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One-pot synthesis of benzaldehyde derivatives in $PdCl_2$-catalyzed reactions with H_2O_2 in alcoholic solutions

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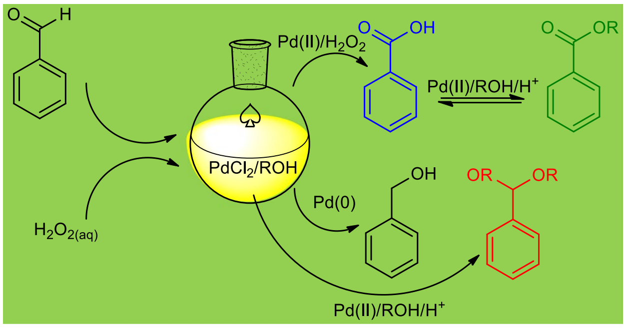
Abstract

Abstract The activity of the palladium salt catalysts was investigated on the benzaldehyde reactions with H_2O_2. The $PdCl_2$ salt was the most efficient catalyst for the formation of the goal products. In CH_3OH, benzaldehyde was selectively oxidized to benzoic acid and posteriorly esterified to methyl benzoate. In this process, the reaction of the $PdCl_2$ catalyst with aqueous H_2O_2 provided H^+ ions, which also promoted the esterification and acetalization reactions. The oxidant load played a key role in the selectivity controlling; while a large excess (9:1) gave benzoic acid (90%), with a lower ratio (3:1), acid and ester were formed with selectivity of 58 and 35%, respectively. With H_2O_2 at an equimolar ratio, the Pd(0) reduced the benzaldehyde to benzyl alcohol (30%). In absence of the oxidant, $PdCl_2$ (2.5 mol %) condensated benzaldehyde and alcohol to acetal (90%). Therefore, $PdCl_2$ directly catalyzed the oxidation and reduction reactions, and participated in acid-catalyzed reactions (i.e., condensation and esterification), generating H^+ ions, demonstrating to be a highly versatile catalyst. An adequate adjusting of reaction conditions allowed to control the reaction selectivity toward the desired products (i.e., benzoic acid or ester benzyl, acetal, or benzyl alcohol).

Graphic Abstract



Keywords Homogeneous catalysis · Chemoselectivity · Oxidations · Reductions · Reaction mechanisms · Coordination chemistry

Introduction

The production of benzoic acid and their esters have gathered a lot of attention, due to extensive use of these products as raw material aiming the industrial production of fibbers, cosmetics, plasticizers, dyestuffs (Ilyas and Sadiq 2009; Chumbhale et al. 2005). Benzoic acid has been industrially produced through toluene oxidation in liquid or vapor phase

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at high temperatures, in a one-pot process that consumes environmentally unfriendly oxidants, which are expensive and generates residues at stoichiometric amounts; in addition, in these processes, low yields have been reached (Dash et al. 2009; Sedelmeier et al. 2010; Yuan et al. 2011; Mukhopadhyay and Datta 2008).

For these reasons, environmentally benign routes for the benzaldehyde oxidation using clean oxidants have gradually replaced the stoichiometric oxidation processes (Coronel et al. 2019). Undoubtedly, molecular oxygen is abundant, cheap and a green oxidant. However, aerobic oxidation reactions involve a combination of the palladium catalysts with metal reoxidants, which trigger various parallel reactions that compromise the oxidation selectivity (Keith and Henry 2009).

Hydrogen peroxide is an atom-efficient oxidant, easily handled, non-flammable, whose consumption results in water as a by-product, being thus a reactant highly desired to oxidize the benzaldehyde (Muzart 2003; Viana et al. 2018). Notwithstanding, hydrogen peroxide should be primarily activated, a step that requires the presence of homogeneous or heterogeneous metal catalysts (Bernini et al. 2005; da Silva et al. 2018; Tandon et al. 2005). However, some peroxide-based methods commonly require additives to control the pH, in addition to needs phase transfer catalysts due to the solubility problems (Cong et al. 2006; Jeong et al. 2014).

It is known that solid supported catalysts can activate the hydrogen peroxide in the solution, making them an attractive option to oxidizing alcohols and aldehydes (Sousa et al. 2011; Farsani et al. 2014; Zhou et al. 2013). Although the immobilization of homogeneous catalyst on solid support remains a widely explored field, there are some drawbacks that motivate the search for a better understanding of how these catalysts work in solution (Hübner et al. 2016). Notwithstanding, several advances obtained in the study of the homogenous catalysts as the transition metal salts, have been useful to optimize their use as heterogeneous catalysts in oxidation processes with hydrogen peroxide (Balula et al. 2013; Pathan and Patel 2011, 2013).

In this present study, palladium salts were used as catalysts in reactions of the benzaldehyde with hydrogen peroxide in an alcoholic solution. Without any addition of Brønsted acid, the benzoic acid obtained was converted to alkyl ester. At low loads of oxidant, Pd(0) species were formed and reduced benzaldehyde to benzyl alcohol. In the absence of the oxidant, the palladium-catalyzed reaction gave exclusively benzaldehyde acetal. The focus was on correlating the activity and selectivity attained in palladium-catalyzed reactions with the main reaction parameters (i.e., oxidant load, type and concentration of palladium catalyst, reaction temperature**,** and nature of alcohol). Simple experimental data such as pH measurements and products selectivity, allowed to propose reaction pathways that elucidated how the palladium catalyst contributed to the benzaldehyde conversion to main products (i.e., benzoic acid, alkyl benzoate, benzaldehyde acetal, and benzyl alcohol), through distinct reactions (i.e., oxidation, esterification, acetalization, and reduction).

Experimental section

Chemicals

All chemicals are commercially available and were utilized without prior handling. $PdCl_2$, $Pd(acac)_2$, $Pd(CF_3COO)_2$, and $Pd(OAc)_2\cdot$were purchased from Sigma Aldrich (99 wt.%). Benzaldehyde (99 wt.%), alkyl alcohols (i.e., methyl, ethyl, propyl, and butyl) were all Sigma-Aldrich (99.0–99.5 wt.%). Hydrogen peroxide was purchased from Vetec (34 wt.% aqueous solution).

Catalytic runs

Catalytic runs were performed in a glass reactor (50 mL), equipped with a magnetic stirrer and sampling septum. Typically, benzaldehyde (10 mmol, 1.06 g) and Pd(II) catalyst (2.5 mol %, i.e. $PdCl_2 = 0.25$ mmol/44.3 mg) were dissolved in CH_3OH (10 mL solution) and heated to 323 K. Afterward, an aqueous H_2O_2 solution (30 mmol of H_2O_2, 1.02 g) was added drop to drop to the reactor, and then the reaction was initiated.

The reaction progress was followed by GC analysis of samples periodically collected (GC 2010 Shimadzu, capillary column, FID). A calibration curve was built with the authentic samples of reactant (benzaldehyde). It allowed calculate the conversion of substrate (Eq. 1).

$$\%\ \text{Conversion} = \left(A_{t=0} - A_{t=i}\right)/A_{t=0} \times 100, \quad (1)$$

A_0 is the initial area of GC peak of benzaldehyde, A_i is the area of benzaldehyde GC peak detected in the aliquot of reaction.

The Eq. 2 allowed to check the mass balance of reactions.

$$\sum \text{corrected GC peaks area (products)} = \text{Consumed GC peak area (substrate)}. \quad (2)$$

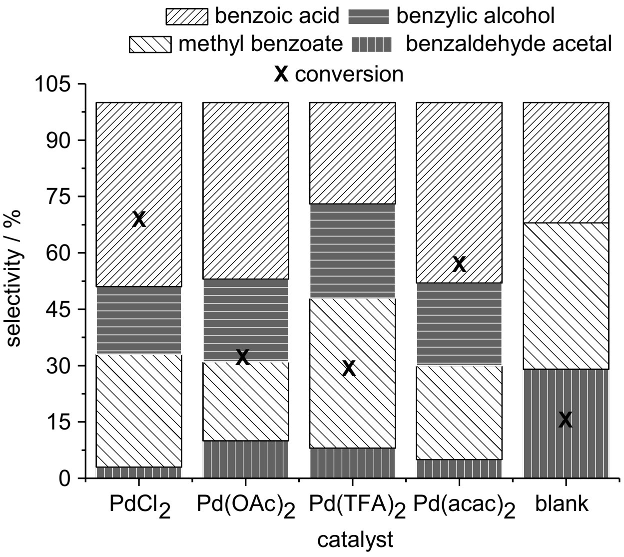


Fig. 1 Conversion and selectivity of benzaldehyde oxidation reactions with H_2O_2 in the presence or absence of palladium catalysts[a]. [a]Reaction conditions: catalyst load (2.5 mol%); temperature (323 K); benzaldehyde (10 mmol): H_2O_2 (30 mmol); CH_3OH (163 mmol); reaction volume (10 mL) time (4 h)

To determine the response factor (i.e., rf, Eq. 3), acetonitrile solutions containing aliquots at the same concentration were prepared from authentic samples (i.e., benzoic acid, benzyl alcohol), or from previously synthesized products (benzoic esters), being then injected in a GC equipment.

$$\text{rf} = \text{Area of GC peak/area of GC peak of the product.} \quad (3)$$

To calculate the reaction selectivity, the Eq. 4 was used. It is important to highlight that all the products were detected by GC analyses, the sum of products selectivity always was 100%.

$$\%\ \text{Selectivity} = \text{GC peak corrected area of product/GC peak consumed area of substrate.} \quad (4)$$

Characterization data

The main reaction products were identified by GC–MS analysis (GC–MS 2010 ultra mass, i.e. 70 eV) (see supplemental material) and co-injection with authentic samples. Furthermore, after the end of the reaction, methyl alcohol was distilled under vacuum and the residue was purified by silica-gel column chromatography, using hexane: ethyl acetate 5:1 as eluent for the purification of the main products.

Proton nuclear magnetic resonance spectra were recorded on a Varian Mercury instrument (300 MHz) with $CDCl_3$ as solvent referenced relative to residual $CHCl_3$ ($\delta = 7.27$ ppm). Chemical shifts are reported in ppm. Carbon NMR spectra were recorded on the same instrument (75 MHz) with total proton decoupling. The signal of $CDCl_3$ at $\delta = 77$ ppm was used as reference in the ^{13}C NMR (see spectra in the supplemental material).

Results and discussion

Screening of the palladium catalyst

In this work, our initial objective was promoting the oxidative esterification of benzaldehyde with hydrogen peroxide in palladium-catalyzed reactions without the addition of Brønsted acid. Initially, we assessed the activity of the different palladium catalysts to understand the role of the palladium and their anionic ligands on these reactions.

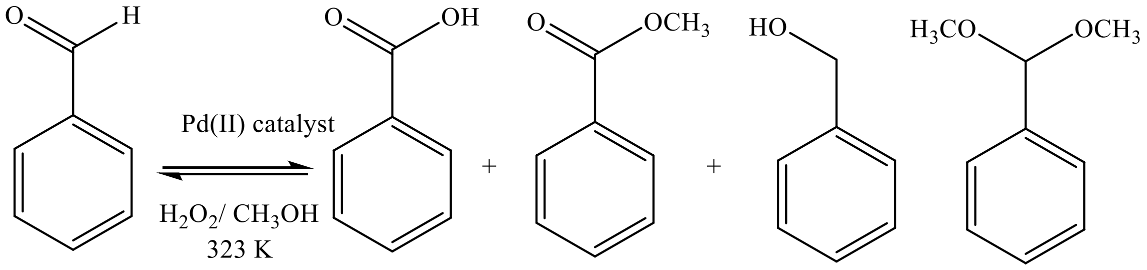
To select the most active catalyst, an initial screening of the palladium salt catalyst was performed, and the main results are displayed in Fig. 1. It is important to know that in this step the reaction conditions were not optimized to achieve the maximum conversion.

Even in the presence of an oxidant excess (molar ratio of 3:1 H_2O_2/benzaldehyde), the reaction carried out in the absence of the catalyst achieved only a poor conversion (i.e., a maximum of 14%). Conversely, in the presence of Pd(II) catalysts, both conversion and selectivity of the reactions were dependent on the nature of the anionic ligand.

The reaction conversions were as follows: $PdCl_2 > Pd(acac)_2 > Pd(OAc)_2 > Pd(TFA)_2$. Therefore, we can conclude that the palladium catalysts with the two stronger ligands were the less active (i.e., acetate and trifluoroacetate, $Pd(OAc)_2$ and $Pd(TFA)_2$, respectively). Probably, the formation of the peroxidized palladium species, which are intermediates common on these reactions was difficult due to the lower lability of the ligands (Oliveira et al. 2009; da Silva et al. 2013). Conversely, the catalyst with a labile ligand was the most active (i.e., $PdCl_2$).

In general, the reactions in the $Pd(II)/CH_3OH/H_2O_2$ system converted benzaldehyde (**1**) to following products; benzoic acid (**2**), methyl benzoate (**3**), benzyl alcohol (**4**), and (dimethoxymethyl)benzene (**5**) (Scheme1).

These products were formed at a variable selectivity depending on the presence and nature of the palladium catalyst. When palladium was absent, benzyl alcohol (**4**), which is a product formed by the reduction of the benzaldehyde was not detected, evidence that the palladium is required for its formation (see blank-reaction, Fig. 1). When $Pd(OAc)_2$ or $PdCl_2$ were the catalysts, the reactions achieved the highest benzoic acid (**2**) selectivity (50%). The formation of (**2**) along the uncatalyzed reaction demonstrated that the



Scheme 1 Reaction of the benzaldehyde in presence of Pd(II)/CH_3OH/H_2O_2

hydrogen peroxide may itself oxidize benzaldehyde through a radical reaction pathway, even though with low conversion. An increase of selectivity for (**2**) as well as the higher benzaldehyde conversion assure that palladium effectively participated in this oxidative process.

On the other hand, the reactions gave two products that are commonly obtained in the presence of Brønsted acid catalysts: benzaldehyde acetal (**5**) and methyl benzoate (**3**). It is possible that the palladium catalyst may have been hydrolyzed by aqueous hydrogen peroxide generating the H^+ ions, which acted as catalysts in acetalization and esterification reactions. These aspects will be addressed in the next section.

Discussion about the reaction pathways

In addition to the expected oxidation product [i.e., benzoic acid (**2**)], the system Pd(II)/H_2O_2/CH_3OH gave three products that were formed through distinct catalytic processes; benzyl alcohol (**4**), a product obtained via benzaldehyde reduction, methyl benzoate (**3**) and benzaldehyde acetal (**5**), compounds typically generated in the presence of Brønsted acid catalysts. A route for these reactions will be addressed in next sections.

$PdCl_2$-catalyzed oxidation of the benzaldehyde with H_2O_2 to benzoic acid followed by reduction of the benzaldehyde by Pd(0) to benzyl alcohol

Palladium catalysts are well known by their ability in promoting either reaction of oxidation as well as reduction, introducing oxygen atoms or hydrogen in the organic substrates such as alcohols and olefins (da Silva et al. 2009; da Silva and Berlini 2016). Substrates as the benzaldehyde can be potentially converted to oxidation or reduction products in processes carried out in the presence of Pd(II) or Pd(0) catalysts, respectively. The novelty of this present work is that both reactions have occurred in one-pot process (Fig. 2).

Before our mechanistic proposal, it is important to consider an important aspect. Benzaldehyde can undergo a classical reaction (i.e., Cannizzaro reaction), where it is disproportionated to benzyl alcohol and benzoic acid. Although common, this reaction requires the presence of a strong base, to attack the benzaldehyde and generating a carboxylate, which reacts with another aldehyde molecule giving the alcohol and acid as products. No strong base was present or was generated during the reaction described herein.

We verified that $PdCl_2$/H_2O_2 combination was efficient to oxidize benzaldehyde to benzoic acid if compared to the other palladium catalysts (Fig. 1). Hydrogen peroxide provided the oxygen atom that was incorporated into the benzaldehyde. Palladium hydroperoxidic species (ClPdOOH and/or HOPdOOH) formed by the addition of H_2O_2 to the $PdCl_2$ seems to be the most likely active intermediate in this reaction (Remias and Sen 2002).

In Wacker-type systems, palladium species coordinated to the water are also possibly formed. However, as demonstrated by da Silva and Berlini, no reaction progress in terms of oxidation is observed when a mixture $PdCl_2$/H_2O is used (i.e., without H_2O_2) (da Silva and Berlini, 2016).

On the other hand, after an oxidation step, it is possible that Pd(0) species have been formed in the reaction medium. It could be expected that the presence of H_2O_2 in the solution should quickly oxidize these reduced species, recovering the Pd(II). Indeed, no palladium-black precipitation was observed throughout the reactions. We suppose that despites the short lifetime, the reduced palladium species were formed by an enough time to catalyze the reduction of the benzaldehyde to benzyl alcohol (**4**), which was also a product significantly formed in the reactions (Fig. 1).

Thus, as depicted in Fig. 2, we suppose that another benzaldehyde molecule can react with the Pd(0) species in the presence of HCl previously formed, which provide hydrogen atoms to be incorporated in the aldehyde (**1**), generating benzyl alcohol (**4**) and, consequently, oxidizing Pd(0) to $PdCl_2$. Although this dual behaviour of the palladium in a one-pot system is relatively rare, the literature describes

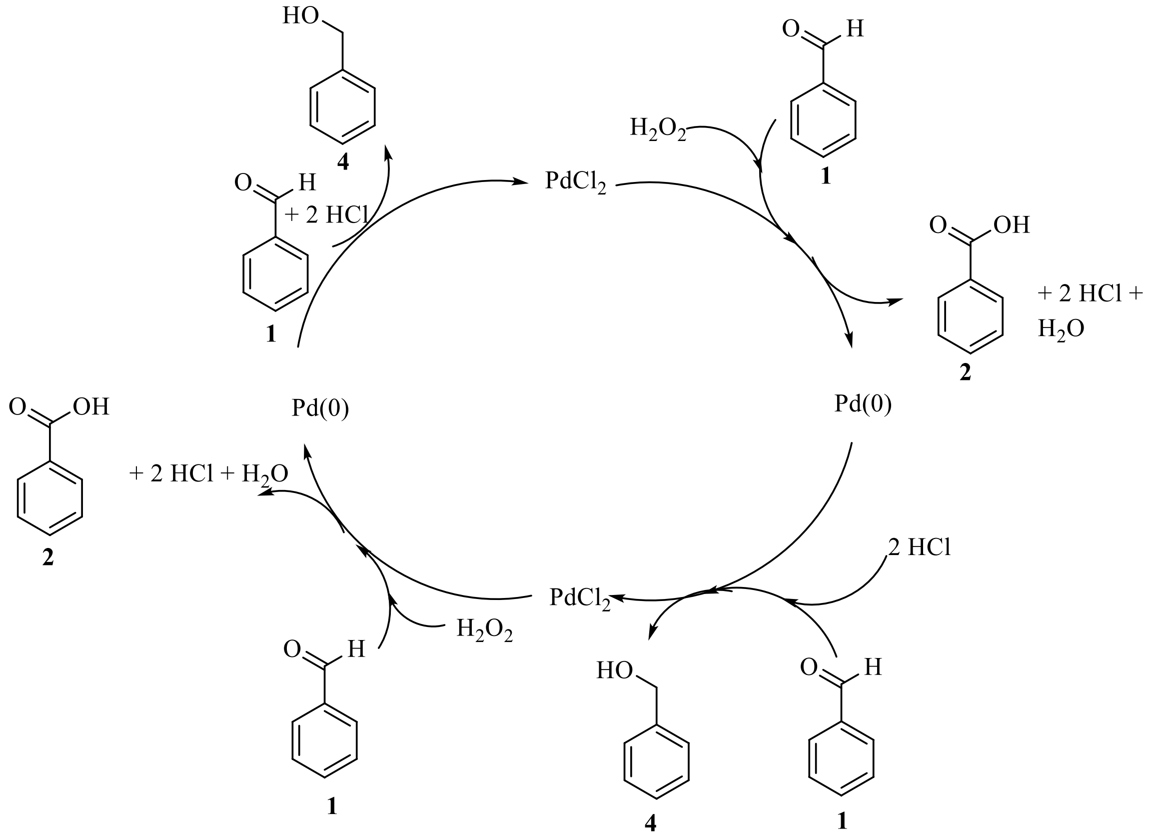


Fig. 2 Proposal for reactions of oxidation and reduction of benzaldehyde promoted by the palladium catalysts

that palladium catalysts promoted the dehydrogenation/hydrogenation of the cyclohexene in one-pot reactions giving cyclohexane and benzene (da Silva and Berlini, 2016).

Esterification of the benzoic acid to methyl benzoate in the system $PdCl_2/CH_3OH/H_2O_2$

After benzaldehyde (**1**) has been oxidized to benzoic acid (**2**), it was esterified to methyl benzoate (**3**); all these reactions were carried in one-pot route in the presence of aqueous H_2O_2 in methyl alcohol solutions containing catalytic amounts of the $PdCl_2$.

Typically, esterification reactions are catalyzed by solid or soluble Brønsted acids (Pasquale et al. 2012). However, herein no Brønsted acid was added to the solution. Although it could be possible that the Pd(II) species may polarize the carbonyl group of acid and facilitate its attack by the alcohol (Rubio-Caballero et al. 2014), we believe that in the present process, it happened through another reaction pathway. Measurements of pH were performed in CH_3OH, $PdCl_2/CH_3OH$, and $PdCl_2/CH_3OH/H_2O_2$ solutions, and demonstrated that an addition of $PdCl_2$ triggered an increase of medium acidity; the values of pH were 8.0 (i.e., CH_3OH), 5.2 (i.e., $PdCl_2/CH_3OH$), and 3.2 (i.e., $PdCl_2/CH_3OH/H_2O_2$), respectively. It is evidence that H^+ ions were released in solution.

In Scheme SM1 (supplemental material), we are proposing that initially, the $PdCl_2$ react with aqueous H_2O_2 or methyl alcohol releasing H^+ cations, as observed in hydrolysis reactions of metal cations (da Silva et al. 2015). Afterward, the reaction follows a typical route of Brønsted acid-catalyzed esterification (Rubio-Caballero et al. 2014; da Silva et al. 2015).

Therefore, we conclude that $PdCl_2$ preferentially reacted with one of the protic species present in the solution (i.e., H_2O_2, H_2O or even CH_3OH), generating H^+ ions (Eq. 1, supplemental material). The generated H^+ cations can then to catalyze the esterification reaction of the benzoic acid (**2**) to methyl benzoate (**3**) (Scheme SM1, supplemental material).

After the protonation of the carbonyl group of the benzoic acid, the attack by the methyl alcohol on the carbonylic carbon is favoured (Scheme SM1). After the protonated intermediate has been formed, it undergoes a prototropism step, then, it releases water and benzyl ester (**4**).

Condensation of the benzaldehyde with CH_3OH generating benzaldehyde acetal in the presence of the $PdCl_2$

The condensation reactions of aldehydes with alcohols are frequently catalyzed by Brønsted acids (Chen et al. 2018). Herein, H^+ cations were generated by the reaction of the $PdCl_2$ catalyst with aqueous H_2O_2. A traditional route of acetalization is depicted in Scheme SM2 (supplemental material) (da Silva et al. 2015).

After the initial protonation of the benzaldehyde (**1**) by H^+ cations (step 1, Scheme SM2), occurs a nucleophilic attack of the carbonylic carbon atom by the methyl alcohol (step 2, Scheme SM2), generating a positively charged oxonium intermediate. This intermediate undergoes a prototropism (step 3, Scheme SM2), resulting in a positively charged tetrahedral intermediate, that will then release a water molecule (step 4, Scheme SM2) and to be again attacked by another alcohol molecule (step 5, Scheme SM2). Finally, the proton is released, and the acetal benzaldehyde (5) is formed (step 6, Scheme SM2).

Effects of main reaction parameters on the benzaldehyde oxidation in $PdCl_2/H_2O_2/$ alcohol system

Effect of the reactants molar proportion

The oxidant load played a pivotal role in $PdCl_2$-catalyzed benzaldehyde oxidation with H_2O_2 in CH_3OH solutions. Figure 3 displays the main data of conversion and selectivity obtained in reactions with different amount of oxidant. When the oxidant was absent (1:0 proportion, Fig. 3), solely a minimum amount of benzoic acid (**2**) was detected (2.0%), assigned to the stoichiometric oxidation of benzaldehyde (**1**) by the $PdCl_2$. In this case, the oxygen source is the solvent or any residual water. Equally, a minimum amount of benzyl alcohol (**4**) was formed, due to the stoichiometric reduction of (**1**) by the Pd(0), which was resulting from the benzaldehyde oxidation reaction.

Notwithstanding, this redox sequence was stopped, and these reactions did not go on. The $PdCl_2$ should have reacted with CH_3OH, releasing H^+ ions, which were able to promote the condensation reaction. In this case, the pH was reduced from 8.0 to 5.2. However, the Pd alkoxide was stable and became inactive for the stoichiometric oxidation/reduction reactions.

Expectedly, the addition of the hydrogen peroxide to the system has improved the benzaldehyde conversion as well as enhanced the selectivity of the oxidation product (**2**) (Fig. 3). Nonetheless, the formation of the benzyl alcohol (**4**) was not immediately suppressed; it was detected in reactions with loads of benzaldehyde:H_2O_2 of 1:1–1:7. Although an increase of H_2O_2 load has resulted in a reduction of the selectivity of benzyl alcohol (**4**), only when a 1:9 molar ratio of substrate: oxidant was used it was not formed.

The increase of the oxidant load was also a reason for the decreasing of the selectivity of the condensation product (**5**). It was significantly formed only until loads of 1:4 between benzaldehyde: oxidant.

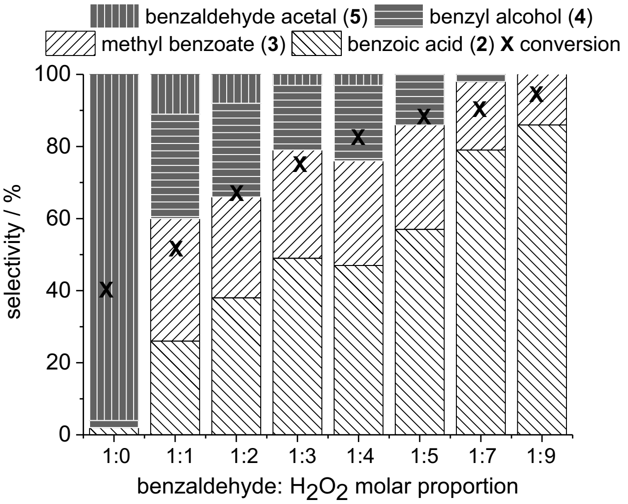


Fig. 3 Effect of the oxidant load on conversion and selectivity of the benzaldehyde oxidation by H_2O_2 in the presence of palladium chloride catalyst[a]. [a]Reaction conditions: catalyst load (2.5 mol%); temperature (323 K); benzaldehyde (10 mmol); CH_3OH (163 mmol); reaction volume (10 mL) time (4 h)

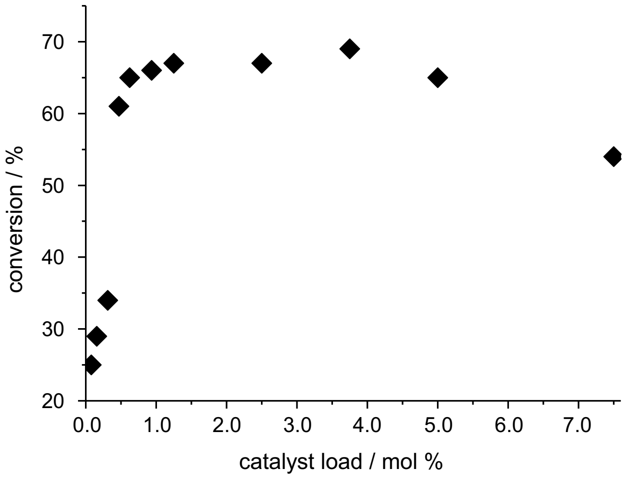


Fig. 4 Effect of the catalyst load on conversion of the benzaldehyde in $PdCl_2$-catalyzed reactions with hydrogen peroxide[a]. [a]Reaction conditions: benzaldehyde (10 mmol); H_2O_2 (30.0 mmol); CH_3OH (163 mmol); temperature (323 K); reaction volume (10 mL) time (4 h)

Effect of the $PdCl_2$ catalyst load on the benzaldehyde oxidation by H_2O_2 in CH_3OH

The effect of catalyst load was investigated in wide range (0.078–7.5 mol %, Fig. 4). We have found that regardless the catalyst concentration, all the reactions had a maximum conversion after 2 h reaction (values presented in Fig. 4); afterward, the conversions remained almost constant. Nonetheless, the runs were performed by 4 h.

The highest conversion was achieved in reaction with 3.75 mol % of $PdCl_2$; on the catalytic runs with loads higher than this, a decrease was observed, which was assigned to the quick decomposition of the hydrogen peroxide triggered by the high catalyst concentration (Fig. 4).

It is important to know that H_2O_2 is always the last reactant to be added, aiming minimize its decomposition. There is another relevant point; even it (H_2O_2) have been decomposed to water and molecular oxygen, it has not a beneficial effect for the reaction. An additional experiment demonstrated that no oxidation product was detected when we carried out the reaction under oxygen atmosphere (i.e., without H_2O_2). It reinforces the result shown in Fig. 3, where only acetal was obtained.

Unlikely the conversion, the reactions selectivity was much more affected by the variation of the catalyst load. We are presenting the selectivity data in two different levels of catalyst concentration; at low and high loads (Figs. 5 and 6, respectively).

When a low catalyst load was used, no formation of benzyl alcohol was observed (i.e., 0.078 and 0.156 mol %, Fig. 5). It is consequence of a higher proportion peroxide: palladium, which difficulted the formation of Pd(0) species, responsible by the reduction of benzaldehyde to alcohol (**4**). Conversely, benzaldehyde acetal (**5**) was the major product until loads of 0.312 mol % of catalyst; at loads higher than this, benzoic acid (**2**) and their ester (**3**) became the major products (Fig. 5). This trend was confirmed when the reactions were carried out with higher $PdCl_2$ load (Fig. 6).

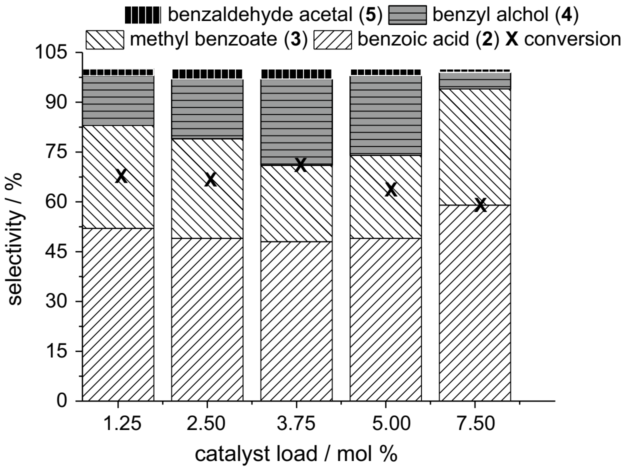


Fig. 6 Effect of the catalyst load on the conversion and selectivity of the benzaldehyde oxidation by H_2O_2 in the presence of $PdCl_2$[a]. [a]Reaction conditions: catalyst load (1.25–7.50 mol%); temperature (323 K); benzaldehyde (10 mmol); H_2O_2 (30 mmol); CH_3OH (163 mmol); reaction volume (10 mL) time (4 h)

These experimental data suggests that the two pairs of concurrent reactions, the first one, oxidation/ reduction (i.e., reactions that are directly palladium-catalyzed), and the second one, esterification/ condensation (i.e., reactions that are

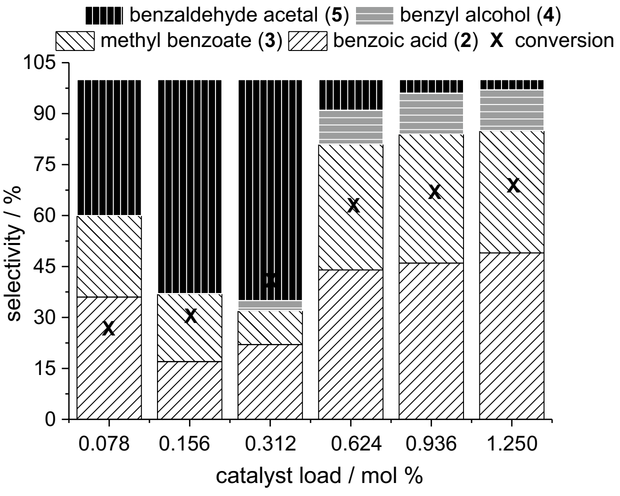


Fig. 5 Effect of the catalyst load on the conversion and selectivity of the oxidation reaction of benzaldehyde with H_2O_2 in the presence of $PdCl_2$[a]. [a]Reaction conditions: catalyst load (0.078–1.25 mol%); temperature (323 K); benzaldehyde (10 mmol); H_2O_2 (30 mmol); CH_3OH (163 mmol); reaction volume (10 mL) time (4 h)

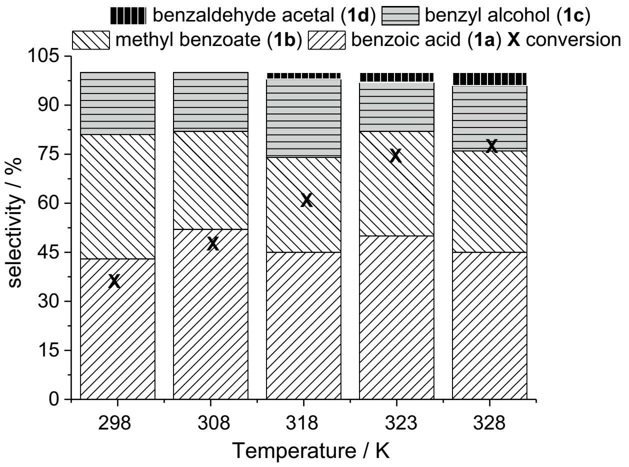


Fig. 7 Effect of the temperature on the conversion and selectivity of the $PdCl_2$-catalyzed oxidation reactions of the benzaldehyde by H_2O_2[a]. [a]Reaction conditions: catalyst load (2.50 mol%); benzaldehyde (10 mmol); H_2O_2 (30 mmol); CH_3OH (163 mmol); reaction volume (10 mL) time (4 h)

H^+ ions-catalyzed generated by the $PdCl_2$), were sensitive to the variation on the catalyst load. A positive aspect of this oxidative process is that in reactions with concentrations of $PdCl_2$ equal or higher than 0.624 mol %, a high selectivity combined for ester/ acid (i.e., 2 /3) was achieved, which varied of 75–95%.

Effect of the temperature on the $PdCl_2$-catalyzed oxidation of benzaldehyde by H_2O_2 in CH_3OH

Temperature effects on the conversion and selectivity were also investigated (Fig. 7). An increase of the reaction temperature resulted in a higher conversion of benzaldehyde, nonetheless, the selectivity combined acid/ester was less affected.

At these reaction conditions, benzaldehyde acetal (**5**) was always obtained in a minor amount (318–328 K), or totally absent (298 and 308 K). Nonetheless, regardless the reaction temperature, the pair benzoic acid/methyl benzoate were always the main products. At range of temperature of 298–328 K, benzyl alcohol (**4**) was formed with a variable selectivity (10–18%).

Effect of alcohol on the $PdCl_2$-catalyzed oxidation of benzaldehyde by H_2O_2

The steric hindrance on hydroxyl group of the alky alcohols may be an important feature that distinguish their reactivity in esterification and condensation reactions. In addition, due to different pKa values of alcohols, the acidity strength of medium may be also affected. The activity of $PdCl_2$ catalyst was assessed in reactions of benzaldehyde and H_2O_2 using different alcohols as solvent (Fig. 8).

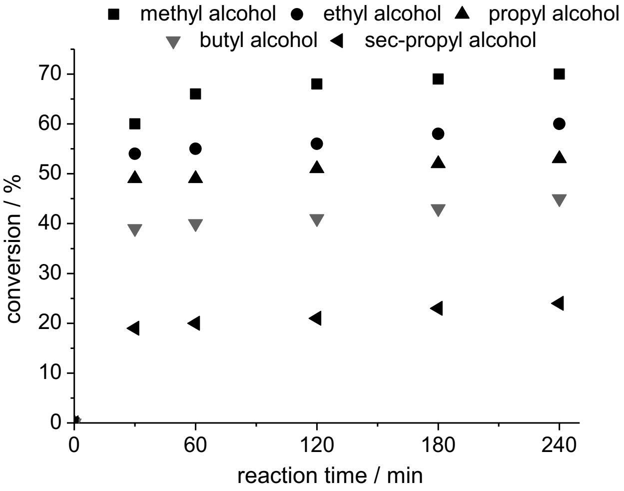


Fig. 8 Effect of the alcohol nature on the $PdCl_2$-catalyzed reactions of the benzaldehyde with $H_2O_2{}^a$. ^{a}Reaction conditions: catalyst load (2.50 mol%); benzaldehyde (10 mmol); H_2O_2 (30 mmol); ROH (163 mmol); reaction volume (10 mL) time (4 h)

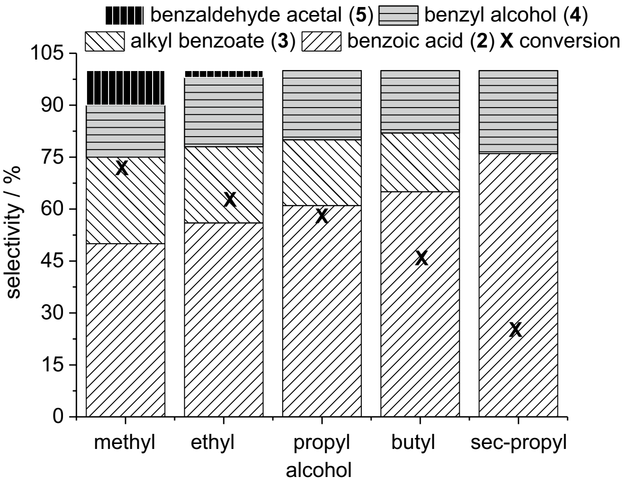


Fig. 9 Effect of the alcohol nature on the conversion and selectivity of $PdCl_2$-catalyzed oxidation reactions of the benzaldehyde by $H_2O_2{}^a$. ^{a}Reaction conditions: catalyst load (2.50 mol%); benzaldehyde (10 mmol); H_2O_2 (30 mmol); ROH (163 mmol); reaction volume (10 mL) time (4 h)

The alcohols reactivity followed the trends $CH_3OH > C_2H_5OH > C_3H_7OH > C_4H_9OH >$ *sec*-C_3H_7OH. An increase on carbon chain size reduced the reactivity of the alcohol, and consequently, the conversion of the reactions was lower (Fig. 8). Moreover, the secondary hydroxyl group was the less reactive. Independently of the alcohol, all the reactions achieved a maximum conversion within first hour of run. Afterward, no significant progress has occurred, and the conversions stayed almost constant.

The effects of type alcohol on the conversion and reaction selectivity were also evaluated. Figure 9 summarizes the main results of conversion and selectivity.

In all the reactions, the benzoic acid (**2**) was the major reaction product. While the selectivity of this reaction was independent of the alcohol nature (i.e., only $PdCl_2$ and H_2O_2 participate in this reaction), the selectivity for the products formed in the concurrent reactions (i.e., esterification and condensation) was reduced. Consequently, the selectivity of (**2**) product was being gradually enhanced.

An increase of the carbon chain size affected the ester selectivity (**3**), which was being progressively lowered when primary alcohols with lengthier chain size were used. However, (**3**) product was not formed when a secondary alcohol was the substrate (Fig. 9). The condensation reaction was highly sensitive in relation the alcohol nature. An increase of the chain carbon size decreased the benzaldehyde acetal selectivity (**4**); it was detected only in the reactions with methyl and ethyl alcohols. Conversely, the selectivity for the reduction product (**3**) was less impacted by the alcohol nature.

Conclusion

In this paper, the oxidation of the benzaldehyde by hydrogen peroxide was performed in the presence of palladium catalysts solved in alcoholic solutions. Among the catalysts assessed, $PdCl_2$ was the most active. The main aspects that drives the reaction selectivity were studied. Benzoic acid and alkyl ester were obtained in one-pot process. The formation of the two side-products was carefully investigated (i.e., benzyl alcohol and benzaldehyde acetal). Palladium chloride was the most versatile catalyst, promoting different reactions such as oxidation, reduction, esterification and acetalization. Depending on the reaction conditions (i.e., catalyst and oxidant loads), benzaldehyde was selectively oxidized to benzoic acid, or reduced, giving benzyl alcohol. The oxidant: benzaldehyde molar ratio as well as the $PdCl_2$ concentration were the key aspects that governed these reactions. We demonstrated that $PdCl_2$ reacts with the aqueous hydrogen peroxide or alcohol molecules resulting in H^+ ions, which are active catalysts in condensation and esterification reactions. The reactivity of the different alcohols was assessed, and we verified that an increase on chain carbon size of the alcohol decreased their reactivity toward acetalization and esterification reactions. An adequate adjusting of the oxidant load on the $PdCl_2$/ H_2O_2 allowed maximize both benzaldehyde conversion and selectivity of acid/ ester.

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