)_2$ (11.2 mg, 0.5×10^{-4} mol) and triphenylphosphine (26.3 mg, 1×10^{-4} mol) into 10 mL of dichloromethane. 0.2 mL of this solution was added to the mixture of [BMI][Br] and formic acid as described above. The final concentration of palladium in ionic liquid was 1×10^{-3} mol L^{-1}.

Synthesis of catalyst ionogels for the coupling reaction of 4-vinyl pyridine with 4-iodo-*N*,*N*-dibutylaniline. The palladium(II) complex was prepared by mixing $Pd(OAc)_2$ (1 eq.) and PPh_3 (2 eq.) in dichloromethane (concentration in Pd(II) 1.2×10^{-2} mol L^{-1}) and stirring at room temperature for 2 h. 250 μL of tetramethoxysilane (TMOS) and 250 μL of methyltrimethoxysilane (MTMOS) were mixed with 0.37 g of [BMI][Br] and 1 mL of formic acid. After few minutes, the ionic liquid was totally dissolved. 150 μL of the palladium complex solution in CH_2Cl_2 were added so that the palladium concentration in the ionic liquid was 3.6×10^{-3} mol L^{-1}. (Additional experiments indicated that, if the concentration of Pd(II) per litre was higher than 3.6×10^{-3} mol L^{-1} in the ionic liquid, the resulting ionogels were not transparent and the results were not reproducible). After a short stirring to obtain



Scheme 2 Heck coupling of 4-vinylpyridine and 4-iodo-*N*,*N*-dibutylaniline.

Fig. 1 Pd-doped ionogel pellet.

an orange homogeneous mixture the solution can be cast in one pellet or distributed into 4 Eppendorf tubes to generate several duplicates of ionogels showing the same shape, the same active surface and the same amount of Pd(II).

This step must be done before the gelation which occurred within 2 h. After aging for two weeks at room temperature the ionogels were obtained as orange transparent pellets or small cones (each containing 4.5×10^{-7} mol of Pd) (Fig. 2).

Coupling reaction of ethyl acrylate with iodobenzene. The ionogel encapsulating the Pd catalyst was put in the glass "basket" of the reactor. Toluene (17 mL), iodobenzene (0.1 mL, 0.90 mmol), ethyl acrylate (0.2 mL, 1.8 mmol) and triethylamine (0.2 mL, 1.4 mmol) were added under nitrogen atmosphere. The palladium loading for the phosphine free reaction was 1.1% and in the case of the phosphine reaction, 0.1%. The solution was stirred at 100 °C and the reaction was monitored by GC (dihexyl ether as internal reference). When the reaction was complete, the reactor was left to cool to room temperature. Excess toluene and triethylamine were evaporated affording ethyl cinnamate.

Coupling reaction of 4-vinyl pyridine with 4-iodo-*N*,*N*-dibutylaniline. 150 μl of $Pd(OAc)_2$–PPh_3 solution in CH_2Cl_2 ($1.2\ 10^{-2}$ mol L^{-1}) were introduced, after 2 h of mixing, into two tubes A and B. After evaporation of CH_2Cl_2 the tubes A and B contained 1.8×10^{-6} mol of Pd. 0.37 g of ionic liquid [BMI][Br] were added to the tube B. 4 small ionocats were added into a third tube C (entry 3) in order to have the same amount of Pd in tubes A, B and C. 1.8 ml of toluene–NEt_3 (4/1, v/v) containing 1.8×10^{-4} mol of 4-vinylpyridine and 4-iodo-*N*,*N*-dibutylaniline were added under nitrogen atmosphere into tubes A, B and C and stirred with an orbital shaker at 80 °C for 72 h.

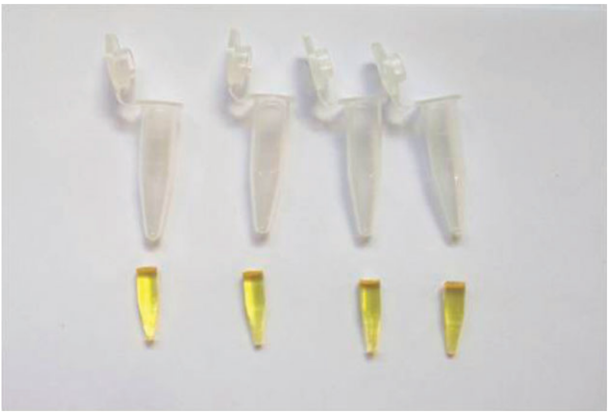


Fig. 2 Pd-doped cone ionocats.

After cooling to room temperature, the solution in tube B was separated from the ionic liquid by means of a liquid–liquid extraction. The ionogel was filtrated and washed with toluene. In all cases, the solvent was removed under reduced pressure affording the target compound. The conversion and selectivity *E*/*Z* of crude product were determined by ^{1}H-NMR.

^{1}H-NMR ($CDCl_3$) *E* isomer: δ 8.54 (2H, d, J = 6 Hz), 7.38 (2H, d, J = 9 Hz), 7.26 (2H, d, J = 6 Hz), 7.15 (1H, d, J = 16 Hz), 6.73 (1H, d, J = 16 Hz), 6.62 (2H, d, J = 9 Hz), 3.32 (4H, q, J = 7 Hz), 1.57 (4H, m), 1.37 (4H, m), 0.97 (6H, t, J = 7 Hz).

^{13}C-NMR ($CDCl_3$) *E* isomer: δ 149.65 (2 CH Ar), 128.98 (1 CH=), 128.56 (2 CH Ar), 120.34 (2 CH Ar, 1 CH=), 111.11 (2 CH Ar), 50.75 (2 CH_2), 29.48 (2 CH_2), 20.35 (2 CH_2), 14.02 (2 CH_3).

^{1}H-NMR ($CDCl_3$) *Z* isomer: δ 8.44 (2H, d, J = 6 Hz), 7.22 (2H, d, J = 6 Hz), 7.09 (2H, d, J = 9 Hz), 6.59 (1H, d, J = 12 Hz), 6.20 (1H, d, J = 12 Hz), 6.47 (2H, d, J = 9Hz), 3.26 (4H, q, J = 7 Hz), 1.57 (4H, m), 1.37 (4H, m), 0.96 (6H, t, J = 7 Hz).

^{13}C-NMR ($CDCl_3$) *Z* isomer: δ 149.73 (2 CH Ar), 134.02 (1 CH=), 130.33 (2 CH Ar), 123.51 (2 CH Ar), 122.98 (1 CH=), 110.96 (2 CH Ar), 50.68 (2 CH_2), 29.44 (2 CH_2), 20.35 (2 CH_2), 14.02 (2 CH_3).

Results and discussion

Choice of the ionic liquid

Preliminary tests were carried out to check the solubility and stability of $Pd(OAc)_2$ in different imidazolium salts: [BMI][Br], [BMI][PF_6] and [BMI][TFSI]. Clear yellow solutions were obtained in the cases of [BMI][PF_6] and [BMI][TFSI]; nevertheless these solutions turned into black colloids within a few hours under ambient conditions. This phenomenon was even worse in the presence of formic acid (Fig. 3). However, the behavior of [BMI][Br] was different, affording a yellow solution when mixed with $Pd(OAc)_2$ in diluted form, or red solution when concentrated, and remaining stable over weeks even in the presence of formic acid (Fig. 3). The formation of

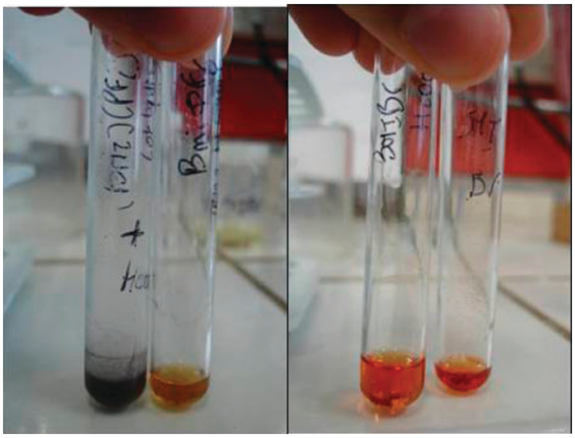


Fig. 3 $Pd(OAc)_2$ in [BMI][PF_6] (left) before and after addition of HCOOH; $Pd(OAc)_2$ in [BMI][Br] (right) before and after addition of HCOOH.

carbene ligand, which would be able to stabilize palladium species,[37] was first assumed, but no carbene was detected at room temperature by ^{1}H NMR. The red color is more likely to be related to the formation of $[PdBr_4]^{2-}$ species.[43]

Accordingly, the ionogels, the synthesis of which spreads over weeks, were prepared from 1-butyl-3-methylimidazolium bromide. The ionogels were synthesized using a sol–gel route first described by Sharp[44] and already applied to the synthesis of monolith ionogels.[13] Typically, silica precursors (1 eq.) and formic acid (7.8 eq.) were dissolved in [BMI][Br] (0.5 eq.) and stirred at room temperature. After gelation, the gels were left for aging until a constant weight (no more volatiles evolved) was obtained affording yellow homogeneous pellets or cones (Fig. 1 and 2).

Model reaction: coupling reaction of ethyl acrylate with iodobenzene

The activity of catalyst ionogels was first evaluated in the coupling reaction of ethyl acrylate with iodobenzene (Scheme 1) using a glass "basket" reactor (Fig. 4), so that the Pd-doped ionogel soaked in toluene solvent (17 mL) whereas it was not ground by the stirring magnet (the glass featured small holes allowing free exchange from the solvent to the ionogel).

For comparison, the coupling reaction was also carried out in toluene under classical homogeneous catalysis conditions, in the presence and absence of triphenylphosphine. The loading of palladium was 1.1% in the case of phosphine free systems, but due to solubility restrictions the loading with $Pd(OAc)_2$–PPh_3 was 0.11%. Long reaction times were observed, in relation to the very low substrate concentrations used. The progress of coupling reactions under homogeneous conditions and that of reactions in the presence of catalyst ionogels are compared in Fig. 5. A marked initiation period is visible in ionogel systems in the absence of phosphine, whereas in the presence of triphenylphosphine the initial rate is higher than under homogeneous conditions. Comparing the two ionogel systems, the reaction rate was higher in the presence of phosphine even though the catalyst concentration was 10 times lower. Note that an increase in maximal conversion was noticeable in ionogel systems, particularly in the presence of phosphine. At the end of the reaction, the ionogel which was fragmented, black and embedded in the salt products was removed with the basket. No leaching of the ionic liquid to the solvent mixture was observed based on the ^{1}H NMR spectrum of the filtrate after evaporation of volatiles.

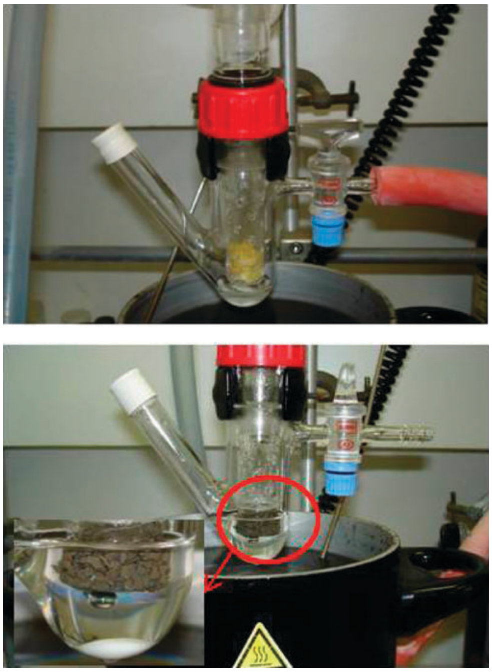


Fig. 4 Basket reactor before (top) and after reaction (bottom).

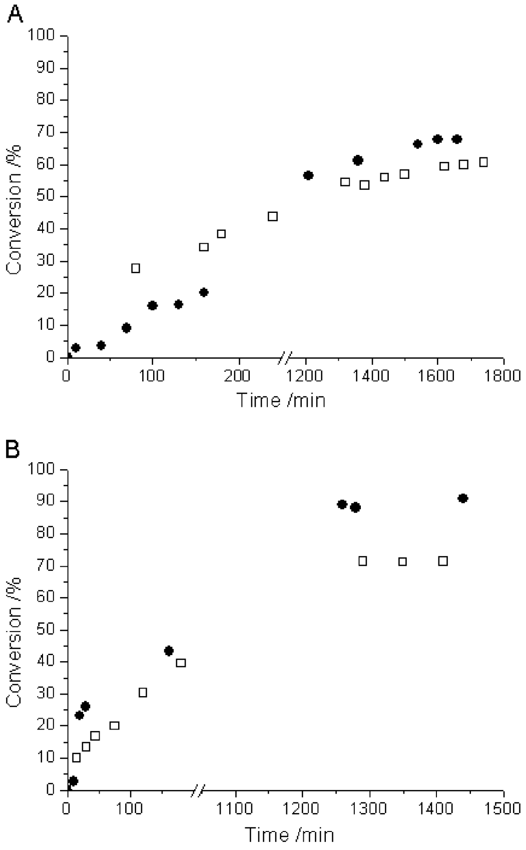


Fig. 5 Heck reaction of 4-iodobenzene and ethyl acrylate as a function of time (A) without phosphine (B) with phosphine; ● ionogel, □ homogeneous.

A key point for heterogeneous catalysis is the leaching of metal species. Here the absence of palladium leaching was checked by the "hot filtration technique".[45] The hot reaction mixture was filtered off from the reactor at a low conversion ratio while the temperature was held at 100 °C. As displayed in Fig. 6, the coupling reaction stopped at this moment, thus evidencing that the palladium catalyst species were kept encapsulated within the ionogel while the reaction ran. This supported the catalyzed reaction actually taking place in the ionic liquid phase confined in the silica network. This point was confirmed by trace analysis of Pd measured by ICP-MS: $0.9 \leq x \leq 1$ ppm (≤ 0.4 wt%) was detected in the filtrate. Note that ionogel pellets underwent significant fragmentation during the reaction course (Fig. 4), which could be related to

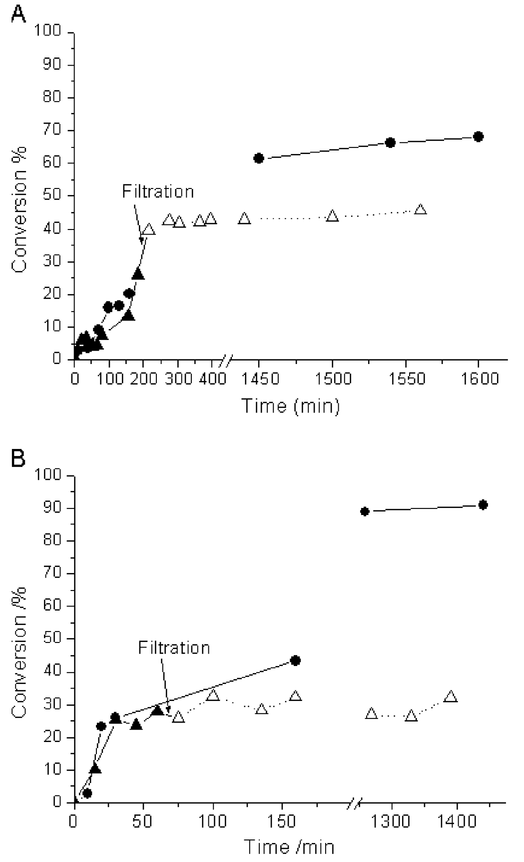


Fig. 6 Hot filtration analysis using ionogels (A) without phosphine (B) with phosphine; ● continuous reaction, ▲ reaction before hot filtration, Δ reaction after hot filtration.

the action of triethylamine base on the silica network or/and the extensive formation of triethylammonium bromide within the mesopores.

Coupling of 4-iodo-*N*,*N*-dibutylaniline and 4-vinyl pyridine

The preparation of ionogels was slightly modified by using a 50 : 50 TMOS–MTMOS mixture as starting silicon alkoxides. The idea was to decrease the hydrophilicity of pore walls, which could favor the diffusion of organic reactants. The absence of leaching in toluene was checked again, using a somewhat different protocol. Toluene was added to the Pd(II)–PPh_3 containing ionogel. After heating for 2 hours at 80 °C, the solution was removed and engaged in the Heck coupling reaction under the usual conditions; once again no catalysis was detected. On the other hand, the ionogel pellet heated for 2 h at 80 °C in toluene was shown to be still able to induce the catalytic coupling reaction.

The catalytic properties of the Pd(II) catalyst-containing ionogel for the coupling of *p*-vinylpyridine and 4-iodo-*N*,*N*-dibutylaniline were checked in toluene–NEt_3 (4/1 v/v) at 80 °C for 72 h. An orbital shaker (Syncore system from Buchi) was used, rather than a classical magnetic stirrer, to prevent grinding the pellet to dust. Drawing advantage from the opportunity to easily generate duplicates of catalysts from the same mother solution by dispatching the sol–gel solution into small tubes before gelation, a series of cone ionogels, hereafter referred to as *ionocats*, were prepared (Fig. 2), each containing 4.5×10^{-7} mol of Pd and 0.092 g of [BMI][Br]. Three parallel experiments were performed (Table 1) to compare the homogeneous catalyst, the homogeneous catalyst in the presence of ionic liquid and the ionocats. The palladium–substrate ratio was kept constant at 1% and the dilution was the same. After 72 hours, similar conversions were obtained as shown in Table 1. However, a second use of ionogel catalysts was found to result in a considerable lowering of the yield ($<5\%$). Moreover an important fragmentation of the pellets was observed, as in the ethyl cinnamate synthesis.

Discussion

Similar reaction rates were found under classical homogeneous conditions and in the presence of Pd catalyst encapsulated in ionogels, without apparent limitations related to the diffusion of reactants and products between the internal ionic liquid and the external solvent, whereas leaching tests showed that catalysis actually took place in the ionic liquid phase confined within the silica matrix. It is a major advantage to implement coupling reactions without any contamination of products with metal traces, for such application as drugs and molecular probes in life science.

Another feature was that the triethylammonium salt by-product was not dispatched in the toluene phase, but was kept in the ionic liquid. The extensive formation of salt in the course of the reaction resulted in dramatic fragmentation and embedding of catalyst ionogels. The question arises, to what extent the continuous *in situ* formation of triethylammonium iodide modifies the nature of the ionic liquid medium and accordingly the course of the reaction. Unfortunately washing the catalyst ionogels for reusing is not possible since [BMI][Br] is water soluble. However, this efficient salt trapping by ionogels represents a practical advantage. Usually, homogeneous Heck–Mizoroki coupling reaction involves a purification step to separate metal residues, salts and target products. This purification step, generally column chromatography or liquid–liquid extraction with water, is time-consuming and needs significant amounts of solvent. Using catalyst ionogels, simply decanting could be enough to eliminate both metal and salt residues when coupling reactions are quantitative. Alternatively a *tea-bag-like* reaction could be carried out, using a basket, as in the coupling of ethyl acrylate with iodobenzene.

The last interest for the encapsulation of Pd catalyst into ionogels is the opportunity to generate duplicates of catalysts from the same mother solution by dispatching the sol–gel solution into small tubes before gelation. One can easily use one, two or more of these ionocats containing the same amount of Pd catalyst, depending on the amount required for the reaction.

As supported ionic liquid films (SILF), ionocats involve low amounts of ionic liquids and combine the advantages of homogeneous catalysis and of heterogeneous catalysis. However, the processing of metal catalyzed reactions is quite different in ionogels and SILF. In the latter, reactants diffuse through the residual voids in pores, the walls of which are only

Table 1 Conversion and selectivity %

Entry	Conditions[a]	Conversion[b] (%)	Selectivity[b] E/Z (%)
1	Toluene–NEt_3–$Pd(OAc)_2$–$2PPh_3$	25	95/5
2	Toluene–NEt_3–[BMI][Br]–$Pd(OAc)_2$–$2PPh_3$	20	97/3
3	Toluene–NEt_3–ionocats	20	98/2

[a] Ratio of palladium to substrate: 1%. [b] Measured by ^1H NMR.

coated with the liquid catalyst film. On the other hand, in ionogels, reactants diffuse in the 3D continuous liquid phase which fills all the pores. Similarly products diffuse back out of the material according to the two different routes. Thus, diffusion should be by far easier in SILF. However, in the liquid phase SILF are subjected to the risk of extensive leaching, in relation to the minute amount of ionic liquid on the support. Even in the case of complete immiscibility in the feedstock–product mixture, the ionic liquid film may be mechanically removed from the support by the liquid flow. As a consequence, SILF look like the most convenient process for continuous gas-phase reactions, whereas it is demonstrated here that ionogels offer an interesting alternative for liquid-phase reactions.

Conclusion

In conclusion, Pd containing ionogels prepared by the incorporation of a Pd complex into the ionic liquid solution before gelation were shown to be active in the Heck–Mizoroki coupling reaction. These ionogels could be cast as small cones containing identical Pd contents, thus providing convenient ready-to-use catalyst doses for organic synthesis. No significant difference was noticeable by comparison with corresponding homogeneous catalysis. No leaching of catalytic species took place during the reaction. Moreover, ammonium salts were shown to be trapped in the ionogels. This provides an efficient method for isolating the products, free of metal and salt residues, and offers some advantages over SILF when operating in the presence of an organic solvent.

Acknowledgements

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