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Pd-Based Polysaccharide Hydrogels as Heterogeneous Catalysts for Oxidation of Aromatic Alcohols

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Abstract: Immobilization of $Pd(OAc)_2(TPPTS)_2$ in various renewable polysaccharides hydrogels, yielded heterogeneous catalysts that were successfully used, for the first time, in the aerobic oxidation of benzylic alcohol. The new catalysts were easily removed from the reaction mixture and recycled with some loss of activity. Among all tested polysaccharides, iota-carrageenan was found to be the most suitable support, using calcium chloride as a gelation agent.

Keywords: aerobic oxidation; heterogenization; hydrogels; iota-carrageenan; palladium

1. Introduction

Polysaccharides can form several types of solid gels, among which the most applicable as supports for catalysis are hydrogels and xerogels [1,2]. A hydrogel is a three-dimensional polymeric network that has the ability to swell and hold a water within its structure, but without dissolving in its aqueous media. Hydrogels can be synthesized in several "classical" chemical ways [3,4], one of which is to combine a polyelectrolyte with a univalent/multivalent ion of the opposite charge. However, their stability is dependent on the level of cross-linking and/or the ionic, H-bonding, or hydrophobic forces between the molecules. On the other hand, xerogel is a dry support obtained by evaporation of the liquid phase of a gel by different techniques [2].

Renewable polysaccharide-based-hydrogels have become attractive materials that are used in many applications (including textile, food, printing, biomedical and pharmaceutical, toxic ion removal, and water purification [3,5–9]) due to their characteristics such as biodegradability, biocompatibility, abundance, stimuli-responsive characteristics, and biological functions. Among them, carrageenan forms are well-known by their high capacity to absorb water, abundant availability, and non-toxicity [10,11].

Polysaccharide hydrogels have also been used as supports for catalysts [12–14]. For instance, enzymes and living cells were immobilized in different polysaccharide hydrogel systems as these preserve the aqueous surroundings that are critical to proper enzyme and cell performance [15,16]. Furthermore, hydrogel systems were also found to be useful for the heterogenization of transition metal complexes (TMCs) [17], although the use of polysaccharides for such a purpose is still in its infancy.

In our ongoing effort to explore the use of polysaccharide-based heterogeneous systems, we prepared palladium and rhodium catalysts supported on various polysaccharide supports in the form of xerogel [18–21] and hydrogel [22]. The catalysts were used in Suzuki cross-coupling, Heck coupling, and transfer hydrogenation of olefins. Recently, for the first time, we also used palladium-based polysaccharide xerogels as a low-cost and recyclable heterogeneous catalyst in the aerobic oxidation of benzylic alcohols [23]. It was found that this palladium catalyst in the form of an xerogel yielded an increase in activity in every reuse due to the reduction of palladium and formation of nanoparticles during the reaction in ethanol.

In general, alcohol oxidation is a fundamental organic transformation that can proceed with various organic and inorganic oxidants [24–27]. Yet, among all oxidation pathways, aerobic oxidation is the simplest, cheapest, and most environmentally friendly route, as oxygen is readily available and water is the only by-product [28,29].

Herein, we report for the first time on the aerobic oxidation of benzylic alcohol in several solvents, using Pd(OAc)$_2$(TPPTS)$_2$ that was immobilized on different renewable polysaccharide hydrogels, according to a method that we published before, as heterogeneous catalyst (Figure 1). Beside the importance to find greener routs that use environmentally friendly oxidant and recyclable catalyst, using aerobic oxidation as a model reaction also allow exploring the use of such catalytic system in three phase reaction.
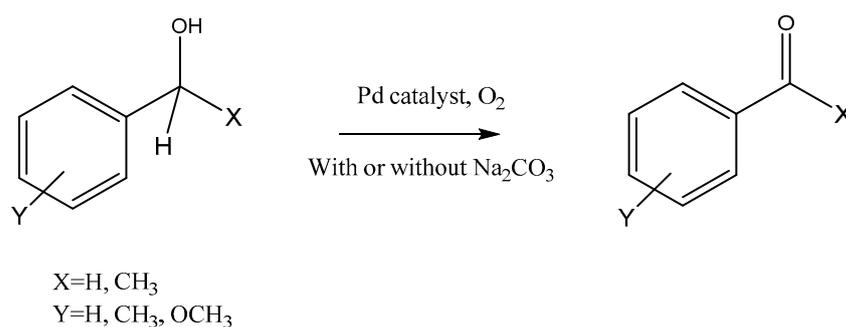

X=H, CH$_3$
Y=H, CH$_3$, OCH$_3$

Figure 1. Aerobic oxidation of benzylic alcohols.

2. Experimental Section

2.1. Polysaccharides Catalyst and Reagents

All the materials used i.e., polysaccharides, catalysts, solvents, and substrates analytical grades) were purchased from Sigma Aldrich Israel.

2.2. Preparation of Hydrogel Beads with Calcium Chloride (I-CaCl$_2$)

The hydrogels with calcium chloride were prepared by dissolving 1 g of each polysaccharide (iota (I), kappa (K), alginate (A) and guar gum (G)) in 100 mL double distilled water (DDW) while heating the solution to 50 °C, and stirring the mixture for several hours until a homogeneous solution was obtained. In the next step, palladium acetate (10 µmol) was added together with 3 mL distillated water and 30 µmol of 3,3′,3″-Phosphanetriyltris trisodium salt (TPPTS), to a vial, and mixed at room temperature for 5 min. Then, 3 mL of the polysaccharide solution (1 wt.%) was added to the vial with the catalyst solution and mixed by vortexing until an homogenized solution was obtained.

To prepare the hydrogel beads, a 1 mL disposable plastic pipette was used, to drop the homogenized solution with the catalyst into a solution of calcium chloride in DDW (0.5 M). Then, it was magnetically stirred, and the separation of the beads from the solution was done with a tweezer. Finally, the beads were washed with DDW, and transferred fresh to the reaction mixture.

2.3. Preparation of Hydrogel Beads with Chitosan (I-C)

The hydrogels with Chitosan (C) were prepared using the complex-polysaccharide solution (prepared as detailed above). In this case, 6 mL of each complex-polysaccharide solution was dropped with a 1 mL disposable plastic pipette into a vial that contained 3 mL of 1 wt.% chitosan solution, which was prepared as detailed above with the addition of 300 µL acetic acid. Then, the mixture was stirred for short period and the hydrogel beads, which were separated from the solution with a tweezer, were washed with DDW and transferred fresh to a reaction mixture.

2.4. Reaction Procedure

A typical procedure was performed by adding 10 μmol of palladium catalyst (homogenous or heterogeneous) and 0.925 mmol benzyl alcohol to a vial with 5 mL ethanol. Then, the mixture was magnetically stirred in a preheated oil bath at 60 °C for 24 h. Afterward, the reaction mixture was cooled and was filtered through a 0.45-μm Millex LH. The organic phase filtrate was analyzed by gas chromatograph (GC) using HP-5 column. In an alternative system, a 10 mL vial with a 5 mL reaction mixture was shaken in a Julabo SW22 water bath at 90 rpm and 60 °C for 24 h. Finally, for high pressure reactions, a home-made 10 mL stainless steel reactor with magnetic stirring was used, following the same procedure.

Leaching of the catalysts was tested in three ways: (1) a second reaction was performed after the removal of the catalyst from the original reaction mixture following by the addition of the catalyst to a fresh reaction mixture with similar amounts of fresh substrates, and running the reaction mixture under the same reaction conditions for an additional 24 h; (2) running the reaction mixture under similar conditions for an additional 24 h after the removal of the catalyst, to check whether the conversion increases with time; and (3) by detecting palladium leftovers in the reaction medium following the 24 h of the first cycle, using ICP-OES (Arcos, Spectro), to check for traces of palladium in the reaction solution.

2.5. Scanning Electron Microscope (SEM) Analysis

Scanning electronic microscopy (SEM) (FEI Quanta 200 (ThermoFisher), with acceleration voltage of 25 Kw) was used to scan the hydrogel beads that were coated with gold.

2.6. High-Resolution Transmission Electron Microscopic (HRTEM) Analysis

High-resolution transmission electron microscope (HRTEM–FEI Talos F200C TEM operated at 200 kV at room temperature) was used to scan the beads that were prepared by depositing a drop of ethanol suspension of the crushed solid catalyst on a carbon-coated Cu grid.

3. Results and Discussion

The investigation initiated with the homogeneous aerobic oxidation of benzyl alcohol in several representative solvents differing in their polarities, in the presence of a palladium acetate ($Pd(OAc)_2$) or palladium acetate complex ($Pd(OAc)_2(TPPTS)_2$) (Table 1). The reaction with palladium acetate yielded high performance in both the most polar and least polar solvents, ethanol, and hexane respectively (Table 1, entry 1 and 4). This might be attributed to the fact that the polarity of the solvent affect both reactants and catalyst solubilities, and while the solubility of the catalyst increases in more polar solvents, the solubility of oxygen decreases.

Table 1. Reactions conversions in representative solvents [a].

Entry	Solvent	RP [b]	Pd(OAc)$_2$	Pd(OAc)$_2$(TPPTS)$_2$	I-CaCl$_2$	I-C
1	Ethanol	0.654	50	40 (78) [c]	25	4
2	Ethyl acetate	0.228	26	28 (59) [c]	16	3
3	Petroleum ether	0.111	31	25 (55) [c]	38	14
4	Hexane	0.009	48	47 (86) [c]	66	35

[a] Reaction conditions: 0.925 mmol benzyl alcohol, 10 μmol catalyst, 5 mL solvent, 60 °C, 1 atm air, 24 h; [b] Relative polarity that was normalized from measurements of solvent shifts of absorption spectra [30]; [c] 1 mL of water and 4 mL solvent.

It is well-known that addition of ligand to the metal center can activate the catalyst and/or reduce deactivation of the catalysts due to formation of palladium black. Thus, the water-soluble phosphine, TPPTS, which is also used in the heterogenization of the metal to the polysaccharides, was added to palladium acetate, yielding a significantly higher conversion rate in ethanol which is the most polar solvent (Table 1, entry 1).

As previously stated, hydrogel beads can be easily prepared by adding polysaccharide and catalyst to calcium chloride or chitosan solutions [22]. Hence, in the next step, $Pd(OAc)_2(TPPTS)_2$ was immobilized in iota-carrageenan (I), where the preparation done by dropping an aqueous solution of the complex and I into an aqueous solution of calcium chloride to yield I-$CaCl_2$ beads (Figure 2A). As ICP-OES detection did not reveal any palladium in the solution after separation of the beads, it was concluded that the amount of palladium in the hydrogels is also 10 micromoles. The SEM and TEM images of I-$CaCl_2$ beads are shown in Figure 2B,C, respectively; The shape of the hydrogels is spherical and their size ranges from 1.5 to 3 mm. Furthermore, the beads have a sealed surface texture and no palladium nanoparticles were detected.
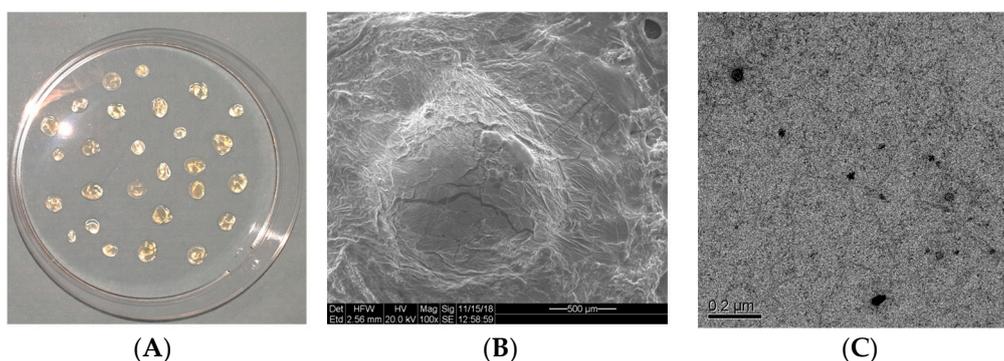

(**A**) (**B**) (**C**)

Figure 2. I-$CaCl_2$ (10 µmol $Pd(OAc)_2(TPPTS)_2$ supported on I with 0.5 M $CaCl_2$ aqueous solution) (**A**) Photo image (**B**) SEM image (**C**) TEM image.

Employing the new heterogeneous system in the aerobic oxidation of benzyl alcohol yielded the highest conversion in hexane, which was even higher than the conversion of both tested homogeneous reactions with the palladium salt or with the palladium complex (Table 1, entry 4). Also, in the case of petroleum ether the heterogeneous system was more active than the corresponding two homogeneous reactions (Table 1, entry 3), whereas in the polar solvents the conversions were lower in comparison to their homogeneous analogs. Notably, in the presence of ethanol the conversion rate of the heterogeneous catalyst was much lower than the parent homogeneous complex (Table 1, entry 1). Moreover, it was observed that the beads that were mixed in ethanol were crumpled, while the beads in petroleum ether and hexane kept their form. Thus, it is suggested that the water that was embedded in the hydrogel split from the gel and mixed with the ethanol, while in the case of the apolar solvents the hydrogels retained the water. Furthermore, it was found that addition of water to the homogeneous reactions yielded higher conversion rates with all the solvents (column 4 in brackets), leading to the conclusion that water accelerates the reaction. Thus, it seems that the water which was left in the hydrogel when hexane and petroleum ether were used as solvents is what increased the product yield.

Preparing hydrogel by dropping an aqueous solution of $Pd(OAc)_2(TPPTS)_2$ and I, which has bare sulfate groups on its backbone, into an aqueous solution of chitosan with which has ammonium groups on the polymer chain, also yielded hydrogels that immobilized the complex. However, the beads that were formed by this preparation procedure were much smaller and stiffer, leading also to lower conversion rates in all solvents. In addition, the conversion rates in hexane and petroleum ether were still the highest (Table 1, entries 4 and 5, respectively).

In the next step, four representative polysaccharides with different structure and functional groups were used (Table 2): I and K- carrageenan forms with hydroxyl and anionic sulfate groups in their structure; A with carboxylate and hydroxyl groups; and Gthat has only hydroxyl groups on its backbone. All of these were used to immobilize the palladium complex via the first preparation technique with calcium chloride (Table 2). It was found that adding $I/K/A$-$Pd(OAc)_2(TPPTS)_2$ solutions to an aqueous 0.5 M calcium

chloride solution yielded stable beads, but when G was used instead, no beads were formed. This informs us that the existence of acidic groups on the polysaccharide— either sulfate groups in iota and kappa or carboxylic groups in alginate—which can interact with the calcium ions, is necessary to form a hydrogel.

Table 2. Characteristics and performance of heterogeneous systems with representative polysaccharides [a].

Polysaccharide	Branched/Linear	Building Block	Functional Groups	Conversion (%)
Iota (I)	Linear	D-Gal-4-sulfate,3,6-anhydro-D-Gal-2-sulfate	$-OH, -OSO_3^-$	66 71 [b] 40 [c]
Kappa (K)	Linear	D-Gal-4-sulfate,3,6-anhydro-D-Gal	$-OH, -OSO_3^-$	44
Alginate (A)	Linear	β-(1 → 4)-linked mannose and α-L guluronate	$-OH, -COO-$	34
Guar gum (G)	Branched	β-(1 → 4)-linked mannose	$-OH$	-

[a] The hydrogels were prepared with 0.5 M $CaCl_2$. Reaction conditions: 0.925 mmol benzyl alcohol, 10 μmol catalyst, 5 mL hexane, 60 °C, 1 atm air, 24 h; [b] The hydrogels were prepared with 0.25 M $CaCl_2$; [c] The hydrogels were prepared with 1 M $CaCl_2$.

At the next stage, the investigation was focused on the reactions with the polysaccharide-based hydrogels in hexane, which was selected on account of its performance qualities. Conversion rates decreased in the order of I > K > A (Table 2). It can be suggested that both the structure and the acidity of the functional groups may play a critical role in the reaction performance. For example, I that has more sulfate ester in its structure in comparison to K yielded higher conversion rates (Table 2). In addition, I and K that bare sulfate ester groups on their backbone, which are more acidic than the carboxylate groups on A, yielded higher conversion rates. It seems that the nature of the functional groups on the polysaccharides affects both the structure of the hydrogel beads and hence the permeability of the substrate through the beads, and the amount of water that was retained in the beads, thus effecting the reaction performance. Finally, changing the concentration of $CaCl_2$ in the solution in the range of 0.25–1 M, yielded a decrease in the conversion rates, probably because the I-$CaCl_2$ hydrogels were more condensed. Yet when the beads were prepared with a 0.25 M $CaCl_2$ solution they were less stable but yielded the highest conversions (Table 2).

The I-based catalyst was recycled for multiple runs in hexane in order to better evaluate the catalyst potential of the new heterogeneous system (I-$CaCl_2$) (Table 3). Notably, the catalyst could easily be recycled after it was separated from the reaction mixture. In addition, redoing the reaction with the reaction mixture after filtration of the catalysts did not yield an increase of the conversion—implying that the catalyst had not leached into the solution. Furthermore, as detected by ICP-OES, no palladium leftovers were found in the filtrated reaction mixture, indicating that there was no palladium leaching. However, the conversion rates were tremendously decreased in each reuse, which could be attributed to the fact that the hydrogel was crushed by the stirrer, thus leading to some catalyst loss during recycling, and to the loss of water, which as noted before enhance the reaction (Table 3, entries 2 and 3). This suggested that using a shaker instead of magnetic stirring might improve the ability to recycle the hydrogels. However, as was expected, due to the lower mixing ability of the shaker, the conversion rate decreased from 66% to 49% in the first run (Table 3, entries 1 and 4, respectively), but again the second and third runs yielded a much lower conversion rate (Table 3, entry 5 and 6, respectively). Finally, the hydrogels were also recycled in ethanol, and the drop in conversion from one cycle to another was lower (Table 3, entries 14–16).

To improve the reaction performance, the effect of air pressure was tested, as it was suggested that increasing the partial oxygen pressure would lead to a higher oxygen concentration in the solvent. Indeed, increasing the air pressure from 1 atm to 3.8 atm slightly increased the conversion rates (Table 3, entries 1 and 8, respectively). However, when oxygen was used instead of air, conversion rates slightly decreased (Table 3, entries 9 and 10, Table 3). Finally, different benzylic alcohols were employed, and their oxidation

with the new heterogeneous catalysts was also successful. Moreover, it was found that the addition of an electron donating group, such as methoxy, tremendously increased the conversion rate (Table 3, entries 11–13). However, when aliphatic alcohols were used, only negligible conversion rates were detected.

Table 3. Catalyst recycling and effect of oxygen concentration and substrate type on performance in hexane [a].

Entry	Mixing	Substrate	Pressure (atm)	Cycle	Conversion (%)
1	Stirring	Benzyl alcohol	1	1	66
2	Stirring	Benzyl alcohol	1	2	33
3	Stirring	Benzyl alcohol	1	3	10
4	Shaking	Benzyl alcohol	1	1	49
5	Shaking	Benzyl alcohol	1	2	28
6	Shaking	Benzyl alcohol	1	3	25
7	Stirring	Benzyl alcohol	1	1	22
8	Stirring	Benzyl alcohol	3.8	1	69
9	Stirring	Benzyl alcohol	1 [b]	1	60
10	Stirring	Benzyl alcohol	3.8 [b]	1	55
11	Stirring	1-Phenyl ethanol	1	1	63
12	Stirring	4-Methylbenzyl alcohol	1	1	69
13	Stirring	4-Methoxylbenzyl alcohol	1	1	99
14	Stirring	Benzyl alcohol [c]	1	1	25
15	Stirring	Benzyl alcohol [c]	1	2	23
16	Stirring	Benzyl alcohol [c]	1	3	19

[a] Reaction conditions: 0.925 mmol substrate, 10 μmol catalyst (I-CaCl$_2$), 5 mL Hexane, 60 °C, 24 h; [b] Oxygen instead of air; [c] The solvent used was 5 mL Ethanol.

4. Conclusions

Heterogeneous palladium catalysts, prepared using a very simple and straightforward method, were successfully employed in the aerobic oxidation of benzylic alcohols. The new hydrogels, which were prepared by addition of Pd(OAc)$_2$(TPPTS)$_2$ and a polysaccharide aqueous solution to either CaCl$_2$ or chitosan aqueous solutions, yielded a recyclable catalyst, in which the metal did not leach into the reaction mixture. It was found that the hydrogels prepared with CaCl$_2$ were less stiff and yielded higher conversion rates then the hydrogels prepared with chitosan. In addition, among all the polysaccharides tested, the hydrogels that were prepared with iota-carrageenan yielded the highest performance rates.

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