Gold Nanoparticles Supported on Poly(2,6-dimethyl-1,4-phenylene oxide) as Robust, Selective and Cost-Effective Catalyst for Aerobic Oxidation and Direct Oxidative Esterification of Alcohols

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A new catalytic system based on gold nanoparticles (AuNPs) incarcerated in poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) matrix has been synthesized and successfully tested in aerobic oxidation of alkyl alcohols. PPO is a cheap and commercially available polymer, showing nanoporous morphology, high glass transition temperature ($T_g = 220^\circ$C), semi-crystallinity, excellent thermal stability, and interesting chemo-physical properties. The synthesis of the AuNPs-PPO catalyst is simple, cost-effective and allows a fine control of the gold concentration, as well as an optimal dispersion of 7–8 nm sized AuNPs in the polymer matrix. AuNPs-PPO is an efficient, robust and selective catalyst active in the aerobic oxidation and oxidative esterification of alcohols in water under mild reaction conditions (35°C, atmospheric pressure of oxygen). The testing of AuNPs-PPO in aerobic oxidation of 1-phenylethanol to acetophenone, as a benchmark reaction, highlighted that this gold catalyst exhibits activity values among the highest so far reported for polymer-supported AuNPs under mild reaction conditions. The oxidation of primary alcohols, such as benzyl and cinnamyl alcohols, could be addressed to the corresponding aldehyde or carboxylate derivatives. Alkyl cinnamates were obtained with efficiency in the one-pot aerobic oxidation of cinnamyl alcohol in the presence of alkyl alcohols, such as n-butanol or n-hexanol. The role of the polymer matrix and the reaction conditions on both activity and selectivity of the AuNPs-PPO catalyst were also investigated and discussed.

Introduction

Nanostructured gold, differently from the bulk metal, presents extraordinary chemo-physical properties due to the high surface area and, primarily, the quantum size effect.[1] The confinement of gold as nanosized particle discloses novel features to this metal, substantially inert in the bulky form. Gold nanoparticles (AuNPs) catalyse several organic transformations under mild and green conditions, with high selectivity and activity.[2] A number of inorganic and organic supports have been used for preventing coalescence of the nanoparticles and enhancing both selectivity and activity in catalytic applications. Organic polymers are versatile supports because of their wide commercial availability and the extended possibility of functionalization.[2a,3] The polymer matrix not only serves as a stabilizer to prevent metal leaching during the catalytic application, but also assists the catalytic process by controlling the chemical environment surrounding the catalytic sites (Figure 1).[2a]

The swelling of the polymer matrix by treatment with solvents or reagents enhances the accessibility of the reactants to the catalytic sites, locating these nanohybrid catalysts at the interface between heterogeneous and homogeneous catalysis.[2b] Porous polymers, in particular micro- and mesoporous polymers with pore sizes smaller than 2 nm and in the range 2–50 nm, respectively, intrinsically show superior permeability to small organic molecules.[2a,k] To date, only two polymers comprising porous crystalline phases with high permeability to organic molecules are known to produce co-
crystalline structures: syndiotactic polystyrene (sPS)\textsuperscript{[4]} and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO)\textsuperscript{[5]}. sPS and its multiblock copolymer with cis-1,4-polybutadiene (sPSB) have been used as support of AuNPs and exhibited interesting catalytic patterns\textsuperscript{[2a]} in aerobic oxidations of alcohols\textsuperscript{[6]}, nitroarene reduction\textsuperscript{[7]}, and hydroamination of alkynes with anilines\textsuperscript{[8]}, with unprecedented selectivity and activity under mild to moderate reaction conditions. The careful choice of the solvent, reaction temperature and crystalline structure of the polymer matrix allowed to address the reaction course toward the formation of the desired reaction product in high yields. Worth of mention is the application of the sPSB-AuNPs catalyst in the valorisation of the biosourced platform molecule 5-hydroxymethylfurfural (HMF): at the variance of the reaction conditions, it was possible to address the species permeating the organic support and the synthesis of a library of HMF derivatives of industrial interest.\textsuperscript{[6c]}

PPO is cheap, commercially available, and thermally stable plastics showing high glass transition temperature ($T_g$ = 215 °C) and excellent chemical and physical resistance. PPO has been recently recognized as a polymorphic nanoporous polymer\textsuperscript{[5b]} that efficiently absorbs small organic molecules, also in traces, from air or water\textsuperscript{[9]}; both these features are of interest for designing catalytic application of PPO supported AuNPs. Herein we describe the synthesis of AuNPs embedded in PPO and the application of this nanocomposite in the aerobic oxidation of alcohols as well as in the direct oxidative esterification reaction of alcohols. The synthesis of AuNPs-PPO is simple and cost-effective and allows the complete entrapment of gold determining a fine regulation of the metal content in the catalyst. AuNPs-PPO resulted highly active in the oxidation of 1-phenylethanol to acetophenone, as a benchmark reaction, even in water as a solvent, atmospheric pressure of oxygen and 35 °C. Additionally, the catalyst allowed addressing the reaction course toward the formation of the desired products in the oxidation of primary alcohols, such as benzyl and cinnamyl alcohol. Considering the pharmacological and cosmetic applications of alkyl cinnamates\textsuperscript{[6b,10]} the production of these derivatives via direct oxidative esterification of cinnamyl alcohol with alkyl alcohols has been also explored. The origins of the activity and selectivity of the novel catalytic system were also investigated and discussed.

**Results and Discussion**

**Synthesis and characterization of AuNPs-PPO**

The procedure adopted for the synthesis of AuNPs-PPO is straightforward and efficient, leading to small-sized AuNPs (about 7 nm, see Figure 2 and 3) homogeneously dispersed in the polymer matrix. The entrapment of gold is quantitative, allowing a programmable composition of the catalyst. In brief, tetrachloroauric acid was compounded with PPO in THF, followed by reduction of the gold precursor with sodium tetraethyl-borohydride at room temperature; the catalyst was recovered by precipitation in methanol, filtration and drying in vacuo at room temperature. The gold content (pre-set to 2 wt\% Au) was assessed by ICP-OES analysis of the catalyst mineralized by digestion with sulfuric acid, hydrogen peroxide and aqua regia (see Experimental part).

![Figure 2. HR-TEM micrographs of: i) AuNPs-PPO (a) with corresponding magnification of a single AuNPs (b); SAED of the sample region (c); ii) AuNPs-PPO170; (d) with corresponding AuNPs magnification (e) and SAED (f).](image)
The aerobic oxidation of 1-phenylethanol to acetophenone is the benchmark reaction in which the nanogold catalysts are typically tested. Under the typical conditions adopted for this reaction,\(^\text{[4d]}\) (gold loading = 4 mol%; KOH as a base, 1 : 1 molar ratio with the substrate, atmospheric pressure of oxygen and temperature of 35\(^\circ\)C) the alcohol conversion in water is 80% within 6 h, corresponding to a turnover frequency (TOF) of 3.32 mol\(_{\text{alcohol}}\)/mol\(_{\text{Au}}\) h\(^{-1}\) (entry 1, Table 1). As it can be readily envisioned, crystallization of the host polymer matrix resulting from annealing with temperature (entries 2–3, Table 1) reduces the permeability of PPO to organics and the activity of the catalyst, as a consequence.\(^\text{[6]}\)

The thermal treatment of the catalyst at 170\(^\circ\)C or 230\(^\circ\)C produced a worsening of the catalytic activity, which decreased from 3.32 to 1.12 and 0.26 mol\(_{\text{alcohol}}\)/mol\(_{\text{Au}}\) h\(^{-1}\), respectively (compare 1 with entries 2–3 of Table 1). The AuNPs-PPO-(H\(_2\)O&CHCl\(_3\)), AuNPs-PPO-(H\(_2\)O&Tol) and AuNPs-PPO-(H\(_2\)O&CCl\(_4\)) catalysts also worse performed (entries 4–6, Table 1). In conclusion, the PPO matrix acts as a harvester, i.e. a concentrator and conveyor, of the alcohol from the water medium to the gold catalytic sites but crystallization of the polymer support reduces permeability and catalytic activity.

The increase of the reaction temperature strongly enhances the oxidation rate of 1-phenylethanol yielding an alcohol conversion of 92% in 3 h at 80\(^\circ\)C, with a corresponding TOF of 7.70 mol\(_{\text{alcohol}}\)/mol\(_{\text{Au}}\) h\(^{-1}\) (compare entry 7 with 1 of Table 1). A further increase of the reaction temperature to 100\(^\circ\)C did not produce an increase in the catalytic activity (TOF = 4.63 mol\(_{\text{alcohol}}\)/mol\(_{\text{Au}}\) h\(^{-1}\); compare entry 8 with 7 of Table 1). The increase of the reaction temperature to 80\(^\circ\)C improves the diffusivity of the reactant in the polymer matrix and thus the catalytic activity (entry 7, Table 1). The further increase of the reaction temperature to 100\(^\circ\)C did not result in a further increase in the activity (entry 8, Table 1) likely because of the drop in oxygen solubility at the boiling point of water.

The concentration of KOH strongly affects the reaction rate; the increase of the Brønsted base concentration from 3 to 6 equiv. changed the catalytic activity from 4.57 to 5.79 mol\(_{\text{alcohol}}\)/h.
mol\textsubscript{Au}^{-1} h\textsuperscript{-1} (compare entries 9–10 with 1 of Table 1 and with entries 1–2 of Table 3). This effect agrees with the generally accepted mechanism for aerobic oxidation of alcohol catalysed by AuNPs. The Brønsted base deprotonates the alcohol favouring its coordination to the AuNPs surface\cite{12} later on it promotes the hydride shift from the carbynol group to the gold surface determining alcohol oxidation\cite{13,14} and finally catalyses the decomposition of the hydroperoxide species on the surface of gold\cite{12} resulting from the two-electron reduction of dioxygen with Au–H\cite{14}. It was previously observed that the addition of chloroform to water as solvent enhances the gold catalyst performance in alcohol oxidation.\cite{16} In the case of AuNPs-PPO this solvent mixture affords crystallization of the polymer matrix (Figure 3) and produces thus lower permeability to the reactants. The activity of AuNPs-PPO in 1-phenylethanol oxidation in neat water is thus higher than that in water/chloroform (entries 11–13, Table 1); a moderate improvement of the catalytic activity was observed with AuNPs-PPO\textsubscript{170} and AuNPs-PPO\textsubscript{310} (compare entries 12–13 with 2–3 of Table 1) likely as a result of the polymer swelling of the crystalline phase into the organic solvent.

The catalyst resulted reusable: under the reaction condition of entry 7 in Table 1, i.e., in water, 80 °C and atmospheric pressure of oxygen, AuNPs-PPO preserved its activity for at least five utilizations (see Table S1 of Supporting information).

**Table 1. Aerobic oxidation of 1-phenylethanol to aceto phenone promoted by AuNPs-PPO.**

| Entry[a] | Catalyst       | T  | KOH/Alcohol | Solvent | Time | Yield [b] | TOF [c] |
|----------|----------------|----|-------------|---------|------|-----------|---------|
| 1        | AuNPs-PPO      | 35 | 1           | H\textsubscript{2}O | 6    | 80        | 3.32    |
| 2        | AuNPs-PPO\textsubscript{170} | 35 | 1           | H\textsubscript{2}O | 6    | 27        | 1.12    |
| 3        | AuNPs-PPO\textsubscript{310} | 35 | 1           | H\textsubscript{2}O | 5    | 5         | 0.26    |
| 4        | AuNPs-PPO-(H\textsubscript{2}O&CH\textsubscript{2}Cl\textsubscript{2}) | 35 | 1           | H\textsubscript{2}O | 5    | 4         | 0.20    |
| 5        | AuNPs-PPO-(H\textsubscript{2}O&Tol) | 35 | 1           | H\textsubscript{2}O | 5    | 9         | 0.43    |
| 6        | AuNPs-PPO-(H\textsubscript{2}O&CH\textsubscript{2}Cl\textsubscript{2}) | 35 | 1           | H\textsubscript{2}O | 5    | 3         | 0.16    |
| 7        | AuNPs-PPO      | 80 | 1           | H\textsubscript{2}O | 3    | 92        | 7.70    |
| 8        | AuNPs-PPO      | 100| 1           | H\textsubscript{2}O | 5    | 93        | 4.63    |
| 9        | AuNPs-PPO      | 80 | 3           | H\textsubscript{2}O | 4    | 73        | 4.57    |
| 10       | AuNPs-PPO      | 80 | 6           | H\textsubscript{2}O | 4    | 93        | 5.79    |
| 11       | AuNPs-PPO      | 35 | 1           | H\textsubscript{2}O&CH\textsubscript{2}Cl\textsubscript{2} \, (e) | 6    | 35        | 1.46    |
| 12       | AuNPs-PPO\textsubscript{170} | 35 | 1           | H\textsubscript{2}O&CH\textsubscript{2}Cl\textsubscript{2} \, (e) | 8    | 69        | 2.17    |
| 13       | AuNPs-PPO\textsubscript{310} | 35 | 1           | H\textsubscript{2}O&CH\textsubscript{2}Cl\textsubscript{2} \, (e) | 6    | 34        | 1.42    |

[a] Reaction conditions: [a] 1-phenylethanol = 0.51 mmol; gold loading = 4 mol% w.r.t 1-phenylethanol; PO\textsubscript{2} = 1 atm; KOH; anisole internal standard = 0.51 mmol; solvent volume = 6 mL, [b] Determined by GC-MS, selectivity for formation of aceto phenone > 99.9%, [c] v/v = 1/1.

Aerobic selective oxidation of benzyl alcohol

To widen the reaction scope, the AuNPs-PPO catalyst was tested in aerobic oxidation of benzyl alcohol in water; the alcohol conversion is 60% and the benzoic acid vs benzaldehyde selectivity was of 90.2 (entry 1, Table 2). The calculated TOF value of 2.50 mol\textsubscript{Alcohol} mol\textsubscript{Au}^{-1} h\textsuperscript{-1} is lower than that found in 1-phenylethanol oxidation (compare entry 1 of Table 2 with entry 1 of Table 1). Also in this case, the thermally treated catalysts AuNPs-PPO\textsubscript{170} and AuNPs-PPO\textsubscript{310} worse performed in this reaction (compare entries 2–3 with 1 of Table 2) because of the not permeable polymer phase. Noteworthy the solvent annealing of the catalyst (see entries 4–5 of Table 2) or the presence of organic solvents changes the selectivity in favour of benzaldehyde which is the only reaction product in H\textsubscript{2}O/H\textsubscript{2}OCH\textsubscript{2}Cl\textsubscript{2} (entry 6–7, Table 2) whereas benzoic acid is selectively obtained in water (compare entries 1–2 with entry 6, Table 2). The aerobic oxidation of primary alcohols to carboxylic acids over gold catalyst proceeds through the oxidation of the alcohol to aldehyde that, in turn is oxidized to the corresponding carboxylic acid after the formation of the gem-diol intermediate (see Scheme 1). To understand the origin of selectivity in primary alcohol oxidation by AuNPs-PPO, the speciation and the species-repartition in water and chloroform was analysed by \textsuperscript{1}H NMR spectroscopy (see Figure S1 in the Supplementary Material). Benzyl alcohol and benzaldehyde were vigorously stirred in H\textsubscript{2}O/CH\textsubscript{2}Cl\textsubscript{2} (entry 6–7, Table 2) whereas benzoic acid is selectively obtained in water (compare entries 1–2 with entry 6, Table 2).
Selective oxidation and oxidative esterification of cinnamyl alcohol

The selective oxidation of cinnamyl alcohol and the oxidative esterification of this alcohol to alkyl cinnamates yield products of interest for pharmaceutical and cosmetic industry. The ability of the AuNPs-PPO catalyst in these reactions was thus investigated and the main results are reported in Table 3.

Under the reaction conditions of entry 11 of Table 1 and entry 6 of Table 2, the aerobic oxidation of cinnamyl alcohol proceeds slowly affording alcohol conversion of only 3.7% with a TOF of 0.27 mol_{alcohol} mol_{Au}^{-1} h^{-1} (entry 1, Table 3); selectivity is also rather low as a result of the formation of cinnamaldehyde and 3-phenylpropan-1-ol in comparable amounts. Interestingly, both catalytic activity and selectivity significantly increased when the concentration of KOH was increased to 6 equiv.; the alcohol conversion is 97% in 1.5 h, corresponding to a TOF of 16.19 mol_{alcohol} mol_{Au}^{-1} h^{-1} and selectivity of 96.9% in cinnamaldehyde (entry 2, Table 3). The oxidation of cinnamyl alcohol in the presence of 1-butanol yields the corresponding alkyl cinnamates in high yield and selectivity. The oxidative esterification of cinnamyl alcohol with 1-butanol produced 93% conversion of the alcohol in 6 h and selective formation (93.3%) of butyl cinnamate (entry 3, Table 3). The corresponding reaction with 1-hexanol led to 89% of alcohol conversion with a selectivity of 65.9% in hexyl cinnamate (entry 4, Table 3).

In the light of the reaction mechanism above discussed, one can assume that, under mild reaction conditions, primary alkyl alcohols are not oxidised whereas aryl and allyl alcohols do it. Therefore, the selective oxidation of a mixture of alkyl alcohols with benzyl or allyl alcohols leads to the synthesis of alkyl carboxylates via hemiacetal intermediates resulting from the nucleophilic attack of the primary alcohols to the unsaturated aldehyde. The presence of an organic solvent in the reaction mixture or of a hydrophobic polymer support can contribute to avoiding alcohol over oxidation to carboxylic acid representing the resting state in the cascade of oxidation reactions.

Table 2. Aerobic oxidation of benzyl alcohol promoted by AuNPs-PPO.

| Entry | Catalyst | Solvent | Time | Conv. | Benzaldehyde | Benzoic acid | TOF[^c] |
|-------|----------|---------|------|-------|--------------|--------------|---------|
| 1     | AuNPs-PPO | H2O     | 6    | 60    | 5.9          | 9.8          | 54.1    |
| 2     | AuNPs-PPO | H2O     | 6    | 59    | 1.2          | 1.9          | 57.8    |
| 3     | AuNPs-PPO | H2O     | 6    | 36    | 18           | 50.1         | 18      |
| 4     | AuNPs-PPO | H2O     | 6    | 24    | >99.9        | -            | -       |
| 5     | AuNPs-PPO | H2O     | 6    | 1     | >99.9        | -            | -       |
| 6     | AuNPs-PPO | H2O     | 24   | 76    | 76           | >99.9        | -       |
| 7     | AuNPs-PPO | H2O     | 24   | 33    | 33           | >99.9        | -       |

[^a]: Reaction conditions: benzyl alcohol = 0.51 mmol; gold loading = 4 mol% w.r.t. benzyl alcohol; PO2 = 1 atm; KOH/benzyl alcohol molar ratio = 1; anisole internal standard = 0.51 mmol; solvent volume = 6 mL; 35 °C, [b]: Conversion of benzyl alcohol determined by 1H NMR, [c]: Determined by 1H NMR, [d]: v/v = 1/1.
Table 3. Aerobic oxidation of cinnamyl alcohol and direct oxidative esterification of cinnamyl alcohol with alkyl alcohols promoted by AuNPs-PPO.

| Entry | Alkyl alcohol | KOH/ cinnamyl alcohol | Time | Conv. | Cinnamaldehyde | 3-Phenylpropan-1-ol | TOF \( \text{h}^{-1} \) |
|-------|---------------|------------------------|------|-------|----------------|---------------------|----------------|
| 1     | –             | 1                      | 3    | 3.7   | 1.5            | 40.5                | 2.2            |
| 2     | –             | 6                      | 1.5  | 97    | 94.0           | 96.9                | 3.0            |
| 3     | 1-butanol     | 6                      | 93   | 3.7   | 4.0            | 2.5                 | 2.7            |
| 4     | 1-hexanol     | 6                      | 89   | 27.5  | 30.9           | 2.8                 | 3.2            |

[a] Reaction conditions: cinnamyl alcohol = 0.51 mmol; alkyl alcohol = 5.1 mmol; gold loading = 4 mol% w.r.t. cinnamyl alcohol; \( \text{PO}_2 = 1 \) atm; KOH; anisole internal standard = 0.51 mmol; solvent = \( \text{H}_2\text{O}/\text{CHCl}_3 \) (v/v = 1/1); 6 mL; 35 °C. [b] Conversion of cinnamyl alcohol determined by \( ^1\text{H} \) NMR. [c] Determined by \( ^1\text{H} \) NMR.

Conclusion

The AuNPs-PPO has been easily synthesized with fine regulation of gold content and optimal dispersion of the nanosized metal particles in the polymer matrix. The excellent chemophysical properties of PPO provided thermal robustness to the catalytic system and the possibility of addressing the reaction pathway with efficiency and selectivity. 1-phenylethanol was oxidised in water to acetophenone under mild reaction conditions with high selectivity and high mobility of the organics through the polymer support that acts as a conveyor and concentrator of the reactants towards the catalytic sites. The hydrophobic AuNPs-PPO catalyst is highly active in 1-phenylethanol and benzyl alcohol oxidation even in water. Interestingly the selectivity of the oxidation pathway can be addressed at variance of the solvent; the addition of an organic solvent such as chloroform or hexane allowed the selective formation of benzaldehyde whereas benzoic acid was the main reaction product in water. This result was explained considering that the oxidation of the benzyl alcohol proceeds in the first step to benzaldehyde which is then further oxidized to benzoic acid via gem-diol in water. In chloroform/water solvent mixture, the speciation of benzaldehyde demonstrates that the aldehyde is protected in organic solvent from hydration to gem-diol and thus towards the further oxidation to acid. This concept explains the possibility of selective syntheses of alkyl esters by means of direct oxidative esterification. The oxidation of cinnamyl alcohol was addressed to cinnamaldehyde or alkyl cinnamates depending on the reaction conditions.

In conclusion, AuNPs-PPO is an efficient and versatile catalyst for the synthesis of fine chemicals, showing high selectivity in aerobic oxidation and oxidative esterification of alcohols.

Experimental Section

Materials. HAuCl₄·3H₂O (Sigma-Aldrich), poly(2,6-dimethyl-1,4-phenylene oxide) (PPO, Sigma-Aldrich), sodium triethylborohydride (1.0 M in THF; Sigma–Aldrich), (±)-1-phenylethanol (>99%, Sigma–Aldrich), benzyl alcohol (>99%, Sigma–Aldrich), benzaldehyde (>99% Sigma–Aldrich), cinnamyl alcohol (97% Fluka), methanol (HPLC grade; Sigma), ethanol (99.8% Fluka), isopropyl alcohol (99.8% Sigma–Aldrich), 1-butanol (98%; Labscan), 1-hexanol (98% Sigma–Aldrich), hydrochloric acid (37%; Sigma–Aldrich), potassium hydroxide (85%; Sigma–Aldrich), anisole (99% Sigma–Aldrich), water (HPLC grade; Panreac), tolune (HPLC grade; Romil), chloroform (HPLC grade; Romil) and deuterated solvents (Euriso-Top or Sigma–Aldrich), unless otherwise stated, were used as received. Oxygen (5.0) was supplied by Linde and used as received. The Au(III) standard solution (Carlo Erba; 1.000 ± 0.002 g L⁻¹ in aqueous HCl solution, 2 %w/w), for the AAS and ICP-OES measurements, was used as received.

Instrumentation and methods. Nuclear magnetic resonance (NMR) spectra were recorded with Bruker AVANCE spectrometers (600, 400 and 300 MHz for \(^1\text{H} \) NMR). Chemical shifts were referenced to tetramethylsilane, as an external reference, using residual protio signals of deuterated solvents. Wide-angle x-ray diffraction (WAXD) patterns were obtained in reflection mode with an automatic Bruker D8 powder diffractometer using the nickel-filtered CuKα radiation. High resolution-transmission electron microscopy (HR-TEM) analysis was carried out with a Tecnai 20 (FEI) microscope operated at 200 kV. The specimens for TEM analysis were sonicated in 2-propanol, then transferred (10 mL) onto a copper grid covered with a lacey carbon film supplied from Assing. The gold loading in AuNPs-PPO was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) with an Optima 7000 DV spectrometer from Perkin-Elmer. The AuNPs-PPO catalyst (50 mg) was acid digested in a Kjeldahl flask by treatment with concentrated hydrochloric acid (5 M) with addition of a sodium hydroxide solution (5 M) until the appearance of a neutral reaction mixture. The final solution was filtered, diluted with water and the concentration of the Au content was determined by ICP-OES.
sulfuric acid (2.5 mL, 98 wt%) at 250 °C for 30 min and then at room temperature with hydrogen peroxide (4.0 mL, 30 wt%). The resulting suspension was heated at 250 °C until to produce a clear solution. Aqua regia (1.5 mL) was added at room temperature and the solution was diluted with an aqueous solution of HCl (10 v/%) to the final volume of 10.0 mL. The calibration was performed using seven solutions with variable concentrations of gold(III), prepared by progressive dilution of a standard solution (1.000 ± 0.002 g/L in water with 2 wt% of HCl) with water and an aqueous solution of HCl (10 v%). Gas chromatographic (GC) analyses were performed with a GC-MS 7890 A/5975 C chromatograph, from Agilent Technologies, equipped with a mass-selective detector (MSD) and a flame ionization detector (FID), by using a DB-5 capillary column (polyethylene glycol, 30 m, 0.25 mm ID) or an Optima 17MS column (1:1 diphenylpolysiloxane/dimethylpolysiloxane, 30 m, 0.25 mm ID).

**Synthesis of AuNPs-PPO.** A 1 L round-bottomed three-necked flask equipped with a magnetic stirrer bar was charged with finely ground PPO (4.90 g) and anhydrous THF (800 mL). The mixture was stirred for 24 h at room temperature under a nitrogen protective atmosphere and then heated to reflux of the solvent for 1 h to complete the swelling of the polymer. HAuCl₄ · 3H₂O (0.200 g; 5.08 × 10⁻³ mol) was added at room temperature, kept under agitation for 1 h, and a solution of sodium triethylborohydride (4.1 mL, 1 M) in THF was added at room temperature, producing a rapid change of the colour from pale yellow to red. The catalyst was rapidly precipitated in methanol, recovered by filtration, washed with fresh methanol and dried in vacuo at room temperature.

**General procedure for oxidation of alcohols in water catalysed by AuNPs-PPO (referred to entry 1 of Table 1).** A 50 mL round-bottom two-necked flask equipped with a magnetic stirrer bar was charged with H₂O (3 mL), KOH (28 mg, 0.51 mmol), anisole as an internal standard (55 μL, 0.51 mmol), 1-phenylethanol (HP-Inn) 0.51 column and catalyst (200 mg). The mixture was stirred at 35 °C under atmospheric pressure of O₂. Aliquots of the reaction mixture were sampled at the desired reaction time and treated with plenty of acetonitrile. The polymer was separated by filtration and the filtrate was analysed by GC-MS and ¹H NMR spectroscopy. At the end of the reaction, the polymer was coagulated in plenty of acetonitrile. The catalyst was recovered by filtration and the filtrate was analysed.

**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

**Keywords:** alcohol oxidation · esterification · gold nanoparticles · nanoporous · polymer support

**Acknowledgements**

The authors are grateful for funding from the Ministero dell'Università e della Ricerca MUR (PRIN2017 grant) and from the Università degli Studi di Salerno (FARB grants). Open Access Funding provided by Università degli Studi di Salerno within the CRUI-CARE Agreement.

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