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# Importance of the Conditioning of the Chitosan Support in a Catalyst-Containing Ionic Liquid Phase Immobilised on Chitosan: The Palladium-Catalysed Allylation Reaction Case

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**Abstract:** Catalysts containing ionic liquid phase immobilised on chitosan are successfully applied to the palladium-catalysed allylation reaction. A strong influence of the conditioning of chitosan not only on the activity and enantioselectivity but also on the re-

cyclability and reusability of the catalyst is demonstrated.

**Keywords:** allylation; chitosan; enantioselectivity; immobilized catalysts; ionic liquids

## Introduction

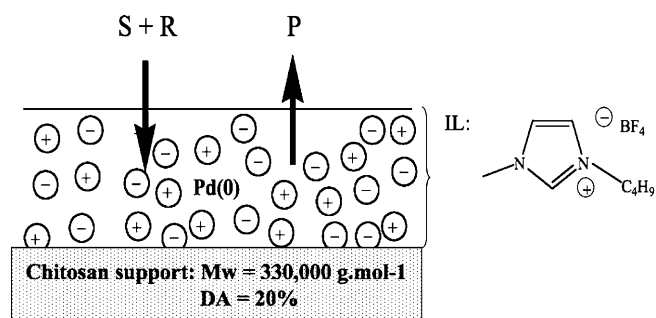
The formation of carbon-carbon bonds is one of the main goals in organic chemistry. Since the first description of palladium-catalysed allylic substitution by Tsuji in 1965,<sup>[1]</sup> the reaction has become one of the most versatile catalytic C–C bond-forming reactions.<sup>[2]</sup> Extensive investigations have defined substrate and nucleophile tolerance, regioselectivity and stereoselectivity.<sup>[3]</sup> The main problems still to be addressed in this topic are, as for numerous other homogenous catalytic processes, the efficient catalyst separation from the product, and the catalyst and solvent recycling.<sup>[4]</sup> Since the reaction is usually conducted by mixing and heating stabilised carbanions with a substrate/catalyst mixture in THF,<sup>[5]</sup> this goal is undoubtedly difficult.<sup>[6]</sup> In general, immobilisation of homogeneous catalysts has been investigated in an attempt to overcome these limitations and the common strategies include covalent bonding of the catalyst to a polymer,<sup>[7]</sup> grafting it onto inorganic materials<sup>[8]</sup> or use of a fluorous phase.<sup>[9]</sup> However, these approaches have often met with limited success due to lowered catalytic activity<sup>[8c]</sup> and/or enantioselectivity.<sup>[8c,10]</sup> Furthermore, the catalytic sites are randomly oriented among the supports and the microenvironment around the active

sites is usually not clear. It is thus difficult, or even impossible, to fine-tune both catalytic activity and enantioselectivity. Furthermore, the immobilisation strategy often requires a multistep sequence, which has a negative consequence on the price of the process. Recently, a partial solution has been brought with the use of ionic liquids (ILs).<sup>[11]</sup> Although enabling the catalyst recycling, the extraction of the organic product from the IL is still tedious. Another limitation arises from the high cost of ILs compared to that of traditional solvents. Their use as solvent (in large amounts) also raises the question of their reprocessing.<sup>[12]</sup> To overcome these problems, the immobilisation of ILs onto a support is a highly attractive and inexpensive strategy, which allows one to minimise the amount of ILs used.<sup>[13]</sup> Additionally, supported ILs have the advantage of an easier separation and recycling as well as the potential for the development of continuous processes.

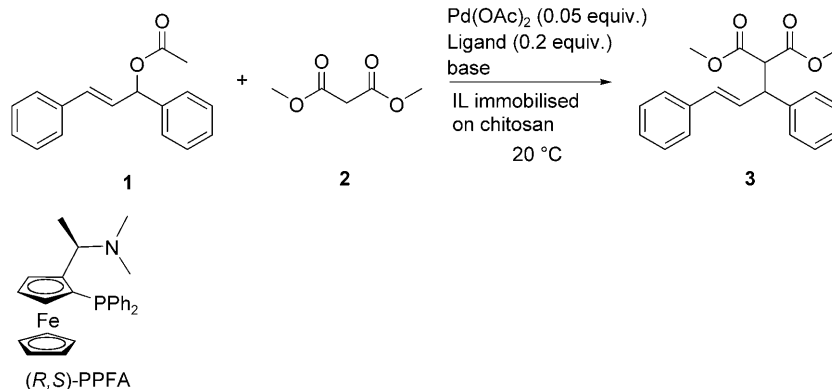
We recently reported the immobilisation of an ionic liquid phase containing a palladium catalyst on a bio-organic polymer, that is, chitosan. The new catalytic system was prepared by adsorption of the catalyst-containing ionic liquid layer onto the surface of freeze-dried chitosan beads.<sup>[14]</sup> One of the greatest advantages of chitosan over most of other polysaccha-

rides (e.g., cellulose, starch) and other potent materials used as support (e.g., silica) is that slightly acidic solutions of chitosan can be readily cast into beads, films, fibres or scaffolds, allowing for a great flexibility in the conditioning of chitosan.<sup>[15]</sup> This property accounts for the unique potential of chitosan as a support for catalysis. Moreover, it offers an opportunity to develop continuous fixed-bed reactors.

Our preliminary study on the use of chitosan for immobilising a catalyst-containing ionic liquid phase was related to the achiral palladium-catalysed amination reaction.<sup>[14]</sup> This approach provided major advantages over other heterogenised catalytic systems and reactions conducted in pure ILs such as i) the use of a small amount of ionic liquid, ii) the ease of product extraction, iii) the efficient recycling and reuse of the catalytic system. We report herein the application of these catalyst-containing ionic liquid phases immobilised on chitosan in the palladium-catalysed C–C bond formation (Tsuji–Trost allylation reaction) in both racemic and enantioselective versions. Interestingly, the conditioning of the chitosan support proved to play a major role on the activity, selectivity and recycling of the catalyst.



**Figure 1.** Chitosan-IL phase catalytic system.



**Scheme 1.** Palladium-catalysed allylic substitution (Ligands = PPh<sub>3</sub>, TPPTS).

## Results and Discussion

The catalyst-containing IL phase immobilised on chitosan, which is used, is represented in Figure 1.

Typically, the catalytic system is prepared by impregnation of lyophilised chitosan beads using [bmim][BF<sub>4</sub>] containing 0.05 equivalent of the palladium catalyst [Pd(OAc)<sub>2</sub>] and 0.2 equivalent of PPh<sub>3</sub> as ligand with a polymer concentration of 14.3% (w/v). After stirring at room temperature for 30 min, the chitosan and the ionic liquid-based catalytic system is ready for use. The allylation reaction between (*E*)-1,3-diphenyl-3-acetoxyprop-1-ene **1** and dimethyl malonate **2** using NEt<sub>3</sub> as base was selected as a model reaction (Scheme 1). This quite complex reaction involving a substrate, a reagent and a base to generate the reactive anion was selected to study the scope and limitation of these new catalysts.

The reaction was completed after 48 h at 20 °C, affording the expected allylated malonate **3** in good yield (80%) (Table 1, entry 1). In the absence of phosphine ligand (PPh<sub>3</sub>), the reaction was unsuccessful, indicating that the complexation of the Pd to chitosan does not occur or that the organometallic complex formed is inactive.

Recycling tests were next performed. They showed a decrease in activity from the second run, seven days

**Table 1.** Allylic substitution using lyophilised chitosan beads.<sup>[a]</sup>

| Entry | Ligand           | Cycle | Time | Conversion [%] | Isolated yield [%] |
|-------|------------------|-------|------|----------------|--------------------|
| 1     | PPh <sub>3</sub> | 1     | 48 h | 92             | 80                 |
| 2     | PPh <sub>3</sub> | 2     | 7 d  | 22             | 20                 |
| 3     | TPPTS            | 1     | 46 h | > 98           | 81                 |
| 4     | TPPTS            | 2     | 7 d  | 56             | 47                 |

<sup>[a]</sup> Reactions performed at 20 °C with 0.05 equiv. of Pd(OAc)<sub>2</sub>, 0.2 equiv. of ligand, 1.2 equiv. of NEt<sub>3</sub> and 1.4 equiv. of **2**.

at room temperature leading only to a partial conversion (22%) (Table 1, entry 2). This poor recycling ability of the catalyst was attributed to the neutral character of the PPh<sub>3</sub> ligand, which favours the leaching of the palladium catalyst during the extraction of **3**.<sup>[14]</sup> To get a better anchoring of the Pd complex in the IL layer and to avoid the catalyst leaching, the neutral triphenylphosphine ligand was replaced by the ionic TPPTS ligand [P(*m*-C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>Na)<sub>3</sub>]. The catalytic system was then evaluated in the model reaction described above. An excellent conversion was achieved leading to the expected product **3** in good yield (81%) (Table 1, entry 3). Recycling and reuse were next examined. Surprisingly and contrarily to what was observed in the palladium-catalysed amination reaction,<sup>[14]</sup> the replacement of the neutral PPh<sub>3</sub> ligand by the ionic TPPTS afforded no improvement in the catalyst recycling (Table 1, entry 4).

Considering the recycling problems, the influence of the base used for the reaction was considered. Indeed, NEt<sub>3</sub> leads to the formation of the corresponding ammonium salt during the reaction. This salt is not extracted with the product and stays in the immobilised ionic liquid layer of the catalytic system, leading to the modification and probably the degradation of the latter. This assumption was confirmed by the fact that addition of triethylammonium chloride to the chitosan-IL phase catalyst dramatically decreases the activity of the catalyst. To avoid the poisoning of the chitosan-IL phase catalyst, NEt<sub>3</sub> was replaced by BSA/AcOK, a classical basic system used in the allylic alkylation.<sup>[16]</sup> Hence, using this basic system in the model reaction described in Scheme 1, and using PPh<sub>3</sub> as ligand, compound **3** was obtained in a good yield (86%) (Table 2, entry 1). Interestingly, the catalyst could be recycled and reused in a second run without loss of activity. However, in the third run, the activity dramatically decreased (Table 2, entry 3).

Replacement of PPh<sub>3</sub> by TPPTS as ligand led to a considerable improvement in the activity and the recovery and reusability of the catalyst. Hence, compound **3** was obtained in good yield (85%) in only 18 h compared to the 40 h previously required with PPh<sub>3</sub> ligand (Table 2, entry 4). The recycling tests showed that the chitosan-IL phase catalyst could be successfully reused at least four cycles with a good conversion (>93%) (Table 2, entries 4–7), although a decrease in the activity was noticed in the fourth run. Hence, four days at 20 °C were required for a complete conversion instead of 18 h in the three first runs. In the 5th cycle, conversion dropped to 52% (Table 2, entry 8). Detection of palladium by ICP-MS in the extraction phases showed a significant leaching of the metal in the two first cycles (5% and 9%, respectively) (Table 3).

Although we were able to define conditions to perform the allylation reaction using the chitosan-immobilised

**Table 2.** Allylic substitution using lyophilised or scCO<sub>2</sub> dried chitosan beads.<sup>[a]</sup>

| Entry | Chitosan drying process | Ligand           | Cycle | Time | Conversion [%] | Yield [%] |
|-------|-------------------------|------------------|-------|------|----------------|-----------|
| 1     | lyophilised             | PPh <sub>3</sub> | 1     | 40 h | >98            | 86        |
| 2     | lyophilised             | PPh <sub>3</sub> | 2     | 40 h | >98            | 85        |
| 3     | lyophilised             | PPh <sub>3</sub> | 3     | 3 d  | 2              | –         |
| 4     | lyophilised             | TPPTS            | 1     | 18 h | >98            | 85        |
| 5     | lyophilised             | TPPTS            | 2     | 18 h | >98            | 85        |
| 6     | lyophilised             | TPPTS            | 3     | 18 h | >98            | 85        |
| 7     | lyophilised             | TPPTS            | 4     | 4 d  | 93             | 80        |
| 8     | lyophilised             | TPPTS            | 5     | 6 d  | 52             | 50        |
| 9     | scCO <sub>2</sub>       | TPPTS            | 1     | 4 h  | >98            | 98        |
| 10    | scCO <sub>2</sub>       | TPPTS            | 2     | 4 h  | >98            | 98        |
| 11    | scCO <sub>2</sub>       | TPPTS            | 3     | 4 h  | >98            | 94        |
| 12    | scCO <sub>2</sub>       | TPPTS            | 4     | 5 h  | >98            | 98        |
| 13    | scCO <sub>2</sub>       | TPPTS            | 5     | 22 h | >98            | 90        |
| 14    | scCO <sub>2</sub>       | TPPTS            | 6     | 5 d  | 22             | 16        |

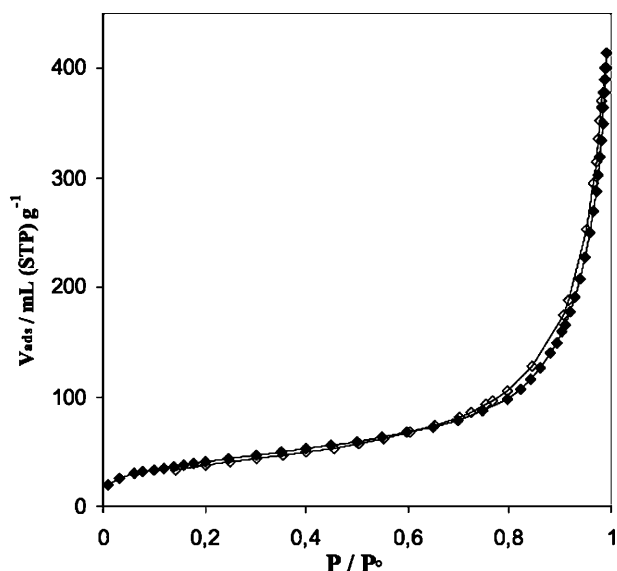
<sup>[a]</sup> Reactions performed with 0.05 equiv. of Pd(OAc)<sub>2</sub>, 0.2 equiv. of ligand, 3 equiv. of BSA, 0.05 equiv. of AcOK, and 3 equiv. of **2**.

**Table 3.** Recycling and reuse of lyophilised chitosan-IL phase catalyst in the allylic substitution.

| Cycle               | 1   | 2   | 3   | 4  | 5  |
|---------------------|-----|-----|-----|----|----|
| Conversion [%]      | >98 | >98 | >98 | 93 | 52 |
| % Pd <sup>[a]</sup> | 5   | 9   | 2   | 2  | 1  |

<sup>[a]</sup> Percentage of leaching palladium in the ether phase as compared to total palladium introduced.

bilised IL phase catalysts, the results obtained in this first part of the work needed improvement in both catalyst activity and recycling. As the surface area of the support can play a major role in heterogeneous catalysis, our attention next focused on the chitosan conditioning with the aim to improve the catalytic activity and the recycling of the catalyst-containing IL phase immobilised on chitosan. Recently, in a remarkable work, Quignard et al. have reported the efficiency of a supercritical CO<sub>2</sub> (scCO<sub>2</sub>) drying of chitosan gels to favour the formation of highly porous materials.<sup>[17]</sup> This technique is commonly processed with inorganic solids and is expected to enable the drying without leading to the collapse of the structure, affording an aerogel with high surface area.<sup>[18]</sup> Hence, preparations of scCO<sub>2</sub> dried chitosan beads were implemented. The comparison of the textural properties of the different materials synthesised (lyophilised chitosan beads and scCO<sub>2</sub> dried chitosan beads) was performed by nitrogen adsorption-desorption isotherms at 77 K (Figure 2). The isotherms of lyophilised beads merged with the axes, indicating that these chitosan



**Figure 2.** N<sub>2</sub> adsorption isotherms of ScCO<sub>2</sub> dried chitosan beads. Full symbol corresponds to the adsorption branch and empty symbol to the desorption branch.

samples are non-porous materials with very low surface areas (Table 4).

Contrarily, the samples issued from the scCO<sub>2</sub> drying process are porous materials with high specific

**Table 4.** Textural properties obtained by nitrogen physisorption at 77 K.

| Chitosan conditioning         | V <sub>pore</sub> [mL g <sup>-1</sup> ] | S <sub>BET</sub> [m <sup>2</sup> g <sup>-1</sup> ] | C <sub>BET</sub> | Pore size [nm] |
|-------------------------------|---|--|------------------|----------------|
| Lyophilised beads             | und.                                    | 2 ± 1  | 22               | und.           |
| scCO <sub>2</sub> dried beads | 0.62                                    | 146 ± 1  | 82               | 50             |

surface areas. These results are clearly observed in the SEM picture (Figure 3). The scCO<sub>2</sub> dried chitosan beads exhibit a nearly type II isotherm in the IUPAC

classification, indicating the presence of ultralarge mesopores (cell-like pores) with a size distribution that is more in the range of the macroporosity. The surface area measured is about 146 m<sup>2</sup> g<sup>-1</sup>, a value close to that reported by Quignard et al.<sup>[17a]</sup>

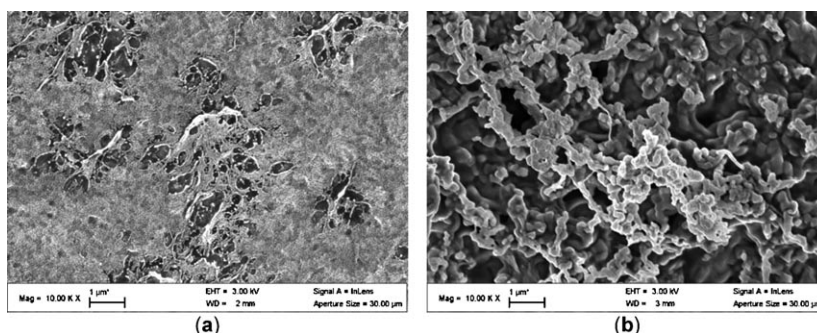
The catalytic activity of the scCO<sub>2</sub> dried chitosan-immobilised IL phase catalyst was then evaluated in the model reaction described in Scheme 1, with TPPTS as ligand. The results are reported in Table 2 (entries 9–14). As expected, compound **3** was obtained in good yield (98%). The most important feature of this new catalytic system is its high activity. The reaction was completed in 4 h at 20 °C instead of the 18 h required with the catalytic material made of lyophilised chitosan beads (Table 2, entry 9). Recycling of the catalytic material was next performed and we were pleased to see that the scCO<sub>2</sub> dried chitosan material enabled the recycling of the catalyst for at least 5 cycles with a 100% conversion (see Table 2, entries 9–13). In the 6th run, a significant decrease of the catalytic activity was measured (22% after 5 days at 20 °C, see Table 2, entry 14). Analysis by ICP-MS of the extraction phases showed a leaching of the metal in the four first cycles (5% for each) (Table 5).

Although the leaching of the palladium can partially explain the decrease in conversion, we are more inclined to believe that there is a progressive deactivation of the catalyst related to the mechanical alteration of the catalytic system. This deactivation can be associated to an accumulation of base-derived products in the ionic liquid layer and to the alteration of the chitosan support during the recycling processes.

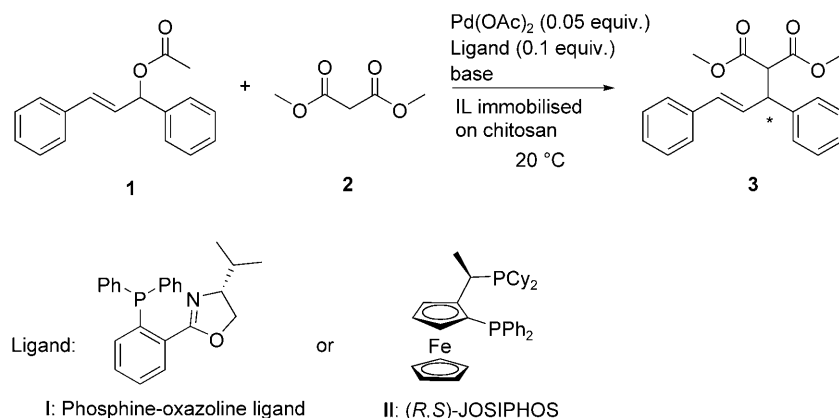
**Table 5.** Recycling and reuse of scCO<sub>2</sub> dried chitosan-IL phase catalyst in the allylic substitution.

| Cycle               | 1   | 2   | 3   | 4   | 5   |
|---------------------|-----|-----|-----|-----|-----|
| Conversion [%]      | >98 | >98 | >98 | >98 | >98 |
| % Pd <sup>[a]</sup> | 5   | 5   | 5   | 5   | 1   |

<sup>[a]</sup> Percentage palladium leached in the ether phase as compared to total palladium introduced.



**Figure 3.** SEM pictures of the surface of the chitosan beads: lyophilised bead (a) and scCO<sub>2</sub> dried bead (b).



**Scheme 2.** Enantioselective allylic substitution reaction.

Reports concerning applications of supported ionic liquids for asymmetric catalysis are scarce,<sup>[19]</sup> and precedents on the use of a biopolymer as support do not exist. Hence, we embark on the study of the chiral version of the allylation reaction. Chiral ligands such as (*R,S*)-JOSIPHOS and the phosphine-oxazoline ligand developed by Pfaltz, ligands which are commonly used in the asymmetric allylation reaction under homogeneous conditions,<sup>[20]</sup> were evaluated in the benchmark enantioselective Pd(0)-catalysed allylation of dimethyl malonate using (*rac*)-(*E*)-1,3-diphenyl-3-acetoxyprop-1-ene **1** as substrate (Scheme 2). Both the lyophilised and the scCO<sub>2</sub>-dried chitosan-IL phase catalysts were evaluated.

The reactions were carried out at 20 °C using the BSA/AcOK couple as base. The enantiomeric ratios obtained in the different experiments were determined by chiral HPLC. The isolated yields in **3** and the enantiomeric ratio are given in Table 6.

To evaluate the influence of the support, the reaction was first performed under homogeneous conditions directly in pure [bmim][BF<sub>4</sub>] using (*R,S*)-JOSIPHOS as ligand. After 20 h, the conversion reached

poorly 18%. Nevertheless, a good enantioselectivity (*er*=93/7) was measured in favour of the (*S*) enantiomer (Table 6, entry 3). After six days, the reaction was still incomplete (76% conversion) and enantioselectivity was unchanged. The reaction was next performed with the ionic liquid phase catalyst immobilised on lyophilised chitosan beads. The selected ligands I and II associated to the Pd complex provided the expected product **3** in moderate yields (45 to 64%) after 20 h at room temperature (Table 6, entries 2 and 1). Interestingly, upon using the ionic liquid phase catalyst immobilised on scCO<sub>2</sub> dried chitosan beads under similar conditions (20 h, 20 °C), a great improvement in the conversion and the isolated yields was obtained for both ligands (74 and 80%, respectively, Table 6, entries 4 and 5). The ultralarge cell-like pores (up to 50 nm), which minimise the diffusion limitation problem, generally encountered in heterogeneous catalysis and a possible positive confinement effect<sup>[19a,21]</sup> presumably account for the highest activity of the scCO<sub>2</sub> dried beads compared to reactions conducted with lyophilised beads or under homogeneous conditions in [bmim][BF<sub>4</sub>]. Dealing with enantioselectivity, the results were rather different depending on the ligand used. With (*R,S*)-JOSIPHOS, a quite similar *ee* was obtained (*er*=95/5) whatever the drying process of chitosan beads. However, with phosphine-oxazoline ligand, the enantioselectivity was greatly improved using the catalyst-containing IL phase immobilised on scCO<sub>2</sub>-dried chitosan [*er*=3/97 instead of 18/82 for the lyophilised chitosan-IL phase catalysts (Table 6 entries 4 and 1)], indicating a support-mediated selectivity modulation. Hence, in addition to improving the activity of the catalyst, the scCO<sub>2</sub> chitosan support also improves the enantioselectivity of the reaction. Although the existence of a support effect on the selectivities was already demonstrated in SILF (supported ionic liquid film) catalysts,<sup>[19a]</sup> this is the first time that the influence of the conditioning of the support is demonstrated in such

**Table 6.** Enantioselective allylic substitution using lyophilised or scCO<sub>2</sub> dried chitosan beads.<sup>[a]</sup>

| Entry            | Chitosan drying process | Ligand | Time | Conv. [%] | Yield [%] | <i>er</i> [%] S/R |
|------------------|-------------------------|--------|------|-----------|-----------|-------------------|
| 1                | lyophilised             | I      | 20 h | 75        | 64        | 18/82             |
| 2                | lyophilised             | II     | 20 h | 51        | 45        | 94/6              |
| 3 <sup>[b]</sup> | –                       | II     | 20 h | 18        | 17        | 93/7              |
| 4                | scCO <sub>2</sub>       | I      | 20 h | 80        | 74        | 3/97              |
| 5                | scCO <sub>2</sub>       | II     | 20 h | 89        | 80        | 95/5              |

<sup>[a]</sup> Reactions performed with 0.05 equiv. of Pd(OAc)<sub>2</sub>, 0.1 equiv. of ligand, 3 equiv. of BSA, 0.05 equiv. of AcOK and 3 equiv. of **2**.

<sup>[b]</sup> Reaction performed under homogeneous conditions in [bmim][BF<sub>4</sub>].



catalytic materials. These preliminary results emphasised the major role played by the drying mode upon the polymer framework structure.

## Conclusions

In this work, we have shown that a catalyst-containing IL phase immobilised on chitosan can be successfully applied to the palladium-catalysed allylation reactions. This study emphasised the major role of the drying process of the chitosan support. Hence, performing alcohol exchange and supercritical CO<sub>2</sub> drying have proven to be an efficient method to provide macroporous chitosan with a high specific surface area (in the range of 150 m<sup>2</sup> g<sup>-1</sup>). This characteristic can be directly related to the high efficiency of these new supported catalysts both in terms of activity, recycling and reuse (5 cycles with 100% conversion). Dealing with the enantioselectivity aspect, the role of the chitosan drying process was particularly emphasised with phosphine-oxazoline ligand, with a great enhancement of the enantioselectivity when using the scCO<sub>2</sub> chitosan-IL phase catalyst.

The influence of the support on the catalytic results being clearly shown, further studies dealing with the preparation of the catalyst-containing IL phase immobilised on chitosan using other conditionings (such as scaffolds, hollow fibers, etc.) and their exploration for catalysis are currently under way.

## Experimental Section

Chitosan was obtained from Fluka with an average molar mass of 330,000 g mol<sup>-1</sup> (determined by viscosimetry) and a degree of deacetylation determined by <sup>1</sup>H NMR of 80%. Ionic liquids were supplied by Solvionic (Toulouse, France). All commercially available compounds were used as received. Thin layer chromatography was carried out on silica gel 60 F<sub>254</sub> (1.1 mm, Merck) with spot detection under UV light or through I<sub>2</sub> or KMnO<sub>4</sub> oxidation. Chromatographic separations were achieved on Merck silica gel column (Geduran Si 60, 0.040–0.063 mm). High-performance liquid chromatograph (HPLC) analysis was performed on a Waters apparatus equipped with diode array ultraviolet (UV) detector and Daicel Chiralpak AD-H column. N<sub>2</sub> physisorption isotherms have been acquired for four samples using an ASAP 2000 instrument from Micromeritics. The powdered sample of mass about 200 mg was evacuated overnight at 353 K prior adsorption, i.e., under degradation. Total porous volume V<sub>pore</sub> is from the volume adsorbed under relative pressure 0.99. The surface morphology and surface fracture of chitosan beads were examined using a scanning electron microscope (SEM) from ZEISS Supra 55 at relatively low voltage (<10 kV) after coating with gold (Fine coat JFC1100).

### Preparation of Chitosan-SILP Catalyst

Pre-degassed [bmim][BF<sub>4</sub>] (0.5 mL) was added to Pd(OAc)<sub>2</sub> (0.02 mmol, 0.05 equiv.), the ligand [PPh<sub>3</sub>] (0.079 mmol, 0.2 equiv.), TPPTS (0.079 mmol, 0.2 equiv.), (*R,S*)-JOSIPHOS (0.04 mmol, 0.1 equiv.) or Pfaltz ligand (0.04 mmol, 0.1 equiv.), and the purified chitosan (100 mg). The resulting mixture was stirred 30 min at room temperature under an inert atmosphere.

### Preparation of Lyophilised Chitosan Beads

1 g of chitosan was dissolved in 100 mL of a 0.2% HCl solution. After complete dissolution, the solution was filtered on a Büchner funnel, and added dropwise into an NaOH solution (0.25 mol L<sup>-1</sup>) through a syringe needle. Chitosan beads were rinsed with water to attain the water conductivity. Beads were then freeze-dried.

### Preparation of Supercritical CO<sub>2</sub> Dried Chitosan Beads

The procedure follows the method described by Quignard et al.<sup>[17a]</sup> 1 g of chitosan was dissolved in 100 mL of an acetic acid solution (0.055 mol L<sup>-1</sup>). After complete dissolution, the solution was filtered on a Büchner funnel and added dropwise into an NaOH solution (4N) through a syringe needle. The chitosan beads were stored in the NaOH solution for 2 h and then dehydrated by successive immersion in a series of water/ethanol baths (90/10, 70/30, 50/50, 30/70, 10/90, 0/100) for 15 min each. Then, the chitosan beads were dried with supercritical CO<sub>2</sub> (74 bar, 31.5 °C) using a Polaron 3100 apparatus.

### General Procedure for Pd-Catalysed Allylic Substitution of (*E*)-1,3-Diphenyl-3-acetoxyprop-1-ene with Dimethyl Malonate<sup>[16a]</sup>

(*E*)-1,3-Diphenyl-3-acetoxyprop-1-ene (100 mg, 0.40 mmol, 1 equiv.), AcOK (0.02 mmol, 0.05 equiv.), BSA (1.19 mmol, 3 equiv.) and dimethyl malonate (1.19 mmol, 3 equiv.) were added to the chitosan-SILP catalyst. The mixture was stirred at room temperature under an inert atmosphere and monitored by TLC. Products were extracted with diethyl ether (monitored by TLC). The combined organic layers were washed with water, dried over MgSO<sub>4</sub>, filtered and concentrated under reduced pressure. After the extraction of the product, the chitosan-SILP catalyst was dried under vacuum and reused for another catalytic cycle.

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