



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

M. Isabel Burguete^a, Eduardo García-Verdugo^{b,*}, Ignacio Garcia-Villar^c, Fabien Gelat^a, Peter Licence^c, Santiago V. Luis^{a,*}, Victor Sans^a

^a Department of Inorganic and Organic Chemistry, University Jaume I, Avda. Sos Baynat s/n, Castellón E-12071, Spain

^b Instituto de Catálisis y Petroleoquímica, CSIC, Campus de la UAM, C/Marie Curie, 2, Cantoblanco, Madrid E-28049, Spain

^c School of Chemistry/SChEME, University of Nottingham, University Park, Nottingham NG7 2RD, United Kingdom

ARTICLE INFO

Article history:

Received 16 July 2009

Revised 2 November 2009

Accepted 2 November 2009

Available online 4 December 2009

Keywords:

Catalysis

C–C coupling

Functional polymers

Supported catalysts

Pd

Supported ionic liquid

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.

© 2009 Elsevier Inc. All rights reserved.

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,

* Corresponding authors.

E-mail addresses: egverdugo@icp.csic.es (E. García-Verdugo), luis@qio.uji.es (S.V. Luis).

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:CH₂Cl₂ (1:1), and CH₂Cl₂ and dried in a vacuum oven.

2.2. General procedure for anion metathesis (BF₄⁻, SbF₆⁻ and NTf₂⁻)

The polymer was suspended in MeOH, 30 equivalents of the corresponding salt was dissolved in miliQ[®] 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 CH₂Cl₂. Finally the polymer was vacuum dried.

2.3. General procedure for anion metathesis of (TfO⁻)

The polymer was suspended in CH₂Cl₂. 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 CH₂Cl₂. 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)₂ was added and the system was heated for

3 h at 50 °C. Afterwards, the polymer was filtered and washed with THF, MeOH, and CH₂Cl₂. 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)₂ was added and the system was heated for 3 h at 50 °C. Afterwards, the polymer was filtered and washed with THF, MeOH, and CH₂Cl₂. Finally, the polymer was dried under vacuum.

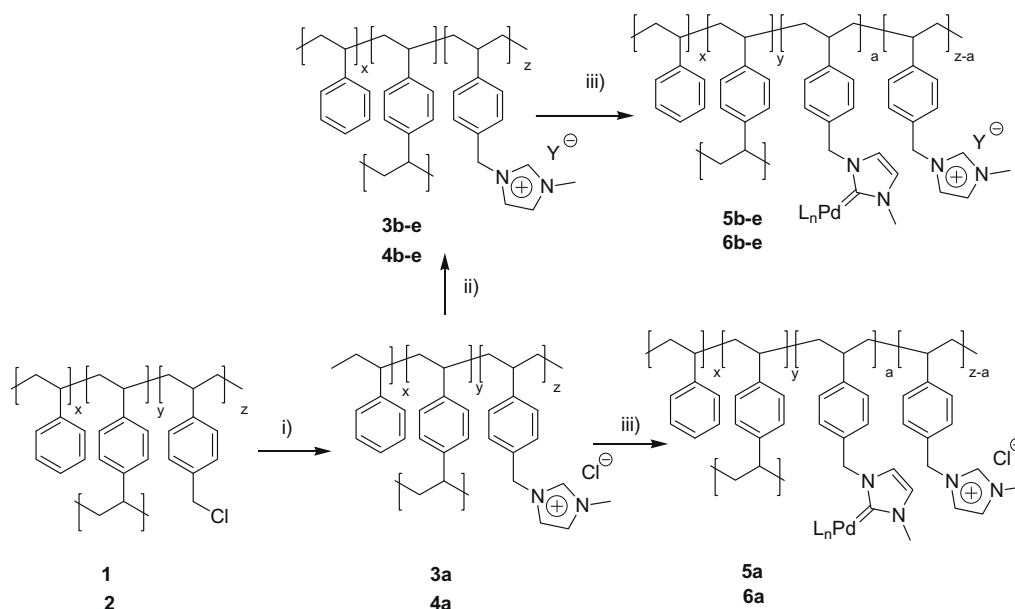
2.6. General procedure for the heterogeneous Heck reaction

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[®] 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 Et₃N 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 CH₃CN. After completion of the reaction, the mixture was filtered to recover the catalyst. The polymer was washed with MeOH and CH₂Cl₂, 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 CH₂–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 (NaBF₄, CF₃SO₃H, NaSbF₆, and LiNTf₂, 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 CH₂Cl 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



Scheme 1. Synthesis of supported Pd–NHC complexes. (i) Merrifield resin, 1-methylimidazole, 90 °C. (ii) Metathesis, ZY or HY, MeOH/H₂O. (iii) Bu^tOK, Pd(OAc)₂, 50 °C, 3 h.

Table 1
Functionalization of the g-SILLPs and the corresponding Pd–g-SILLPs.

Entry	g-SILLPs	X ⁻	Loading (mmol SILLP/g) ^a	Mass % IL ^b	Pd–g-SILLPs	Pd loading (mmol/g) ^c	Mass % Pd
1	3a	Cl	0.93	22	5a	0.17	1.8
2	4a	Cl	3.02	71	6a	0.34	3.6
3	3b	BF ₄	0.89	25	5b	0.16	1.5
4	4b	BF ₄	2.65	69	6b	0.28	3.0
5	3c	TfO	0.84	29	5c	0.20	2.1
6	4c	TfO	2.30	80	6c	0.18	1.9
7	3d	NTf ₂	0.79	38	5d	0.17	1.8
8	4d	NTf ₂	1.62	78	6d	0.27	2.9
9	3e	SbF ₆	0.71	34	5e	0.18	1.9
10	4e	SbF ₆	1.61	85	6e	0.21	2.2

^a Determined by elemental analysis.

^b Calculated as g-SILLP/g-polymer.

^c Determined by ICP-MS

NHC:Pd stoichiometries. On the other hand, the polarity of the surfaces of the polymer, and accordingly the microenvironment of the catalytic sites containing Pd, can be significantly modified [27]. We have recently demonstrated, quantitatively, the *change on polarity* of the microenvironment at the surfaces of g-SILLPs as compared to the standard PS-DVB supports (from $\epsilon < 5$ to $\epsilon \geq 10$ –20) [27]. It is worth mentioning that those values reflect that the functional surfaces on the polymers containing IL-like moieties essentially maintain the same polarity of the bulk room temperature ILs.

The corresponding NHC palladium complexes (**5** and **6**) were prepared by reaction of the different g-SILLPs with Pd(OAc)₂ using Bu^tOK as the base to ensure deprotonation of the C2-H of the imidazolium ring [26,28,29]. The same amount of palladium was used in all the different g-SILLPs. For the g-SILLPs with low loadings (**3a–e**) 1 mol of Pd(OAc)₂ was added per mol of imidazolium subunit. In the case of g-SILLPs **4a–e** this ratio was ca. 2–3 times lower. The Pd loading of complexes was found out by ICP-MS (see Table 1) to be 0.17–0.34 mmol/g (ca. 1.5–3.6% by weight) for all the catalysts prepared (see Table 1). Thus, the imidazolium:Pd ratio for resins **5a–e** is ca. 4–5, being 6–10 for resins **6a–e**. Accordingly, the incorporation of Pd is smaller than expected even for the formation of 2:1 NHC:Pd stoichiometries. In this regard, it must be considered that the formation of those 2:1 stoichiometries should be accompanied by an increase in the actual crosslinking of the

polymeric chains, reducing their mobility and hampering the formation of additional 2:1 complexes [13b].

The FT-IR spectra for resins **5** showed a strong reduction in intensity for the bands characteristic of imidazolium subunits at 1160 and 620 cm⁻¹ (C–H bands of the C2 position of the imidazolium ring) and this can be ascribed to the formation of the Pd–NHC complexes [29]. The Pd–g-SILLPs were also analyzed by XPS (Table 2). Some interesting differences were obtained. The low loading Pd–g-SILLPs (**5**) showed a red-brown color, indicative of the presence of Pd(II) species corresponding to the carbene complexes. This

Table 2
XPS bands observed for the different Pd–g-SILLPs.

Entry	Polymer	Anion ^a	Pd 3d _{5/2} (eV)		Pd 3d _{3/2} (eV)	
			Pd(II) ^b	Pd(0)	Pd(II)	Pd(0)
1	5a	Cl	337.4 (100)	–	343.0	–
2	6a	Cl	338.3 (45)	335.5 (55)	343.5	340.7
3	6b	BF ₄	337.7 (100)	–	343.0	–
4	6c	TfO	337.7 (52)	335.7 (48)	343.0	340.9
5	6d	NTf ₂	338.5 (73)	336.2 (27)	343.7	341.3
6	6e	SbF ₆	338.0 (72)	335.8 (28)	343.4	341.1

^a Charges omitted for clarity.

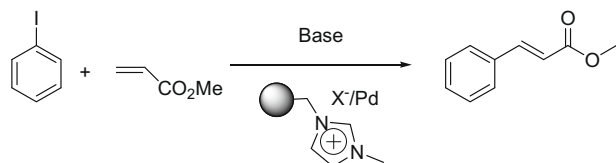
^b Relative percentages are given in parentheses.

was confirmed by XPS (entry 1, similar data found for the other resins **5**), where bands corresponding to Pd(II) were only detected. However, for the high loading polymers both Pd(II) and Pd(0) species were detected. The presence of Pd(0) is not easy to rationalize but can be associated to the affinity to polar solvents of the higher loading *g*-SILLPs. In this way, significant amounts of MeOH used during the synthesis could be adsorbed on the polymer, leading to a partial reduction of the Pd. This is in good agreement with the fact that the more polar *g*-SILLPs ($X = \text{Cl}^-$ and $X = \text{TfO}^-$) showed a higher proportion of Pd(0). In the case of BF_4^- , only Pd(II) was again detected. SEM images for the high loading polymers revealed the formation of black microparticles that were confirmed by EDX microanalysis to be Pd(0) clusters [30].

For a proper evaluation of resins **5** and **6** as catalysts, we selected the Heck reaction between iodobenzene and methylacrylate (Scheme 2) as the benchmark reaction. The reaction and substrates were chosen due to their high reactivity. It has been proposed that at high temperatures the Heck reaction works through a leaching mechanism in which soluble Pd(II) species are the molecular catalysts [3,10]. The mechanism of the Suzuki reaction, however, is controversial. Thus, both mechanisms at the NPs surface [31] and involving homogeneous molecular Pd(II) catalysts [32] have been suggested. Besides, phenyl boronic acids are found to act as a stabilizer of the PdNPs binding strongly to the surface of the NPs during the catalytic process, whereas iodobenzene seems not to have any effect. The selected Heck benchmark reaction is not expected to limit the overall process, allowing to study the efficiency of these materials as the so-called “boomerang catalysts” [33] operating by releasing, stabilizing, and recapturing the active species involved in the catalytic cycle. Our preliminary studies focused on determining the influence of different reaction parameters such as the base, the reaction temperature, and the catalyst loading on the reaction rates.

Initial studies were carried out at 90 °C using DMF or DMF/H₂O mixtures as the solvent and using either NEt₃ or NaOAc as the base. Some of the results achieved are gathered in Fig. 1. For all the cases, the coupling reaction took place with good to excellent yields (from ca. 80% to 99%) after 3 h. Two equivalents of base were required to get a full conversion of PhI into the desired product. When NaOAc was assayed as the base, a DMF/H₂O mixture was used as the solvent to ensure complete dissolution of the base. Under such conditions, a slight decrease of the catalytic activity was observed. Noteworthy, the addition of water to the reaction medium not only led to an incomplete conversion of PhI, but also gave a significant reduction of the reaction rate. In fact, the TOF (at 50% conversion of PhI) for pure DMF (Et₃N as the base) was 3.4 fold higher than that for the DMF/water mixture under the same conditions (50% of yield in 25 min for pure DMF vs. 85 min for the DMF/H₂O mixture). Therefore, the DMF/H₂O mixture seems to be less efficient than DMF as the reaction solvent, but this is not surprising as the nature of the solvent is known to have a dramatic effect on the catalytic activity for this reaction [34].

The influence of the temperature was also studied using Et₃N as the base and DMF as the solvent. Temperatures ranging from 90 to 130 °C (gradient by 10 °C) were investigated. The results obtained for catalyst **6a** are summarized in Fig. 2. As expected, a small in-



Scheme 2. Benchmark Heck reaction.

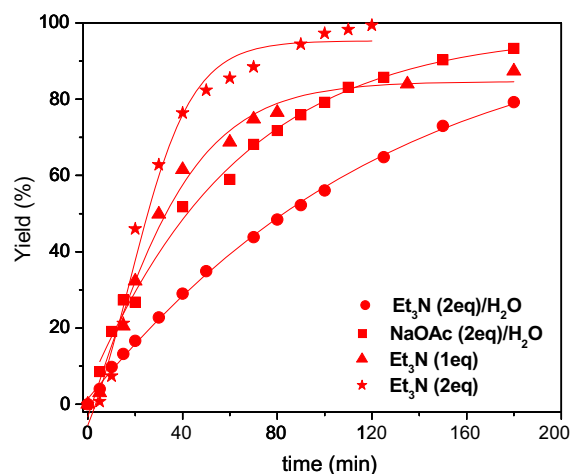


Fig. 1. Plots of yield vs. time for the Heck reaction of methylacrylate (7.5 mmol) and iodobenzene (5 mmol) at 90 °C catalyzed by 0.02% mol of **6a**. (i) Triangles: 5 mL DMF, 1 equivalent of NEt₃. (ii) Stars: 5 mL DMF, 2 equivalents of Et₃N. (iii) Squares: 5 mL DMF/H₂O (1:1), 2 equivalents of NaOAc. (iv) Dots: 5 mL DMF/H₂O (1:1), 2 equivalents of Et₃N.

crease in the temperature led to a significant increase in the catalytic activity. It is important to note that the kinetics of the reaction at the different temperatures studied showed a sigmoidal curve (see Fig. 2), where the induction period was clearly reduced with the increase in the temperature. A 48-fold increase of the TOF at 50% conversion was observed when going from 90 °C (ca. 12 h was required to achieve a 50% yield of the desired product; ca. 194 mol *trans*-methyl cinnamate/mol Pd × h⁻¹) to 130 °C (16 min, TOF ca. 9375). In general, the reaction is slightly slower than the one taking place through the catalysis by Pd(OAc)₂ under similar conditions [17,21a].

The sigmoidal kinetic plots observed in all the cases are consistent with an autocatalytic model for Pd nanoparticles formation, whereby the soluble nanoclusters generated “*in situ*” are actively involved in the catalytic process [12a,35]. Therefore we tried to fit our results to the two-step mechanism model of autocatalysis proposed by Finke [35,36]. This mechanistic model has been demonstrated to determinate the rate of many processes involving initial formation of catalytic metal NPs for which the rates of product formation are much faster than the rates for soluble nanocluster generation. Thus, according to this model, the overall reaction rate is expected to be limited by the formation of those catalytic soluble nanoclusters. The resulting Pd nanoparticles could act catalytically by oxidative addition of PhI on their surface, giving place to the formation of soluble anionic species that initiate the catalytic cycle (Fig. 3) [37]. The first pseudo-elementary step is the reduction of the precatalyst to yield Pd(0) molecular species, whereas the autocatalytic growth of the active soluble Pd species should be the second step (k_2). The experimental kinetic data showed a good fit to this model, providing the pseudo-elementary rate constants k_1 and k_2 [35,36]. The values calculated for these constants at each temperature tested follow Arrhenius’ law. Thus, for resin **6a**, the characteristic parameters for each constant are shown in Table 3. In this model, the induction period is associated to k_1 , i.e. to the build up of a concentration of Pd(0) molecular species high enough to favor the autocatalytic association into nanoclusters or nanoparticles, while the slope of the sigmoidal curve is associated to the growth of the NPs.

In agreement with the former observations, an analysis of the final solution and the polymer, after the reaction was completed at 90 °C, revealed that at least 10% of the Pd originally present on the resin was released to the final solution with either **5e** or **6e**.

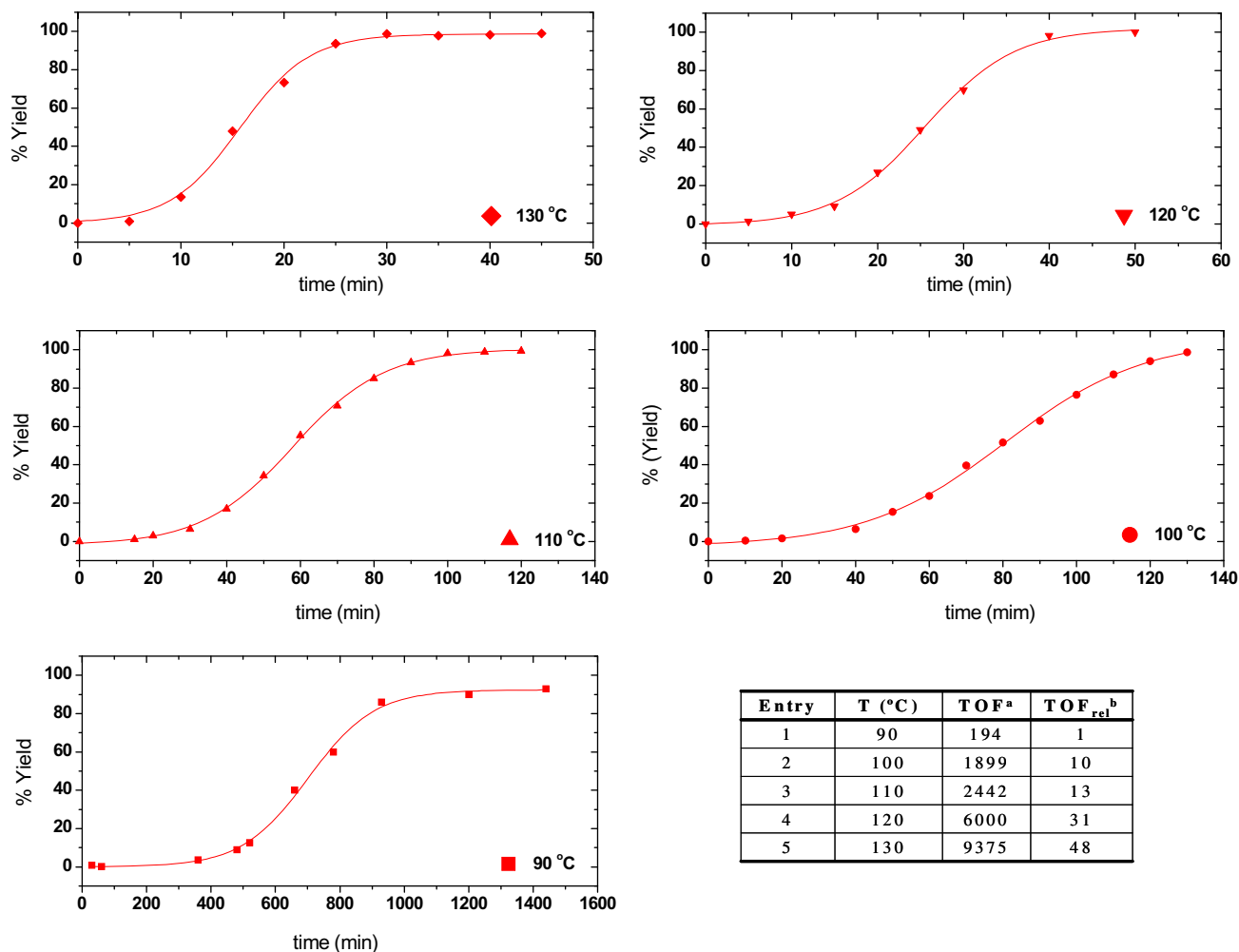


Fig. 2. Plots of yield vs. time for the Heck reaction of methylacrylate (7.5 mmol) and iodobenzene (5 mmol) at different temperatures catalyzed by 0.02% mol of **6a** in 5 mL DMF, in the presence of 2 equivalents of Et₃N. (a) TOF = mol of *trans*-methylcinnamate/mol Pd × h⁻¹ at 50% of conversion. (b) TOF_{rel} = TOF_T/TOF₉₀.

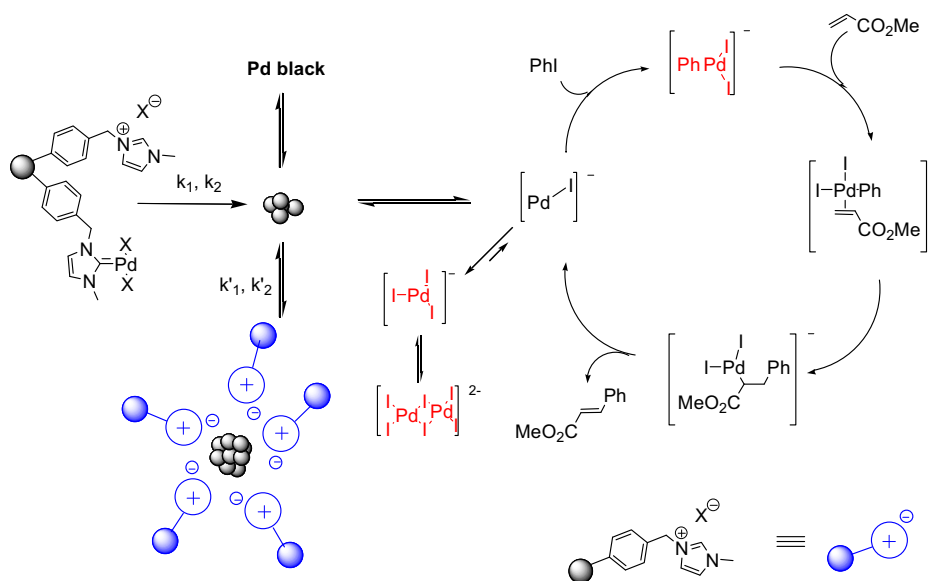


Fig. 3. Proposed reaction mechanism (red compounds correspond to species detected by ESI-MS). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 3

Preexponential factor and activation energy for Pd–g-SILLP 6a calculated for constants k_1 and k_2 at different temperatures accordingly with Arrhenius' law.

Entry	A	E_A (J/mol) $\times 10^{-4}$	R^2
1 ^a	7.97E+05	6.61	0.995
2 ^b	6.00E+18	91.44	0.993

^a Calculated for k_1 (min⁻¹) at 90, 100, 110, 120, and 130 °C.

^b Calculated for k_2 (min⁻¹ M⁻¹) (min⁻¹) at 90, 100, 110, 120, and 130 °C.

Fortunately, when the reaction was carried out at 130 °C with high loading resin **6e**, no leaching was observed. Accordingly, g-SILLPs are capable to scavenge soluble palladium species from solution, and this scavenging seems to be quantitative at 130 °C for the high loading resins. It has been shown that, when homogeneous precatalysts are used, agglomeration to form Pd black particles is favored at the higher temperatures at the end of the reaction. Slow deposition of those particles can decrease the amount of Pd contained in the final solution [38]. Several functional materials have been used to favor the recovering of those Pd black particles (for instance, Quadrapure-TU and polyvinylpyridine), but, in general, the palladium adsorbed on such materials is inactive in further reaction cycles without previous reactivation [10,39]. Thus, for instance, pretreatment with iodine has been described as a methodology for reactivation [40,3a]. On the contrary, initial experiments with our recovered resins from the former experiments revealed that they were still active for consecutive catalytic cycles without the need of any additional pretreatment, as it will be discussed below.

In the light of the former results, we can consider the existence of a “catch and release” mechanism that can be schematically summarized as shown in Fig. 3.

The initial Pd–g-SILLPs prepared (**5** and **6**) act as precatalytic species. Those Pd–NHC complexes give place, under the reaction conditions, to the formation of soluble Pd species, which are responsible for the catalytic activity [10,12]. Soluble Pd species include different molecular species in equilibrium with soluble clusters or NPs, according to the general mechanism observed in solution [43]. The agglomeration of the soluble Pd clusters/NPs would give place to the formation of inactive Pd black particles, but the presence of g-SILLPs provides a different outcome, as those soluble clusters can be recaptured and stabilized to form new supported PdNPs–g-SILLPs. As we have mentioned above, the process of agglomeration increases at high temperatures and, according to our data, those conditions also favor the recapture by the functional polymer, which predominates over the formation of Pd black particles and seems to be also operative during the reaction [22,23]. Those PdNPs–g-SILLP supported species are able to provide again the active soluble species for the next run without the need of any previous activation. Thus, the polymer bearing ionic liquid-like units behaves as the analogous ILs in solution stabilizing the PdNPs against the aggregation [23,41]. In this regard, three main steps seem to be involved in our system: (1) the release to the solution of the active catalytic species from the supported Pd complexes; (2) the catalytic cycle involving different soluble molecular species; and (3) the recapture by the resin of the soluble species in the form of stabilized Pd–g-SILLPs NPs.

The evidences gathered from the observation of leaching and the presence of sigmoidal kinetics support the release mechanism. In order to confirm the nature of the active catalytic species involved, we decided to study in more detail the reaction at 90 °C. At this temperature, higher concentrations of soluble Pd species seem to be formed, and thus their study seems to be more accessible [10,12]. Various hot filtration tests (HFTs) were carried out at this temperature to evaluate the activity of the soluble fraction [42]. Table 4 gathers some results obtained from tests performed

Table 4

Hot filtration test for the Heck reaction in the presence of resins **5e** and **6e** and after hot filtration.^a

Entry	Catalyst	Time (min)	TON ^d
1	5e	20	1936
2	5e	60	4500
3	HFT ^b	60	4800
4	6e	100	1215
5	6e	240	4900
6	HFT ^c	240	3915

^a All reactions were carried out with methylacrylate (7.5 mmol) and iodobenzene (5 mmol) in 5 mL DMF with 2 equivalents of Et₃N at 90 °C. The HFT was performed by filtering off the resin and monitoring the solution under identical reaction conditions.

^b Resin **5e** was filtered after 20 min of reaction.

^c Resin **6e** was filtered after 100 min of reaction.

with a 0.02% molar of the palladium catalyst, using **5e** and **6e** as the catalysts with low and high loadings of ionic liquid-like moieties, respectively. After reaching ca. 20–40% conversion, the resins were filtered off and the transformation of the substrate was again monitored to evaluate the conversion of PhI in the absence of the solid Pd–g-SILLP. In both cases, catalytic activity was detected after the filtration of the solid “catalyst” revealing the presence of catalytic species in the solution. The reaction on the filtrate (filtration after 20 min) using resin **5e** (low loading resin) proceeded at similar or slightly higher rates than the reaction in the presence of the supported system, demonstrating that species in solution are responsible for the catalytic activity. Rather interestingly, in the case of **6e** (high loading resin, filtration after 100 min), the filtrate solution, although active, displayed a lower reaction rate than that of the heterogeneous system, suggesting a contribution of the supported species.

On the other hand, when catalyst **6e** was heated up at 90 °C in pure DMF, in the absence of any other reactants, for 28 h, no leached palladium was observed. However, upon the addition of Et₃N a small degree of leaching to the organic phase (ca. 8% of the palladium used) was found by ICP-MS. In a second experiment, when PhI and Et₃N were added simultaneously the amount of palladium leached increased up to 10–16%. This suggests that the Pd–NHC complex may initially undergo oxidative addition of aryl iodine to form [ArPdI₂]⁻ [12d]. Indeed, ESI-MS studies under the same conditions confirmed the presence of [PhPdI₂]⁻ anionic species in solution. Additionally, other species such as [PdI₃]⁻ and its dimer [Pd₂I₆]²⁻ were also detected. Therefore, the mechanism involves the presence of soluble anionic intermediate palladium species that can operate via a homeopathic catalytic Pd(0)–Pd(II) cycle, in agreement with the one recently proposed by de Vries [3,43].

The observation of catalytic activity in the recovered resins can be used as an indirect evidence of the recapture process. A more direct support, however, was obtained using soluble Pd catalysts/precatalysts. As can be seen in Fig. 4, when using Pd(OAc)₂ as a ligand-free catalyst, under similar conditions to those used with Pd–g-SILLPs, the Heck reaction, takes place slightly faster than the ones observed using **5**, with a quantitative transformation of the substrate in ca. 40 min instead of ca. 60–90 min, being the rate for the supported system highly dependent of the anion. A clear reduction in the rate was observed for the resins with higher ionic liquid-like loading **6**. Thus in the cases of **6a–d** 4–6 h was required to achieve a complete conversion of iodobenzene. On the other hand, a clear reduction in the rate was found when the palladium ligand-free experiment was carried out, under the same conditions, but in the presence of g-SILLPs **4a**. Thus, the TOF at 50% of conversion of PhI is reduced from ca. 5500 to ca. 4400. This indicates the capacity of those resins to remove active Pd species from solution.

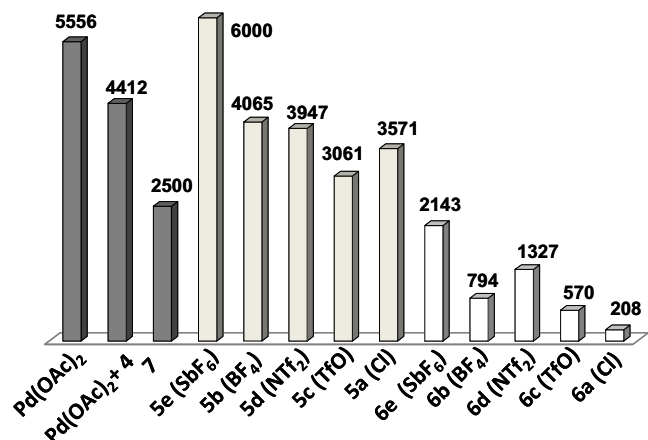


Fig. 4. TOF at 50% conversion vs. catalyst type for the Heck reaction of methylacrylate (7.5 mmol) and iodobenzene (5 mmol) at 90 °C catalyzed by 0.02% mol of Pd(OAc)₂, Pd(OAc)₂ + 100 mg of **4a**, **7** (recovered resin from the former experiment), Pd-g-SILLPs **5a–e** and **6a–e** in 5 mL DMF, with 2 equivalents of Et₃N.

The capacity of those resins to recapture Pd species in the form of active-supported PdNPs–g-SILLPs was further confirmed by carrying out an additional experiment that showed how, after filtering and washing, the resulting resins (**7**) were active for a new run of the Heck reaction. In this case a complete conversion was attained after ca. 2.5 h. Additionally, SEM experiments revealed the presence of Pd(0) NPs on those resins. It is worth mentioning that the PS-DVD polymer by itself is not able to scavenge palladium species from the reaction mixture. When the former experiment was repeated in the presence of PS-DVB, no appreciable effects on the rate of the reaction were detected and the resulting polymer at the end of the reaction did not show any catalytic activity in a new run.

It is interesting to note that although the reaction with a homogeneous source of palladium is faster than when Pd–g-SILLPs are used, the kinetic results obtained compare with great advantage with the results obtained for the Heck reaction using ILs as solvents [44]. This is clearly illustrated by the results summarized in Table 5. It can be seen that a quantitative conversion of iodobenzene can be obtained at 90 °C in DMF, after 1 h, using Pd(OAc)₂ and Et₃N as the base. Under the same conditions, 4.5 h is required for a quantitative transformation of the substrate using the same loading of **6b** as the precatalyst. The reactions using ILs as solvents are significantly slower. Thus, only a 43% of conversion was obtained in [bmim][BF₄] at the same temperature after 24 h even when a 1% molar loading of Pd(OAc)₂ was used. The reaction was even slower when an isolated Pd–NHC biscarbene complex derived from [bmim][Br] was used as the Pd source. In this case only a 35% conversion was observed after 24 h [44]. This large reduction in rate

has been attributed to the formation of tetrakis-carbenes of very low catalytic activity [44,45]. Site isolation effects associated to the immobilization of the imidazolium subunits to the polymeric matrix [46] are, most likely, responsible for the no participation of this deactivation pathway.

Given the above-mentioned mechanism, the microenvironment surrounding the active sites in the polymer-supported precatalyst can play an important role in determining the rate, yield, and selectivity for product formation [14,46]. Finke's model can be applied as a tool to characterize in a quantitative way the effect of the g-SILLPs on the formation, release, and recapture of active species from the reaction medium.

Thus, the kinetic profiles for polymers **5** and **6** on the model reaction were evaluated at 90 °C. Again this temperature was selected to properly observe the sigmoidal kinetics and to identify the induction period for all resins. The results achieved are shown in Fig. 5. The Pd/IL-like fragments ratio significantly affects the critical parameters of the process as are the overall reaction rates and the ability of the support to release and recapture the soluble Pd species. Indeed, a clearly different behavior was observed for the Pd–g-SILLPs with low (**5a–e**) or high (**6a–e**) loading of ionic liquid-like moieties. Pd–g-SILLPs **5a–e** were more active catalysts, giving high conversions of PhI (85–99%) in less than 2 h. On the contrary, a period of 3–5 h was required to obtain similar conversions for highly functionalized polymers (**6a–e**). A second factor that can affect the course of the reaction is the nature of the counteranions present in the IL-like moieties not transformed into Pd–NHC functionalities. This effect was more important for the solids with a high loading of ionic liquid-like units. For them the reaction rates increased in the order SbF₆[−] (**6e**) > BF₄[−] (**6b**) > Tf₂N[−] (**6d**) > TfO[−] (**6c**) > Cl[−] (**6a**). Differences on reaction rates were also observed for the resins with low IL-like moieties loadings, although the effect was not so pronounced, the order being very similar: SbF₆[−] (**5e**) > Tf₂N[−] (**5d**) ≈ BF₄[−] (**5b**) > TfO[−] (**5c**) > Cl[−] (**5a**). In all the cases, the kinetic curves were fitted to Finke's model to obtain the values corresponding to the pseudo-elementary rate constants for the nucleation (*k*₁) and for the autocatalytic growth (*k*₂), which is shown in Table 6.

A linear relationship was found between the TOFs calculated at 50% conversion of PhI and the values of *k*₂ calculated for each anion in both series, high and low loading of ionic liquid-like units (see Fig. 6). The differences in catalytic activity of the resins are clearly associated to the coordinative ability of the counteranions. The reactions performed with catalysts based on g-SILLPs containing more coordinating anions (Cl[−] and CF₃SO₃[−]) show a lower activity. Similar trends are observed when the effects of counteranions on *k*₁ are considered. Fig. 7 shows the existence of a linear relationship between *k*₁ and the amount of palladium leached to the reaction medium for polymers **6** after 2 h of reaction at 90 °C. Again, the more coordinating anions are associated with lower values for *k*₁ and to a reduction of leaching. The presence of strong coordinating

Table 5

Comparison of the results obtained for the Heck reaction between iodobenzene and methyl or ethyl acrylate in DMF and ILs or SILLPs.

Entry	Catalyst	Solvent	Base	<i>T</i> (°C)	<i>t</i> (h)	Conversion ^a	Selectivity ^b
1	Pd(OAc) ₂ ^c	DMF	Et ₃ N ^d	90	1	100	100
2	6b ^c	DMF	Et ₃ N ^d	90	4.5	95	100
3 ^e	Pd(OAc) ₂ ^f	[bmim][BF ₄]	NaOAc ^g	90	24	43	68
4 ^e	PdNHC ^f	[bmim][BF ₄]	NaOAc ^g	90	24	35	56

^a Conversion of iodobenzene.

^b Selectivity to *trans* cinnamate.

^c 0.02 mol% relative to iodobenzene.

^d 2 equivalents.

^e Data taken from Ref. [44].

^f 1 mol% relative to iodobenzene.

^g 1.1 equivalents.

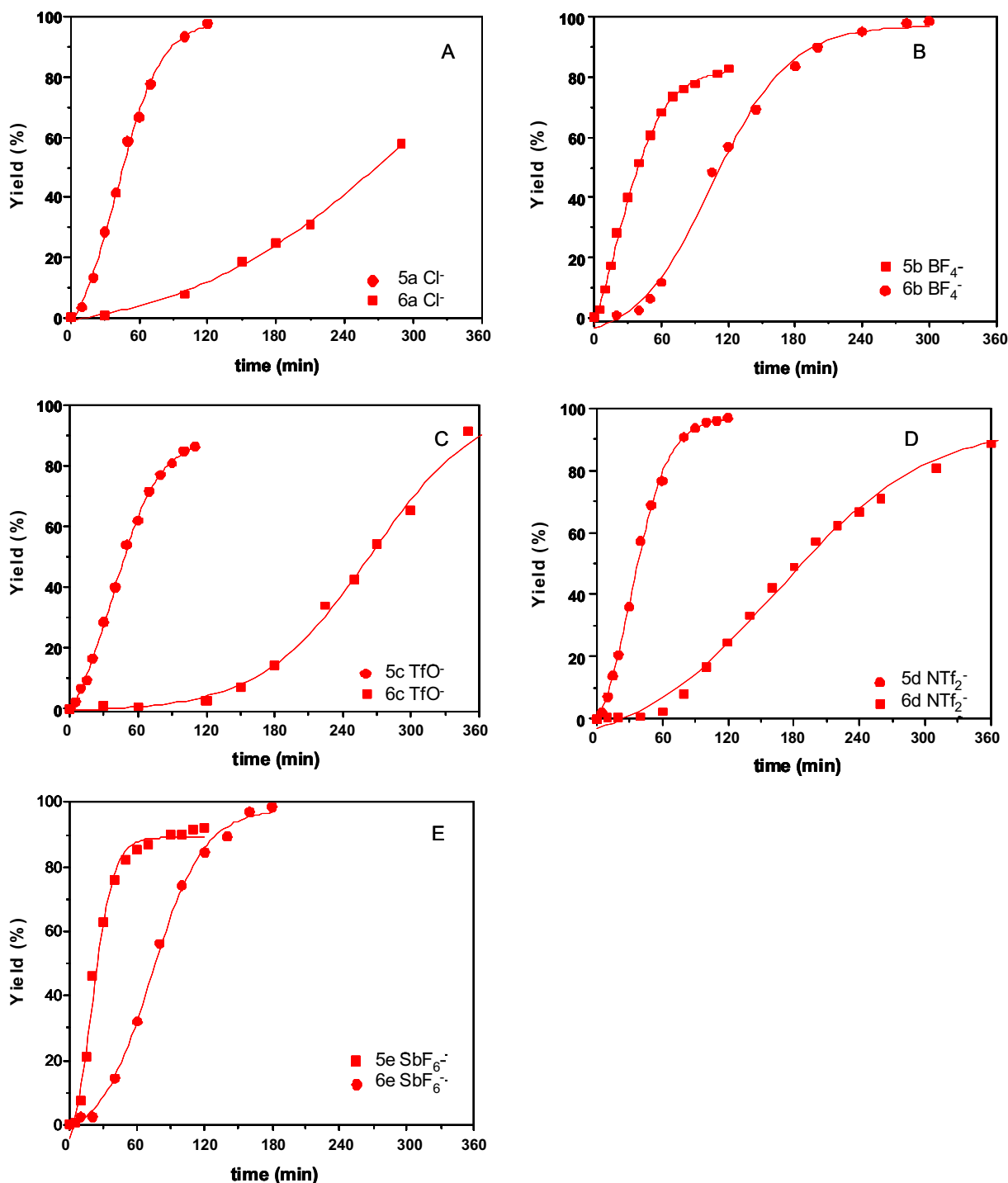


Fig. 5. Plots of yield vs. time for the Heck reaction of methylacrylate (7.5 mmol) and iodobenzene (5 mmol) at 90 °C catalyzed by 0.02% mol of Pd-g-SILLPs **5a–e** and **6a–e** in 5 mL DMF, with 2 equivalents of Et₃N. (A) **5a** (X = Cl⁻, low loading of IL-like units) and **6a** (X = Cl⁻, high loading of IL-like units). (B) **5b** (X = BF₄⁻, low loading of IL-like units) and **6b** (X = BF₄⁻, high loading of IL-like units). (C) **5c** (X = TfO⁻, low loading of IL-like units) and **6c** (X = TfO⁻, high loading of IL-like units). (D) **5d** (X = Tf₂N⁻, low loading of IL-like units) and **6d** (X = Tf₂N⁻, high loading of IL-like units). (E) **5e** (X = SbF₆⁻, low loading of IL-like units) and **6e** (X = SbF₆⁻, high loading of IL-like units).

counteranions is expected to stabilize the Pd-g-SILLPs complexes, as well as the Pd-NPs-g-SILLPs once formed, thus reducing the rate for the generation of Pd(0) (k_1).

The former effect of the counteranion is remarkable as the Heck reaction considered here occurs with the concomitant formation of significant amounts of Et₃NI that does not seem to interfere nor compete with the imidazolium subunits in the stabilization of the Pd-NPs formed.

The significant leaching of Pd observed at 90 °C is accompanied by a decrease in the activity for successive runs. Thus, for **6e**, the first and second run produced a quantitative transformation of the substrates, but conversion falls dramatically after the third use to yield only 20% of the product. This was expected, since SbF₆ is the less coordinative anion employed and therefore a faster release and less capability to stabilize and recapture the active species was anticipated [47]. It could be expected that using longer

Table 6
Catalytic activity of the Pd-*g*-SILLPs in the Heck reaction. Kinetic parameters.

Entry	Pd- <i>g</i> -SILLP	X ⁻	$k_1 \times 10^4$ (min ⁻¹)	$k_2 \times 10^{-6}$ (M ⁻¹ min ⁻¹) ^a
1	5a	Cl	27.4	1.68
2	6a	Cl	2.55	0.43
3	5b	BF ₄	45.4	1.75
4	6b	BF ₄	4.92	1.00
5	5c	TfO	30.3	1.50
6	6c	TfO	1.03	0.48
7	5d	NTf ₂	37.0	1.78
8	6d	NTf ₂	4.37	0.59
9	5e	SbF ₆	55.3	2.73
10	6e	SbF ₆	9.93	1.36

^a k_2 values corrected by a stoichiometric factor [30].

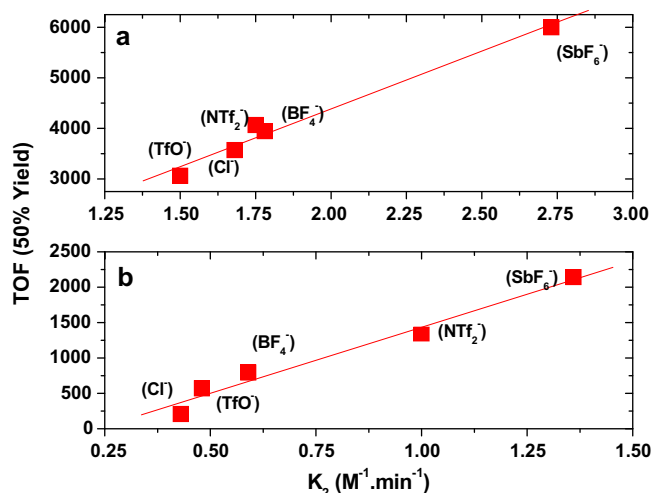


Fig. 6. Plots of TOF (50% yield) vs. k_2 (M⁻¹ min⁻¹) for the Heck reaction of methylacrylate (7.5 mmol) and phenyliodide (5 mmol) at 90 °C using 0.02% mol of different Pd-*g*-SILLPs in 5 mL DMF, with 2 equivalents of Et₃N. (a) Polymers **5** with low loading of IL-like moieties; $y = -187 + 2286x$; $R^2 = 0.989$. (b) Polymers **6** with high loading of IL-like moieties; $y = -431 + 1864x$; $R^2 = 0.985$.

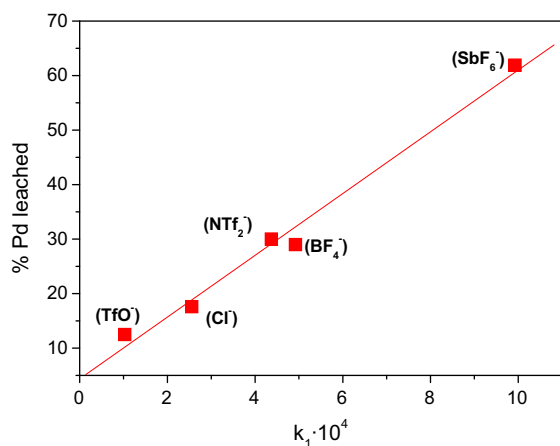


Fig. 7. Plot of % Pd leached vs. k_1 (min⁻¹) for the Heck reaction of methylacrylate and phenyliodide at 90 °C, 0.02% mol of **6a–e** in 5 mL DMF, with 2 equivalents of Et₃N. $y = 4.7 + 5.7x$, $R^2 = 0.986$.

reaction times, a higher degree of redeposition could be obtained, although problems of excessive aggregation could affect the reusability of the system in further reaction cycles, needing the addition of an oxidant agent, such as iodide [40,3a]. However, when the reaction is carried out at 130 °C, no leaching is detected and

the number of efficient cycles largely increases. This is a much more efficient approach. For the same resin (**6e**) nearly quantitative yields were achieved for a constant reaction time (180 min) for more than five cycles. Nevertheless, kinetic profiles for the different cycles are a more realistic tool to analyze the long-term stability of those systems than conversion or yields [7]. In this regard, some reduction on the reaction rates (Fig. 8) was observed, relative to the first cycle, for the second run. We must be aware that obviously different kinetics parameters must apply for the first and for consecutive cycles. Once the Pd-NPs are formed and stabilized by the *g*-SILLPs surfaces, the precatalytic species are those Pd-NPs-*g*-SILLPs and not the initially supported Pd-NHC species. The k'_1 and k'_2 (see Fig. 3) values should reflect the rates for the formation of the true catalytic species from those Pd-NPs-*g*-SILLPs. The recapture of the active species is also quite efficient, since no leaching was detected by ICP-MS. Moreover, SEM images from the polymer after the first cycle showed the presence of Pd(0). In regard to the activity of the palladium species recaptured onto the *g*-SILLPs, this material was used in four additional runs. Remarkably, in all the reuses, yields >95% for the main product, after 180 min, were achieved without the need of any additional oxidizing agent. Furthermore, as it can be observed in Fig. 8, the kinetic profiles in the successive runs are very similar. More importantly, the slope of the sigmoidal profile was found to be 1.295 ± 0.026 min⁻¹ in the cycles 2–5, indicating that activity remains essentially constant for successive cycles and fully confirming that our supported Pd system maintains the activity for the successive cycles and is fully recoverable. This also demonstrates that the active species and the mechanisms are the same in all recycles assayed.

Finally, some additional experiments were carried out to explore the scope of our catalytic system. Thus, the Heck reaction was examined for different iodo and bromobenzenes and with different acrylates as well as styrene and some results are gathered in Table 7. Resin **6a** was chosen as the catalyst and the solvent and base used were *N*-methylpyrrolidone and NaOAc to favor the reactivity of the less reactive substrates. All aryl iodides were rapidly converted to the corresponding Heck products with excellent yields, regardless of the nature of the alkene (Table 7, entries 1–3). Reaction of *p*-bromoacetophenone and *p*-nitrobromobenzene with methyl acrylate gave the corresponding product in 95% and 97% yield, respectively, in 18 h (entries 4 and 5). Nevertheless, as could be expected, when the less active substrates *p*-methoxybromobenzene and bromobenzene were assayed, lower yields of product were observed for the same period of time. Resin **6a** was not active, however, for the Heck reaction with an activate chloroarene and methyl acrylate.

Once the system proved to be active and recyclable, we also tested different C–C coupling reactions employing the same system (Table 7, entries 9 and 10). The Sonogashira coupling between iodobenzene and phenylacetylene proved to be very straightforward. Noteworthy, the reaction was carried out under aerobic conditions and without the use of CuI as a co-catalyst. The Suzuki reaction between iodobenzene and phenylboronic acid was also carried out successfully. In this case 24 h of reaction time was necessary to obtain yields over 90%.

4. Conclusions

In summary, the Heck reaction was effectively catalyzed by different Pd-*g*-SILLPs. Excellent values of TON and TOF can be achieved for the coupling of phenyliodide and methylacrylate. The reaction system can be easily handled, being stable against moisture and air. The reaction mechanism seems to involve the formation of soluble species of molecular and colloidal nature. The initial Pd-NHC supported complexes are mere precatalysts of

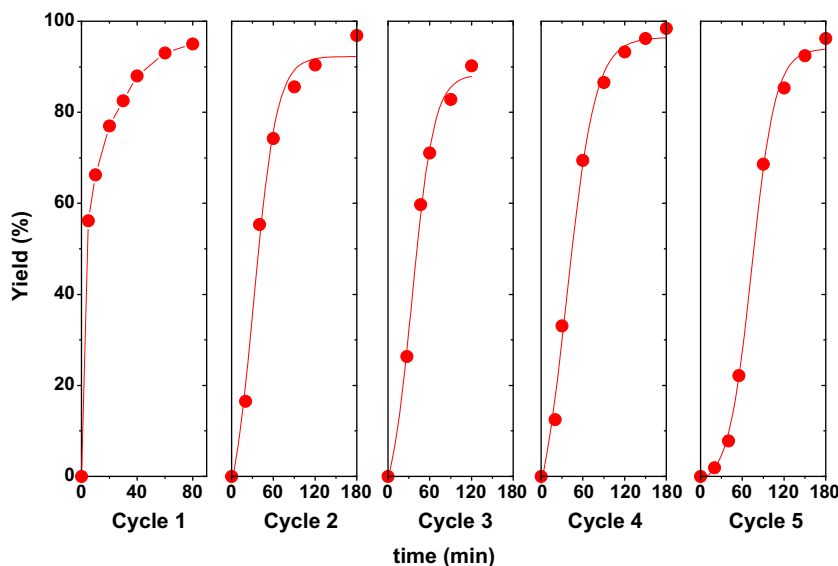


Fig. 8. Recycling test. Plots of yield vs. time for the Heck reaction of metylacrylate (7.5 mmol) and iodobenzene (5 mmol) at 130 °C by 0.1% mol of **6e** in 5 mL DMF, 2 equivalents of Et₃N.

Table 7
Cross-Coupling reactions of haloarenes catalyzed by Pd-*g*-SILLP **6a**.

Entry	R ₁	X ⁻	R ₂	Z	Time (h)	Yield (%)
<i>R₁X + R₂Z → R₁-ZR₂</i>						
1	H	I	CH ₂ =CH	CO ₂ Me	4	97
2	H	I	CH ₂ =CH	Ph	4	95
3	H	I	CH ₂ =CH	CN	4	89
4	4-NO ₂	Br	CH ₂ =CH	CO ₂ Me	18	97
5	4-CH ₃ CO	Br	CH ₂ =CH	CO ₂ Me	18	95
6	4-CH ₃ O	Br	CH ₂ =CH	CO ₂ Me	18	15
7	H	Br	CH ₂ =CH	CO ₂ Me	18	30
8	4-CHO	Cl	CH ₂ =CH	CO ₂ Me	18	–
9	H	I	HC≡C	Ph	18	95
10	H	I	B(OH) ₂	Ph	24	91

Z-R² (7.5 mmol) and haloarene (5 mmol) at 140 °C by 0.04% mol of **6a** in 5 mL NMP, 1.5 equivalents of NaOAc.

the active species, released into the medium by the effect of the phenyliodide and the base. The release is controlled by the micro-environment of the palladium complexes provided by the functional surfaces containing imidazolium moieties. The soluble nanoclusters can further aggregate, but the presence of the IL-like modified surfaces stabilizes the clusters formed and limits their aggregation to form large, non-active Pd(0) particles. Important differences in activity were observed depending on the nature and loading of the *g*-SILLPs. Higher loadings of ionic liquid-like species led, in all cases, to lower activities but efficient recovery. The presence of more strongly coordinating anions, such as chloride and triflate also provided reduced activities. On the contrary, weak coordinating anions, such as SbF₆⁻ and BF₄⁻, led to higher activities, but worst recyclability. In this way, the functional polymers are able to control the release of active species and efficiently recapture them, and become a reservoir of Pd species being able to participate in successive catalytic runs, leading to an efficient reusable system. The truly reusable character of the supported Pd species formed after the first cycle is confirmed by the constant performance of the resins at 130 °C not only in terms of yield but also in terms of the main kinetics parameters. This efficient recycling can be achieved without the need of additional reactivation of the redeposit Pd species. The present catalysts have also been shown to efficiently catalyze the Heck reaction of iodides and

bromides with different alkenes, and are also active for related processes such as Sonogashira and Suzuki reactions.

Acknowledgments

We thank the Spanish Ministerio de Ciencia y Tecnología (CTQ2008-04412/BQU and CTQ2008-04309/BQU), Generalitat Valenciana (GV2007/107 and ARVIV/2007/081), and Bancaixa-UJI (P1 1A2007-11) for financial support. E.G.-V. thanks MCYT for personal financial support (Ramón y Cajal program).

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jcat.2009.11.002](https://doi.org/10.1016/j.jcat.2009.11.002).

References

- [1] (a) R.F. Heck, *Acc. Chem. Res.* 12 (1979) 146; (b) I.P. Beletskaya, A.V. Cheprakov, *Chem. Rev.* 12 (2000) 3009; (c) M. Beller (Ed.), *Transition Metals for Organic Synthesis, Building Blocks and Fine Chemicals*, Wiley-VCH, Weinheim, 2004.
- [2] J.-C. Hierro, M. Beaupérin, P. Meunier, *Chem. Eur. J.* 13 (2007) 6908.
- [3] (a) A.H.M. de Vries, F.J. Parlevliet, L. Schmieder-van de Von-dervoort, J.H.M. Mommers, H.J.W. Henderickx, M.A.N. Walet, J.G. de Vries, *Adv. Syn. Catal.* 344 (2002) 996; (b) A.H.M. de Vries, J.M.C.A. Mulders, J.H.M. Mommers, H.J.W. Henderickx, J.G. de Vries, *Org. Lett.* 5 (2003) 3285; (c) J.G. de Vries, *Dalton Trans.* 421 (2006).
- [4] (a) For a general overview on metal nanoclusters and their applications in catalysis, see J.S. Bradley, E. Hill, M.E. Leonowicz, H. Witzke, *J. Mol. Catal.* 41 (1987) 59; (b) J.D. Aiken III, R.G. Finke, *J. Mol. Catal. A* 145 (1999) 1; (c) H.B. Nnnemann, R.M. Richards, *Eur. J. Org. Chem.* (2001) 2455.
- [5] L. Yin, J. Liebscher, *Chem. Rev.* 107 (2007) 133.
- [6] A. de Meijere, F. Diederich (Eds.), *Metal-Catalyzed Cross-Coupling Reactions*, vol. 1, Wiley-VCH, Weinheim, 2004.
- [7] For the "Ideal Catalysts" concept see J.A. Gladysz, *Pure Appl. Chem.* 73 (2001) 1319.
- [8] (a) B.M. Bhanage, M. Arai, *Catal. Rev.* 43 (2001) 315; (b) C.E. Garret, K. Prasad, *Adv. Syn. Catal.* 346 (2004) 889; (c) E.J. Flahive, B.L. Ewanicki, N.W. Sach, S.A. O'Neill-Slawecki, N.S. Stankovic, S. Yu, S.M. Guinness, J. Dunn, *Org. Process Res. Dev.* 12 (2008) 637.
- [9] V. Polshettiwar, Á. Molnár, *Tetrahedron* 63 (2007) 6949.
- [10] N.T.S. Phan, M.V.D. Sluys, C.W. Jones, *Adv. Syn. Catal.* 348 (2006) 609.
- [11] A. Biffis, M. Zecca, M. Basato, *J. Mol. Catal. A* 173 (2001) 249.
- [12] (a) K. Yu, W. Sommer, J.M. Richardson, M. Weck, C.W. Jones, *Adv. Syn. Catal.* 347 (2005) 161;

- (b) W. Sommer, K. Yu, J.S. Sears, J. Ji, X. Zheng, R.J. Davis, C.D. Sherill, C.W. Jones, M. Weck, *Organometallics* 24 (2005) 4351;
(c) J.M. Richardson, C.W. Jones, *J. Catal.* 251 (2007) 80;
(d) M. Weck, C.W. Jones, *Inorg. Chem.* 46 (2007) 1865.
- [13] (a) See monographic issue J.A. Gladysz, *Chem. Rev.* 102 (2002) 3215;
(b) F. Albericio, Tulla-Puche (Eds.), *The Power of Functional Resins in Organic Synthesis*, Wiley-VCH, Weinheim, 2008.
- [14] (a) B. Altava, M.I. Burguete, J.M. Fraile, J.I. García, S.V. Luis, J.A. Mayoral, M.J. Vicent, *Angew. Chem. Int. Ed.* 39 (2000) 1506;
(b) H. Hagiwara, Y. Masahiro, Y. Sugawara, T. Hoshi, T. Suzuki, *Chem. Commun.* 23 (2005) 2942;
(c) B. Altava, M.I. Burguete, E. Garcia-Verdugo, S.V. Luis, M.J. Vicent, *Green Chem.* 8 (2006) 717;
(d) N. Madhavan, C.W. Jones, M. Weck, *Acc. Chem. Res.* 41 (2008) 1153.
- [15] (a) B. Helms, S.J. Guillaudeu, Y. Xie, M. McMurdo, C.J. Hawker, J.M.J. Fréchet, *Angew. Chem. Int. Ed.* 44 (2005) 6384;
(b) C. K.-W. Kwong, R. Huang, M. Zhang, H. Shi, P.H. Toy, *Chem. Eur. J.* 13 (2007) 2369;
(c) A. Dahan, M. Portnoy, *J. Am. Chem. Soc.* 129 (2007) 5860.
- [16] A. Kirschning, W. Solodenko, K. Mennecke, *Chem. Eur. J.* 12 (2006) 5972.
- [17] (a) N. Karbass, V. Sans, E. García-Verdugo, M.I. Burguete, S.V. Luis, *Chem. Commun.* 29 (2006) 3095.
- [18] P. Lozano, E. García-Verdugo, R. Piamtongkam, N. Karbass, T. De Diego, M.I. Burguete, S.V. Luis, J.L. Iborra, *Adv. Syn. Catal.* 349 (2007) 1077.
- [19] M.I. Burguete, H. Erythropel, E. García-Verdugo, S.V. Luis, V. Sans, *Green Chem.* 10 (2008) 401.
- [20] (a) C.P. Mehnert, *Chem. Eur. J.* 11 (2005) 50;
(b) A. Riisager, R. Fehrmann, M. Haumann, P. Wasserscheid, *Eur. J. Inorg. Chem.* (2006) 695;
(c) Y. Gua, G. Li, *Adv. Syn. Catal.* 351 (2009) 817.
- [21] (a) Initial studies with metal NHC complexes based on supported imidazolium salts can be found in B. Altava, M.I. Burguete, E. García-Verdugo, N. Karbass, S.V. Luis, A. Puzary, V. Sans, *Tetrahedron Lett.* 47 (2006) 2311;
(b) W. Gil, K. Boczoń, A.M. Trzeciak, J.J. Ziolkowski, E. Garcia-Verdugo, S.V. Luis, V. Sans, *J. Mol. Catal. A* 309 (2009) 131–136.
- [22] Metal nanoparticles with narrow size distributions have been synthesized in imidazolium-based ILs. The IL acts as a template for the formation of nanoscale structures and stabilizes the metal nanoparticles by the formation of “protective” anionic and cationic layers avoiding particle aggregation see Ref. [23].
- [23] (a) P. Migowski, J. Dupont *Chem. Eur. J.* 13 (2007) 32;
(b) X. Yang, Z. Fei, D. Zhao, W. Han Ang, Y. Li, Paul J. Dyson, *Inorg. Chem.* 47 (2008) 3292;
(c) M. Ruta, G. Laurenczy, P.J. Dyson, L. Kiwi-Minsker, *J. Phys. Chem. C* 112 (2008) 17814;
(d) E. Redel, R. Thomann, C. Janiak, *Chem. Commun.* (2008) 1789.
- [24] (a) B. Altava, M.I. Burguete, E. García-Verdugo, S.V. Luis, M.J. Vicent, *Tetrahedron* 57 (2001) 8675;
(b) B. Altava, M.I. Burguete, E. García-Verdugo, S.V. Luis, M.J. Vicent, *Tetrahedron Lett.* 42 (2001) 8459.
- [25] F. Galindo, B. Altava, M.I. Burguete, R. Gavara, S.V. Luis, *J. Combin. Chem.* 6 (2004) 859.
- [26] (a) J.-W. Byun, Y.-S. Lee, *Tetrahedron Lett.* 45 (2004) 1837;
(b) D.-W. Kim, D.-Y. Chi, *Angew. Chem. Int. Ed.* 43 (2004) 483;
(c) J.H. Kim, B.H. Jun, J.W. Byun, Y. S Lee, *Tetrahedron Lett.* 45 (2004) 5827;
(d) D.-W. Kim, D.-J. Hong, K.-S. Jang, D.-Y. Chi, *Adv. Syn. Catal.* 348 (2006) 1719;
- (e) D.-H. Lee, J.-H. Kim, B.-H. Jun, H. Kang, J. Park, Y.-S. Lee, *Org. Lett.* 10 (2008) 1609;
(f) V. Polshettiwar, R.S. Varma, *Tetrahedron* 64 (2008) 4637.
- [27] M.I. Burguete, F. Galindo, E. Garcia-Verdugo, N. Karbass, S.V. Luis, *Chem. Commun.* 29 (2007) 3087.
- [28] W.J. Sommer, M. Werk Coor, *Chem. Rev.* 251 (2007) 860.
- [29] J.H. Kim, J.W. Kim, M. Shokouhimehr, Y.S. Lee, *J. Org. Chem.* 70 (2005) 6714.
- [30] It is worthy to mention that both materials SILLPs and palladium complex-SILLPs can be easily synthesized in grams scale under aerobic conditions being storable without any significant modifications during months.
- [31] R. Narayanan, M.A. El-Sayed, *J. Am. Chem. Soc.* 125 (2003) 8340.
- [32] J. Hu, Y.B. Liu, *Langmuir* 21 (2005) 2121.
- [33] (a) I.W. Davies, L. Matty, D.L. Hughes, P.J. Reider, *J. Am. Chem. Soc.* 123 (2001) 10139;
(b) B.H. Lipshutz, S. Tasler, W. Chrisman, B. Spliethoff, B. Tesche, *J. Org. Chem.* 68 (2003) 1177.
- [34] (a) F. Zhao, M.B. Bhanage, M. Shirai, M. Arai, *J. Mol. Catal. A* 142 (1999) 383;
(b) K. Kohler, R.G. Heidenreich, J.G.E. Krauter, M. Pietsch, *Chem. Eur. J.* 8 (2002) 622.
- [35] (a) M.A. Watzky, R.G. Finke, *J. Am. Chem. Soc.* 119 (1997) 10382;
(b) K.S. Weddle, J.D. Aiken III, R.G. Finke, *J. Am. Chem. Soc.* 120 (1998) 5653;
(c) J.A. Widegren, J.D. Aiken III, S. Azkar, R.G. Finke, *Chem. Mat.* 13 (2001) 312;
(d) J.A. Widegren, M.A. Bennett, R.G. Finke, *J. Am. Chem. Soc.* 125 (2003) 10301;
(e) J.A. Widegren, R.G. Finke, *J. Mol. Catal. A* 198 (2003) 317.
- [36] The kinetics can be adjusted to a nucleation pseudo-elementary step, $A \rightarrow B$ (rate constant k_1) followed by an autocatalytic surface-growth pseudo-elementary step, $A + B \rightarrow 2B$ (rate constant k_2), in which metal species are added to a soluble nanoparticle (where A is the Pd complex and B is soluble Pd(0)). When combined with the pseudo-elementary step for the Heck reaction, $B + \text{olefin} + \text{iodoarene} \rightarrow B + \text{HI} + \text{coupling product}$, these steps can be fit to the kinetic data (see supporting information). Ref. [35].
- [37] (a) M.B. Thathagar, J.E. ten Elshof, G. Rothenberg, *Angew. Chem. Int. Ed.* 45 (2006) 2886;
(b) A.V. Gaikwad, A. Holuigue, M.B. Thathagar, J.E. ten Elshof, G. Rothenberg, *Chem. Eur. J.* 13 (2007) 6908;
(c) A.M. Trzeciak, J.J. Ziolkowski, *Coord. Chem. Rev.* 251 (2007) 1281.
- [38] F. Zhao, M. Shirai, Y. Ikushima, M. Arai, *J. Mol. Catal. A* 180 (2002) 211.
- [39] J.D. Webb, S. MacQuarrie, K. McEleney, C.M. Crudden, *J. Catal.* 252 (2007) 97.
- [40] (a) G. Budroni, A. Corma, H. García, A. Primo, *J. Catal.* 251 (2007) 345;
(b) K. Köhler, R.G. Heidenreich, S.S. Soomro, S.S. Pröckla, *Adv. Syn. Catal.* 350 (2008) 2930.
- [41] X. Mu, J. Meng, Z.-C. Li, Y. Kou, *J. Am. Chem. Soc.* 127 (2005) 9694.
- [42] R.A. Sheldon, M. Wallau, I.W.C.E. Arends, U. Schuchardt, *Acc. Chem. Res.* 31 (1998) 485.
- [43] D. Astruc, *Inorg. Chem.* 46 (2007) 1884.
- [44] L. Xu, W. Chen, J. Xiao, *Organometallics* 19 (2000) 1123.
- [45] W.A. Herrmann, J. Schwarz, M.G. Gardiner, M. Splieger, *J. Organomet. Chem.* 575 (1999) 80;
W.P. Fehlhammer, T. Bliss, U. Kernbach, I. Brüdgam, *J. Organomet. Chem.* 490 (1995) 149.
- [46] (a) C. Yaroslavsky, A. Patchornik, E. Katchalski, *Tetrahedron Lett.* 11 (1970) 3629;
(b) S.D. Alexandratos, D.H.J. Miller, *Macromolecules* 29 (1996) 8025;
(c) S.D. Alexandratos, D.H.J. Miller, *Macromolecules* 33 (2000) 2011.
- [47] L.S. Ott, R.G. Finke, *Chem. Mater.* 20 (2008) 2592.