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Nitrogen functionalized carbon nanostructures supported Pd and Au–Pd NPs as catalyst for alcohols oxidation

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ABSTRACT

Carbon nanofibers (CNFs) PR24-PS and carbon nanotubes (CNTs) Baytubes were functionalized by oxidation with nitric acid and further amination with gaseous NH_3. Thus Au and Au–Pd nanoparticles were prepared by PVA/$NaBH_4$ system and anchored on the surface of pristine carbon nanostructures (CNS) and N-CNS (nitrogen functionalized carbon nanostructures). TEM analysis revealed that the introduction of nitrogen functionalities improves the dispersion of the metal nanoparticles on the surface of the support. This phenomena leads to an improved activity of N-CNS based catalysts with respect to pristine CNS when tested in the liquid phase oxidation of alcohols.

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1. Introduction

The oxidation of alcohols to their corresponding carbonyl compounds catalyzed by supported noble metal has been recently the subject of growing interest [1–3]. Due to the high costs of the noble metal it is necessary to extend and enhance their catalytic performance by depositing them homogenously on the support in order to optimize the active surface [4]. For this purpose the choice of the support is of fundamental importance influencing also the stability of the metal nanoparticles. Recently CNTs attracted a lot of attention as support for metal nanoparticles [5–9]. In particular their morphology suggests their use as support for liquid phase reactions as benzyl alcohol oxidation [10] and cinnamaldehyde hydrogenation [11,12]. On the contrary to activated carbons where there are many inaccessible active sites, CNTs are advantageous substrate since most of the metal nanoparticles are expected to be exposed and accessible to reactant thus acting as effective catalysts [13]. However due to the inertness of the pristine CNTs a selective metal deposition requires activation [14]. Jiang et al., for example, observed that the introduction of nitrogen groups on the surface of CNTs drastically increase the dispersion and stability of the metal nanoparticles [15], due to the strong interaction of metal–nitrogen. Metal/N-CNTs system resulted more active than metal/pristine when tested in different reactions. For example, highly dispersed metal nanoparticles immobilized on nitrogen doped CNTs showed better activity than pristine CNTs for methanol oxidation [16] and hydrogenation of cinnamaldehyde [17,18] and Heck reaction of iodobenzene and styrene [19]. We recently reported the preparation of N-CNFs sample by a gas phase procedure [20]. The CNFs used (PR24-PS) are characterized by large diameter (∼100 nm) and the presence of impurities, like amorphous carbon on the surface and inhomogeneity in size [21]. N-functionalized CNFs were obtained by previous acid oxidation and further amination with gaseous NH_3. XPS and TG-MS revealed that these samples mainly contain pyridinic and pyrrolic groups. In the present work we extended the functionalization method to CNTs, Baytubes, with the aim to study the effect of the diameter of the tubes and the presence of impurities on the surface on the metal nanoparticles dispersion and on the catalytic activity. Baytubes, in fact, are characterized by a smaller diameter than PR24-PS (10 nm instead 100 nm) with a better homogeneity in size and morphology, and they exhibited only little amorphous carbon on their surface [20]. Pristine CNS and N-CNS were used as support for Pd and Au–Pd nanoparticles prepared by colloidal method using PVA (polyvinyl alcohol) as protective agent [22]. The catalysts were characterized by TEM in order to investigate the effect of the nitrogen functionalities on the dispersion of the metal nanoparticles. All the catalysts were tested in the liquid phase oxidation of benzyl and cinnamyl alcohol.

2. Experimental

2.1. Materials

Commercial CNFs PR24-PS and CNTs Baytubes were supplied respectively from Applied Science and from Bayer. PR24-PS consist

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of tubular fibers with an average diameter of 88 ± 30 nm and a specific surface area of 43 $m^2 g^{-1}$ [21] whereas Baytubes have an average diameter of 10 ± 2 nm and a specific surface area of 288 $m^2 g^{-1}$ [21]. $NaBH_4$ (Fluka, >96%), polyvinylalcohol (PVA) (mw = 13,000–23,000, 87–89% hydrolysed, Aldrich), $NaAuCl_4 \cdot 2H_2O$ and $Na_2PdCl_4 \cdot 2H_2O$ (Aldrich, 99.99% purity) were used in these experiments. Gaseous oxygen from SIAD was 99.99% pure.

2.2. Catalyst preparation

2.2.1. Monometallic catalysts

Pd sol: solid Na_2PdCl_4 (0.043 mmol) and 0.22 ml PVA solution (2%, w/w) (Pd/PVA 1:1, w/w) were added to 130 ml of H_2O. After 3 min, 0.860 ml of 0.1 M $NaBH_4$ solution was added to the yellow-brown solution under vigorous magnetic stirring. The brown Pd(0) sol was immediately formed. An UV–visible spectrum of the palladium sol was recorded for ensuring the complete reduction of Pd(II). Within few minutes from their generation, the colloids (acidified at pH 2, by sulphuric acid) were immobilized by adding the support under vigorous stirring. The amount of support was calculated in order to obtain a final metal loading of 1 wt% (on the basis of quantitative loading of the metal on the support). The metal loading was also confirmed by burning off the CNS and performing ICP (Jobin Yvon JV24) analyses of the solution.

2.2.2. Bimetallic catalysts

Bimetallic catalysts have been prepared following the procedure reported in [22]. Solid $NaAuCl_4 \cdot 2H_2O$ (0.072 mmol) was dissolved in 140 ml of water (final 10^{-4} M) and 0.706 ml of PVA (2%, w/w) was added (Au/PVA 1:1, w/w). The yellow solution was stirred for 3 min and 2.9 ml of 0.1 M $NaBH_4$ (0.285 mol, Au/$NaBH_4$ 1:3 mol/mol) was added under vigorous magnetic stirring. The ruby red Au(0) sol was immediately formed. An UV–visible spectrum of the gold sol was recorded to check the complete $AuCl^{4-}$ reduction and the formation of the plasmon peak. Within a few minutes of sol generation, the gold sol was immobilized by adding carbon nanotubes (acidified until pH 2 by sulphuric acid) under vigorous stirring. The amount of support was calculated as having a gold loading of 0.73 wt%. After 2 h the slurry was filtered, the catalyst was thoroughly washed with distilled water (neutral mother liquors). ICP analyses were performed on the filtrate using a Jobin Yvon JV24 to verify the total metal loading on carbon. The 0.73 wt% Au/CNTs prepared was then dispersed in 140 ml of water; Na_2PdCl_4 (0.048 mol) and 0.225 ml of PVA solution (0.2%, w/w) (Au/PVA 1:1, w/w) were added. H_2 has been bubbled (50 ml/min) under atmospheric pressure and room temperature for 2 h. After additional 18 h, the slurry was filtered; the catalyst was thoroughly washed with distilled water. ICP analyses were performed on the filtrate using a Jobin Yvon JV24 to verify the quantitative metal loading on the support. The final total metal loading was 1 wt%. The total metal loading and Au/Pd ratios were also confirmed by burning off the CNS and performing ICP (Jobin Yvon JV24) analyses of the solution.

2.3. Catalytic test

The reactions were carried out in a thermostatted glass reactor (30 ml) provided with an electronically controlled magnetic stirrer connected to a large reservoir (5000 ml) containing oxygen at 2 atm. The oxygen uptake was followed by a mass flow controller connected to a PC through an A/D board, plotting a flow/time diagram. The oxidation experiments were carried out in solventless (0.0125 mol substrate, substrate/metal = 35,000 (mol/mol), 120 °C, pO_2 = 1.5 atm) or in the presence of water as solvent (alcohol 0.3 M, substrate/metal = 5000 (mol/mol), 60 °C, pO_2 = 1.5 atm). In the case of solventless reaction, periodic removal of samples from the reactor was performed, whereas in the case of water solvent, after the end of the reaction the catalyst was filtered off and the product mixture was extracted with CH_2Cl_2. Recoveries were always $98 \pm 3\%$ with this procedure. For the identification and analysis of the products a GC–MS and GC (a Dani 86.10 HT Gas Chromatograph equipped with a capillary column, BP21 30m × 0.53 mm, 0.5 μm film, made by SGE), were used by comparison of the authentic samples. For the quantification of the reactant-products the external calibration method was used.

2.4. Catalyst characterization

The metal content was checked by ICP analysis of the filtrate or, alternatively, directly on the catalyst after the carbon was burned off, using a Jobin Yvon JY24 instrument. A Hitachi S-4800 SEM equipped with EDX detector for elemental analysis was used to investigate the surface morphologies of the CNS. Morphology and microstructures of the catalysts were characterized in a Philips CM200 FEG electron microscope, operating at 200 kV and equipped with a Gatan imaging filter, GIF Tridiem.

Powder samples of the catalysts were ultrasonicated in ethanol and dispersed on copper grids covered with a holey carbon film. The particle size distribution for each catalyst was determined by measuring the mean diameter of over 300 particles from different areas. Each size distribution can be fitted by a log-normal function.

3. Results and discussion

Carbon nanotubes are a promising support and an effective alternative to activated carbons for liquid phase reaction. We

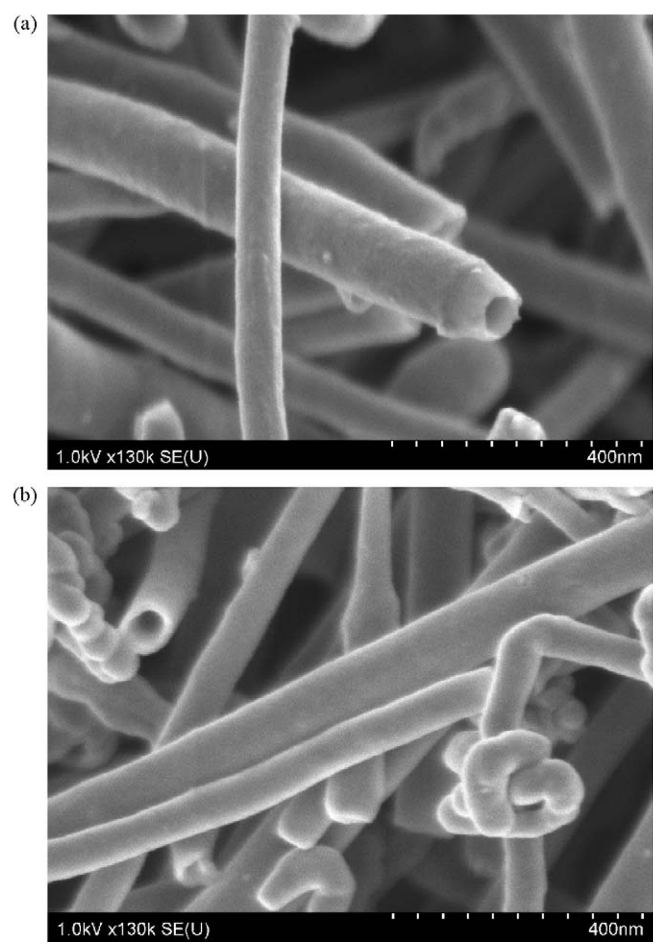

Fig. 1. SEM overview of (a) pristine PR24-PS-PS and (b) N-functionalized PR24-PS-PS.

previously observed that Pd nanoparticles supported on CNTs (Baytubes) showed a better stability and limited leaching in comparison to activated carbon when tested in the liquid phase oxidation of benzyl alcohol [11]. However Pd/CNTs showed a lower activity than Pd/AC, according to the lower metal dispersion observed on CNTs compared to AC. This phenomenon can be addressed to the inertness of the surface of pristine CNTs. Thus in order to improve the metal–support interaction it is necessary to introduce functionalities on the surface of carbon nanotubes.

In this study, two different carbon nanostructures, CNTs Baytubes and CNFs PR24-PS were considered. Baytubes are characterized by small diameter (10 nm), and homogenous morphology whereas PR24-PS by larger diameter (100 nm), more inhomogeneous morphology and the presence of a large amount of impurities on the surface [21]. Furthermore, the CNS were functionalized with nitrogen groups, following a procedure that we recently report [20]. In brief, the CNS were first oxidized with nitric acid at 100 °C and further aminated with gaseous NH_3 at 600 °C. The acid treatment introduces oxygen functionalities on

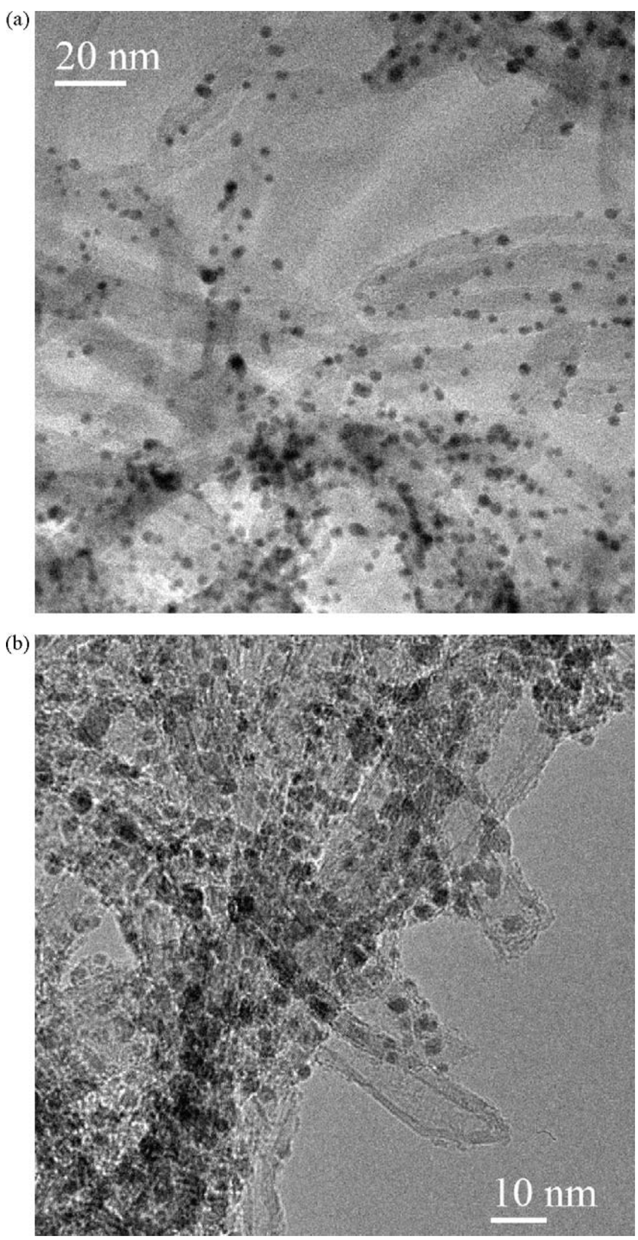

Fig. 2. The TEM overview image for (a) Pd/Baytubes and (b) Pd/N-Baytubes.

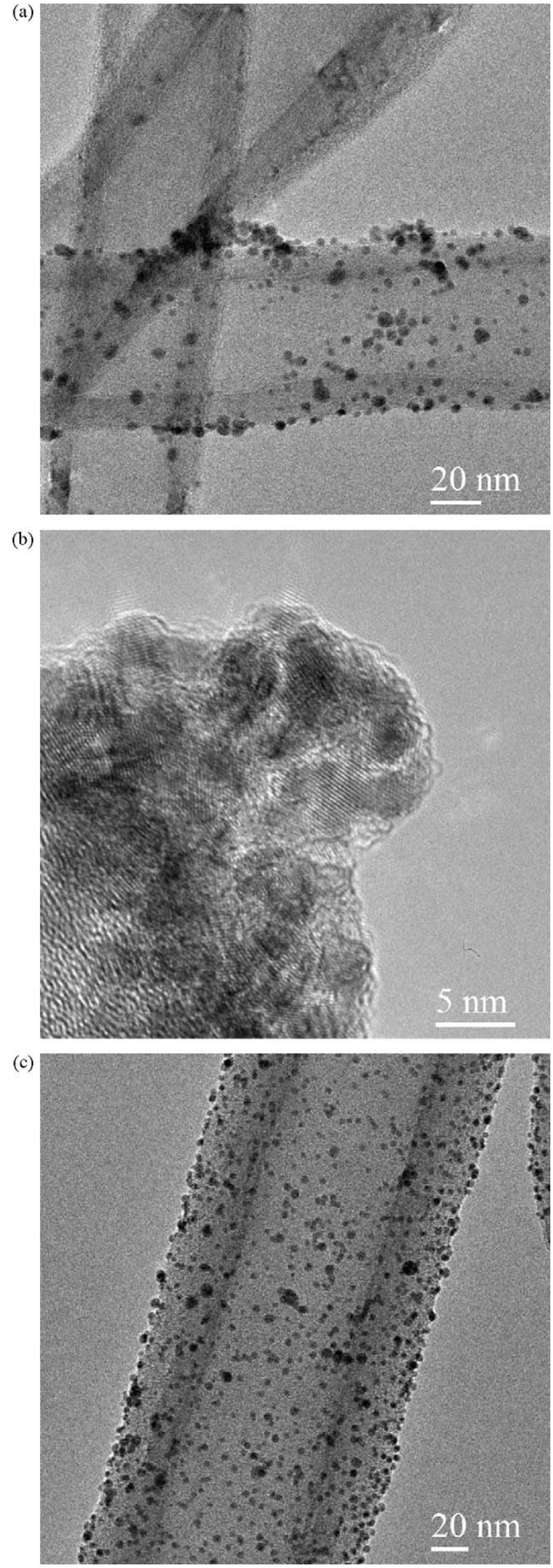

Fig. 3. The TEM overview image for (a) and (b) Pd/PR24-PS and (c) Pd/N-PR24-PS.

the surface but at the same time removes some impurities present. SEM images of pristine and functionalized CNS shows, in fact, that after the functionalization the impurities present on the surface of the tube (bright dots) (Fig. 1a) disappeared and the surface of the tube shows better homogeneity (Fig. 1b). XPS revealed that these samples after amination mainly contain pyridinic and pyrrolic groups [20].

We synthesized Pd/CNS and Pd/N-CNS via sol immobilization method ($NaBH_4$/PVA); for Au–Pd a two step procedure that ensures the formation of uniform alloyed Pd/Au nanoparticles has been used [22]. The metal sols were generated in the presence of a protective agent (polyvinyl alcohol) which provides both steric as well as electrostatic stabilization of the metal nanoparticles.

All the catalysts have been fully investigated by HRTEM. For Baytubes based catalysts we can observe that Pd particles size is almost the same as for pristine and functionalized carbon nanotubes being 3.35 nm and 3.34 nm for Pd/Baytubes and Pd/N-Baytubes. In the case of bimetallics, Au–Pd/N-Baytubes shows smaller particles than Au/Baytubes (respectively 3.41 nm and 3.53 nm) (Table 1). TEM images of Pd/Baytubes and Pd/N-Baytubes were reported as example for Baytubes based catalysts (Fig. 2a and b). In both cases the dispersion of metal nanoparticles on the tubes is not completely homogeneous. In particular on Baytubes based catalysts several CNTs were found without metal nanoparticles, whereas in the case of N-Baytubes catalyst the empty tubes can be considered exception. The same trend was observed for Au–Pd/Baytubes and Au–Pd/N-Baytubes catalysts.

More differences were observed using pristine and functionalized PR24-PS. Pd and Au–Pd supported on pristine PR24-PS showed bigger particles than the corresponding on N-PR24-PS (4.28 nm and 4.5 nm for Pd/PR24-PS and Au–Pd/PR24-PS whereas 3.28 nm and 3.70 nm for Pd/N-PR24-PS and Au–Pd/N-PR24-PS respectively) (Table 1). Fig. 3 shows TEM images of Pd/PR24-PS (Fig. 3a and b) and Pd/N-PR24-PS (Fig. 3c) respectively. For pristine PR24-PS several tubes were found without Pd nanoparticles, whereas many Pd particles are observed as aggregates. Some metal nanoparticles are anchored to the amorphous carbon present on the surface of the CNFs (Fig. 3b). The metal–support interaction is probably promoted on the amorphous carbon being full of defects. Moreover TEM observation confirmed that well dispersed nanoparticles decorate the walls of the nitrogen functionalized PR24-PS quite uniformly and no empty tubes are present (Fig. 3c).

The catalysts were tested in the liquid phase oxidation of benzyl and cinnamyl alcohols. These reactions have been widely studies in the literature being two models of oxidation of aromatic and activated alcohols [1].

Table 2 reports the results of Pd and Au–Pd supported on CNS and N-CNS for benzyl alcohol oxidation in solventless conditions. For comparison Pd and Au–Pd on AC have been also showed. For these experiments we used the following conditions: 0.0125 mol substrate, substrate/metal = 35,000 mol/mol, 120 °C, pO_2 = 1.5 atm.

In these reaction conditions Pd based catalysts show better activity than Au–Pd. This result contradicts what reported in the literature, that the addition of Au to Pd increases the catalytic performances in the oxidation of alcohols [23,24], but it has to be considered that the effect of the addition of gold normally has been studied in the presence of solvent. In terms of selectivity the addition of Au increases the selectivity to aldehyde from 62–68% for Pd based catalysts to 74–76% for Au–Pd based catalysts as also previously observed [10,23,24].

For PR24-PS based catalyst a dramatic increase of activity was observed using functionalized instead pristine CNFs. In fact the TOF increases from 7260 h^{-1} to 65,876 h^{-1} for Pd based catalysts and from 9076 h^{-1} to 52,638 h^{-1}. However the functionalization appears not to affect the selectivity to benzaldehyde. The increasing of activity from pristine to functionalized CNFs can be address to the smaller nanoparticles and better dispersion present of N-PR24.

On the contrary the effect of the N-functionalization for Baytubes based catalysts is not so important. Baytubes catalysts showed a better activity than PR24-PS but when N-modified, the effect was small (TOF of 43,281 h^{-1} and 50,387 h^{-1} for Pd/Baytubes and Pd/N-Baytubes, and 33,580 h^{-1} and 43,479 h^{-1} for Au–Pd/Baytubes and Au–Pd/N-Baytubes respectively).

With respect to activated carbon, nitrogen functionalized CNS based catalysts showed a better activity whereas pristine CNS are

Table 1
Statistical median and standard deviation of particle size analysis for Pd and Au/Pd catalysts.

Catalyst	Statistical media (nm)	Standard deviation (σ)
Pd/Baytubes[a]	3.35	0.87
Pd/N-Baytubes	3.34	0.71
Pd/PR24-PS	4.28	1.41
Pd/N-PR24-PS	3.28	0.93
Au–Pd/Baytubes[a]	3.53	0.78
Au–Pd/N-Baytubes	3.41	0.68
Au–Pd/PR24-PS	4.50	1.46
Au–Pd/N-PR24-PS	3.70	0.93

[a] Data from Ref. [10].

Table 2
Oxidation of benzyl alcohol solventless.

Catalyst	TOF[a] (h^{-1})	Selectivity[b]				
		Toluene	Benzaldehyde	Benzoic acid	Benzyl benzoate	Benzene
Pd						
PR24-PS[c]	7260	24	62	4	5	5
Baytubes	43,281	21	62	10	5	2
N-PR24-PS	65,876	26	64	2	1	7
N-Baytubes	50,387	20	68	6	5	1
AC	47,834	21	67	3	7	2
Au–Pd						
PR24-PS[c]	6076	18	74	3	1	4
Baytubes	33,580	13	75	7	4	1
N-PR24-PS	52,638	15	75	4	4	1
N-Baytubes	43,479	11	76	7	5	1
AC	35,426	12	76	6	3	3

Reaction conditions: solventless; alcohol/metal: 1/35,000; T = 120 °C; pO_2 = 1.5 atm.
[a] TOF calculated after 15 min of reaction based on the total metal loading.
[b] Selectivity calculated at 90% conversion.
[c] Selectivity calculated at 50% conversion.

Table 3
Oxidation of benzyl and cinnamyl alcohol in water.

Catalyst	Benzyl alcohol		Cinnamyl alcohol	
	TOF[a] (h^{-1})	Selectivity[b]	TOF[a] (h^{-1})	Selectivity[b]
Pd				
PR24-PS	10	92	52	75
Baytubes	625	91	248	77
N-PR24-PS	836	93	494	76
N-Baytubes	951	94	706	78
Au–Pd				
PR24-PS	24	96	51	81
Baytubes	747	97	300	82
N-PR24-PS	1099	97	517	82
N-Baytubes	1070	96	803	85

Reaction conditions: alcohol 0.3 M in water; alcohol/metal: 1/500; $T = 60\,^{\circ}C$; $pO_2 = 1.5$ atm.
[a] TOF calculated after 15 min of reaction based on the total metal loading.
[b] Selectivity calculated at 90% conversion.

less active. This increasing of activity can be addressed to the increasing of metal dispersion being correlated to the introduction of N-functionalities.

When water was used as the solvent (0.3 M, 60 °C, alcohol/metal 1/500 and 1.5 atm O_2), the activities decreased as expected. Under such conditions we also tested cinnamyl alcohol as the reactant. As already observed [23] the addition of Au to Pd had a positive effect not only on the selectivity but also on the activity of the catalysts (Table 3). As in the previous case the Baytubes catalysts appeared more active than PR24-PS-ones and the effect of N-functionalization result in an important increasing of activity only in the case of PR24-PS. The same trend was observed in the case of cinnamyl alcohol, where the introduction of N-functionalities increased the activity of the catalyst without affecting the selectivity to aldehyde.

The addition of Au to Pd has usually a positive effect on the selectivity but also on the catalytic activity for the liquid phase oxidation of polyols and alcohols [22–24]. This is the first time where the addition of Au to Pd has a positive or negative effect according to the reaction conditions using the same substrate.

4. Conclusion

The synthesis of nitrogen doped carbon nanostructures has been achieved by oxidation with nitric acid and further amination with gaseous NH_3. SEM revealed that this procedure is able to purify the surface of the CNS from impurities like amorphous carbon, in particular on PR24-PS. The introduction of nitrogen functionalities on the surface of CNS has a positive effect on the metal dispersion.

The functionalized N-CNS based catalysts were tested in the selective oxidation of alcohols and compared to pristine CNS based ones. Nitrogen functionalities incorporation led to a significant improvement of the catalytic performance. The activity improvement was attributed to a better dispersion of the metal nanoparticles on the surface. Moreover the increasing of the local basic environment did not affect the selectivity to aldehyde.

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