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 Na₂PdCl₄ with NaBH₄ 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, O₂, 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/TiO₂ 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...
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 benzylic 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 benzylic alcohol derivatives [12]. Pd(0) NPs deposited on mesoporous carbon nanocomposites correspond to a rare example of catalyst oxidizing benzylic 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–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 NaBH₄. 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 TiO₂ P25 (specific surface area 57 m² g⁻¹) obtained from Evonik.

2.2 Synthesis of Pd NPs in Water

A first solution was prepared by dissolving Na₂PdCl₄ (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 NaBH₄ (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 TiO₂

Pd/TiO₂ 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). TiO₂ 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 ºC), and calcined under air flow (450 ºC, 2 ºC min⁻¹, N₂/O₂ 80/20, 60 mL min⁻¹) for 3 h. Reduction under H₂ flow (300 ºC, 2 ºC min⁻¹, 60 mL min⁻¹) for 3 h followed by passivation with 1% O₂/N₂ (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.
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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/HNO₃ 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/TiO₂ (277 mg, 7.05 × 10⁻⁵ mol Pd) in 20 mL of HPLC-grade water, was introduced in the flask. NaHCO₃ (400 mg) was added and the mixture heated at 80 °C under vigorous stirring. The reactant (7.05 × 10⁻⁵ 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 O₂ 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 ℃, T detection 250 ℃). 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 H₂PdCl₄, K₂PdCl₄ or Na₂PdCl₄ solutions are used as Pd sources, after conventional [40] or microwave heating [41]. Most often NaBH₄ 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 Na₂PdCl₄ was dissolved in water along with polyvinylpyrrolidone (PVP). Pd reduction occurred through addition of NaBH₄ 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 TiO₂

The as-synthetized Pd NPs stabilized by PVP were used to prepare immobilized Pd NPs on TiO₂. TiO₂ 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/TiO₂ 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$_2$. 

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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 TiO₂. 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 TiO₂ 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 m² g⁻¹ showing no significant difference compared to TiO₂ (57 m² g⁻¹). Moreover DRX analysis (Fig. 4) indicates that no modification of TiO₂ 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
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 NaHCO₃ 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 NaHCO₃, 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 O₂ atmosphere in place of air to assess possible balance of reaction time and oxidant.
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Concentration. Thus in this second set of experiments, various conditions under O₂ 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 O₂ 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/TiO₂ [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, N₂ 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

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Table 1 Vanillic alcohol oxidation with Pd NPs stabilized by PVP under O₂

| Entry | Time (h) | T (°C) | NaHCO₃ (g L⁻¹) | Yield of vanillin (%)<sup>a</sup> |
|-------|----------|--------|----------------|---------------------------------|
| 1     | 3        | 80     | 0              | 100                             |
| 2     | 3        | 80     | 5              | 65                              |
| 3     | 6        | 80     | 10             | 100                             |
| 4     | 1        | 80     | 20             | 91                              |
| 5<sup>b</sup> | 1        | 80     | 20             | 80                              |
| 6<sup>b</sup> | 1        | 80     | 20             | 66                              |
| 7<sup>c</sup> | 1        | 80     | 20             | 36                              |

H₂O (20 mL); substrate 100 mol equiv./Pd; Pd: 7.05 × 10⁻⁵ mol; air flow, ambient pressure

<sup>a</sup> Maximum yield observed

<sup>b</sup> 1st and 2nd recycling

<sup>c</sup> In the presence of Pd/TiO₂
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/TiO₂ 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 O₂ 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/H₂O₂ 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/O₂/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/TiO₂ which was particularly not able to transform hydrobenzoin. Note that optimization
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of conditions has not been attempted with Pd/TiO₂ but these results nevertheless highlight the probably higher accessibility of the Pd nanoparticles dispersed in water than supported on TiO₂, 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/TiO₂ 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/TiO₂ 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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References

1. Parmeggiani C, Cardona F (2012) Transition metal based catalysts in the aerobic oxidation of alcohols. Green Chem 14:547–564
2. Davis SE, Ide MS, Davis RJ (2013) Selective oxidation of alcohols and aldehydes over supported metal nanoparticles. Green Chem 15:17–45
3. Chan-Thaw CE, Savara A, Villa A (2018) Selective benzyl alcohol oxidation over Pd catalysts. Catalysts 8:431/431-431/421
4. Durndell LJ, Lee AF, Bailie DS, Muldoon MJ (2015) Selective palladium-catalysed aerobic oxidation of alcohols. RSC Green Chem Ser 28:92–132
5. Muzart J (2003) Palladium-catalysed oxidation of primary and secondary alcohols. Tetrahedron 59:5789–5816
6. Bourbiaux D, Pu J, Rataboul F, Djakovitch L, Geantet C, Laurenti D (2021) Reductive or oxidative catalytic lignin depolymerization: an overview of recent advances. Catal Today (Under revision)
7. Sun Z, Fridrich B, de Santi A, Elangovan S, Barta K (2018) Bright side of lignin depolymerization: toward new platform chemicals. Chem Rev 118:614–678
8. Zakzeski J, Bruijninx PCA, Jongerius AL, Weckhuysen BM (2010) The catalytic valorization of lignin for the production of renewable chemicals. Chem Rev 110:3552–3599
9. Ma R, Guo M, Zhang X (2018) Recent advances in oxidative valorization of lignin. Catal Today 302:50–60
10. Vangeel T, Schutyser W, Renders T, Sels BF (2018) Perspective on lignin oxidation: advances, challenges, and future directions. Top Curr Chem 376:30
11. Dell’Anna MM, Mali M, Mastorriili P, Cotugno P, Monopoli A (2014) Oxidation of benzyl alcohols to aldehydes and ketones.
under air in water using a polymer supported palladium catalyst. J Mol Catal A 386:114–119
12. Zhang W, Xiao Z, Wang J, Fu W, Tan R, Yin D (2019) selective aerobic oxidation of alcohols over gold–palladium alloy catalysts using air at atmospheric pressure in water. ChemCatChem 11:1779–1788
13. Ganji N, Karimi B, Najafvand-Derivi-kand S, Vali H (2020) Palladium supported on a novel ordered mesoporous poly-pyrrole/ carbon nanocomposite as a powerful heterogeneous catalyst for the aerobic oxidation of alcohols to carboxylic acids and ketones on water. RSC Adv 10:13616–13631
14. Favier I, Pia D, Gómez M (2020) Palladium nanoparticles in poly-ols: synthesis, catalytic couplings, and hydrogenations. Chem Rev 120:1146–1183
15. Axet MR, Philippot K (2020) Catalysis with colloidal ruthenium nanoparticles. Chem Rev 120:1085–1145
16. Astruc D, Lu F, Aranzaes JR (2005) Nanoparticles as recyclable catalysts: the frontier between homogeneous and heterogeneous catalysis. Angew Chem Int Ed 44:7852–7872
17. Prati L, Villa A (2014) Gold colloids: from quasi-homogeneous to heterogeneous catalytic systems. Acc Chem Res 47:855–863
18. Denicourt-Nowicki A, Roucoux A (2016) Odyssey in polyphasic catalysis by metal nanoparticles. Chem Rec 16:2127–2141
19. Wang X, Huang C, Li X, Cie C, Yu S (2019) PVA-encapsulated palladium nanoparticles: eco-friendly and highly selective catalyst for hydrogenation of nitrobenzene in aqueous medium. Chem Asian J 14:2256–2272
20. I. Llevot A, Monney B, Sehlinger A, Behrens S, Meier M (2017) Highly efficient Tsuji–Trost allylation in water catalyzed by Pd nanoparticles. Chem Commun 53:5175–5178
21. Levi N, Neumann R (2013) Diastereoselective and enantiospecific direct reductive amination in water catalyzed by palladium nanoparticles stabilized by polyethyleneimine derivatives. ACS Catal 3:1915–1918
22. Ohtaka A, Teratani T, Fujii R, Ikekshita K, Kawashima T, Tsutumi K, Shimomura O, Nomura R (2011) Linear polystyrene-stabilized palladium nanoparticles-catalyzed C–C coupling reaction in water. J Org Chem 76:4052–4060
23. Sawoo S, Srimani D, Dutta P, Lahiri R, Sarkar A (2009) Size controlled synthesis of Pd nanoparticles in water and their catalytic application in C–C coupling reactions. Tetrahedron 65:4367–4374
24. La Sorella G, Sperni L, Canton F, Coletti L, Fabris F, Strukul G, Scarso A (2018) Selective hydrogenations and dechlorinations in water mediated by anionic surfactant-stabilized Pd nanoparticles. J Org Chem 83:7438–7446
25. Zhang Y, Zhu J, Xia Y-T, Sun X-T, Wu L (2016) Efficient hydrogenation of nitrogen heterocycles catalyzed by carbon-metal covalent bonds-stabilized palladium nanoparticles: synergistic effects of particle size and water. Adv Synth Catal 358:3039–3045
26. Noël S, Leger B, Ponchel A, Philippot K, Denicourt-Nowicki A, Roucoux A, Monflier E (2014) Cyclodextrin-based systems for the stabilization of metallic(0) nanoparticles and their versatile applications in catalysis. Catal Today 235:20–32
27. Mehta V, Panchal M, Kongor A, Panchal U, Jain VK (2016) Synthesis of water-dispersible Pd nanoparticles using a novel oxal-lamine derivative and their catalytic application in C–C coupling reactions. Catal Lett 146:1581–1590
28. Dhara K, Parasar B, Patil AJ, Dash J (2019) Microwave assisted cross-coupling reactions using palladium nanoparticles in aqueous media. Synth Commun 49:859–868
29. Dewan A, Bharali P, Bora U, Thakur AJ (2016) Starch assisted palladium(0) nanoparticles as in situ generated catalysts for room temperature Suzuki–Miyaura reactions in water. RSC Adv 6:11758–11762
30. Prastaro A, Ceci P, Chiancone E, Boffi A, Cirilli R, Colone M, Fabrizi G, Stringaro A, Cacchi S (2009) Suzuki–Miyaura cross-coupling catalyzed by protein-stabilized palladium nanoparticles under aerobic conditions in water: application to a one-pot chemoenzymatic enantioselective synthesis of chiral biaryl alcohols. Green Chem 11:1929–1932
31. Iben Ayad A, Belda Marín C, Colaco E, Lefevre C, Methivier C, Ould Driss A, Landoulsi J, Gueuni E (2019) “Water soluble” palladium nanoparticle engineering for C–C coupling, reduction and cyclization catalysis. Green Chem 21:6646–6657
32. Ge J, Jiang J, Yuan C, Zhang C, Liu M (2017) Palladium nanoparticles stabilized by phoshine ligand for aqueous phase room temperature Suzuki–Miyaura coupling. Tetrahedron Lett 58:1142–1145
33. Asensio JM, Tricard S, Coppel Y, Andres R, Chaudret B, de Jesus E (2017) Synthesis of water-soluble palladium nanoparticles stabilized by sulfonated N-heterocyclic carbenes. Chem Eur J 23:13435–13444
34. Hou W, Dehm NA, Scott RJW (2008) Alcohol oxidations in aqueous solutions using Au, Pd, and bimetallic AuPd nanoparticle catalysts. J Catal 253:22–27
35. Baltsa T, Strobl JR, Fowler C, Dash P, Scott RJW (2011) Selective aerobic oxidation of cyrtoyl alcohol using AuPd core-shell nanoparticles. ACS Catal 1:425–436
36. Giachi G, Oberhauser W, Frediani M, Passaglia E, Capozzoli L, Rosi L (2013) Pd-nanoparticles stabilized by pyridine-functionalized poly(ethylene glycol) as catalyst for the aerobic oxidation of α, β-unsaturated alcohols in water. J Polym Sci A 51:2518–2526
37. Matsura VA, Potekhin VV, Ukrainstev VB (2002) Kinetics of hydrogenation and oxidation of benzyl alcohol in the presence of colloidal palladium in situ. Russ J Gen Chem 72:105–109
38. Behling R, Valange S, Chatel G (2016) Heterogeneous catalytic oxidation for lignin valorization into valuable chemicals: what results? What limitations? What trends? Green Chem 18:1839–1854
39. Hanson SK, Baker RT (2015) Knocking on wood: base metal complexes as catalysts for selective oxidation of lignin models and extracts. Acc Chem Res 48:2037–2048
40. Dong Y, Jin Y, Wang J, Shu J, Zhang M (2017) Pd nanoparticles stabilized by a simple pH-sensitive p(acrylamide-co-acrylic acid) copolymer: a recyclable and highly active catalyst system in aqueous medium. Chem Eng J 325:303–312
41. Zhang J, Bai X (2017) Microwave-assisted synthesis of Pd nanoparticles and their catalysis application for Suzuki cross-coupling reactions. Inorg Nano-Met Chem 47:672–676
42. Zhao Y, Baeza IA, Koteswarao R, Calvo L, Gilarrranza MA, Li YD, Lefferts L (2014) Unsupported PVA- and PVP-stabilized Pd nanoparticles as catalyst for nitrite hydrogenation in aqueous phase. J Catal 318:162–169
43. Zhu J-F, Tao G-H, Liu H-Y, He L, Sun Q-H, Liu H-C (2014) Aqueous-phase selective hydrogenation of phenol to cyclohexanone over soluble Pd nanoparticles. Green Chem 16:2664–2669
44. Narayanan R, El-Sayed MA (2003) Effect of catalysis on the stability of metallic nanoparticles: Suzuki reaction catalyzed by PVP-palladium nanoparticles. J Am Chem Soc 125:8340–8347
45. Tarnowicz S, Alsalahi W, Mieczynska E, Trzecki AM (2017) Heck arylation of allyl alcohol catalyzed by Pd(0) nanoparticles. Tetrahedron 73:5605–5612
46. Uberman PM, Pérez LA, Martín SE, Lacconi GI (2014) Electrochemical synthesis of palladium nanoparticles in PVP solutions and their catalytic activity in Suzuki and Heck reactions in aqueous medium. RSC Adv 4:12330–12341
47. Rautiainen S, Chen J, Vehkamäki M, Repo T (2016) Oxidation of alcohols to carboxylic acids and ketones in water mediated by anionic surfactant-stabilized Pd nanoparticles. J Org Chem 83:7438–7446
48. Bayer T, Milker S, Wiesinger T, Winkler M, Mihovilovic MD, Rudroff F (2017) In vivo synthesis of polyhydroxylated
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...compounds from a “hidden reservoir” of toxic aldehyde species. ChemCatChem 9:2919–2923

49. Zhu Y, Liu J, Liao Y, Lv W, Ma L, Wang C (2018) Degradation of vanillin during lignin valorization under alkaline oxidation. Top Curr Chem 376:29

50. Wu M, Pang J-H, Song P-P, Peng J-J, Xu F, Li Q, Zhang X-M (2019) Visible light-driven oxidation of vanillyl alcohol in air with Au–Pd bimetallic nanoparticles on phosphorylated hydrotalcite. New J Chem 43:1964–1971

51. Enache DI, Edwards JK, Landon P, Solsona-Espriu B, Carley AF, Herzing AA, Watanabe M, Kiely CJ, Knight DW, Hutchings GJ (2006) Solvent-free oxidation of primary alcohols to aldehydes using Au–Pd/TiO2 catalysts. Science 311:362–365

52. Chen G, Wu S, Liu H, Jiang H, Li Y (2013) Palladium supported on an acidic metal–organic framework as an efficient catalyst in selective aerobic oxidation of alcohols. Green Chem 15:230–235

53. Layek K, Maheswaran H, Arundhati R, Kantam ML, Bhargava SK (2011) Nanocrystalline magnesium oxide stabilized palladium(0): an efficient reusable catalyst for room temperature selective aerobic oxidation of alcohols. Adv Synth Catal 353:606–616

54. Anderson M, Afewerki S, Berglund P, Córdova A (2014) Total synthesis of capsaicin analogues from lignin-derived compounds by combined heterogeneous metal, organocatalytic and enzymatic cascades in one pot. Adv Synth Catal 356:2113–2118

55. Hinde CS, Ansovini D, Wells PP, Collins G, Aswegen SV, Holmes JD, Hor TSA, Raja R (2015) Elucidating structure–property relationships in the design of metal nanoparticle catalysts for the activation of molecular oxygen. ACS Catal 5:3807–3816

56. Fu W, Yue L, Duan X, Li J, Lu G (2016) Acceptor-free dehydrogenation of 4-hydroxy-3-methoxybenzyl alcohol to vanillin over a palladium complex. Green Chem 18:6136–6142

57. Zhang Z, Khrouz L, Yin G, Andrioletti B (2019) Efficient oxidation of benzylaldehyde and aliphatic alcohols using a bioinspired cross-bridged cyclam manganese complex with H2O2. Eur J Org Chem 2019:323–327

58. Dadras A, Naimi-Jamal MR, Moghaddam FM, Ayati SE (2018) Green and selective oxidation of alcohols by immobilized Pd onto triazole functionalized Fe3O4 magnetic nanoparticles. J Chem Sci 130:162

59. Lu Y-M, Zhu H-Z, Liu J-W, Yu S-H (2015) Palladium nanoparticles supported on titane nanobelts for solvent-free aerobic oxidation of alcohols. ChemCatChem 7:4131–4136

60. Abad A, Almela C, Corma A, García H (2006) Efficient chemoselective alcohol oxidation using oxygen as oxidant. Superior performance of gold over palladium catalysts. Tetrahedron 62:6666–6672

61. Buffin BP, Clarkson JP, Belitz NL, Kundu A (2005) Pd(II)-biquinoline catalyzed aerobic oxidation of alcohols in water. J Mol Catal A 225:111–116

62. Kim A, Bae HS, Park JC, Song H, Park KH (2015) Surfactant-free Pd@SiO2 yolk–shell nanocatalysts for selective oxidation of primary alcohols to aldehydes. New J Chem 39:8153–8157

63. Olmos CM, Chinchilla LE, Cappella AM, Villa A, Delgado JJ, Hungria AB, Blanco G, Calvino JJ, Prati L, Chen X (2018) Selective oxidation of vaneryl alcohol over Au–Pd/Ce0.62Zr0.38O2 catalysts synthesized by sol-immobilization: effect of Au:Pd molar ratio. Nanomaterials 8:669/661-669/616

64. Yang Z-W, Zhao X, Li T-J, Chen W-L, Kang Q-X, Xu X-Q, Liang X-X, Feng Y, Duan H-H, Lei Z-q (2015) Catalytic properties of polygorskite supported Ru and Pd for efficient oxidation of alcohols. Catal Commun 65:34–40

65. Zhang L, Li P, Yang J, Wang M, Wang L (2014) Palladium supported on magnetic core-shell nanoparticles: an efficient and reusable catalyst for the oxidation of alcohols into aldehydes and ketones by molecular oxygen. ChemPlusChem 79:217–222

66. Mecozzi F, Dong JJ, Saisaha P, Browne WR (2017) Oxidation of vicinal diols to α-hydroxy ketones with H2O2 and a simple manganese catalyst. Eur J Org Chem 2017:6919–6925

67. De Crisci AG, Chung K, Oliver AG, Solis-Ibarra D, Waymouth RM (2013) Chemoselective oxidation of polyols with chiral palladium catalysts. Organometallics 32:2257–2266

68. Steele AM, Zhu J, Tsang SC (2001) Noble metal catalyzed aerobic oxidation of alcohols to aldehydes in supercritical carbon dioxide. Catal Lett 73:9–13

69. Iwahama T, Yoshino Y, Keitoku T, Sakaguchi S, Ishii Y (2000) Efficient oxidation of alcohols to carbonyl compounds with molecular oxygen catalyzed by N-hydroxyphthalimide combined with a Co species. J Org Chem 65:6502–6507

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