



## Pd catalysts immobilized onto gel-supported ionic liquid-like phases (g-SILLPs): A remarkable effect of the nature of the support

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### ABSTRACT

New polymeric materials containing functional sites analogous to ionic liquids have been synthesized. Those materials are a supported reservoir for the active Pd species. Their catalytic activity has been evaluated for the Heck reaction proving an excellent performance in terms of both activity and recyclability. Although soluble Pd species seem to participate in the catalytic cycle, as for many other supported Pd-systems, the g-SILLPs present the ability to efficiently release and recapture those soluble species. This allows to dramatically reduce or eliminate the amount of Pd leached to the final solution, in particular at higher temperatures, and opens the way, based on a *release and catch* strategy, for the development of active-supported Pd catalytic systems, easily recoverable and reusable for a large number of catalytic cycles. The exact nature of the polymer (SILLPs) has a remarkable influence on the overall process. The appropriate design of the g-SILLPs is a key factor for the optimization of the *release and catch* system. The functionalized polymers prepared can be reused for a significant number of catalytic cycles without any loss in performance.

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### 1. Introduction

The palladium-catalyzed C–C forming reactions are of great interest in synthetic organic chemistry, and the Heck coupling of aryl halides with terminal olefins is one of the most important reactions [1]. Different strategies have been evaluated to develop efficient catalytic systems for this reaction: (i) development of highly active homogeneous catalyst at parts per million concentrations based on palladium complexes [2], “ligand-free” Pd catalyst [3] or stabilized Pd clusters [4]. (ii) immobilization of palladium onto the adequate support [5].

A current challenge in this area is the development of efficient immobilized systems that could simultaneously fulfill the usual targets of achieving high TON values and facilitate recovering and reuse as well as the need for obtaining Pd-free final products [6,7], meeting the strict purity specifications for the pharmaceutical industry [8].

In this regard, different types of heterogeneous precatalysts have been prepared with the goal of achieving catalyst recovery and recycling [5,8a,9]. However, despite the numerous reports claiming palladium heterogeneous catalysis for Heck reactions,

there are only a few examples for which this has been demonstrated [10]. In most cases, experiments to distinguish homogeneous from heterogeneous catalytic species reveal that leached, soluble palladium species are the true catalytic species and not the supported particles [11,12].

The current paradigm for the development of polymer-supported catalysts establishes that the support must be both electronically and sterically “inert” towards the reaction and/or the catalyst [13]. However, designing the support to play an active role in the catalytic reaction, as the environment in which processes take place, might lead to improvements in the catalytic performance or even to change the course of the catalytic reaction [14].

The modification of the functional support with the introduction, besides the catalytic center, of appropriate modifiers, can produce different positive effects: (1) assisting to the activation of the catalyst, (2) generating novel catalytic species, (3) improving the stability of the catalyst, (4) optimizing immobilization and recyclability, (5) facilitating product isolation, and (6) influencing the selectivity of the reaction. Thus, one important concept to be explored is to promote reactions in restricted spaces on functional or multifunctional polymers [15], where the support is able to stabilize catalytic species, to define the mass transport of substrates and products in and out of the catalytic site, to immobilize reactants, and to play an active role in overall the reaction mechanism, leading to more efficient catalytic processes. Additionally,

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the supported catalysts will present the general advantages of the solid materials, as are the easy separation and recyclability as well as their potential use for the development of continuous processes [16].

In this context, we and others have recently synthesized and characterized a series of *supported ionic liquid-like phases* (SILLPs) by covalent anchoring of functional moieties with IL-like structure onto polystyrene-divinyl benzene (PS-DVB) solid supports [17–19]. The use of ionic liquid-like functionalities as modifiers in supported systems is highly interesting, since, ideally, they will tune the nature of the material, transferring the ILs properties at molecular and nanoscale level [20]. This approach allows obtaining tailored structured materials able to present most characteristics and properties of ILs as molecular solvents, playing an active role in the immobilization and stabilization of different catalytic moieties [17–20].

Here we report on the detailed study of a catalytic system, in which palladium is immobilized onto *gel-supported ionic liquid-like phases* (*g*-SILLPs) based on gel-type PS-DVB resins. The catalytic behavior of the corresponding supported Pd species has been investigated for the Heck coupling reaction. Palladium is initially supported onto the *g*-SILLPs as Pd–NHC complexes [21]. The micro-environment of the palladium complexes allows a controlled release, under the reaction conditions employed, of the active species to the homogeneous phase. Besides, the presence of additional IL-like moieties contributes to stabilize and recapture the palladium species released to the solution, being the catalyst easily recoverable, reusable and with essentially no Pd leaching at the end of the reaction under the appropriate conditions [22,23].

## 2. Materials and methods

### 2.1. General procedure for the synthesis of *g*-SILLPs

Merrifield resin (5 g, 2% crosslinking, 4.3 mmol/g, 21.5 mmol) was introduced in a round-bottomed flask and suspended in 20 mL of 1-methylimidazole (243.5 mmol). The suspension was heated at 80 °C for 3 h. Afterwards, the suspension was filtered and the polymer was washed with MeOH, MeOH:CH<sub>2</sub>Cl<sub>2</sub> (1:1), and CH<sub>2</sub>Cl<sub>2</sub> and dried in a vacuum oven.

### 2.2. General procedure for anion metathesis (BF<sub>4</sub><sup>-</sup>, SbF<sub>6</sub><sup>-</sup> and NTf<sub>2</sub><sup>-</sup>)

The polymer was suspended in MeOH, 30 equivalents of the corresponding salt was dissolved in miliQ<sup>®</sup> water and added to the suspension. The system was stirred for 24 h at r.t. Afterwards, the polymer was filtered and washed (3 × 20 mL) with MeOH, MeOH:water (1:1), MeOH, and CH<sub>2</sub>Cl<sub>2</sub>. Finally the polymer was vacuum dried.

### 2.3. General procedure for anion metathesis of (TfO<sup>-</sup>)

The polymer was suspended in CH<sub>2</sub>Cl<sub>2</sub>. Afterwards, three equivalents of HOTf was added and the suspension was stirred for 24 h at r.t. The polymer was then filtered and washed (3 × 20 mL) with MeOH, MeOH:water (1:1), MeOH, and CH<sub>2</sub>Cl<sub>2</sub>. Finally the polymer was vacuum dried.

### 2.4. Synthesis of Pd-supported species (low loading: 5a–e)

The corresponding low loading *g*-SILLP (0.5 g, 0.46 mmol) was introduced in a round-bottomed flask containing 30 mL of dry THF under an inert atmosphere. Then, 2 equivalents of potassium *tert*-butoxide was introduced. After 10 min of stirring at r.t., 1 equivalent of Pd(OAc)<sub>2</sub> was added and the system was heated for

3 h at 50 °C. Afterwards, the polymer was filtered and washed with THF, MeOH, and CH<sub>2</sub>Cl<sub>2</sub>. Finally, the polymer was dried under vacuum.

### 2.5. Synthesis of Pd-supported species (high loading: 6a–e)

The corresponding high loading *g*-SILLP (0.5 g, 1.53 mmol) was introduced in a round-bottomed flask containing 30 mL of dry THF under an inert atmosphere. Then, 0.6 equivalents of potassium *tert*-butoxide was introduced. After 10 min of stirring at r.t., 0.3 equivalents of Pd(OAc)<sub>2</sub> was added and the system was heated for 3 h at 50 °C. Afterwards, the polymer was filtered and washed with THF, MeOH, and CH<sub>2</sub>Cl<sub>2</sub>. Finally, the polymer was dried under vacuum.

### 2.6. General procedure for the heterogeneous Heck reaction

The polymer-supported catalyst (0.02 mol% respect to the aryl halide) was introduced in a round-bottomed flask, containing a magnetic stirrer and used as a standard batch reactor, previously washed with nitric acid and miliQ<sup>®</sup> water and vacuum dried, and suspended in 5 mL of DMF. Afterwards, 5 mmol of aryl halide, 7.5 mmol of alkene, 3 mmol of mesitylene (internal standard), and 10 mmol of Et<sub>3</sub>N were added. Then the flask was introduced in a thermostated oil bath. The reaction was followed by HPLC, taking 5 μL aliquots from the reaction and diluting them with 1 mL of CH<sub>3</sub>CN. After completion of the reaction, the mixture was filtered to recover the catalyst. The polymer was washed with MeOH and CH<sub>2</sub>Cl<sub>2</sub>, vacuum dried and stored for a new run.

## 3. Results and discussion

The *g*-SILLPs, 3a and 4a were synthesized through modification of commercially available Merrifield resins by covalent attachment of IL-like units (Scheme 1). The resins were allowed to react with methyl imidazole, used as solvent and reagent, at 80 °C, to give the corresponding supported methyl imidazolium salts in quantitative yields [17–19]. Two gel-type resins with different chlorine loadings (1.1 and 4.3 meq of Cl/g) were selected in order to obtain different ratios of Pd/IL-like moieties. The reaction progress was followed by Raman spectroscopy and polymers 3a and 3b were characterized by the NBP test [24,25]. The combined use of both techniques allowed us to observe that the reaction time required to achieve a quantitative conversion of the CH<sub>2</sub>–Cl groups is much shorter than previously reported for related systems (30 min vs. 12–78 h) [26]. From 3a and 4a, *g*-SILLPs 3b–e and 4b–e, having different counteranions, were prepared by the metathesis reaction of the chloride anion using the corresponding salts or acid reactants (NaBF<sub>4</sub>, CF<sub>3</sub>SO<sub>3</sub>H, NaSbF<sub>6</sub>, and LiNTf<sub>2</sub>, respectively). The anion exchange was followed by FT-IR and Raman spectroscopy. The elemental analyses for the different *g*-SILLPs allowed calculating the loadings shown in Table 1. Those were in good agreement with a quantitative conversion both for the transformation of the CH<sub>2</sub>Cl groups and for anion exchange. Polymers 4a–e were also analyzed by XPS showing the characteristic peaks corresponding to the ionic liquid structure. The binding energies obtained were similar to those of their homogeneous counterparts. This indicates that the supported phases show similar properties than the related ILs.

According to this, two different families of *g*-SILLPs were obtained. The first family (3a–e) displayed a low loading of IL-like moieties (from 22% to 34% by weight), while the second family (4a–e) displayed a high loading of IL-like moieties (from 66% to 85% by weight). The presence of a high loading of imidazolium subunits on the polymer can play two different roles. On the one hand, it can favor the formation of pseudo pincer structures with 2:1

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