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PAPER

One-pot synthesis of lignin-stabilised platinum and palladium nanoparticles and their catalytic behaviour in oxidation and reduction reactions†

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A one-pot green method to synthesise Pt and Pd nanoparticles is reported. Two natural aromatic polymers, lignin and fulvic acid, were used as both reducing and stabilising agents at moderate temperature (80 °C) in water and under aerobic conditions. Full characterisation was performed using TEM, UV-vis, XRD, ¹⁹⁵Pt and ¹H NMR, FT-IR and GC-MS techniques. In the TEM images, we observed spherical nanoparticles of diameters in the range of 16 nm to 20 nm, in the case of Pd, and smaller ones of not so well defined shapes for Pt. GC-MS of the organic fractions formed during the preparation of the nanoparticles showed defined amounts of vanillin, a well known degradation product of these polymers. This finding indicates that the active participation of lignins and fulvic acids in the metal reduction step. The catalytic activity of the nanoparticles was tested for the NaBH₄ reduction of 4-nitrophenol and for the aerobic oxidation of alcohols, reactions that are always conducted under green conditions. Both Pt and Pd nanoparticles show good catalytic activity in the reduction reaction, while in the aerobic oxidation reaction only the Pt nanoparticles were effective.

Introduction

There is growing interest in the synthesis of metal nanoparticles (NPs) as they can show novel, and sometimes unexpected, properties with respect to their bulk aggregations.¹ Such NPs have the possibly of being used in a variety of fields (e.g. medicine, catalysis and biosensors).²

The general preparation of NPs involves the reduction of the metal ions to the zero-valent state, followed by the formation/stabilisation step for the NPs in a solvent, which is often of an organic nature. The conventional procedures to reduce the metal ions are often carried out in the presence of a not so benign agents, such as sodium borohydride, hydrazine, dimethyl formamide, hydrogen or polyols, or at high temperatures in the gas phase.³ Furthermore, capping or encapsulating agents are necessary to stabilise the metal NPs that are formed, among which there are a variety of polymeric materials, dendrimers, surfactants, organic ligands and polyoxometalates.⁴ Recently, an interesting study by Sheldon *et al.* reported the preparation *in situ* of

palladium–neocuproine NPs stabilised by both the organic ligand and the ethylene carbonate co-solvent, which were used to effectively catalyse the oxidation of alcohols in aqueous solution.⁵

In view of new and important commercial opportunities, it is important to meet the green chemistry principles for the overall procedure of the preparation of metal NPs, to minimise reactant consumption and by-product production, and to use, if possible, renewable materials and benign solvents. Indeed, in the past, some studies have reported the formation of Au, Ag, Pt and Pd NPs by natural products, like starch, carbohydrates, wood nano-materials, cellulose nanocrystallites, hydrocolloid gums and various plant extracts.⁶

Lignin is a heterogeneous and amorphous polymer of a phenolic nature, and it is the second-most-abundant biopolymer on Earth, second only to cellulose. Lignin is the only biomass constituent that is based on aromatic units. It contains about 40% of the overall organic carbon, and it constitutes 25% to 30% of the dry mass of wood.⁷ Moreover, as a waste product from the wood pulp industry, lignin is available in large amounts. Structurally, it has many hydroxylic groups that show both aliphatic and aromatic behaviours, and several aromatic methoxy, carboxylic, carbonylic and ethereal moieties.⁸ The humic materials that are present in the soil are closely related to lignins: brown- to black-coloured substances of relatively high molecular weight that are formed by secondary synthesis reactions. Among these humic substances, fulvic acids represent the only water-soluble fraction at acidic pH, and is the polymer family with a lower average molecular weight.

Our interest in reactions in water media⁹ prompted us to investigate the interactions between lignins and humic substances

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with some transition metals in their oxidised form. Fulvic acid fractions and two sulphonated lignins, such as Ca^{2+} and NH_4^+ derivatives (CaLig and AmLig), were considered. Among humic substances, we selected fulvic acid, which is the only fraction soluble in both acidic and alkaline conditions, while in the case of lignins we selected the lignosulfonate derivatives, as again they are the most soluble in water, compared, for example, with other lignins, such as organosolv, pyrolytic, steam explosion and Kraft lignins. These natural compounds contain several easily oxidisable functional groups (*e.g.* $-\text{OH}$) that can act as reducing agents for high valent metal ions, like Pt^{IV} and Pd^{II} , to form their zero state, thus inducing, in principle, the formation of NPs.

In the present study, we describe a successful and totally green method to prepare Pt and Pd NPs starting from H_2PtCl_6 and PdCl_2 , respectively, using the above-mentioned natural polymeric substrates. The NPs were then tested as catalysts for oxidation of alcohols and for reduction of 4-nitrophenol.

Experimental

Materials

The ammonium and calcium derivatives of the lignin samples (AmLig and CaLig) were a gift from Burgo Group S.p.A. (Tolmezzo, Italy). They were obtained by cooking red pine in a calcium hydrogen sulphite solution. Both of these lignins are brown powders that are highly soluble in water. Fulvic acid was obtained according to the following procedure: 5 mL of commercial concentrated humic extract from leonardite (LEA S.r.l., Reggiolo, Italy) was diluted to 100 mL with water and the pH of the solution was adjusted to 1.0 by addition of concentrated HCl. At this acidic pH, the humic acids precipitate from the solution, which allowed its separation by centrifugation (1600 g for 10 min) while the supernatant solution, containing fulvic acids, was evaporated by rotavapor. Hexachloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) and palladium chloride (PdCl_2) were purchased from Stream. The remaining reagents used in the catalytic tests were purchased from Aldrich.

Synthesis of Pt and Pd NPs

To 0.06 g lignin (or fulvic acid) in 6 mL water, 0.03 g $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ was added. For the synthesis with fulvic acid, the pH was adjusted to 7 using NaOH. The solution was heated to 80 °C for 3 h. In the case of palladium, 0.06 g lignin (or fulvic acid) in 10 mL water and 0.01 g PdCl_2 were used. For the synthesis with fulvic acid, the pH was adjusted to 7 using NaOH. Again the solution was heated to 80 °C for 3 h. Formation of NPs was shown by the change in the colour of the solution: from dark orange to dark brown for Pt, and from brown to black for Pd. This NP solution was used as such in the catalytic experiments.

NP characterisation

The samples for the UV-vis measurements were prepared by diluting 40 μL of the NP solution by the addition of 140 μL ultrapure water, with the resulting solutions analysed in 0.1 cm quartz cuvettes (Hellma). The UV-vis instrument was a Jenway

6505 spectrophotometer; with a spectral window range of 200 nm to 600 nm.

The samples for transmission electron microscopy (TEM) analysis were prepared by placing 5 μL of a 10-fold diluted solution of the metal NPs onto 3 mm, 300 mesh, formvar/carbon nickel grids (Agar Scientific Ltd), with the necessary time allowed for the evaporation of the solvent at room temperature (24 h). The TEM measurements were performed under vacuum using a 109 Zeiss EM equipped with built-in electromagnetic objective lenses and a camera (Oberkochen, Germany).

The samples for nuclear magnetic resonance (NMR) analysis were prepared by concentrating the NP solutions six-fold for platinum and 10-fold palladium. The NMR spectra were obtained using a Bruker Avance 300 spectrometer (7.05 Tesla) equipped with a high resolution multinuclear probe that operated in the range of 30 MHz to 300 MHz. To eliminate the dominant water signal in the ^1H NMR spectra, water suppression was carried out using a presaturation sequence of a composite pulse (zgpcpr Bruker sequence). A co-axial capillary tube that contained a 30 mM D_2O solution of 3-(trimethylsilyl) propionic-2,2,3,3- d_4 acid, sodium salt, was used as the reference. ^{195}Pt NMR were recorded using a saturated water solution of K_2PtCl_6 as the reference.

The samples for X-ray diffractometer (XRD) analysis were prepared by evaporation of the solvent of the entire NP solution, with the resulting solid powder placed on the glass plate of the instrument. The XRD analysis was performed on a Miniflex II Rigaku automated power XRD system ($\text{Cu K}\alpha$ radiation, 45 kV, 100 mA) (RINT 2500, Japan). Diffraction data were recorded using continuous scanning at 3°min^{-1} , with 0.010° steps.

The samples for Fourier transform infrared (FT-IR) analysis were prepared by first evaporating off the water solvent from the NPs. The resulting solid residue was milled with KBr (1%, w/w) to form a very fine powder that was compressed into a thin pellet and analysed using the FT-IR instrument (Perkin Elmer 1600), using a spectral window of 4000 cm^{-1} to 400 cm^{-1} .

The samples for gas chromatography-mass spectroscopy (GC-MS) analysis were obtained by using a 10 mL separation funnel to extract 5 mL NP water solution with 3 mL chloroform. The organic fractions were dried with anhydrous sodium sulphate, and 1 μL of these was injected into the GC-MS apparatus. The GC-MS comprised a Thermo Scientific Focus series gas-chromatograph coupled to an ISQ mass-selective detector equipped with a split-splitless injection system (injections made in splitless mode) and an HP5 MS (cross-linked 5% phenyl methyl siloxane) capillary column (length, 15 m; diameter, 0.25 mm; film thickness, 0.1 μm), using helium as the carrier gas at a constant pressure of 50 kPa. The acquisition parameters were: source, 250 °C, transfer line, 250 °C, 3 min delay in the acquisition time at the beginning of the analysis, mass range, 33 amu to 350 amu, injector temperature, 250 °C, initial temperature of the analysis, 50 °C (for 1 min), then $8^\circ \text{C min}^{-1}$ up to 120 °C (for 0 min), and $20^\circ \text{C min}^{-1}$ up to 250 °C (for 5 min), for a total acquisition time of 20 min.

Reduction and oxidation procedures

Reduction reaction of 4-nitrophenol to 4-aminophenol: here, 25 mg NaBH_4 was added to 33 mL 1 mM 4-nitrophenol with

30 μL Pd NP solution (0.17 μmol ; 194 : 1 molar ratio reagent to catalyst) or 15 μL Pt NP solution (0.18 μmol ; 183 : 1 molar ratio reagent to catalyst). These were then stirred for 4 h.

Oxidation reaction of alcohols: here, 250 μL Pt NP solution (3.0 μmol ; 120 : 1 molar ratio reagent to catalyst) or 500 μL Pd NP solution (2.8 μmol ; 128 : 1 molar ratio reagent to catalyst) was put in 12 mL 30 mM alcohol in water solution at 80 $^{\circ}\text{C}$ for 72 h under continuous stirring and under static aerobic conditions.

Results

Pt^{IV} and Pd^{II} ions were reduced to their zero-valent states in the water solution at 80 $^{\circ}\text{C}$, and under aerobic conditions in the presence of the water-soluble lignins and fulvic acid. The stable NPs obtained were fully characterised by UV-vis, ^1H NMR, ^{195}Pt NMR, TEM and XRD, and their behaviours as catalysts were tested for the reduction of 4-nitrophenol to 4-aminophenol, and for the oxidation of alcohols to their corresponding carbonyl derivatives.

The reduction of the metal ions was followed in the case of Pt^{IV} by the disappearance of the diagnostic absorption at 257 nm (Fig. 1); when lignins replaced the fulvic acids, a strong absorption band was observed at 280 nm at the end of the reaction, which was attributable to phenolic units that were completely covered at the start of the reaction by the above H_2PtCl_6 band (see ESI †). In the presence of Pd^{II} , which does not show intense and characteristic absorption peaks, the formation of Pd NPs was followed by the appearance of weak absorbances in the visible region (Fig. 2), which are probably related to the amount and size of the nanoparticles formed.¹⁰

The ^{195}Pt NMR spectra of the Pt^{IV} ion showed two diagnostic signals at 0 ppm and 503 ppm, which are attributable to the chloroplatinate PtCl_6^{2-} and $\text{PtCl}_5(\text{H}_2\text{O})^-$ species, respectively.¹¹ These progressively disappeared with the formation of the NPs. Acetic acid, formic acid and methanol were detected in the reaction mixtures (by ^1H NMR), which clearly indicates (partial) oxidation/degradation of the lignin structure.

NPs could be directly observed under TEM. Fig. 3 shows the general differences between the Pd (Fig. 3, left) and Pt (Fig. 3, right) NPs: the Pd NPs were always spherical particles, while the Pt NPs were smaller in size and of a more irregular form, with a

tendency to aggregate into irregular clusters. The sizes of the Pd NP spheres were influenced a little by the nature of the stabilising ligand, and they ranged from 16 nm (for AmLig and fulvic acid) to 20 nm (CaLig). They were also influenced by pH: strong alkaline media favoured the formation of smaller particles that were always of a spherical shape in the presence of lignins (in the presence of fulvic acid, Pd NPs were formed only at neutral to alkaline pH). Finally, the dimensions and the forms of the NPs were not affected by the amount of organic polymer used.

The XRD analysis indicated a crystalline structure for the Pd and Pt NPs, with peaks at 39.9 $^{\circ}$, 46.3 $^{\circ}$, 46.38 $^{\circ}$, 82.5 $^{\circ}$ and 86.9 $^{\circ}$ for the Pd NP dried powder, and at 39.82 $^{\circ}$, 46.37 $^{\circ}$, 64.56 $^{\circ}$ and 81.36 $^{\circ}$ for the Pt NP dried powder; these can be assigned, respectively, to the diffraction of the (111), (200), (220), and (311) planes of the face-centred cubic metal crystal with the same space group (*Fm3m*). For both of the metals, the XRD patterns did not change by replacing AmLig with CaLig (Fig. 4), while with fulvic acid, a more complicated pattern was seen, probably due to the presence of small amounts of a variety of divalent and trivalent metal ions that were already present in their complexed forms in the humic substances.

The sizes of the nanoparticles can also be calculated by treating the XRD data with the Scherrer formula, which takes into

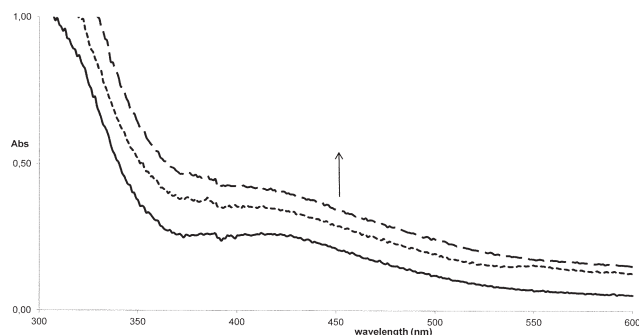


Fig. 2 UV-vis spectra acquired (0, solid line; 2 h, short-dashed line; 4 h, long-dashed line) during the formation of Pd NPs in the presence of fulvic acid.

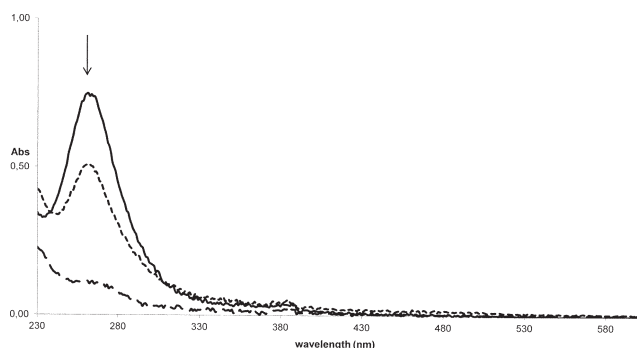


Fig. 1 UV-vis spectra acquired (0 h, solid line; 2 h, short-dashed line; 4 h, long-dashed line) during the formation of Pt NPs in the presence of fulvic acid.

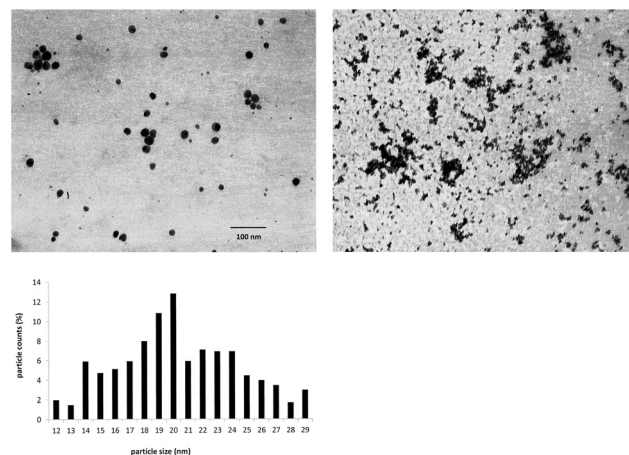


Fig. 3 TEM images of Pd (top, left) and Pt (top, right) NPs obtained through 1% aqueous CaLig solution. The particle size distribution histogram is referred to the Pd NPs.

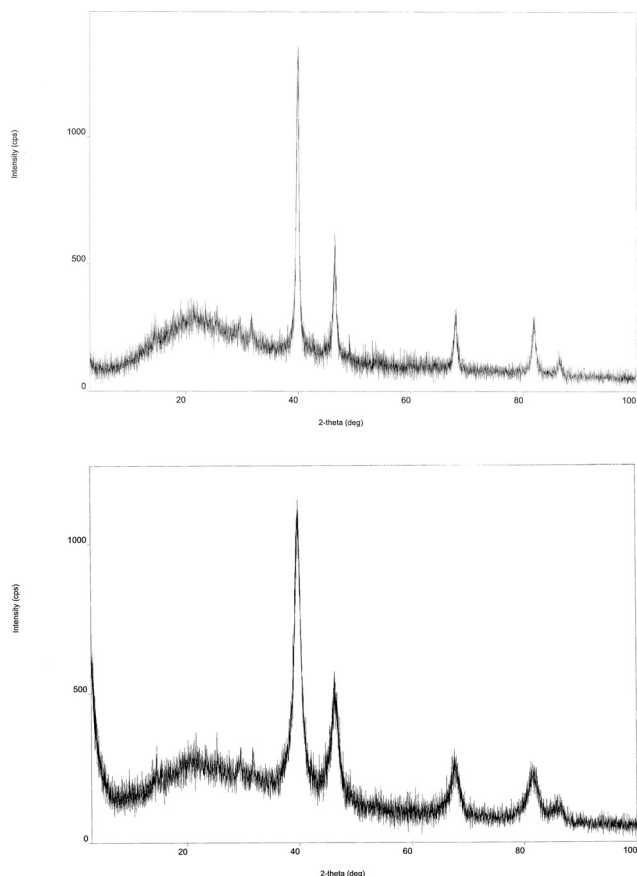


Fig. 4 XRD patterns of Pd (top) and Pt (bottom) CaLig NPs. The broad signal at 20–25 degrees is due to the sample holder.

consideration the half widths of the major diffraction peaks (111):¹²

$$d = K\lambda/B\cos\theta,$$

where d is the nanoparticle size, K (0.89) is the Scherrer constant that is related to the shape and index (hkl) of the crystals, λ is the wavelength of the X-rays (1.54056 Å), θ is the diffraction angle, and B is the corrected full-width-at-half-maximum (in radian). Such formula can be applied only if a variety of conditions are satisfied, *i.e.* NPs size below roughly 100 nm, uniform distribution of spherical shape and sizes, almost amorphous material surrounding the crystals, peak not superimposed on other peak, and related to one only phase and width at half maximum of the largest diffraction peak not affected by instrumental broadening. After a careful analysis of TEM and XRD data, we considered these assumptions valid to calculate the diameter of our NPs.

The average crystallite size was about 23 nm for Pd CaLig NPs, 18 nm for Pd AmLig NPs (both in good agreement with the data obtained by TEM), 6 nm for Pt CaLig NPs, and 8 nm for Pt AmLig NPs. Since the application of the Scherrer equation requires a clear and well resolved XRD pattern, fulvic acid NPs were not considered here.

The IR analysis was carried out to evaluate the extent of the changes in the lignin and fulvic acid structures during the

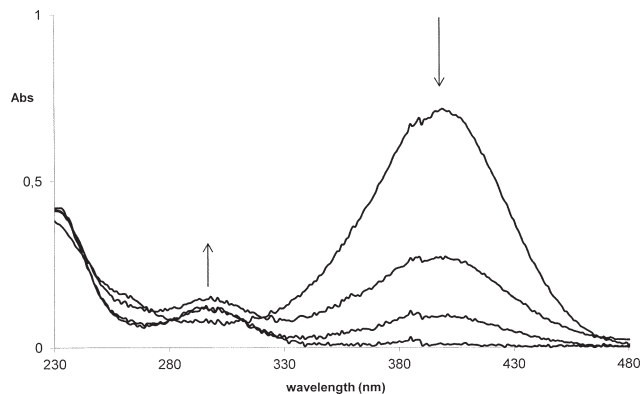


Fig. 5 Time course of reduction of 4-nitrophenol in the presence of Pt AmLig (0, solid line; 5 min, short-dashed line; 10 min, medium-dashed line; 15 min, long-dashed line).

formation of the NPs.¹³ In the IR spectra of the lignin NPs, the bands attributable to methoxyl C–O (1000–1250 cm^{-1}) and to aromatic ring vibrations (1430 and 1510 cm^{-1}) remained practically unchanged, while a weak shoulder appeared at 1730 cm^{-1} that was attributable to muconic acids and esters. Also in the spectra of the fulvic acid NPs, only negligible changes were observed in the C–O stretching and O–H deformation of COOH (1200–1280 cm^{-1}), and in the 1430 cm^{-1} to 1510 cm^{-1} regions. These findings indicate that NP formation does not significantly affect the polymer structures (see ESI†). In all cases, the GC-MS spectra of the chloroform extracts showed large amounts of vanillin (in particular for lignins), together with minor quantities of a variety of other organics, such as phenol, 2-(hydroxymethyl)phenol, salicyl alcohol salicylaldehyde, phenylethanone, phenylethanol, tetramethylbutylphenol and 2-methoxy-1,4-benzenediol (see ESI†).

Pt and Pd NPs were tested as catalysts for the reduction of 4-nitrophenol to 4-aminophenol by NaBH_4 , which has become a model reaction for evaluation of catalytic activity of metal NPs. This is because this reaction is thermodynamically favoured but kinetically hindered, and it speeds up noticeably with tiny amounts of colloidal metal NPs.¹⁴

The reaction was conducted in water and at room temperature, and it was easily monitored by UV-vis (4-nitrophenol maximum absorbance is at 399 nm, whereas that of 4-aminophenol is at 292 nm). It is important to keep in mind that aerial oxygen (the reaction is carried out under aerobic conditions) can interfere, as it can act as an oxidant of both the reactant NaBH_4 and the product 4-aminophenol: therefore, it is advised to operate in an excess of NaBH_4 , thus allowing the hydrogen formed in the water to act as oxygen purging. With 4-nitrophenol always smaller than 5% after 48 h reaction in the uncatalysed experiments, its conversions were quantitative after only 15 min reaction in the presence of fulvic acid and AmLig Pt NPs (Fig. 5). In contrast, with CaLig Pt NPs, the reduction rapidly proceeded up to about 60% conversion, but then remained unchanged even after reaction times longer than 4 h (Table 1). In the presence of Pd NPs, conversions were always lower than those obtained with the corresponding Pt NPs, and they were never quantitative. The best results were observed in the presence of fulvic acid and AmLig (96% and 74%, respectively, after 4 h).

NP-catalysed aerobic oxidation of cyclohexanol to cyclohexanone occurs only in the presence of Pt NPs, and with 100% selectivity (Table 2). Other alcohols were tested with Pt NPs (Table 3), such as saturated diols, which were recovered unchanged after 48 h of reaction, and 1-butanol and 2-butanol, which were rapidly oxidised to the corresponding carbonyl derivatives. Here, for a primary alcohol, the aldehyde was further oxidised into the carboxylic acid, thus demonstrating poor selectivity *versus* the aldehyde derivative. For a secondary alcohol, the conversions were lower, but the ketone was stable under the reaction conditions used. Also, the unsaturated alcohol 2-cyclohexenol was quantitatively converted into 2-cyclohexenone in the presence of AmLig Pt NPs, within 24 h. However, with

CaLig and fulvic acid Pt NPs, the 2-cyclohexenone formed underwent over-oxidation, with the formation of phenol and small amounts of unidentified products. The same reaction pattern was observed by direct oxidation of 2-cyclohexenone under the same conditions.

Discussion

Both Pt and Pd NPs are formed by the action of lignins or fulvic acid on the corresponding metal salts, with Pt NPs being generally smaller in size and with extensive aggregation and various geometries. Although it has often been reported that the dimensions of NPs are influenced by the reaction times,¹⁵ in our case we did not notice any significant differences between 30 min and 24 h reaction times.

The Pt and Pd NPs show remarkable stability, with the UV-vis spectra not showing any significant changes, even after one month under aerobic conditions at room temperature.

The presence of vanillin (by GC-MS) in all of the reaction mixtures containing NPs, together with acetic acid, methanol and formic acid (by ¹H NMR), clearly indicates active participation of the natural polymers in the reduction of the metal. It should be noted that the mild oxidation of lignins is actually one of most promising methods to obtain functionalised low-molecular-weight aromatics.¹⁶

Both the Pd and Pt NPs can be used as effective reduction catalysts to obtain 4-aminophenol from 4-nitrophenol. Even if inactivation of the NPs takes place pretty soon (a few hours), quantitative conversions are reached within minutes, in particular with Pt NPs. Lower catalytic effects were seen for larger NPs, *e.g.* Pd CaLig NPs, for which the largest observed (TEM) and calculated (Scherrer equation, XRD) diameters were measured.

Only Pt NPs can catalyse oxidation of alcohols. Here, catalytic activities are observed up to 48 h of reaction, although experiments conducted at longer times do not lead to higher conversions, whereas the solutions start to become heterogeneous, with the separation of brown precipitates. In the catalytic oxidation, the maximum reactivity was for CaLig Pt NPs. A careful

Table 1 Pt and Pd NP catalysis of reduction of 4-nitrophenol to 4-aminophenol (conversions; data obtained by UV-vis) with NaBH₄

Reaction time (h)	Pt FA	Pd FA	Pt CaLig	Pd CaLig	Pt AmLig	Pd AmLig
0.5	100	65	41	18	100	58
2	—	88	59	25	—	73
4	—	96	64	25	—	74

FA, fulvic acid.

Table 2 Pt and Pd NP catalytic aerobic oxidation of cyclohexanol: conversions and cyclohexanone yields (in brackets); data obtained by ¹H NMR

NPs	Reaction time (h)	
	24	48
Pt fulvic acid	13 (13)	22 (22)
Pd fulvic acid	0	0
Pt CaLig	12 (12)	20 (20)
Pd CaLig	0	0
Pt AmLig	9 (9)	17 (17)
Pd AmLig	0	0

Table 3 Pt NP catalytic oxidation of some alcohols after 24 h and 48 h of reaction time

		Reaction time (h)					
		24			48		
Alcohol		Conv.	Carbonyl yields	Acid yields	Conv.	Carbonyl yields	Acid yields
2-Cyclohexenol ^a	FA	100	55	—	100	53	—
	CaLig	100	0	—	100	0	—
	AmLig	100	85	—	100	61	—
1,3-Propandiol	FA	0	—	—	0	—	—
	CaLig	0	—	—	0	—	—
	AmLig	0	—	—	0	—	—
1,2-Cyclohexanediol	FA	<5	—	—	18	8	5
	CaLig	25	<5	15	40	6	32
	AmLig	15	<5	11	29	5	20
1-Butanol	FA	8	8	—	13	13	—
	CaLig	12	12	—	19	19	—
	AmLig	5	5	—	10	10	—

^a 2-Cyclohexenol was totally oxidised by Pt NPs; however, in the presence of Pt CaLig and Pt fulvic acid, the 2-cyclohexenone formed further reacts to give phenol and small amounts of other unidentified products. FA, fulvic acid.

analysis of the TEM images indicated that in the presence of CaLig, Pt NPs look like small spherical particles that tend to form daisy-shaped aggregates. In contrast, in the presence of fulvic acid, and, in particular, of AmLig, the NPs form aggregates of not so well defined shapes, thus suggesting that regular aggregates (CaLig Pt NPs) lead to a more efficient catalyst.

Of note, there is also the reactivity of the NPs in oxidation of 2-cyclohexenol, which leads to high yields of 2-cyclohexenone only in presence of Pt AmLig NPs. The other Pt NPs worked well too, but they also triggered the over-oxidation of the 2-cyclohexenone formed, to phenol, which has typically been detected in other reports of metal catalysis of aerobic oxidation of 2-cyclohexenones.¹⁷ This finding is probably related to the faster degradation of AmLig Pt NPs with respect to the other Pt NPs, which does not allow the catalyst to effectively act in the over-oxidation reaction.

Conclusions

A novel environmentally friendly one-step method to synthesise stable Pt and Pd NPs is reported here. This involves reduction of the corresponding metal ions in aqueous solutions at 80 °C in the presence of two aromatic natural derivatives: lignin and fulvic acid. The polymers act as both stabilising and reducing agents, as indicated by detection of vanillin and some other volatile low-molecular-weight derivatives in the NP reaction mixtures.

The NPs are fully characterised here by TEM, UV-vis and XRD. Pt NPs are smaller in diameter, and show a better catalytic performance in the reduction of 4-nitrophenol by NaBH₄ and the aerobic oxidation of alcohols. Pd NPs work well only in the reduction of 4-nitrophenol.

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