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Tuning hydrophilic properties of carbon nanotubes: A challenge for enhancing selectivity in Pd catalyzed alcohol oxidation

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ABSTRACT

CNTs were prepared by CCVD and functionalized with inorganic acid, with the aim to study the effect of the surface properties on the catalytic performance in the selective alcohol oxidation using polar (water) and apolar (cyclohexane) solvent. The match between properties of the reactant and the solvent allows tuning the selectivity of the reaction.

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1. Introduction

Alcohol oxidation has been always foreseen as an important task for chemical transformation especially in the case of fine chemical production. However in this field a lot of drawbacks have up-to-now limited the development of oxidative processes on an industrial scale. In fact when O_2 is use as the oxidant and reactions are carried out in condensed phase, deactivation of catalyst often occurred and high selectivity are not reached [1].

Lot of efforts has been made in order to increase both selectivity and durability of the catalyst by changing the metallic active sites, the solvent, the temperature and O_2 pressure. Generally speaking catalyst life is increased by using higher temperature, lower oxygen pressure and a metal less prone to be over-oxidize like gold [2–4]. Solventless conditions have been also investigated showing good results in terms of both activity and selectivity. However, as well as gas phase conditions, also carrying out the reaction without solvent can be not applicable to all the substrate. In fact high boiling or thermally unstable alcohol cannot be vaporized to be oxidized in gas phase like solid alcohols cannot be directly oxidized in condensed phase without the addition of a solvent.

From an environmental and safety point of view, water should be considered the solvent of choice but apart from water-soluble substrate, only a few reports in the literature report selective oxidation of alcohol carried out in water. The main problems that can be envisaged to perform the reaction of hydrophobic alcohol in an aqueous media concern with the intimate contact of reactants (alcohol and oxygen with the catalyst) and the lower oxygen solubility in water with respect of organic solvent [5].

Active carbons have been extensively studied as support in the liquid phase oxidation of alcohols [6–9]. However, more recently, it has been demonstrated that the more crystalline (graphene/graphite) nature of carbon nanotubes could be beneficial in terms of activity and durability of catalytic systems [10]. Surfaces of active carbons are normally hydrophobic indeed be wetting in a better way in apolar solvent than in polar ones [11].

In the present paper we investigated the impact of using apolar or polar solvents in the liquid phase oxidation of hydrophilic or hydrophobic alcohol by modifying the surface of CNTs by means of different HNO_3/H_2SO_4 treatment in order to change the hydrophilic/hydrophobic properties of their surface. The final aim of the study is to find out the optimized conditions (support characteristics and solvent) for each class (water-soluble or insoluble) of alcohols in terms of activity and selectivity.

Indeed CVD prepared CNTs have been differently treated for introducing functionalities and defects thus varying surface hydrophilicity. Pd nanoparticles (PdNP) were deposited onto the CNTs producing 1%Pd/CNTs materials which have been used as catalyst for the selective benzyl alcohol oxidation in cyclohexane and in water. In addition the same materials were used in the glycerol selective oxidation as a test of very hydrophilic substrate.



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2. Experimental

2.1. Materials

Carbon nanotubes (CNTs) were prepared by Catalytic Chemical Vapor Deposition (CCVD) of isobutane ($i-C_4H_{10}$) over Fe supported on Al₂O₃ catalyst (iron load 29 wt.%) [12].

The synthesis was carried out placing the catalyst (0.5 g) in a quartz boat inside a quartz tube located in a horizontal electric furnace. The catalyst was reduced at 773 K under a H₂/He flow (volume ratio 1:1, total flow 120 sccm/min) for 1 h then the temperature was raised to 873 K and helium was replaced by isobutane. The H₂/i-C₄H₁₀ volume ratio was 1:1 and the total flow was kept at 120 sccm/min for 2 h. After synthesis, the product was cooled down to room temperature under helium atmosphere.

Support and iron particles are subsequently removed by refluxing the solid discharged from the reaction with a solution of NaOH (1 M) at 353 K and then with a solution of HCl (1 M).

CNTs were finally washed thoroughly with distilled water and dried at 353 K for 12 h.

Oxidation of CNTs in nitric-sulphuric acid mixture was undertaken in an ultrasonic bath at 333 K for 6 h. 3 g of CNTs were weighed and added to 300 mL of acid mixture (67% HNO₃ and 98% H₂SO₄) having a proper volume ratio. Three different nitric-sulphuric volume-ratio mixtures were used, 3:1, 1:1 and 1:3, respectively. After treatment, carbon material was separated by filtration through 0.2 μ m filter paper, washed with water to neutral pH and dried at 353 K for 12 h.

Table 1 reports the catalysts code which summarizes information relative their treatment (CNTs stands for purified and CNTs_{N:S} stands for oxidized). The subscript N:S indicates the nitric–sulphuric volume ratio used for the oxidation.

2.2. CNTs characterization

The purity degree, PD% of the carbonaceous materials, evaluated by measuring the residual weight upon combustion of samples at 1073 K, a temperature largely exceeding the range of temperature the more oxidation-resistant CNTs burns [12], was estimated as 100-w₁, w₁ representing the relative weight of un-combusted impurities.

Water vapor uptake was calculated as:

Water vapor uptake (wt%) = 100
$$\frac{(m_t - m_0)}{m_0}$$

where m_0 represents the CNTs weight after degassing at 150 °C and m_t represents the final total weight (CNTs + H₂O).

Potentiometric titration of the basic sites was carried out using a Mettler Toledo Titrator. Approximately 0.2 g of sample was suspended in 50 mL of KCl 10^{-3} M and then sonicated and equilibrated for several hours. Prior to each measurement, the suspension was continuously saturated with argon to eliminate the influence of CO₂, until the pH was constant. Volumetric standards of HCl (0.01 M) or NaOH (0.10 M) were used as titrant, starting from the initial pH of the CNTs suspension.

The volatile matter content was estimated by Thermogravimetry (TA Instruments SDTQ 600) in the temperature range 473–1273 K, heating rate 20 K min⁻¹. Each sample, placed in a platinum pan, was kept at 473 K in argon until balance stabilisation and subsequently temperature was raised until the desired value.

Specific surface area (m^2/g) , were determined by adsorption-desorption of dinitrogen at -77 K, after outgassing (10^{-4} mbar) the samples at 353 K for 2 h using Surface Area Analyzers – Qsurf Series.

Morphology and dimensions of the CNTs were investigated by using a TEM (JEOL JEM 2010), operating at 200 kV and equipped with a Gatan 794 Multi-Scan CCD camera. The nanotubes were dispersed in isopropanol and deposited on a grid covered with holey carbon film.

A Hitachi S-5200 in lens UHR FE-SEM was used for SEM observation.

Temperature programmed desorption profiles were obtained with a flow reactor equipped with a quadrupole mass spectrometer (HPR 20 HIDEN ANALYTICAL instrument). Samples (30 mg) were placed in a U-shaped quartz tube inside an electrical furnace and heated at 10 K min⁻¹ up to 1373 K using a constant flow rate of helium (30 sccm/min). The mass signals m/z = 28 (CO), 30 (NO), 44 (CO₂), and 64 (SO₂) were monitored during the analysis. The amounts of CO, CO₂, NO and SO₂ were calibrated at the end of each analysis with pure gases. After the treatment of the acquired data, the TPD spectra of CO, CO₂, NO and SO₂ (in µmol $g^{-1} s^{-1}$) were obtained.

Water vapor uptake was evaluated by a thermo-gravimetric technique based on the use of a laboratory McBain. Samples were heated at T = 150 °C in vacuum (P = 0.01 mbar) for 12 h, cooled down to T = 30 °C (in vacuum) and then connected to the evaporator at a (absolute) vapor pressure of P = 10 mbar. Measurements ended when samples reached a stable weight.

2.3. Catalyst preparation

Pd sol: solid Na₂PdCl₄ (0.043 mmol) and 0.22 mL PVA solution (2%, w/w) (Pd/PVA 1:1, w/w) were added to 130 mL of H₂O. After 3 min, 0.860 mL of 0.1 M NaBH₄ solution was added to the yellowbrown solution under vigorous magnetic stirring. The brown Pd(0)sol was immediately formed. An UV-vis 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 catalyst was thoroughly washed with deionized water at 50 °C. TGA performed in the range 100–200 °C revealed the presence of residual PVA in a very low amount (less than 1 wt% respect to the added amount). The metal loading was also confirmed by burning off the CNS and performing ICP (Jobin Yvon JV24) analyses of the solution.

Table 1

Sample code, nitric-sulphuric acid mixture volume ratio used for CNTs oxidation, purity degree (PD%), volatile content (wt.%) and surface area (SA) of purified and oxidized carbon nanotubes.

Code ^a	Nitric-sulphuric (v:v)	PD (%)	Volatile (wt%)	$SA\left(m^2/g\right)$	$\text{CO/CO}_2{}^b(\mu\text{mol}g^{-1})$	NO ^b	$SO_2{}^b(\mu mol~g^{-1})$	Water vapor uptake (%)
CNTs (6.4)	-	94.1	2.0	196	4.4	n.d. ^c	n.d. ^c	2
CNTs _{3:1} (4.4)	3:1	95.4	4.0	195	2.7	3	6	4
CNTs _{1:1} (3.7)	1:1	95.2	12.0	194	1.7	4	182	8
CNTs _{1:3} (2.8)	1:3	96.6	36.0	172	1.3	2	448	11

^a In parenthesis the value of auto-generated pH.

^b CO/CO₂ ratio and concentration (μ mol g⁻¹) of NO and SO₂ as monitored by TPD analysis of carbon materials are also reported. ^c n.d.: not detected.

2.4. Catalyst characterization

Metal particle distribution was investigated by using a TEM (JEOL JEM 2010), operating at 200 kV and equipped with a Gatan 794 Multi-Scan CCD camera. Transmission Electron Microscopy (TEM) was performed with a Philips model CM12 electron microscope operating at 120 kV and directly interfaced with a computer for real-time image processing. The powdered samples were ultrasonically dispersed in isopropyl alcohol, and then a few droplets of the suspension were deposited on a holey carbon support film copper grid. After the solvent evaporated, the specimens were introduced into the microscope column. At least 300 palladium particles were measured from each catalyst to obtain a good statistical particle size distribution.

The average size diameter (*d*) of the palladium particles was calculated using the following formula:

$$d = \frac{\sum n_i d_i}{n_i}$$

where n_i is the number of the metal particles of diameter d_i . The standard deviation (σ) was calculated from the formula:

$$\sigma = \left[\frac{\sum (d_i - d)^2}{\sum n_i}\right]^{1/2}$$

2.5. Catalytic reactions

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. Benzyl alcohol oxidation was carried out in the presence of cyclohexane or water as solvent (0.0125 mol substrate, substrate/metal = 10,000 (mol/mol), Benzyl alcohol/solvent: 50/50 (vol%), $100 \circ C$, $pO_2 = 2$ atm). In the case of cyclohexane as solvent, 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 (Agilent Technologies 7820A Gas Chromatograph equipped with a capillary column, HP-5 $30 \text{ m} \times 0.32 \text{ mm}$, 0.25 μm Film, made by Agilent Technologies), were used by comparison of the authentic samples. For the quantification of the reactant-products the external calibration method was used. Glycerol oxidation was carried out in the presence of water as solvent: 0.3 M Glycerol solution, NaOH (glycerol/NaOH=4 mol/mol) and the Pd catalyst (glycerol/metal = 1000 mol/mol) were added (total volume 10 mL). The reactor was pressurised at 3 atm of O₂ and thermostatted at 50 °C. After an equilibration time of 5 min, the reaction was initiated by stirring and samples were taken every 15 min and analysed by HPLC on a Varian 9010 HPLC equipped with a Varian 9050 UV (210 nm) and a Waters R.I. detector in series. An Alltech OA-1000 column (300 mm \times 6.5 mm) was used with aqueous H₃PO₄ 0.1% wt/wt M (0.5 mL/min) as the eluent. Samples of the reaction mixture (0.5 mL) were diluted (5 mL) using the eluent. Products were assigned by comparison with authentic samples.

3. Results and discussion

3.1. CNTs characterization

CNTs have been prepared by CVD of isobutane according to the procedure reported in [12]. In order to introduce functional groups,

which could enhance the hydrophilicity of the surface, the CNTs have been dispersed in a mixture of HNO_3/H_2SO_4 varying the ratio of HNO_3 to H_2SO_4 from 3:1 to 1:3.

Table 1 summarizes the results of textural and proximate analysis of purified and oxidized CNTs. Specific surface area (SA) of the samples appears to be scarcely influenced by the oxidation conditions. Indeed, as shown in Table 1, close SA values are found for CNTs, $CNTs_{3:1}$ and $CNTs_{1:1}$, while it only slightly reduces for the sample treated with the most sulphuric acid concentrated acid mixture ($CNTs_{1:3}$).

The liquid phase treatment of CNTs leads to a progressive increase of PD as nitric–sulphuric acid mixture volume ratio lowers. The residue obtained upon CNTs oxidation is mainly due to the presence of iron catalyst encapsulated by the graphitic structures during CCVD synthesis [13] that is rather difficult to be dissolved under the mild post synthesis purification with HCl 1 M.

The volatile matter content (wt%) of the investigated samples, reported in Table 1, also progressively increases with the sulphuric acid concentration, i.e. lowering the nitric–sulphuric acid mixture volume ratio. Since these volatiles include products released from the decompositions of the surface groups the above results clearly indicates that sulphuric rich acid mixture is more efficient towards the oxidation of the CNTs surface.

Moreover it was revealed that the water vapor uptake (%) increase increasing the H_2SO_4/HNO_3 molar ratio, meaning that the surface hydrophilicity increased in the order $CNTs_{1:3} > CNTs_{1:1} > CNTs_{3:1} > CNTs$, in agreement with the increase of the volatile matter content, i.e. with amount of functional groups introduced onto the CNTs surface. This fact resulted of great importance by considering the different wetness of surfaces during liquid phase reactions.

Transmission electron microscopy (TEM) analysis of CNTs and CNTs_{N:S}, displayed in Fig. 1, evidences that purified CNTs present as highly entangled long carbon filaments, with external diameter comprised between 5 and 20 nm (Fig. 1a); regardless the liquid phase treatment conditions the tubular structure of carbonaceous material is preserved and that no other carbon structures, such as amorphous carbon and/or graphite platelets, form.

The chemical modification of the carbonaceous materials subjected to the oxidative treatment is evaluated by means of TPD monitoring the CO (m/e = 28) and CO₂ (m/e = 44) molecules resulting from the decomposition of various oxygen containing groups such as carboxyl, carbonyl, phenol, lactones present and/or introduced upon oxidation onto the carbon surfaces. In addition to CO and CO₂, the evolution of NO (m/e = 30) and SO₂ (m/e = 64) molecules, for all the samples is monitored.

The TPD results also allow the identification and quantification of the functional groups present on the materials surface by peak assignment, as described elsewhere [14–16]. TPD spectra are shown in Fig. 2. CNTs release a very low amount of CO₂ in the range of temperature 400–650 K (Fig. 2a), typical of the decomposition of the carboxylic groups [14]. A very narrow CO peak is also observed, at high temperature, likely arising from decomposition of carbonyl groups (Fig. 2b) [14].

SEM analysis of catalysts evidences the presence of discrete bundles with a broad size distribution (($10-100 \,\mu m$). Upon functionalization CNTs is known to agglomerate in a major extent [17].

Upon oxidation with nitric-sulphuric acid mixture CO_2 and CO evolution augments with the increasing of sulphuric acid concentration, indicating an enhancement of functional groups introduced onto the CNTs surface as the oxidative condition become more powerful, in agreement with the increases of the volatile matter content (Table 1). Fig. 2a shows that CO_2 released from $CNTs_{N:S}$ samples occurs in a broad range of temperature (400–1000 K) suggesting that different functionalities such as carboxylic acids, anhydrides and lactones are introduced [14]. CO desorption profiles also



Fig. 1. Morphology of purified and acid treated CNTs as monitored by TEM. Photos refer to CNTs (a), CNTs_{1:1} (b), CNTs_{1:1} (c) and CNTs_{1:3} (d), respectively.

dramatically enlarge due to the overlap of different contribution such as carboxylic anhydride groups, occurring at T < 900 K where CO and CO₂ partly covers, phenols, ethers and carbonyls (Fig. 2b). The sharp CO peak present in the CNTs profile instead progressively decreases for CNTs_{3:1} and CNTs_{1:1} and disappears on the most oxidized CNTs_{1:3} likely due to the over-oxidation of carbonyl functionalities.

NO and SO_2 evolution (not shown) is only observed for the acid treated CNTs. The concentration of the monitored species is reported in Table 1.



Fig. 2. TPD profiles of CNTs and CNTs_{N:S} samples; CO₂ (a), CO (b).

0	n
0	υ

Table 2
Supported PdNPs: mean size and distribution.

Code	Nitric-sulphuric (v:v)	TEM		CO-chemisorption
		Statistical median (nm)	Standard deviation σ	Metallic surface area (m ² /g)
CNTs	_	5.4	4.9	0.92
CNTs _{3:1}	3:1	5.6	0.9	1.03
CNTs _{1:1}	1:1	5.1	1.3	1.04
CNTs _{1:3}	1:3	4.8	1.0	1.03

NO release occurs at low extent in the range of temperature 400–600 K and is due to the decomposition of the nitro-groups introduced by nitration of aromatic rings [22] while SO₂ release, which occurs within 450–800 K, is likely due to the decomposition of thiol and sulfonic acid groups [23,24]. The amount of SO₂ released increases in the order $CNTs_{1:3} > CNTs_{1:1} > CNTs_{3:1}$ in agreement with the increase of sulphuric acid concentration in the oxidant mixture (Table 1).

CO/CO₂ ratio, usually taken as an indicator of the acid/basic properties of the carbonaceous materials [18–21] and reported in Table 1, evidences that CNTs show the higher base character, i.e. higher CO/CO₂ ratio; as result of oxidation by acid mixture the enhancement of the acidic character of CNTs with the increase of sulphuric acid concentration occurs. These evidences agree with the auto-generated pH values (Table 1) that decreases from 6.4 to 2.8 over the most oxidized CNTs_{1:3}.

However it should be also considered that apart the acid functionalities introduced upon oxidation on CNTs surface, the presence of sulphur group can also contribute to the lowering of pH being thyol and sulphonic acid fairly and strong acid respectively.

3.2. Catalyst preparation and characterization

We prepared Pd catalyst using the sol immobilization technique with the aim of obtaining as much as possible similar metal dispersion. The sol was prepared in a unique batch and then divided for four samples: CNTs, $CNTs_{3:1}$, $CNTs_{1:1}$, $CNTs_{1:3}$. Table 2 reported the mean size and standard deviation (σ) of the PdNPs supported on the differently treated support. However, as clearly appeared from TEM images (Fig. 3), deposition of colloidal Pd over pristine CNTs result in the main formation of agglomerate PdNPs while over $CNTs_{N:S}$ a metal dispersion is highly improved. The particle size distribution did not vary appreciably over oxidized CNTs

Indeed the particle distribution on the support become progressively better as the acidic treatment of the support has been more aggressive, i.e. as the H_2SO_4 content increased.

3.3. Alcohol oxidation

Pd on CNTs has been tested in alcohol oxidation using the well studied benzylic alcohol oxidation evaluating the different impact of CNT surface properties on the catalytic performances. The activity of the catalyst has been evaluated in terms of conversion per m² exposed metal per hour and the selectivity as single product over the alcohol converted has been produced. We choose two different systems: the first where the alcohol is completely soluble (cyclohexane) (Table 3), the second where benzyl alcohol is only partly soluble (water) (Table 4). We used a very low amount of catalyst (10 mg,: substrate/metal = 10,000 (mol/mol)) to ensure a kinetic regime. In fact by varying the amount of catalyst in the substrate/metal range 3000-20.000 we observed almost constant TOF. Moreover maintaining the substrate/metal ratio constant, we observed a constant "Mol converted/Pd m² h" by using different loaded catalysts (0.5-2%). According to the latter Madon-Boudart test [25] we can conclude that internal and external diffusion limitation were avoided.

When cyclohexane is used as the solvent the activities of the catalysts follows their hydrophobic properties, being the most hydrophilic support ($CNTs_{1:3}$) the less active (Table 3). All the catalysts behaved similarly in terms of selectivity, producing almost the same amount of benzaldehyde (60–70%) and toluene (25–35%).

As reported by Sumathi et al. [26] and more recently by Hutchings' group [27,28] toluene constitutes the main by-product. A disproportionation mechanism of two mols of benzyl alcohol in a helium atmosphere gives an equimolar amount of benzaldehyde and toluene [27–29]. The toluene amount decrease as the oxygen pressure increase and the oxidation pathway prevails producing a higher amount of benzaldehyde. The ratio between benzaldehyde and toluene was used to roughly quantify the two different mechanisms in which a relevant role was played by the reaction media or the catalytic surface [27]

Looking at our results (Table 3) we could argued that in the case of cyclohexane solvent, the role of the support is limited in determining the preferential reaction route even if its role is important

Та	ble	3

Benzyl alcohol oxidation in cyclohexane.

Catalyst ^a	Mol converted/Pd (m ² h)	benzaldehyde (%)	Toluene (%)	Benzylbenzoate (%)
Pd/CNTs	32.4	75	25	0
Pd/CNTs _{3:1}	34.8	63	37	0
Pd/CNTs _{1:1}	21.7	65	35	0
Pd/CNTs _{1:3}	8.4	64	36	0

^a Reaction conditions: substrate/metal = 10,000 (mol/mol), Benzyl alcohol/solvent: 50/50 (vol%), 100 °C, pO₂ = 2 atm.

Table 4

Benzyl alcohol oxidation in water.

Catalyst ^a	Mol converted/Pd (m ² h)	benzaldehyde (%)	Toluene (%)	Benzoic acid (%)
Pd/CNTs	32.2	74	25	1
Pd/CNTs _{3:1}	34.5	60	40	0.5
Pd/CNTs _{1:1}	21.7	61	38	0.2
Pd/CNTs _{1:3}	24.4	>99	0	0

^a Reaction conditions: substrate/metal = 10,000 (mol/mol), Benzyl alcohol/solvent: 50/50 (vol%), 100 °C, pO₂ = 2 atm.



Fig. 3. TEM images of Pd/CNTs, Pd/CNTs_{3:1}, Pd/CNTs_{1:1}, Pd/CNTs_{1:3}.

in terms of activity. Indeed, it appeared that the more the surface is hydrophobic the more the catalyst becomes active, i.e. the hydrophobic reactant (benzyl alcohol) has an easier access to the active sites.

Using water as the solvent a real biphasic system is obtained dispersing the alcohol in water. Considering the lower solubility of oxygen in water than in cyclohexane, it was quite surprising to obtain almost the same activities in water as in cyclohexane (Table 4). This could be plausible only admitting that in water the elementary steps of the reaction proceeded faster than in cyclohexane. The activity of Pd/CNTs_{1:3} has been the only one considerably increased. This is not surprising as the surface of this catalyst is the

most hydrophilic one and therefore the one that should be taken the highest advantage in the contact surface-solvent.

The selectivities did not change considerably for the different catalysts (Table 4) remaining almost unchanged for pristine, Pd/CNTs_{3:1} and Pd/CNTs_{1:1} with respect to the values obtained using cyclohexane as the solvent. However, we noted a progressive decrease of toluene production with an increase of the hydrophilicity of the support. In the case of Pd/CNTs_{1:3} an almost total selectivity to aldehyde was obtained. We could thus conclude that the beneficial effect of using water as the solvent, in terms of both activity and selectivity, become effective only when the support is highly hydrophilic, i.e. showed a high affinity with the solvent.

Table 5	
Glycerol oxidation	on in water.

Catalyst ^a	Mol converted/Pd (m ² h)	Glycerate and tartronate (%)	Oxalate and glycolate (%)	Formate (%)
Pd/CNTs	2.9	85	10	5
Pd/CNTs _{3:1}	1.9	80	12	8
Pd/CNTs _{1:1}	1.2	78	10	12
Pd/CNTs _{1:3}	1.0	49	25	23

^a Reaction conditions: substrate/metal = 1000 (mol/mol), 0.3 M glycerol, 50 °C, 4 eq NaOH, pO₂ = 3 atm.

Moreover in this latter case the dispropornation mechanism leading to toluene formation is suppressed.

Following these results we investigated what happened when also a hydrophilic reactant is used. We carried out some experiments using glycerol, a highly hydrophilic reactant, as the substrate to oxidize. The results are reported in Table 5.

Contrarily to what expected, also in this case the catalyst activities followed the same trend as before, i.e. the activity decreased by increasing the hydrophilicity of the support surface. The increased affinity of the surface for the reactant seems lowering the desorption of the products thus decreasing the overall rate of the reaction. We can find a confirmation of this in the product distribution: to a highly hydrophilic surface (CNTs_{1:3}) corresponded the highest amount of products derived by C–C bond cleavage (oxalate, glycolate, formate) which raised 48% (Table 5). The adsorbed specie probably due to the high affinity with the surface, desorbed slowly thus lowering the reaction rate but on the same time having time to undergo oxidative cleavage.

4. Conclusions

We prepared Pd catalysts which differ by support surface properties (in particular hydrophilic/hydrophobic property) and tested them in liquid phase oxidation reactions. We changed the solvent (cyclohexane and water) and the reactant (benzyl alcohol and glycerol). The activities of the catalysts depended on the match among reactant, solvent and support surface.

When the reactant is hydrophobic (benzylic alcohol) as the solvent (cyclohexane), the support surface hydrophobicity can improve the activity of the catalyst (but not the selectivity). However, when the solvent is water a complex triphasic system is formed and the hydrophilicity of the surface can mediate the contact between reactant. In this case the selectivity is also affected.

Conversely when the reactant is hydrophilic (glycerol) as well as the solvent (water) it has been showed that the hydrophilicity of the support can limit the activity of the catalyst by lowering the desorption of the reaction products.

Concluding we have shown that it is possible to tune the activity/selectivity of a reaction by accurately matching the hydrophilicity of the surface depending on the solvent and the alcohol to be oxidized.

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