

# Heterogeneous iota carrageenan-based palladium catalysts for organic synthesis

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**Abstract:** Novel heterogeneous iota-carrageenan-based palladium catalysts were prepared and used in Suzuki cross coupling, Heck coupling and the transfer hydrogenation of olefins while using various substrates and solvents. In all of these reactions, heterogeneous systems based on xerogels or hydrogels were found to be active, and in certain cases, they yielded higher conversions than those of the homogeneous parent systems. Moreover, all the catalysts could be easily separated from the reaction mixtures and recycled without loss of activity.

**Keywords:** Polysaccharides; heterogeneous catalysis; heterogenization; Suzuki reaction, Heck reaction, transfer hydrogenation. ©2019 ACG Publications. All right reserved.

## 1. Introduction

Organic synthesis, integral to the development of numerous widely used materials, from fuels to pharmaceuticals to agrochemicals, is vital to our daily lives. The nature of the solvent in which an organic synthesis reaction takes place is among the most important determinants of how efficiently the reaction proceeds. As most organic transformations are performed in the liquid phase with the help of solvents to combine and solubilize reactants and catalyst and to facilitate heat and mass transfer, solvent choice is crucial.<sup>1,2</sup> Furthermore, solvent effects, in terms of physical or chemical modifications, were found to control not only the activity, but also the chemo-, region- and stereo-selectivity of many reactions. In addition, the solvent can also promote reaction workup by enabling both product separation from the solution and catalyst recycling to be done easily.<sup>3-5</sup> In general, reactant solubility was found to be the main factor affecting reaction performance while product solubility in the reaction mixture has the strongest effect on the workup procedure.

In catalytic reactions with transition metal complexes (TMCs), the solvent can also activate or deactivate the catalytic cycle, and it can even redirect the catalytic route and affect reaction selectivity.<sup>6,7</sup> Furthermore, in the case of TMC heterogenization, the advantages of homogeneous catalysis (e.g., high activity and selectivity) can be combined with those of heterogeneous systems (e.g., easy separation and recycling), and often, a particular solvent must be used to ensure heterogeneity.<sup>8-10</sup>

When a heterogeneous system is used, besides the need to avoid the leaching of the metal complex and loss of activity, the complexity and greenness of the preparation procedure and the nature of the support should also be considered. To that end, polymers that comprise diverse functional groups are very attractive matrices for metal complex immobilization via covalent or ionic interactions or by occlusion or

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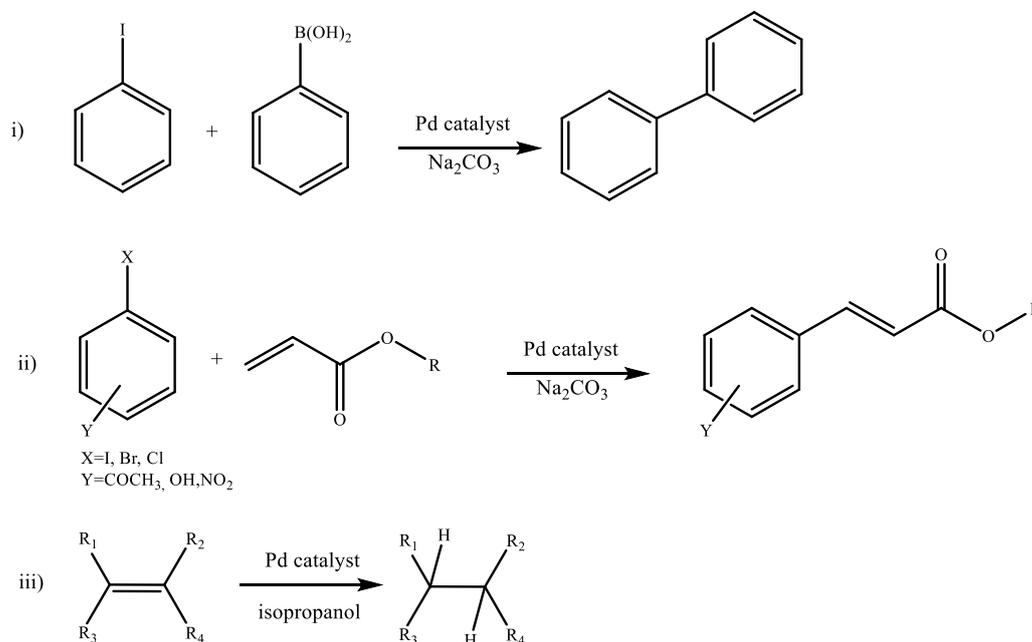
entrapment of the complex in a ship-in-a-bottle-like system.<sup>11,12</sup> Furthermore, non-toxic biopolymers, especially polysaccharides, and biodegradable macromolecules from renewable sources, used already in a wide variety of industries,<sup>13-15</sup> also hold great potential application as catalyst supports.<sup>16-20</sup>

Many organic transformations, from hydrogenation and oxidation to alkylation, carbonylation and C-C coupling, employ palladium-based catalysts. Whether in its metallic form, as a salt or as a metal complex, palladium is a highly versatile and active catalyst.<sup>21-23</sup> Though palladium can exist in number of different oxidation states, most organic synthesis reactions exploit Pd(0) and Pd(II). In addition, to enhance catalytic performance, the properties of the palladium species used must be tailored by combining each palladium species with a ligand.

We recently reported on two novel preparation techniques for the heterogenization of palladium complexes to form polysaccharide-based palladium catalysts in xerogels<sup>24,25</sup> and hydrogels.<sup>26</sup> In both preparations, palladium phosphine complexes with sodium triphenylphosphine trisulfonate (TPPTS) as the ligand were immobilized on various renewable polysaccharides. These new heterogeneous systems were successfully employed through Suzuki cross coupling with various halobenzenes and solvents, wherein the reactions with iodobenzene in ethanol yielded even higher conversions than those with their homogeneous analogues. At the end of the reaction, the new catalysts were successfully filtered from the reaction mixture and recycled.

The results of subsequent spectroscopic analyses led us to conclude that the Pd-complexes were immobilized to different polysaccharides via a new bond that was formed between the sulfonate groups of the TPPTS and the hydroxyl groups of the polysaccharides. In addition, in the xerogel preparation based on iota-carrageenan, both the Pd(II) and Pd(0) species were found. Moreover, it was demonstrated that Pd nanoparticles were formed during the synthesis of the xerogel heterogeneous catalyst.

In this study, we report the results of our in-depth comparative investigation of the performances of palladium iota-carrageenan-based xerogels and hydrogels in three representative reactions: (i) Suzuki cross-coupling of iodoenzenes with phenylboronic acid (Figure 1a), (ii) Heck coupling of halobenzenes and isobutyl acrylate (Figure 1b), and (iii) transfer hydrogenation of olefins (Figure 1c).



**Figure 1.** Representative reactions: (i) Suzuki cross-coupling, (ii) Heck coupling, (iii) transfer hydrogenation of olefins.

## 2. Experimental

### 2.1. Reagents

All polysaccharides and other chemicals (analytical grades) were purchased from Aldrich and see supporting information for details.

### 2.2. Catalyst preparation

#### 2.2.1. Preparation of *I*-PdCl<sub>2</sub>(TPPTS)<sub>2</sub> / *I*-Pd(OAc)<sub>2</sub>(TPPTS)<sub>2</sub> xerogels

A typical procedure for preparation of the heterogeneous xerogel catalyst, designated *I*-PdCl<sub>2</sub>(TPPTS)<sub>2</sub>, was performed as follows: First, 1 g of *i* polysaccharide was dissolved in 100 mL DDW by heating the solution to 50°C. The mixture was then stirred for several hours until a homogeneous solution was obtained. The required quantity of the complex was then prepared by dissolving 10 μmol PdCl<sub>2</sub> or Pd(OAc)<sub>2</sub> and 30 μmol of the TPPTS (Triphenylphosphine-3,3',3''-trisulfonic acid trisodium salt) ligand in 3 mL DDW in a second vial that underwent vortexing for homogenization. The mixed complex was then added, together with 3 mL of 1% wt/v of the *i* solution, to a 15 mL polypropylene tube that was sealed and then vortexed for homogenization. The next step was to deep-freeze the tube at -20°C for 24 h until all the liquid was frozen. The seal was removed, and the tube was then covered with a paraffin sheet pierced by a disposable toothpick and lyophilized for 48 h. At the end of this process, the dried 'sponge-like' catalyst was cut into pieces measuring ~ 1 cm × 1 cm and added to the reaction mixture.

#### 2.2.2. Preparation of hydrogels with chitosan: *I*-C-PdCl<sub>2</sub>(TPPTS)<sub>2</sub> / *I*-C-Pd(OAc)<sub>2</sub>(TPPTS)<sub>2</sub>

First, 1 g of each polysaccharide was dissolved in 100 mL DDW by heating the solution to 50°C, and the mixture was then stirred for several hours until a homogeneous solution was obtained. Furthermore, to dissolve chitosan completely, acetic acid (300 μL) was also added. Then the required quantity of complex (10 μmol PdCl<sub>2</sub> or Pd(OAc)<sub>2</sub> and 30 μmol TPPTS (Triphenylphosphine-3,3',3''-trisulfonic acid trisodium salt) ligand (0.021 g) was dissolved in 3 mL DDW in a vial, to which 3 mL of 1 wt.% of the polysaccharide solution was added, and the vial was mixed by vortexing for homogenization. Lastly, the hydrogel beads were prepared by using a 1 mL disposable plastic pipette to drop 3 mL of complex-polysaccharide solution into a vial that contained 3 mL of 1 wt.% chitosan solution. After several minutes, the hydrogel beads were separated from the solution with a tweezer, washed with DDW and transferred to a reaction mixture.

### 2.3. Reaction procedure

In a typical procedure, 10 μmol of palladium salt with 30 μmol of TPP/TPPTS (homogenous) or TPPTS (heterogeneous – in the form of xerogel or hydrogel) were added, together with the desired reactants in accordance with the reaction type, to a vial with 5 mL solvent.

#### 2.3.1. Suzuki cross coupling

The homogeneous or heterogeneous catalyst was added to a vial with 5 mL solvent together with 0.5 mmol iodobenzene, 0.75 mmol phenylboronic acid and 0.6 mmol Na<sub>2</sub>CO<sub>3</sub>. Then, the vial was placed in a preheated oil bath at 50°C and magnetically stirred for 24 h. At the end of the reaction, the reaction mixture was cooled. For cases in which a heterogeneous catalyst was used, the catalyst was removed by filtration of the reaction mixture through a paper filter. The organic phase was then analyzed to determine the reaction conversion by gas chromatography (GC) by using a HP-5 column.

#### 2.3.2. Heck coupling

In a typical procedure, homogeneous or heterogeneous catalyst was added to a vial with 5 mL solvent together with 0.5 mmol halobenzene, 0.75 mmol isobutyl acrylate and 0.6 mmol Na<sub>2</sub>CO<sub>3</sub>. The

vial was then placed in a preheated oil bath at 50°C and magnetically stirred for 24 h. At the end of the reaction, the reaction mixture was cooled. For cases in which a heterogeneous catalyst was used, the catalyst was removed by filtration of the reaction mixture through a paper filter. The organic phase was then analyzed to determine the reaction conversion by gas chromatography (GC) by using a HP-5 column.

### 2.3.3. Transfer hydrogenation of olefin

The homogeneous or heterogeneous catalyst was added to a vial with 5 mL isopropanol (IPA), which serves as solvent and hydrogen source, together with 0.5 mmol olefin. Then, the vial was placed in a preheated oil bath at 50°C and magnetically stirred for 24 h. At the end of the reaction, the reaction mixture was cooled. For cases in which a heterogeneous catalyst was used, the catalyst was removed by filtration of the reaction mixture through a paper filter. To determine the reaction conversion, the organic phase was then analyzed by gas chromatography (GC) by using a HP-5 column.

### 2.4. Leaching analysis

Catalyst leaching was tested for by using three different approaches: (1) performing a second reaction after the removal of the catalyst from the original reaction mixture and its addition to a fresh reaction mixture with the corresponding amounts of fresh substrates and sodium carbonate, and then testing for comparable catalytic performance; (2) proceeding with the reaction after the removal of the catalyst by running the reaction mixture under similar conditions for an additional 24 h to test whether the conversion increases with time; and (3) performing an inductively-coupled plasma optical emission spectrometry (ICP-OES) (Arcos, Spectro) analysis of the reaction medium after a 24 h reaction time and catalyst removal, to test for leftover palladium in the solution.

### 2.5. Catalyst recycling

Catalysts were recycled by adding the recovered catalyst to a solution with similar amounts of fresh substrates and base and running the reaction mixture under similar reaction conditions for an additional 24 h.

## 3. Results and Discussion

### 3.1. Chemistry

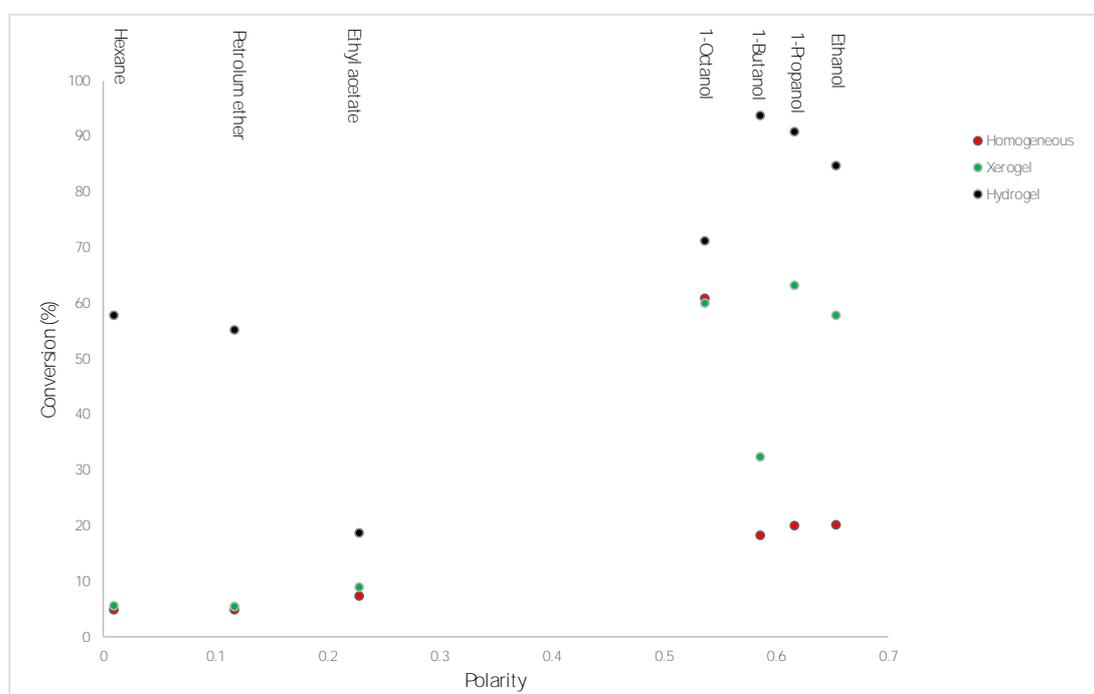
Essential to the successful heterogenization of a metal complex is to design and develop a simple and reproducible procedure in which the support neither dissolves nor undergoes any structural change while in the reaction mixture and the catalyst does not leach. As previously stated, we recently published a novel method for the preparation of a polysaccharide-based heterogeneous catalyst using palladium chloride or acetate with sodium triphenylphosphine trisulfonate (TPPTS) as the ligand.<sup>24-26</sup> Various renewable polysaccharides, and especially carrageenans, which are extracted from red seaweeds, were employed, yielding either xerogel or hydrogel heterogeneous systems that were successfully used in Suzuki cross-coupling. In addition, various chemical and physical spectroscopic and microscopic analytic tools were used in the characterization of the new heterogeneous systems, among them: FTIR, SEM, SEM-EDS, XPS, and TEM, and it was found that the metal complex was covalently immobilized on the polysaccharide via the sulfonate groups of TPPTS, where palladium nanoparticles were also formed. Encouraged by the performances of the new heterogeneous systems, we decided to run in depth study about the effect of the solvent on both xerogels and hydrogels in Suzuki cross-coupling, and to extend our study to new palladium catalyzed reaction such as Heck coupling and transfer hydrogenation of olefins.

In this study, therefore, both homogeneous and heterogeneous reactions, using Pd-based polysaccharides xerogels and hydrogels, were tested and compared in various organic solvents. Solvent choice in homogeneous reactions should ensure the solubility of all the compounds, as they are combined in a single liquid phase. For heterogeneous reactions, since they contain a solvent that dissolves the reactants while having no effect on the solid catalyst a broader range of solvents can be used. However,

the high water solubility of all the currently used polysaccharides precludes the use of water or a highly polar organic solvent, like DMSO, glycerol or methanol, in heterogeneous reactions.

### 3.1. Suzuki cross coupling

The important role of the reaction solvent in catalytic transformations is apparent in the Suzuki cross coupling reaction. Since its discovery in 1979,<sup>27</sup> the Suzuki reaction, involving the cross-coupling of aryl halides with arylboronic acids in the presence of a Pd catalyst and a base, has arguably become one of the most powerful tools for the construction of carbon-carbon bonds (Figure 1a).<sup>28-33</sup> The catalytic cycle of the reaction, which comprises oxidative addition, transmetalation, and reductive elimination, benefits from the use of electron-donating, sterically demanding ligands that promote the reaction's first and last steps.<sup>28</sup> Compared to other Pd-catalyzed cross coupling reactions, the Suzuki cross coupling reaction has clear advantages<sup>31</sup> that include: (i) mild reaction conditions, (ii) ready availability of organoboron reagents, (iii) tolerant toward various functional groups, and (iv) low toxicity of starting materials and by-products.<sup>34</sup> Indeed, these beneficial features have allowed researchers to exploit the reaction mechanism in a wide range of applications, from natural product synthesis to the development of polymeric materials. Choice of reaction solvent in the Suzuki reaction, however, is critical: since it must be able to dissolve hydrophobic halobenzene with hydrophilic arylboronic acid, a base and a catalyst, a polar solvent is usually used.



**Figure 2.** Effect of solvent on the performances of the homogeneous and heterogeneous iota-carrageenan-based Pd catalysts in the Suzuki reaction: ●homogeneous-PdCl<sub>2</sub>(TPP)<sub>2</sub>; ●heterogeneous I-PdCl<sub>2</sub>(TPPTS)<sub>2</sub> xerogel; ●heterogeneous I-C-PdCl<sub>2</sub>(TPPTS)<sub>2</sub> hydrogel.

Reaction conditions: 0.5 mmol iodobenzene, 0.75 mmol phenylboronic acid, 10 μmol PdCl<sub>2</sub>, 0.6 mmol Na<sub>2</sub>CO<sub>3</sub>, 5 mL solvent, 50°C, 4 h.

Due to the importance of the Suzuki reaction, over the last 40 years, numerous homogeneous and heterogeneous palladium catalysts have been synthesized and tested in it. Although the reaction with simple palladium salts, such as palladium chloride and palladium acetate, usually yields good performance, the use of these salts is known to be accompanied by catalyst deactivation due to the formation of palladium black.<sup>35</sup> The addition of phosphine ligands, such as triphenyl phosphine (TPP), can stabilize the catalyst and prevent its deactivation.<sup>36</sup> In recent years, many heterogeneous palladium catalysts have been developed for use in Suzuki cross coupling,<sup>37-39</sup> and among these are several that use polysaccharides as supports.<sup>40-47</sup> As previously stated, we also synthesized various Pd-based polysaccharide xerogels (sponge-like) and hydrogels (beads) (both gels with polysaccharide and CaCl<sub>2</sub>

solution or various polysaccharides and chitosan), and we demonstrated the performance of each in Suzuki cross coupling.<sup>24-26</sup>

The current study began with tests of the effect of the solvent type on the Suzuki cross coupling of iodobenzene with phenyl boric acid (Figure 1a), as illustrated in Figure 2. The solvents were characterized by their polarity, which was calculated based on IR, UV-VIS and mass spectra analyses.<sup>48</sup>

As illustrated in Figure 2, solvent polarity had a profound effect on catalytic activity in all the systems, homogenous and heterogeneous, with xerogel or hydrogels. In general, as expected, the more polar solvents enabled higher activity, which was probably due to the favorable solubility they promote of both reactants with the base. In addition, as previously reported, both heterogeneous systems yielded higher conversions than the homogenous system in all tested solvents. This finding can be attributed to the fact that the use of TPPTS as the ligand stabilizes the metallic center better than when using triphenyl phosphine (TPP). However, due to the high polarity of TPPTS, which renders it insoluble in most reaction solvents, it was replaced by TPP in all homogenous systems. Yet, the enhanced activity of TPPTS observed in the heterogeneous system can also be attributed to the effect of the polysaccharide whose backbone hydroxyl groups cause it to resemble water, that was previously reported to accelerate the Suzuki reaction.<sup>45,49,50</sup>

For all the solvents tested, the hydrogels yielded higher conversions than the xerogels, a finding that is probably due to the retention of water in the hydrogel beads, which, as previously stated, accelerated the reaction (Figure 2). The best result with the beads, a very high conversion of 94%, was achieved in 1-butanol while when xerogel was used, the reaction in 1-propanol achieved the highest conversion of 91%. Hence, it can be assumed that the optimal solvent polarity for the Suzuki reaction is in the range of 0.58-0.62. Finally, leaching and recycling experiments with the different solvents showed that the catalyst did not leach out of either the xerogel- or hydrogel-based heterogeneous system and that the conversions in the second runs were comparable to those in the initial runs.

### 3.2. Heck coupling

Pd-catalyzed C-C coupling of aryl halides with activated alkenes, also known as Heck coupling (Figure 1B), is another useful method for carbon-carbon bond formation.<sup>51-55</sup> To assess the full potential of the new heterogeneous systems, therefore, they were also tested in Heck coupling reactions. Table 1 summarizes the homogeneous and heterogeneous reactions with iodobenzene and isobutyl acrylate in ethanol as the representative solvent. Both palladium chloride and palladium acetate, with and without TPPTS as ligand, were used (entries 1-4), wherein the addition of the ligand increased the conversion slightly. Both types of heterogenous systems—xerogels of iota (I-PdCl<sub>2</sub>(TPPTS)<sub>2</sub> or I-Pd(OAc)<sub>2</sub>(TPPTS)<sub>2</sub>, (entries 5 and 6)) and hydrogels of I and chitosan (I-C-PdCl<sub>2</sub>(TPPTS)<sub>2</sub> or I-C-Pd(OAc)<sub>2</sub>(TPPTS)<sub>2</sub>, (entries 7 and 8))—yielded conversions similar to those observed in the homogeneous parent systems (entries 2 and 4), except the reaction with I-C-PdCl<sub>2</sub>(TPPTS)<sub>2</sub> (entry 7).

**Table 1.** Performances of homogeneous and heterogeneous iota-carrageenan-based Pd catalysts in the Heck coupling reaction<sup>a</sup>

Entry	Catalyst	Conversion (%)
1	PdCl <sub>2</sub>	12
2	PdCl <sub>2</sub> (TPPTS) <sub>2</sub>	15
3	Pd(OAc) <sub>2</sub>	11
4	Pd(OAc) <sub>2</sub> (TPPTS) <sub>2</sub>	13
5	I-PdCl <sub>2</sub> (TPPTS) <sub>2</sub>	12
6	I-Pd(OAc) <sub>2</sub> (TPPTS) <sub>2</sub>	17
7	I-C-PdCl <sub>2</sub> (TPPTS) <sub>2</sub>	7
8	I-C-Pd(OAc) <sub>2</sub> (TPPTS) <sub>2</sub>	15
9 <sup>b</sup>	I-C-Pd(OAc) <sub>2</sub> (TPPTS) <sub>2</sub>	12
10 <sup>c</sup>	I-C-Pd(OAc) <sub>2</sub> (TPPTS) <sub>2</sub>	13

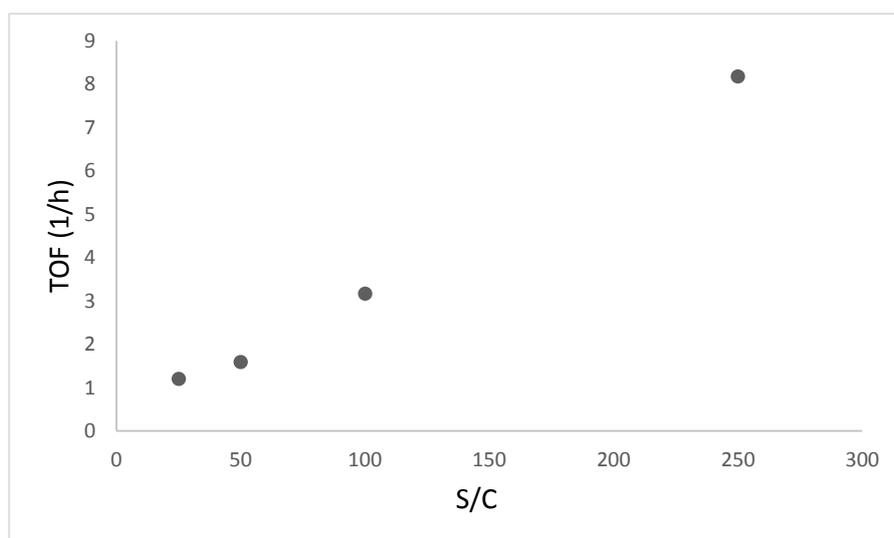
<sup>a</sup>Reaction conditions: 0.5 mmol iodobenzene, 0.75 mmol isobutyl acrylate, 10 μmol Pd salt, 0.6 mmol Na<sub>2</sub>CO<sub>3</sub>, 5 mL ethanol, 50°C, 4 h.

<sup>b</sup>Ethanol replaced by toluene.

<sup>c</sup>Ethanol replaced by ethylacetate.

Moreover, all catalysts were easily separated from their respective reaction mixtures without loss of activity and without leaching of the complex. Finally, the heterogeneous system with I-C-PdCl<sub>2</sub>(TPPTS)<sub>2</sub> was also used in toluene and ethyl acetate, where the conversions were slightly lower, but in both cases, the catalyst was easily and efficiently recycled.

The effect of the substrate to catalyst (S/C) ratio on catalytic performance was also studied with the new I-Pd(OAc)<sub>2</sub>(TPPTS)<sub>2</sub> xerogel-based heterogeneous system in the Heck reaction while maintaining catalyst constant loading. As illustrated in Figure 3, the turn over frequency (TOF) values increased linearly with the S/C ratio, showing that the catalyst can function at high capacity. These results are in agreement to our former results.<sup>25</sup>



**Figure 3.** Effect of S/C ratio on the catalytic performance of I-Pd(OAc)<sub>2</sub> xerogel in the Heck reaction.

Reaction conditions: 10  $\mu$ mol Pd(OAc)<sub>2</sub> in I-Pd(OAc)<sub>2</sub>(TPPTS)<sub>2</sub>, 0.6 mmol Na<sub>2</sub>CO<sub>3</sub>, 5 mL ethanol, 50°C, 4 h. TOF = (S/C)\*Conversion/time.

Finally, the performance of the new heterogeneous catalyst I-Pd(OAc)<sub>2</sub>(TPPTS)<sub>2</sub> xerogel in the Heck reaction was tested with different substrates (Table 2).

**Table 2.** Heterogeneous I-Pd(OAc)<sub>2</sub>(TPPTS)<sub>2</sub> xerogel performance in Heck reactions with representative substrates<sup>a</sup>

Entry	Halobenzene	Conversion (%)
1	Iodobenzene	17
2	Bromobenzene	13
3	Chlorobenzene	11
4	4-Chloroacetophenone	15
5	4-Chlorobenzyl alcohol	36
6	1-Chloro-3-nitrobenzene	37

<sup>a</sup>Reaction conditions: 0.5 mmol halobenzene, 0.75 mmol isobutyl acrylate, 10  $\mu$ mol Pd(OAc)<sub>2</sub> in I-Pd(OAc)<sub>2</sub>(TPPTS)<sub>2</sub>, 0.6 mmol Na<sub>2</sub>CO<sub>3</sub>, 5 mL ethanol, 50°C, 4 h.

Though replacing iodobenzene (entry 1) with bromobenzene (entry 2) or chlorobenzene (entry 3) resulted in a lower conversion value in each case, surprisingly, the conversion while using chlorobenzene, the least active of the halobenzene was tested, was not drastically different from that obtained with iodobenzene. Furthermore, the addition of different groups to the aromatic ring of chlorobenzene yielded higher conversion values than were obtained in the conversion done with chlorobenzene alone (entries 4-6).

### 3.3. Transfer hydrogenation of olefin

Catalytic hydrogenation is a fundamental reaction in chemistry,<sup>56</sup> and one of the best known routes by which to achieve such a transformation is by catalytic transfer hydrogenation.<sup>57</sup> The transfer hydrogenation of olefin can be performed with different TMCs and supported metal catalysts by using a variety of hydrogen donors. In this type of reaction, an organic compound – usually an alcohol, especially a secondary alcohol and often 2-propanol (IPA-isopropanol) – is used as a hydrogen-donor in the presence of a catalyst. A distinct advantage of this pathway is that it is performed in the absence of gaseous hydrogen, the inclusion of which necessitates the use of extra precautionary measures and special, dedicated equipment.

The investigation began by performing the homogeneous transfer hydrogenation reaction of cyclohexen as a representative olefin with different pallidum catalysts in IPA (Table 3). It can be seen that catalysts based on pallidum chloride (entries 1 and 2) showed slightly higher conversions than the reactions with those based on palladium acetate (entries 3 and 4). Furthermore, addition of the TPPTS ligand to both palladium salts resulted in lower conversions.

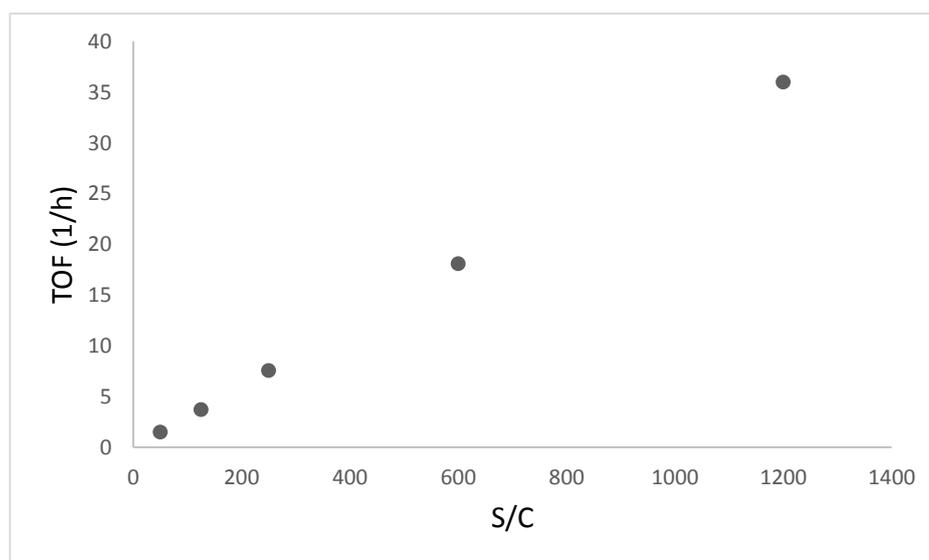
Next the new palladium-based polysaccharide systems were tested for the first time in the transfer hydrogenation reaction. Xerogels of iota (entries 5 and 6) and hydrogels of iota and chitosan (entries 7 and 8) with both palladium complexes were shown to be effective, and again, the catalyst based on PdCl<sub>2</sub>(TPPTS)<sub>2</sub> yielded better performance than those based on Pd(OAc)<sub>2</sub>(TPPTS)<sub>2</sub>. In addition, among the four heterogeneous systems, I-PdCl<sub>2</sub>(TPPTS)<sub>2</sub> (entry 4) yielded the highest conversion, which was also comparable to that of the homogeneous parent system (entry 1). The hydrogel catalysts, in contrast, yielded much lower conversions than the xerogels, a finding that is probably due to the poor solubility of the hydrophobic olefins in the water-rich hydrogel. Replacing the cyclohexene with 1-octene also showed much higher activity with I-PdCl<sub>2</sub>(TPPTS)<sub>2</sub>. Additionally, while the reaction with 3-methyl-2-cyclohexen-1-one resulted in a very low conversion, substituting it with isobutyl acrylate yielded high activity, a result that may be due to the activation of the double bond by the acrylate.

**Table 3.** Performances of homogeneous and heterogeneous I-Pd xerogel and hydrogel systems in olefin transfer hydrogenation reactions<sup>a</sup>

Entry	Catalyst	Substrate	Q3		
			Con.-2h (%)	Con.-5h (%)	Con.-24h (%)
1	PdCl <sub>2</sub>	Cyclohexen	30	50	72
2	PdCl <sub>2</sub> (TPPTS) <sub>2</sub>	Cyclohexen	24	34	55
3	Pd(OAc) <sub>2</sub>	Cyclohexen	19	19	66
4	Pd(OAc) <sub>2</sub> (TPPTS) <sub>2</sub>	Cyclohexen	41	43	50
5	I-PdCl <sub>2</sub> (TPPTS) <sub>2</sub>	Cyclohexen	25	32	72
6	I-Pd(OAc) <sub>2</sub> (TPPTS) <sub>2</sub>	Cyclohexen	11	16	25
7	I-C-PdCl <sub>2</sub> (TPPTS) <sub>2</sub>	Cyclohexen	4	-	20
8	I-C-Pd(OAc) <sub>2</sub> (TPPTS) <sub>2</sub>	Cyclohexen	1	-	3
9	I-PdCl <sub>2</sub> (TPPTS) <sub>2</sub>	1-Octene	35	-	72
10	I-C-Pd(OAc) <sub>2</sub> (TPPTS) <sub>2</sub>	1-Octene	6	-	8
11	I-PdCl <sub>2</sub> (TPPTS) <sub>2</sub>	3-Methyl-2-cyclohexen-1 one	-	-	7
12	I-PdCl <sub>2</sub> (TPPTS) <sub>2</sub>	Isobutyl acrylate	-	-	66

<sup>a</sup>Reaction conditions: 0.5 mmol olefin, 10 μmol catalyst, 5 mL IPA, 50°C. Con: Conversion

The effect of the substrate to catalyst ratio on reaction activity, represented by TOF, was also studied with I-PdCl<sub>2</sub>(TPPTS)<sub>2</sub> (Figure 4). In this case, the TOF was found to increase linearly with the increase in the S/C ratio, revealing that each catalyst molecule as the ability to work in higher capacity.



**Figure 4.** Effect of S/C ratio on the catalytic performance of the I-PdCl<sub>2</sub> xerogel in the transfer hydrogenation reaction.

Reaction conditions: 10  $\mu$ mol of PdCl<sub>2</sub>(TPPTS)<sub>2</sub> in I, 5 mL IPA, 50°C, 24 h.

TOF = (S/C)\*Conversion/time.

#### 4. Conclusion

Palladium-based catalysts with TPPTS as the ligand were successfully immobilized to iota and iota-chitosan polysaccharides to yield xerogels and hydrogels, respectively. The new heterogeneous systems were effectively used in three representative palladium catalyzed organic transformations: Suzuki cross coupling, Heck coupling and the transfer hydrogenation of olefins. In the Suzuki cross-coupling of iodobenzene and phenylboronic acid in various solvents, both the xerogels and the hydrogels exhibited higher activities than that of the homogeneous parent system. Here the performances of the hydrogels were superior, an outcome that is probably due to the presence of water in the beads, which enhances the reaction activity. In addition, catalytic performance was profoundly affected by the polarity of the solvent, which should optimize the solubilities of all reaction components, and the best conditions were obtained with alcohols whose polarities were in the range of 0.58-0.62. The heterogeneous catalysts were also successfully employed in the Heck coupling reaction while using several different substrates and solvents. In contrast to the findings in the Suzuki cross-coupling reaction, in this case, the hydrogels were much less effective than the xerogels. In addition, based on TOF values, increasing the S/C ratio linearly increased the number of cycles per each catalyst molecule. The new catalysts were also tested in the transfer hydrogenations of several olefins where IPA was used as the solvent and hydrogen donor. In this reaction, I-PdCl<sub>2</sub>(TPPTS)<sub>2</sub> was found to be the best choice among all the heterogeneous systems. Lastly, all of the heterogeneous systems were easily filtered from the three reaction mixtures and recycled without loss of activity.

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