The Effect of Alcohol on Palladium Nanoparticles in \( i\text{-Pd(OAc)}_2\text{(TPPTS)}_2 \) for Aerobic Oxidation of Benzyl Alcohol

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Abstract: In the heterogeneous catalyst \( i\text{-Pd(OAc)}_2\text{(TPPTS)}_2 \), Pd(II) was reduced to Pd(0) by using different alcohol solvents, and the catalyst's activity was studied in the aerobic oxidation of benzyl alcohol. We studied the effects of the impregnation time in ethanol as a solvent and the use of various alcoholic solvents on the size of palladium nanoparticles. We found that the reduction of palladium by the various alcohols yielded palladium nanoparticles that were active in the aerobic oxidation of benzyl alcohol. As determined by DLS, TEM, and zeta potential analyses, both the impregnation time in ethanol and the type of alcohol used were observed to affect nanoparticle formation, particle size distribution, and agglomeration, as well as the conversion rate. The palladium nanoparticles' hydrodynamic diameter sizes obtained during the 24 h of impregnation time were in the range of 10–200 nm. However, following 24 h of impregnation in ethanol the nanoparticles tended to form aggregates. The conversion rates of all the primary alcohols were similar, while for secondary alcohol, in which the hydrogen of the hydroxyl is less acidic and there is steric hindrance, the conversion was the lowest. Performing the oxidation using the solvent 1-propanol yielded smaller nanoparticles with narrower distributions in comparison to the reaction that was observed when using the ethanol solvent. On the other hand, the relatively high particle size distribution in 1-hexanol yielded agglomerates.

Keywords: aerobic oxidation; heterogenization; iota carrageenan; nanoparticles; palladium

1. Introduction

The selective conversion of alcohols to their corresponding carbonyl compounds is a fundamental transformation in organic chemistry [1–4]. In this light, among all the oxidation methods, aerobic oxidation is the simplest, cheapest, and most environmentally friendly route to the oxidization of alcohols [5,6]. Moreover, oxygen is an ideal oxidant as it is readily available and tends to form water as a sole by-product.

The aerobic oxidation of alcohols can be performed by using various homogeneous and heterogeneous metal catalysts [7,8]. Various noble metals, such as Pd, Pt, and Ru, with the addition of different activating ligands, were successfully used as homogeneous complexes to this end [9,10]. However, their high prices and tedious preparation, separation, and recycling procedures constitute a huge drawback. Therefore, using heterogeneous systems is advantageous. One method used to prepare an active and selective heterogeneous system is to immobilize metal complexes or metal nanoparticles on a variety of organic and inorganic supports, thus combining the advantages of homogeneous catalysis (high activity and selectivity) with those of heterogeneous catalysis (easy recovery and recycling) [11,12].

Organopalladium chemistry, which deals with organic palladium compounds and their reactions, is widely used in organic synthesis. With its ability to catalyze many reactions, palladium can support a large range of functional groups, among them the aerobic oxidation of alcohols. Various palladium catalysts have been successfully prepared and used for this purpose, wherein both Pd(II) and Pd(0) were found to be the active species [13–15].
We recently heterogenized Pd(OAc)$_2$(TPPTS)$_2$ and PdCl$_2$(TPPTS)$_2$ (TPPTS = sodium triphenylphosphine trisulfonate ligand) on various renewable polysaccharide supports. The new catalysts were successfully employed in Suzuki cross-coupling, Heck coupling and olefin transfer-hydrogenation, using different solvents [16–20]. The palladium complexes that were immobilized on iota Carrageenan (i) were the most producible compared to other polysaccharide-based systems. Moreover, these heterogeneous catalysts, designated i-Pd(OAc)$_2$(TPPTS)$_2$, were also active in the aerobic oxidation of benzyl alcohol in ethanol and were easily separated and recycled without palladium leaching to the reaction mixture [21]. Notably, under reaction conditions in ethanol, the Pd was reduced and formed nanoparticles that, in turn, probably increased its oxidation activity in every re-use.

Palladium salts and their complexes with Pd oxidation state +2 can be reduced by different agents, such as sodium borohydride or hydrazine [22]. Alternatively, alcohols, which bare acidic protons, can also be used to reduce Pd(II) to Pd(0) via the alcohol’s binding to the complex. This is followed by the deprotonation of the alcohol and β-hydride elimination, which produces the corresponding carbonyl compound. The reduction is completed by the reductive elimination of the second proton from the metal (Figure 1) [23].

Figure 1. Mechanism of alcohol reduction of Pd(II) to Pd(0).

Metal nanoparticles can function as heterogeneous catalysts, either as particles in solution or when embedded in different supports; the latter enable the catalyst to be easily separated from the solution and recycled for reuse. However, supported metal nanoparticles tend to undergo agglomeration, which increases their size and reduces their surface area, thereby reducing their reaction performance [24,25].

In this study, we rigorously analyzed the effects of the alcohol types that were used as solvents for the aerobic oxidation of benzyl alcohol on Pd(II) reduction and nanoparticle formation in i-Pd(OAc)$_2$(TPPTS)$_2$. Accordingly, the amount, size, stability, and nature of the palladium nanoparticles were examined following different impregnation times in different
alcohol solvents. The performances of the heterogeneous catalysts were then tested in the aerobic oxidation of benzyl alcohol to benzaldehyde as representative reactions (Figure 2).

**Figure 2.** Aerobic oxidation of benzyl alcohol.

### 2. Materials and Methods

Polysaccharide, catalyst, ligand and reagents: i, palladium salt (Pd(OAc)$_2$), TPPTS, reactant (benzyl alcohol) and alcoholic solvents (analytical grades) were purchased from Sigma-Aldrich Israel.

Catalyst preparation: 10 µmol of Pd(OAc)$_2$ were dissolved in 3 mL of distilled water. Next, 30 µmol of TPPTS were added to the dissolved palladium salt and the mixture was stirred for 5 min at room temperature, yielding a ligand–catalyst mixture. The ligand–catalyst mixture was added to a 15 mL polypropylene tube, together with 3 mL of 1% wt/vol polysaccharide solution in distilled water, and stirred for 5 min. The tube was sealed and deepfrozen at –20 °C for 24 h, and the frozen mixture was then lyophilized. At the end of the process, the lyophylized heterogeneous catalyst (i-Pd(OAc)$_2$(TPPTS)$_2$) was cut into square pieces (~1cm × 1cm) and added to the reaction mixture.

Reaction procedure: The oxidation of benzyl alcohol was carried out as follows.

1. The i-Pd(OAc)$_2$(TPPTS)$_2$ (without or after impregnation with the selected solvent) was added to a vial that contained 5 mL of ethanol with 0.925 mmol of benzyl alcohol.
2. The reaction mixture was preheated using an oil bath at 60 °C and magnetically stirred for 24 h.
3. Following the 24 h reaction, the reaction mixture was cooled, and the solid was removed from the liquid. Next, the remaining liquid was further separated from the left-over solid particles by transferring it through a 0.45 µm Millex LH filter (Millipore, Bedford, MA, USA). The filtered liquid was then analyzed by an HP-5 column to determine the conversion by a GC (Phenomenex, Torrance, CA, USA). First, a sample was injected to the GC without any dilution. Next, the conversion rate was calculated based on a calibration curve, which was built in advance and verified every day. In addition, the identity of the GC peaks observed was verified by a comparison of the retention time of the peaks with the retention time of the known standards.

TEM analysis: HRTEM images were obtained using a FEI Talos F200C electron microscope (Thermo Fisher Scientific, Waltham, MA, USA) operated at 200 kV at room temperature. The samples were prepared by depositing a drop of ethanol suspension of the solid catalyst on a carbon-coated Cu grid, after which they were examined as grain mounts.

Dynamic light scattering (DLS) analysis: The spectra were collected by using a CGS-3, (ALV, Langen, Germany). The laser power was 20 mW at the He-Ne laser line (632.8 nm). The correlograms were calculated by using an ALV/LSE 5003 correlator; they were collected at 90°, and then collected 10 times, over 15 s, at 25 °C. The correlograms were fitted by using the CONTIN program [26].

Zeta potential: The zeta potential was measured by using a Zetasizer Nano ZS (Malvern Panalytical Ltd., Malvern, UK). For each run at 25 °C, between 10 and 100 mea-
measurements, depending on the standard deviation, were taken. A DTS 1060 zeta cell was used (Malvern Panalytical Ltd., Malvern, UK).

3. Results and Discussion

As noted above, the use of i-Pd(OAc)\(_2\)(TPPTS)\(_2\) xerogel as the heterogeneous catalyst in the aerobic oxidation of benzylic alcohols in ethanol led to a reduction in the palladium complex and the formation of palladium nanoparticles during the reaction [21]. We previously report ed that the ratio of Pd(0)/Pd(II) was increased following 24 h of the reaction, based on XPS analysis, i.e., 46% of the Pd(II), derived from Pd(OAc)\(_2\), was reduced to its metallic form during 24 h of reaction [21]. Thus, we have already demonstrated that following 24 h of reaction the formation of palladium nanoparticles is enhanced. Since these nanoparticles were found to have been responsible for reaction acceleration during recycling, we suggested that the impregnation of the catalyst in ethanol before the reaction would yield a higher catalytic performance. As such, we began our study by testing the effect of the impregnation time on the benzyl alcohol conversion rate before starting the reaction. In these tests, the i-Pd(OAc)\(_2\)(TPPTS)\(_2\) xerogel was impregnated in ethanol at 60 °C for different time durations under an air atmosphere. Next, the benzyl alcohol was added to the ethanol with i-Pd(OAc)\(_2\)(TPPTS)\(_2\) and the reaction was carried out for 24 h at 60 °C. As illustrated in Figure 3, the conversion rate reached a maximum value after 24 h of impregnation. It was thus assumed that the impregnation duration time enhanced/reduced the palladium activity due to two opposing effects: (1) The reduction of palladium and formation of nanoparticles that accelerated the reaction, and (2) The growth of palladium nanoparticles and the formation of aggregates, which reduced the palladium outer surface area and may have decreased its activity. Therefore, our hypothesis was that until 24 h the palladium complex was reduced by the ethanol, and, in turn, that the conversion rate increased due to the formation of Pd(0) and the increase in the surface area of the palladium [21]. However, it appears that after 24 h the nanoparticles were agglomerated and, therefore, the outer surface area of the palladium was reduced, hence the reduction of the activity towards benzyl alcohol oxidation. Finally, it should be mentioned that no product other than benzoic acid was detected in any of the reaction mixtures. Furthermore, as reported in our previous work, the catalyst was recycled with some increase of activity three times [21]. However, further reuse of the catalyst resulted in deactivation and a reduction in the conversion rates.

To test our hypothesis, DLS, TEM and zeta potential analyses were applied. At first, the palladium particle size distribution of the different samples (i-Pd(OAc)\(_2\)(TPPTS)\(_2\) that were impregnated in ethanol for different time durations were examined using DLS analysis. It was found that all of the samples contained nanoparticles with hydrodynamic diameter sizes in the range of 10–200 nm (Figure 4). In addition, for impregnation times of up to 4 h, no microparticles were detected, but microparticles were detected when the catalyst was impregnated for longer times. It was also observed that for impregnations times of up to 24 h, the particle size, i.e., the average radius, increased slightly with the increase in impregnation time, such that the particle sizes obtained after very long impregnation times above 24 h were very large, hinting that aggregates were formed.

These findings were also supported by TEM images of the samples (Figure 5), which showed that while the particle sizes were almost the same (i.e., spherical shapes of about 5 nm) regardless of impregnation time duration, the number of particles increased with the impregnation time, and agglomerates formed after long impregnation times. Furthermore, when the xerogel was not impregnated in ethanol, very few nanoparticles formed, which probably occurred during the lyophilization (data not shown).
Figure 3. Effect of catalyst impregnation time on catalytic activity. Impregnation conditions: $i$-Pd(OAc)$_2$(TPPTS)$_2$ (10 µmol Pd), 5 mL ethanol, 60 °C, 1 atm air. Reaction conditions: 0.925 mmol benzyl alcohol, $i$-Pd(OAc)$_2$(TPPTS)$_2$ (10 µmol, Pd) 5 mL ethanol, 60 °C, 1 atm air, 24 h.

Figure 4. Effect of catalyst impregnation time in ethanol on Pd particle size distribution. Impregnation conditions: $i$-Pd(OAc)$_2$(TPPTS)$_2$ (10 µmol, Pd), 5 mL ethanol, 60 °C, 1 atm air.
which probably occurred during the lyophilization (data not shown).

Moreover, when the xerogel was not impregnated in ethanol, very few nanoparticles formed, the impregnation time, and agglomerates formed after long impregnation times. Further-

Table 2. Effect of solvent type on catalytic performance.

| Entry | Solvent     | pKa  | Conversion (%) |
|-------|-------------|------|---------------|
| 1     | Ethanol     | 16.1 | 20.0          |
| 2     | 1-Propanol  | 16.2 | 20.3          |
| 3     | 2-Propanol  | 17.2 | 10.5          |
| 4     | 1-Butanol   | 16.1 | 22.7          |
| 5     | 1-Hexanol   | 16.8 | 19.1          |

The effect of the alcohol type that was used as a solvent on the conversion rate in the aerobic oxidation of benzyl alcohol was also tested (Table 2). As shown in Table 2, both primary and secondary alcohols were used. It is important to note that tertiary alcohols, which reduce the palladium, cannot be used as hydrogen donors. Likewise, methanol was not tested because it dissolves the polysaccharide. The results, after 24 h of reaction, listed in Table 2, show that all the tested primary alcohols yielded similar conversion rates, with a slightly higher conversion rate yielded by 1-butanol. However, as expected, 2-propanol demonstrated a lower conversion rate.

Figure 5. TEM images of i-Pd(OAc)$_2$(TPPTS)$_2$ that impregnated for different duration times in ethanol. Impregnation conditions: i-Pd(OAc)$_2$(TPPTS)$_2$ (10 µmol, Pd), 5 mL ethanol, 60 °C, 1 atm air.

The effect of the impregnation time on nanoparticle stability, zeta potential analysis was performed. The zeta potential value is a key indicator in the evaluation of the stability of colloidal dispersions, and it represents the degree of electrostatic repulsion between adjacent and similarly charged particles in a dispersion. As illustrated in Table 1, the zeta potentials of the particles in all of the samples indicated that they were negatively charged, probably due to the sulfonic groups of the polysaccharide and the ligand, which caused them to repulse each other. In addition, increasing the impregnation time reduced the zeta potential, a finding that was probably due to the increased van der Waals attraction between the particles and/or the reduction of the electronic repulsion as a result of particle aggregation. The magnitude of the zeta potential indicated the interaction between the particles in regard to their charge and shape, whereas the lower values indicated lower stability. Thus, the decreased zeta potential obtained by increasing the impregnation time demonstrates that the stability of the nanoparticles also decreased.

Table 1. Effect of ethanol impregnation duration time on zeta potential of i-Pd(OAc)$_2$(TPPTS)$_2$.

| Impregnation Time (h) | Zeta Potential (mV) |
|-----------------------|----------------------|
| 0                     | -13.37 ± 1.25        |
| 4                     | -10.88 ± 0.62        |
| 24                    | -5.47 ± 0.19         |
| 48                    | -1.80 ± 0.08         |
| 72                    | -0.90 ± 0.02         |

Impregnation conditions: i-Pd(OAc)$_2$(TPPTS)$_2$ (10 µmol, Pd), 5 mL ethanol, 60 °C, 1 atm air.

| Entry | Solvent     | pKa  | Conversion (%) |
|-------|-------------|------|---------------|
| 1     | Ethanol     | 16.1 | 20.0          |
| 2     | 1-Propanol  | 16.1 | 20.3          |
| 3     | 2-Propanol  | 17.2 | 10.5          |
| 4     | 1-Butanol   | 16.1 | 22.7          |
| 5     | 1-Hexanol   | 16.8 | 19.1          |

* Reaction conditions: 0.925 mmol benzyl alcohol, 10 µmol i-Pd(OAc)$_2$(TPPTS)$_2$, 5 mL solvent, 60 °C, 1 atm air, 24 h.
Since the reduction of Pd(II) to Pd(0) was initiated by the dissociation of a proton from the hydroxyl group (Figure 1), the higher the acidity of the alcohol, the greater its ability to reduce the palladium. Furthermore, the ability of larger and branched alcohols to reduce the metal is also influenced by the steric effect. Hence, 2-propanol, which is less polar than all the tested primary alcohols, also exhibited steric hindrance, and, therefore, its ability to reduce the Pd and form nanoparticles was reduced.

The DLS and TEM analyses of the catalysts after carrying out the oxidation reaction in ethanol, 1-propanol, or 1-hexanol for 24 h were also conducted (Figures 6 and 7, respectively). Carrying out the reaction using 1-propanol as a solvent yielded a narrower particle size distribution with smaller nanoparticles in comparison to those observed in the reaction that was carried out using ethanol as a solvent (Figure 6). On the other hand, a wider particle size distribution, characterized by bigger particle sizes, was observed in the reaction that was carried out in 1-hexanol, which also yielded agglomerates that reduced the conversion rate (Figure 6). The TEM micrographs of the three preparations also show that replacing ethanol with 1-propanol and 1-hexanol yielded more and larger agglomerates (Figure 7).

![Graph](image_url)

**Figure 6.** Effect of alcohol type on palladium particle size distribution in i-Pd(OAc)$_2$(TPPTS)$_2$ after 24 h of reaction. Impregnation conditions: i-Pd(OAc)$_2$(TPPTS)$_2$ (10 µmol, Pd), 5 mL alcohol, 60 °C, 1 atm air.
4. Conclusions

In this study, we employed alcohols as reducing agents of Pd(II) in i-Pd(OAc)₂(TPPTS)₂, and tested the activity and stability of the resulting catalysts in the oxidation of benzyl alcohol. Pd nanoparticles were formed on i by reducing the Pd(II) in Pd(OAc)₂(TPPTS)₂ using various alcoholic solvents. It was observed that, during the impregnation or reaction in the alcohol solvents, Pd(II) was reduced and palladium nanoparticles were formed. As determined by DLS, TEM, and zeta potential analyses, both the duration of the impregnation time in the alcohol and the type of alcohol used affected nanoparticle formation and agglomeration. In general, prolonging the impregnation time in ethanol yielded larger amounts of nanoparticles, with slightly larger particle sizes, which eventually yielded agglomerates. Furthermore, the type of alcohol used as the reduction agent also affected the particle sizes and agglomerate formation, whereas using primary alcohols yielded higher conversion rates.

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