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Selective Aerobic Oxidation of Benzyl Alcohols with Palladium(0) Nanoparticles Suspension in Water

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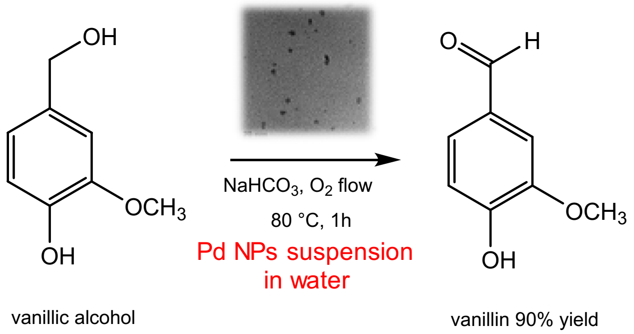
Abstract

This study concerns one of the rare applications of a suspension of palladium nanoparticles in water for oxidation reactions. The aqueous suspension containing well dispersed nanoparticles of 3.85 nm was obtained following a straightforward procedure involving the reduction of Na_2PdCl_4 with $NaBH_4$ in the presence of PVP as stabilizing agent. In the way of oxidative catalytic valorisation of lignin, the aqueous suspension was directly applied as catalytic medium for the selective oxidation of vanillic alcohol into vanillin (80 °C, O_2, 1 h) with more than 90% yield. Reusability of the catalytic medium has been demonstrated, acting as "quasi-homogeneous catalyst". More sophisticated lignin-derived substrates like veratryl alcohol and hydrobenzoin gave yields of 50–80% to the respective aldehyde and ketone. In parallel, this as-synthesized suspension was directly used to prepare a Pd/TiO_2 catalyst, the latter showing less efficiency for the catalytic transformations.

Graphic Abstract



Keywords Metallic nanoparticles · Catalysis · Alcohols oxidation · Aqueous suspension

1 Introduction

The catalytic oxidation of alcohols is an important reaction giving aldehydes, ketones and carboxylic acids as valuable compounds for the chemical industry. Molecular catalysts and organic media are often used for this transformation. Besides, metal nanoparticles (NPs), particularly deposited on a support, are of great potential for oxidation reactions [1, 2] and Pd is one of the most interesting metals [3–5]. Such heterogeneous catalysts are particularly powerful to conduct oxidations in environmentally friendly conditions, i.e. in water using oxygen or air as oxidant, especially if water is the solvent to implement both catalyst preparations and catalytic reactions.

Considering this general context of sustainable chemistry the oxidation of biosourced substrates like lignin is of great potential for the production of molecules of interest. Indeed lignin is a direct renewable source of aromatics and in recent years many studies reported its catalytic valorization under oxidative atmosphere giving oxygenated aromatics [6–8]. The oxidative transformation of lignin

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generally leads to vanillin and related products through the oxidative cleavage of benzylic functions present in the substrate structure [9, 10].

More generally, recent examples reported the aerobic oxidation of benzyl alcohols in water using Pd-based heterogeneous catalysts. For instance Pd(0) nanoparticles supported on a polymer have been directly prepared by the polymerization of the Pd-containing methacrylate monomer giving selective formation of aldehydes or ketones [11]. More recently bimetallic Au–Pd NPs supported on alumina showed higher activity than the monometallic NPs for the selective oxidation of various benzyl alcohol derivatives [12]. Pd(0) NPs deposited on mesoporous carbon nanocomposites correspond to a rare example of catalyst oxidizing benzyl alcohols to the corresponding carboxylic acids [13]. Beside these supported-metal catalysts, a recent approach based on metal suspensions in a solvent gives dispersed (colloidal) nanoparticles having catalytic behaviour often considered as "quasi-homogeneous" [14–17]. If water is used as solvent, a stabilizer soluble in water is required and several systems have been reported to date especially for noble metals [18]. In the case of Pd aqueous suspensions, Pd chloride salts are often used as precursors in the presence of water soluble stabilizers like polymers (polyvinyl alcohol, polyvinyl pyrrolidone, polyethylene diamine, polystyrene, polyethylene glycol) [19–23], short- and long-chain surfactants [24, 25], calixarenes, cyclodextrins [26, 27], natural ligand (glucose, starch, proteins) [28–30] and P- or P–O-based ligands [31, 32]. As for heterogeneous catalysts, the main influencing synthesis parameters are the metal precursor, the solvent, and the stabilizing system. Preparations are generally one-pot (direct) procedures but very different conditions have been applied, leading to Pd(0) NPs through the presence of a reductant such as a base, hydrogen, the stabilizer, and most often $NaBH_4$. Examples of the formation of Pd(II) NPs have also been reported from thermal decomposition of preformed Pd complexes with water-soluble ligands [33]. The application of these Pd aqueous suspensions falls largely in the fields of C–C couplings and to a lesser extent of hydrogenations. It appears to the best of our knowledge that rare examples exist for oxidation reactions in water [34–37].

We wish to report here a straightforward synthesis of Pd catalyst in the form of nanoparticles dispersed in water. The catalytic potential of these suspensions was assessed through oxidation reactions, rarely reported to date with Pd NPs water suspensions. We particularly studied the selective oxidation of benzylic alcohols as lignin model molecules. Indeed studies related to lignin oxidation often involve model molecules to discuss structure/reactivity of novel catalytic systems and highlight the importance of reaction parameters [38, 39].

2 Experimental Section

2.1 Chemicals

All reactants, reagents and products were used as received from Sigma Aldrich except TiO_2 P25 (specific surface area 57 $m^2\ g^{-1}$) obtained from Evonik.

2.2 Synthesis of Pd NPs in Water

A first solution was prepared by dissolving Na_2PdCl_4 (21 mg, 7.05×10^{-5} mol Pd) in HPLC-grade water (8 mL) at room temperature. A second solution was prepared by dissolving PVP K30 (MW ~ 40,000, 78 mg, 10 equiv./Pd) in HPLC-grade water (8 mL) at room temperature. Both solutions were mixed and stirred for 30 min. A third solution of $NaBH_4$ (6.7 mg, 2.5 equiv./Pd) in 4 mL of HPLC-grade water was quickly added into the previous mixture, leading to colour change from yellow to black. The obtained colloidal suspension of Pd nanoparticles (0.035 mol L^{-1} of Pd) was stable over time and could be used for catalytic reactions 24 h after synthesis.

2.3 Synthesis of Pd NPs on TiO_2

Pd/TiO_2 was prepared by immobilisation of preformed Pd nanoparticles (see above). Prior to impregnation, the colloidal suspension of Pd NPs was adjusted to pH 2 by addition of HCl (10% in HPLC-grade water). TiO_2 P25 (750 mg) was then added and the mixture was stirred for 1 h at room temperature. The solid was filtered on Büchner, dried overnight (120 °C), and calcined under air flow (450 °C, 2 °C min^{-1}, N_2/O_2 80/20, 60 mL min^{-1}) for 3 h. Reduction under H_2 flow (300 °C, 2 °C min^{-1}, 60 mL min^{-1},) for 3 h followed by passivation with 1% O_2/N_2 (60 mL min^{-1}) for 30 min at room temperature led to a solid with 2.18 wt% of Pd.

2.4 Nanoparticle Size Determination

Suspended and supported Pd NPs were characterized using transmission electron microscopy on Jeol 2010 apparatus with LaB6 tip at 200 kV. For analysis, a dispersion of the sample crushed in ethanol was deposited on standard holey carbon-covered copper TEM grids. Metal particle size distributions have been determined using FIDJI image program from the measurement of around 200 particles in arbitrarily chosen areas from the images.

2.5 Pd Content Determination

Pd content was determined with an ICP-OES Activa from Horiba Jobin Yvon apparatus. The sample was dissolved with HCl/HNO_3 followed by complete water evaporation before heating further the residue in HCl.

2.6 Crystallinity Determination

Powder X-ray diffraction patterns were obtained on a Bruker D5005 spectrometer using a radiation Cu-Kα (λ = 1.054184 Å). Analysis was performed with DIFFRAC. EVA program.

2.7 Vanillic Alcohol, Veratryl Alcohol and Hydrobenzoin Oxidations

The reactions were performed in a 100 mL round-bottomed flask. A colloidal suspension of PVP stabilized Pd NPs (20 mL, 7.05×10^{-5} mol of Pd), or a dispersion of Pd/TiO_2 (277 mg, 7.05×10^{-5} mol Pd) in 20 mL of HPLC-grade water, was introduced in the flask. $NaHCO_3$ (400 mg) was added and the mixture heated at 80 °C under vigorous stirring. The reactant (7.05×10^{-3} mol for vanillic and veratryl alcohol, 100 equiv./Pd or 7.05×10^{-4} mol for hydrobenzoin, 10 equiv./Pd) was then added. The mixture was heated at the desired temperature stirred under air or O_2 flow, for a determined time with regular sampling for analysis.

2.8 Conversion and Yield Determination

Conversion and yields were determined using a Shimadzu GC-2030 gas chromatograph equipped with a FID detector (Phenomenex Zebron ZB-5HT column, He as carrier gas, T injection 300 °C, T detection 250 °C). Samples were prepared from regular sampling of 500 μL aliquots. Prior to analysis, aqueous samples were extracted with 1 mL of organic solvent (ethyl acetate for vanillic alcohol or dichloromethane for veratryl alcohol and hydrobenzoin experiments), in the presence of NaCl (200 mg). Yields are molar yields and determined through calibration of commercial samples with decane as external standard.

2.9 Recycling Experiments

After a first run, the organics were extracted with 5 mL of ethyl acetate (5 successive times) from the reaction medium until no vanillic alcohol nor vanillin were observed on GC analysis. Then a new charge of vanillic alcohol was added to the obtained aqueous phase and a second run was performed under identical conditions. This procedure was repeated for successive catalyst recycling.

3 Results and Discussion

3.1 Synthesis and Characterization of Water Suspensions of Pd(0) Nanoparticles

Several examples of dispersion of Pd(0) NPs in water stabilized by PVP have been reported, following varied synthetic conditions. Usually H_2PdCl_4, K_2PdCl_4 or Na_2PdCl_4 solutions are used as Pd sources, after conventional [40] or microwave heating [41]. Most often $NaBH_4$ serves as reductant [35, 42, 43] although examples exist using ethanol [41, 44] or even without additional reductant [45] particularly through electrochemical methods [46]. The obtained nanoparticles are of diverse average diameter size depending on the conditions, globally in the 2–5 nm range.

In the present work, we attempted to identify conditions to present a more straightforward synthetic procedure. In particular, colloidal suspensions were prepared at ambient temperature. Palladium precursor Na_2PdCl_4 was dissolved in water along with polyvinylpyrrolidone (PVP). Pd reduction occurred through addition of $NaBH_4$ in water and the mixture was stirred at room temperature. Different preparations were synthesized by varying the stoichiometry of PVP from 5, 10 and 25 molar equivalents (See Sect. 2 for details). This procedure led to colloidal suspensions with 0.035 mol L^{-1} of Pd stable for months under ambient conditions.

As indicated by TEM images (Fig. 1), with PVP/Pd of 5, Pd particles were obtained with a 3.19 ± 1.63 nm average size, which is clearly in line with reported related systems. In this case, it appears that they were encapsulated in PVP micelles but their dispersion was not completely homogeneous. In the case of PVP/Pd of 10, Pd particles possess a mean diameter of 3.85 ± 0.94 nm with a homogeneous dispersion. In the presence of 25 equiv. of PVP, the mean diameter was much higher up to 6.64 ± 1.87 nm, with moreover the presence of aggregates. Therefore, among the three systems, that giving the most dispersed Pd nanoparticles with a relatively small average size was prepared with 10 equiv. of PVP. Therefore, this system was chosen for catalytic studies.

3.2 Synthesis and Characterization of Pd Nanoparticles Supported on TiO_2

The as-synthetized Pd NPs stabilized by PVP were used to prepare immobilized Pd NPs on TiO_2. TiO_2 was chosen since this usual support for heterogeneous catalyst preparation combines structural stability in water and relatively good surface area for Pd NPs immobilisation. The pH value of the suspension was adjusted to 2 by addition of aqueous HCl in order to favour ionic interaction with the support. After impregnation, calcination, reduction and passivation steps gave a Pd/TiO_2 material containing 2.18 wt% of

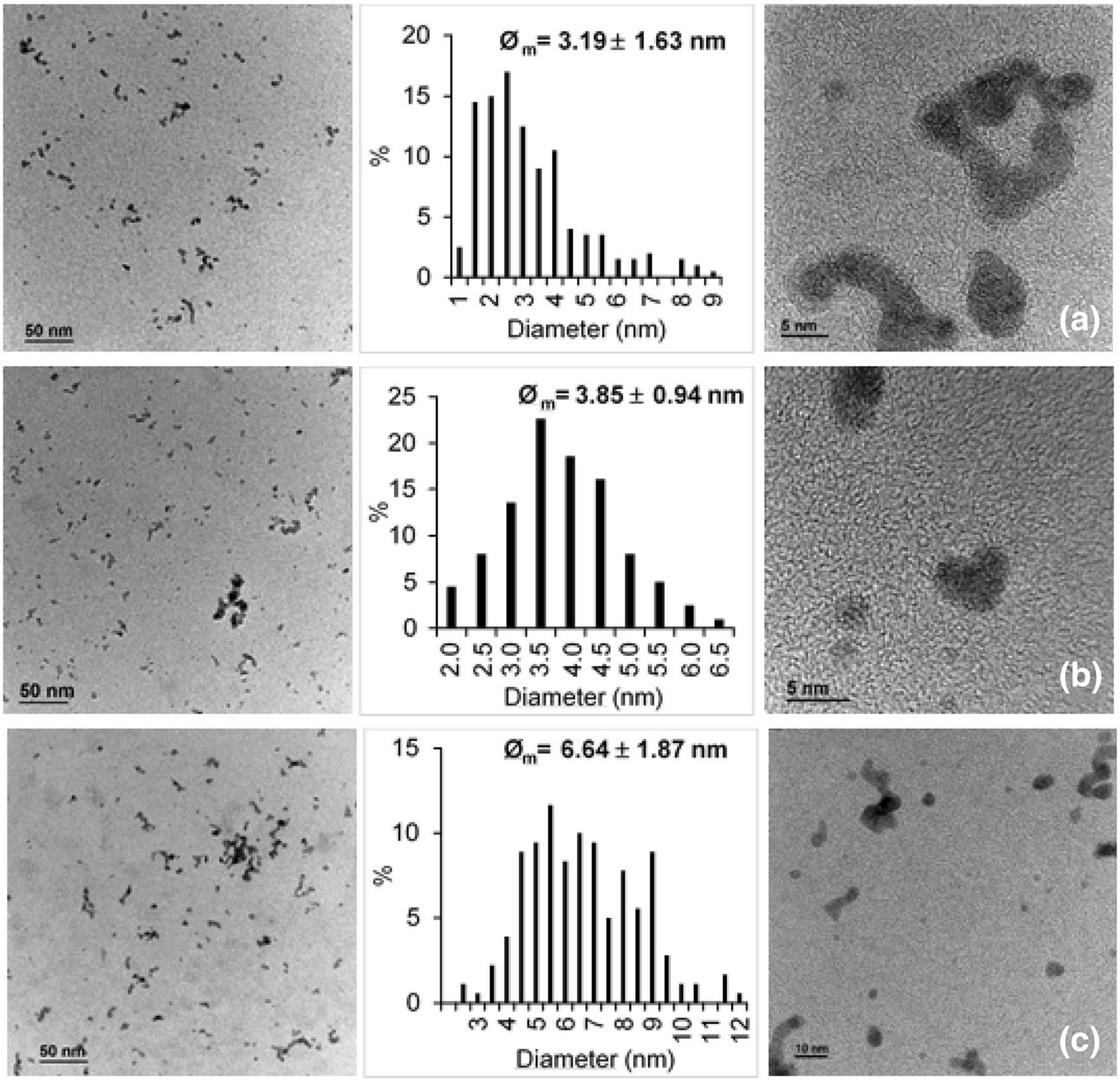


Fig. 1 TEM images and size distribution of Pd NPs prepared with **a** 5; **b** 10; **c** 25 molar equivalents of PVP in water

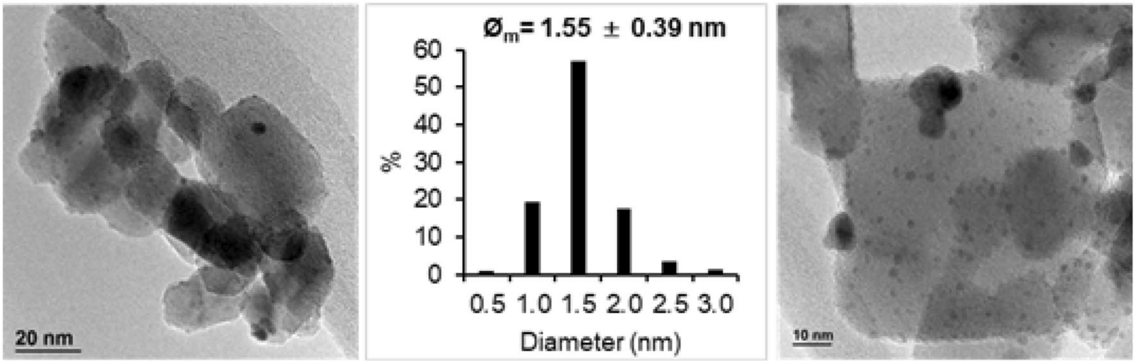


Fig. 2 TEM images and size distribution of Pd NPs deposited on TiO_2

Pd (see Sect. 2 for details). TEM images (Fig. 2) indicates that the preparation not only preserved the nice dispersion of the original nanoparticles without aggregation but also gave smaller nanoparticles with a mean diameter of 1.55 ± 0.39 nm.

To explain the presence of smaller particles, we performed a control experiment consisting of acidifying of a colloidal suspension, but without impregnation on TiO_2. TEM images (Fig. 3) of the resulting mixture indicates that acidification at pH 2.99 decreased the Pd particle sizes. Further acidification to pH 2.65 led to slight increase of the size. Indexing indicated the formation of a layer of palladium oxychloride during the acidification process. At lower pH of 2.00, this shell appeared to dissolve, releasing smaller Pd nanoparticles of lower distribution and agglomeration. When supported onto TiO_2 those NPs were of even smaller size, certainly due to fast stabilization during deposition on the support.

The BET surface area of this material was 61 $m^2\ g^{-1}$ showing no significant difference compared to TiO_2 (57 $m^2\ g^{-1}$). Moreover DRX analysis (Fig. 4) indicates that no modification of TiO_2 phases occurred during the synthesis, and as expected due to small particle size, the absence of signals from Pd.

3.3 Application to the Oxidation of Benzyl Alcohols

The catalytic properties of Pd NPs stabilised by PVP were evaluated in the oxidation of benzyl alcohols. We first studied the oxidation of vanillic alcohol, a simple lignin model. This substrate was chosen for determining the optimal reaction conditions using Pd NPs prepared with 10 equiv. of

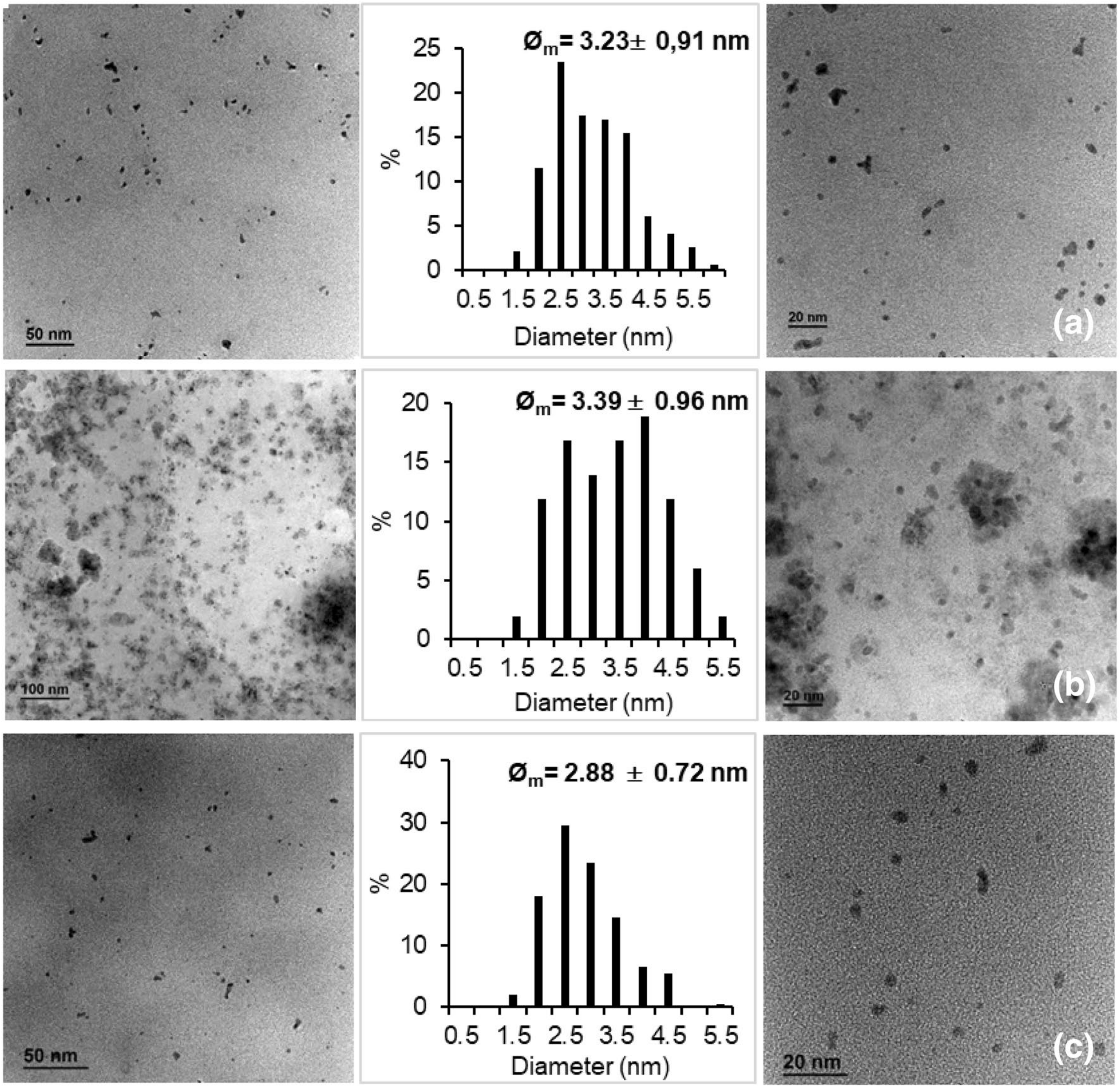


Fig. 3 TEM images and size distribution of Pd NPs after progressive acidification of the suspension, **a** pH 2.99; **b** pH 2.65; **c** pH 2.00

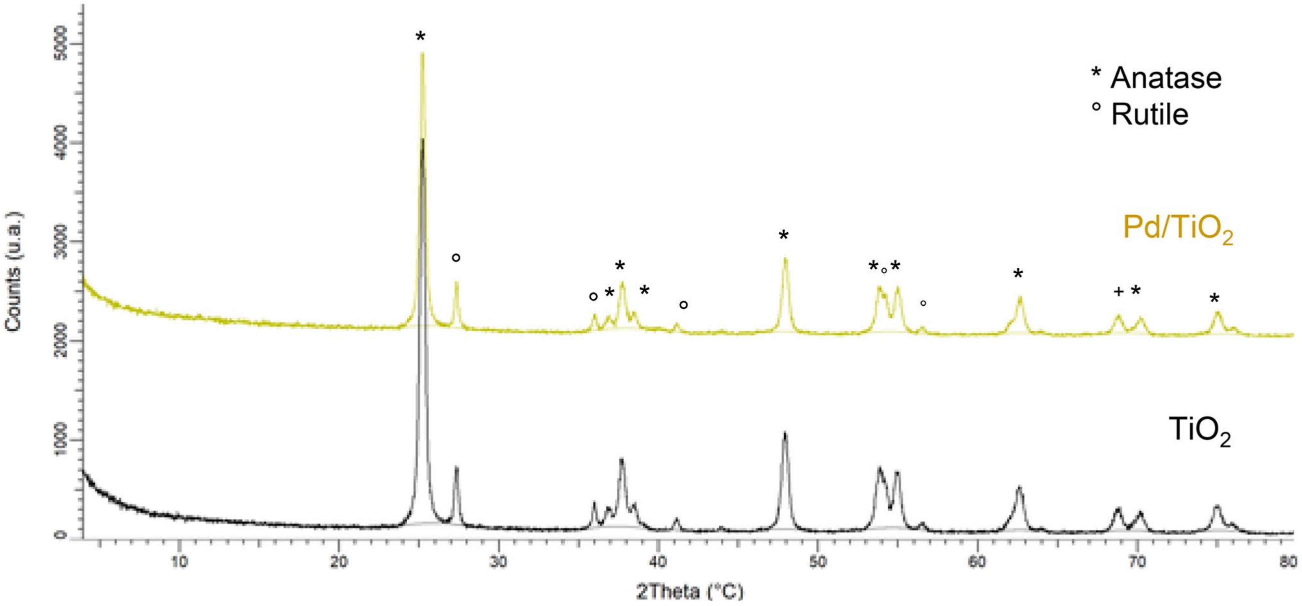
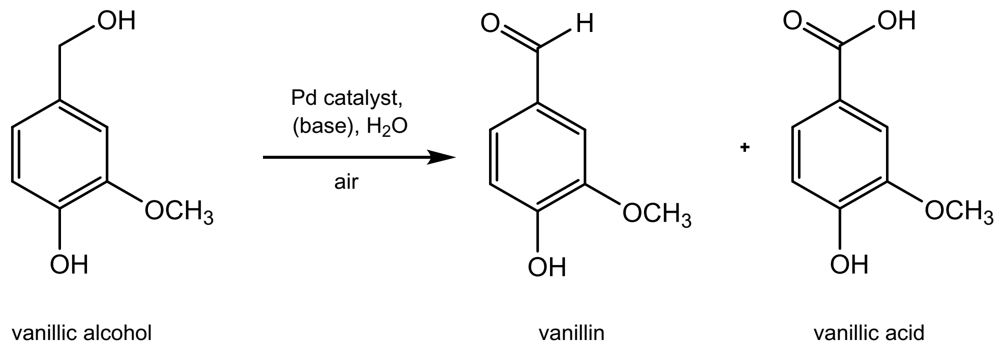


Fig. 4 X-ray diffractograms of TiO$_2$ and Pd/TiO$_2$

PVP. Oxidation of vanillic alcohol can theoretically form the corresponding aldehyde (vanillin) and carboxylic acid (vanillic acid). Note that the latter is rarely formed over classical metallic catalysts [47] while most often obtained with enzymatic catalysts [48] (Scheme 1).

First set of experiments were performed under air flow at 50 and 80 °C, with or without NaHCO$_3$ as base. These conditions were not optimized and realized to observe first tendencies as presented in Fig. 5. Thus, in the absence of a base the transformation was quite efficient for the formation of vanillin with yield of 90–95% after 8 h. The temperature had only a slight influence at the beginning but allows as expected a faster global transformation at 80 °C. The presence of NaHCO$_3$, despite giving close apparent initial rate of reaction, increased significantly the reaction time for maximum vanillin formation. The presence of the base can deactivate the catalyst, or led more probably after a certain time to uncontrolled reactivity of vanillin, successively to its continuous formation. A control experiment confirmed that vanillin was not stable in such conditions after expanded reaction time. Indeed, vanillin treated in the same condition was converted up to 75% after 15 h. As for the experiments performed in the absence of a base, no vanillic acid was observed, excluding therefore this way of transformation. Although we could not definitively identify corresponding products one can propose for example vanillin degradation through aromatic ring opening or even condensation to higher molecular mass compounds [49].

These first results indicate that the Pd NPs aqueous suspension is catalytically active for oxidation reactions and a fine tuning of the conditions has appeared necessary for a more efficient transformation. Therefore we performed the reaction in the presence of O$_2$ atmosphere in place of air to assess possible balance of reaction time and oxidant



Scheme 1 Vanillic alcohol oxidation

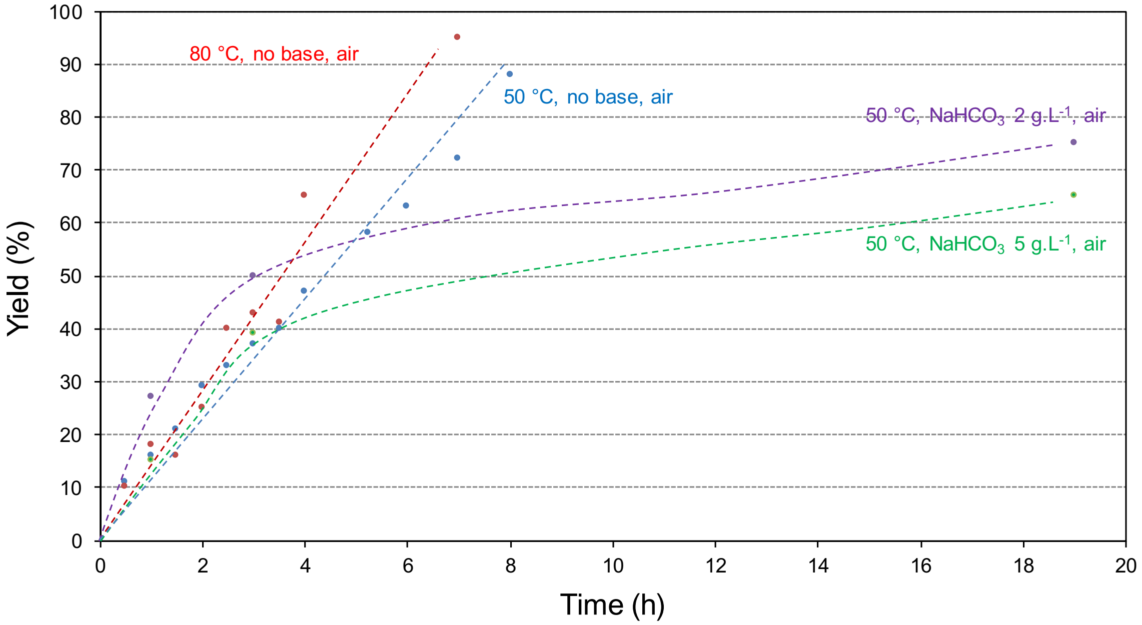


Fig. 5 Vanillic alcohol oxidation with Pd NPs stabilized by PVP under air

Table 1 Vanillic alcohol oxidation with Pd NPs stabilized by PVP under O_2

Entry	Time (h)	T (°C)	$NaHCO_3$ ($g\ L^{-1}$)	Yield of vanillin (%)[a]
1	3	80	0	100
2	3	80	5	65
3	6	80	10	100
4	1	80	20	91
5[b]	1	80	20	80
6[b]	1	80	20	66
7[c]	1	80	20	36

H_2O (20 mL); substrate 100 mol equiv./Pd; Pd: 7.05×10^{-5} mol; air flow, ambient pressure

[a] Maximum yield observed

[b] 1st and 2nd recycling

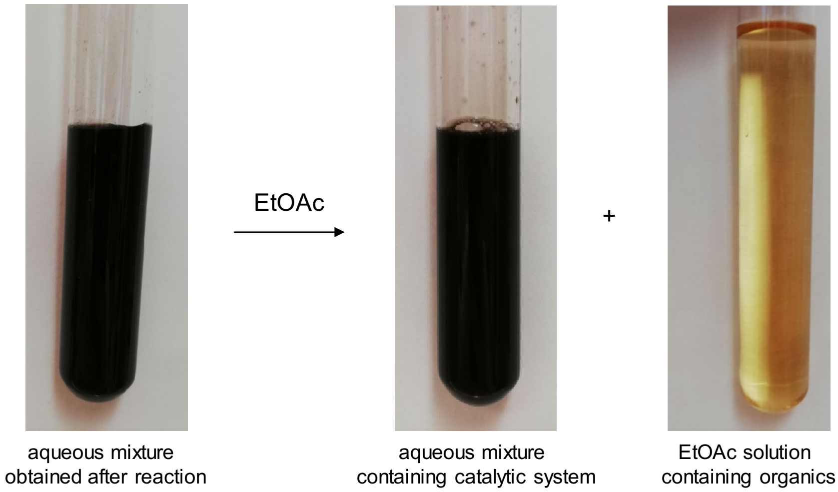
[c] In the presence of Pd/TiO_2

concentration. Thus in this second set of experiments, various conditions under O_2 were evaluated (Table 1). Interestingly in the absence of a base, a complete vanillin formation was obtained at 80 °C within a much shorter reaction time of 3 h (entry 1) than using air as oxidant. This clearly confirms the positive influence of O_2 concentration. Next, the presence of a base gave results somewhat difficult to rationalize (entries 2–4). While lowest concentrations of 5 and 10 g L^{-1} did not seem to influence the reaction, even at longer reaction times, the presence of 20 g L^{-1} allowed a very fast transformation and a yield up to 91% could be obtained after 1 h (entry 4). Note that at this level of base concentration, a noticeably short reaction time was mandatory since a decrease of vanillin yield was also clearly observed while keeping reaction running, as discussed above.

All these tendencies indicate the efficiency of this easily prepared aqueous suspension of Pd nanoparticles as catalyst without the need of purification of catalyst synthesis medium. In the literature there are not many reports of the aerobic oxidation of vanillic alcohol into vanillin with Pd-based catalysts. Examples with supported Pd such as Au–Pd/C(or HT) [50], Au–Pd/TiO_2 [51], Pd/MIL-101 [52], Pd/MgO [53], Pd/MCF [54] or Pd/Cu-chlorophosphate [55] gave interesting results at temperatures from 25 to 170 °C, however in organic solvents like dioxane, toluene or alcohols. It seems that the only example of this reaction in water using single Pd metal was performed using an immobilized Pd(0)-pyridyl-based molecular complex on SBA-15 giving 99% yield of vanillin (80 °C, 7 h, N_2 or air atmosphere, 325 equiv. of Pd) [12, 56]. Therefore, the present results are clearly in line with reported works.

Recyclability has been studied (see Sect. 2 for details). First, as shown in Fig. 6, the Pd suspension appeared to be stable after reaction since no Pd deposit was observed. Then, the organic products were extracted from the reaction medium with EtOAc leaving the catalytic system in the aqueous phase. After addition of vanillic alcohol only, another run was performed under same conditions. Results indicates that the Pd NPs were still active despite a loss of efficiency (Table 1, entries 5–6). TEM images and size distribution (Fig. 7) of Pd nanoparticles after the third run

Fig. 6 Liquid phases obtained through catalyst recycling experiments



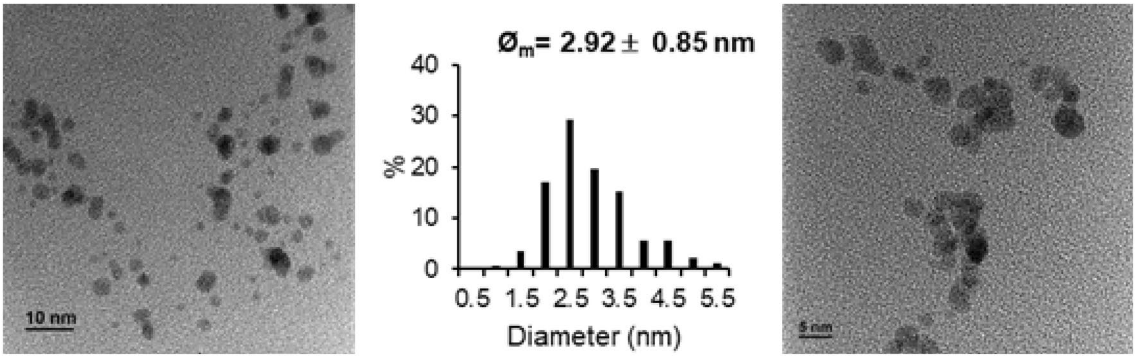


Fig. 7 TEM images and size distribution of Pd NPs after the third run

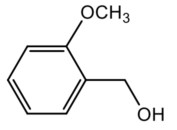
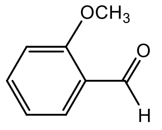
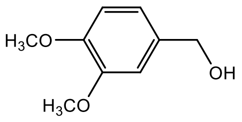
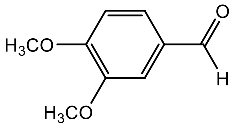
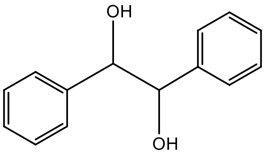
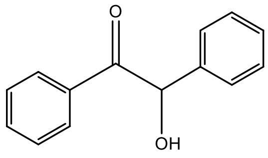
confirmed the stability of the suspension with well dispersed NPs of 2.92 ± 0.85 nm average size, in the same range as before the catalytic reactions. For each recycling, ICP analysis indicates the presence of 0.04% of initial Pd in the organic solution. Despite the fact that this corresponds to a very light loss of Pd from the original suspension, this may be a possibility for the lesser vanillin formation.

Using these last conditions, the potential of Pd/TiO_2 material prepared from the NPs/PVP nanoparticles was compared to that of the parent NPs/PVP suspension (Table 1, entry 7). Here a significant lower efficiency led to a moderate maximum yield of 36% after 1 h.

Based on this, the potential of the NPs suspension was assessed for the oxidation of other substrates modelling the lignin structure under the same conditions [57] (Table 2). First we observed that the reaction was less efficient using 2-methoxybenzyl alcohol (entry 1) with a maximum yield of 21%. Here the presence of a methoxy substituent at the *ortho* position partly prevents the transformation. This phenomenon has been recently observed with Pd-catalysts under similar conditions and steric hindrance was given as the reason for this lower reactivity [58, 59]. Veratryl alcohol oxidation was rarely reported using Pd catalysts, even more with O_2 as oxidant [60–65]. Here, veratryl alcohol reacted similarly to vanillic alcohol with the Pd NPs suspension leading to 83% of veratraldehyde after 2 h (entry 2). This is not surprising since veratryl alcohol structure only slightly differs from vanillic alcohol. Hydrobenzoin is a more sophisticated reactant having vicinal secondary alcohol functions as can be encountered within the lignin structure. Here, it was possible to obtain 58% of benzoin with nice selectivity after 5 h with the Pd NPs suspension (entry 3). Therefore no $(PhCO)_2$ benzil nor C–C cleavage products (e.g. benzaldehyde) were observed. While some reports exist with for example homogeneous Mn/H_2O_2 systems [57, 66], to the best of our knowledge this is the first example of the oxidation of this compound in the presence of a Pd/O_2/water system [67–69]. This is encouraging for the transformation of more functionalized substrates.

In all cases the colloidal suspension of Pd has proven to be much more efficient than Pd/TiO_2 which was particularly not able to transform hydrobenzoin. Note that optimization

Table 2 2-Methoxybenzyl alcohol, veratryl alcohol and hydrobenzoin oxidation under O_2

Entry	Catalytic system	Time (h)	Substrate	Product	Conv/yield (%)
1	Pd NPs suspension	3	 2-methoxybenzyl alcohol	 2-methoxybenzaldehyde	50/21
2	Pd NPs suspension	2	 veratryl alcohol	 veratraldehyde	100/83
	Pd/TiO$_2$	6			45/38
3	Pd NPs suspension	5	 hydrobenzoin	 benzoin	59/58
	Pd/TiO$_2$	6			0.6/0.5

H_2O (20 mL); substrate 10 molar equiv./Pd, Pd: 7.05×10^{-5} mol; O_2 flow, 80 °C, $NaHCO_3$ 20 g L^{-1}, ambient pressure

of conditions has not been attempted with Pd/TiO$_2$ but these results nevertheless highlight the probably higher accessibility of the Pd nanoparticles dispersed in water than supported on TiO$_2$, and that the particle size of the metal phase appeared to be not an exclusive parameter governing that reactivity.

4 Conclusion

We have presented an easy procedure for the synthesis of Pd nanoparticles in water stabilised by PVP. Nanoparticles of 3.85 nm with good dispersion were obtained. This mixture was used to prepare Pd/TiO$_2$ leading to a material having 2.18 wt% of Pd in the form of nanoparticles with a mean diameter of 1.55 ± 0.39 nm. These two systems were used as catalysts for the oxidation of benzyl alcohols as lignin model molecules in water. While Pd/TiO$_2$ presented relatively low efficiency, Pd nanoparticles suspension showed high potential for vanillic alcohol aerobic oxidation in basic medium under mild conditions of pressure and temperature, with a possibility of catalytic system reuse acting therefore as “quasi-homogeneous catalyst”. This system was also efficient for the oxidation of more complex lignin model molecules as veratryl alcohol or hydrobenzoin.

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