Metal nanoparticles on carbon based supports: The effect of the protective agent removal

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ABSTRACT

The sol immobilization technique is widely employed for the synthesis of size- and morphology-controlled supported nanoparticles. The protective agent adsorbed on the surface of nanoparticles can substantially affect the catalytic performances, by limiting the access to the active sites as well as by influencing metal–support and reactant–metal interactions, thus altering not only the activity but also the selectivity of the reaction. Herein, we studied the effect of the capping agent (specifically polyvinyl alcohol, PVA) removal on the catalytic activity and selectivity of gold nanoparticles supported on different carbon based materials using the glycerol oxidation as test reaction.

1. Introduction

Supported noble metal nanoparticles (NPs) are commonly employed as catalysts in several industrially relevant processes [1–4]. Many factors, including particle size and shape, metal dispersion, metal-support interactions, rule out the catalytic performance of metal NPs. Consequently, the control and the optimization of all these parameters represent a challenging issue for the large-scale production of active and selective catalysts. From this point of view, great efforts were devoted to develop synthetic strategies providing tuneable and controllable nanostructures [5–8].

Among the preparation routes, the sol immobilization technique, where pre-formed metal nanoparticles with well-defined particle size are deposited onto the support surface, assures a meticulous morphology control and a wide applicability independently from the nature of the supporting material [9–15]. The stability of metal nanoparticles is conferred by the presence of protecting agent molecules (polymer, surfactant) adsorbed on the surface to reduce their tendency to coalesce. In particular, the use of polyvinyl alcohol (PVA) as the protecting agent has been reported to result in a high metal dispersion whatever the nature of the support [16–19]. Indeed, among various protective agents, PVA has been demonstrated to be the only one able to keep the original sol particle size, even when a support with a high tendency to induce particle coarsening such as activated carbon, is used.

However, to date it is unclear how this protecting ligand influences the catalyst activity, selectivity and stability. On the other hand, the removal of the stabilizer is a delicate process that it requires some precautions. Solvent washing seems to be a quite versatile method for removing the protecting agent without drastically changing particle size and shape [20–22]. Recently, the effect of PVA removal from Au/TiO$_2$ catalysts prepared by the sol immobilization technique has been investigated for various reactions, such as gas-phase CO oxidation [20,22] and liquid phase glycerol oxidation [21]. In the latter case, the presence of PVA has been reported to have a detrimental effect on the activity, probably due to the shielding effect, even if it positively affects the selectivity to glyceric acid and tartronic acid. In addition, the relative amount of PVA seems to be a key factor as small amounts of PVA enhances the activity of the catalyst, probably because of the direct interactions with the substrate [21].

In many cases, the stabilization and the particle morphology after the removal of the protecting agent may be determined by the textural properties of the support and the eventual presence of defects and functional groups on the surface [23,24].

For this reason, here we extended the investigation on the role of the protecting agent in gold NPs catalytic performances when supported on two carbon-based materials with different graphitization degree and crystallinity, namely crystalline graphite and more disordered activated carbon. Indeed, recent studies revealed that the internal bonding of the carbon support (sp^2 vs. sp^3) as well

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as the crystallinity of the support influenced both the immobilization of PVA protected Au NPs and their selective in the oxidation of glycerol [23].

Therefore the different distribution of anchoring sites for metal nanoparticles on the selected supports is expected to differently influence the catalytic activity and selectivity after the removal of the protecting agent.

2. Experimental

2.1. Materials

NaAuCl$_4$·2H$_2$O was from Aldrich (99.99% purity); activated carbon from Camel (X40S; SA = 900–1100 m^2/g; PV = 1.5 cm^3/g; Point of zero charge (pzc) 9–10) and Graphite from Johnson Matthey (SA = 14 m^2/g) were used as supports. NaBH$_4$ of purity >96% from Fluka and poly(vinyl alcohol) (PVA) (Mw = 13 000–23 000, 87–89% hydrolyzed) from Aldrich were used. Gaseous oxygen (99.99%) from SIAD, NaOH from Aldrich and Glycerol (87 wt% solution) from Riedel-de-Häen were used in the catalytic reactions.

2.2. Catalyst preparation

Solid NaAuCl$_4$·2H$_2$O (0.043 mmol) and PVA (Au/PVA = 1:1 wt/wt) solution were added to 130 mL of H$_2$O. After 3 min, 0.1 M NaBH$_4$ (Au/NaBH$_4$ = 1:4 mol mol^{-1}) solution was added to the yellow solution under vigorous magnetic stirring. A ruby red Au(0) sol was immediately formed. Within a 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 catalysts were filtered, washed on the filter (100 mL of distilled water for 1 g of catalyst) and dried at 80 °C for 4 h. Au$_{PVA}$/Support prepared using the Au/PVA ratio 1:1 were poured into a large amount of water (100 mL g^{-1} of catalyst) at room temperature or alternatively at 60 °C and stirred for 8 h. The catalyst was then recovered by filtration and dried at 80 °C for 4 h. In alternative, Au catalysts were further poured into a large amount of water (100 × 5 mL/g of catalyst) at room temperature or in alternative at 60 °C and stirred for 8 h. The catalyst was then recovered by filtration and dried at 80 °C for 4 h.

2.3. Catalyst characterization

The specimens for Transmission Electron Microscopy (TEM) were prepared by dispersing the catalyst powder on TEM grids coated with holey carbon film. They were examined by means of a FEI Titan 80–300 electron microscope, operating at 80 kV equipped with CEOS image spherical aberration corrector, Fischione model 3000 high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) detector.

Metal content in the solution was checked by ICP analysis on a Jobin Yvon JY24 verifying the quantitative loading of Au on the support.

2.4. Catalytic tests

Glycerol (0.3 M) and the catalyst (substrate/total metal = 1000 mol mol^{-1}) were mixed in distilled water (total volume 10 mL) and 4 equivalent of NaOH. The reactor was pressurized at 300 kPa of nitrogen and the temperature sets to 50 °C. Once this temperature was reached, the gas supply was switched to oxygen and the monitoring of the reaction started. The reaction was initiated by stirring. Samples were removed periodically and analyzed by high-performance liquid chromatography (HPLC)

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

Catalyst	Statistical median (nm)	Standard deviation
Au/AC unwashed	2.9	0.1
Au/AC washed at r.t.	3.0	0.2
Au/AC washed at 60 °C	3.4	0.1
Au/Graph. Unwashed	6.7	1.2
Au/Graph. washed at r.t.	5.7	1.5
Au/Graph. washed at 60 °C	6.9	1.8

using a column (Alltech OA-10308, 300 mm_7.8 mm) with UV and refractive index (RI) detectors. Aqueous H$_3$PO$_4$ solution (0.1 wt%) was used as the eluent. Products were identified by comparison with standard samples.

3. Results and discussion

Gold nanoparticles stabilized with poly(vinyl alcohol) were supported on activated carbon and crystalline graphite. To disclose the effect of the protecting agent and its relative amount, the water extraction treatment was carried out on as-prepared catalysts, following the procedure reported by Lopez-Sanchez et al. [20], slightly modified for achieving a gradual removal of the PVA. Catalysts were washed using deionized water at room temperature and at 60 °C. Previous experiments performed on Au$_{PVA}$/TiO$_2$ [21] revealed that the washing treatment at room temperature results in a partial removal of PVA whereas the one at 60 °C is effective in completely extracting residual PVA.

3.1. Catalyst characterization

Compared to thermal and oxidative treatments, the water extraction procedure possesses the undeniable advantage of assuring a facile and effective removal of the protecting agent without altering the size and the morphology of metal nanoparticles [20,21]. To explore the effect of PVA removal on the particle size and distribution, aberration-corrected scanning transmission electron microscopy (STEM) analysis was performed on untreated and treated samples (Figs. 1–2 and Table 1).

STEM data collected on activated carbon supported gold NPs revealed that the gradual removal of PVA resulted in a slight increase in particle size, 2.9–3.4 nm (Table 1) as a consequence of the reduced stability and particle aggregation.

The progressive removal of PVA was also confirmed by HRTEM, where the layer of the protective agent surrounding the particle is clearly observable in the as-prepared sample (Fig. 3a) whereas it is even less evident in the washed samples (Fig. 3b and c). A similar trend was previously observed for Au/TiO$_2$ catalysts where IR spectra also supported these findings [21]. Unfortunately a quantitative measurements of PVA on carbon either by IR or TGA failed.

By successively removing the amount of PVA, an unexpected trend of the mean particle size was observed for Au NPs supported on graphite. Washing at room temperature leads to a decrease of the mean particle size (from 6.7 nm to 5.7 nm) as shown in Table 1 and Fig. 2. Moreover, examining the particle size histograms (Fig. 2b, d and f), a higher amount of nanoparticles smaller than 2 nm was observed after washing at room temperature. Such an unexpected evidence might be ascribed to the presence of small gold clusters in the as-prepared catalyst. These clusters are too small to be detected with STEM, but they coalesce after washing and PVA removal leading to the formation of few nanometer gold particles and to the apparent decrease in mean particle size. Increasing the temperature of washing, the nanoparticles tend to further aggregate (from 5.7 nm to 6.9 nm at room temperature and 60 °C, respectively).
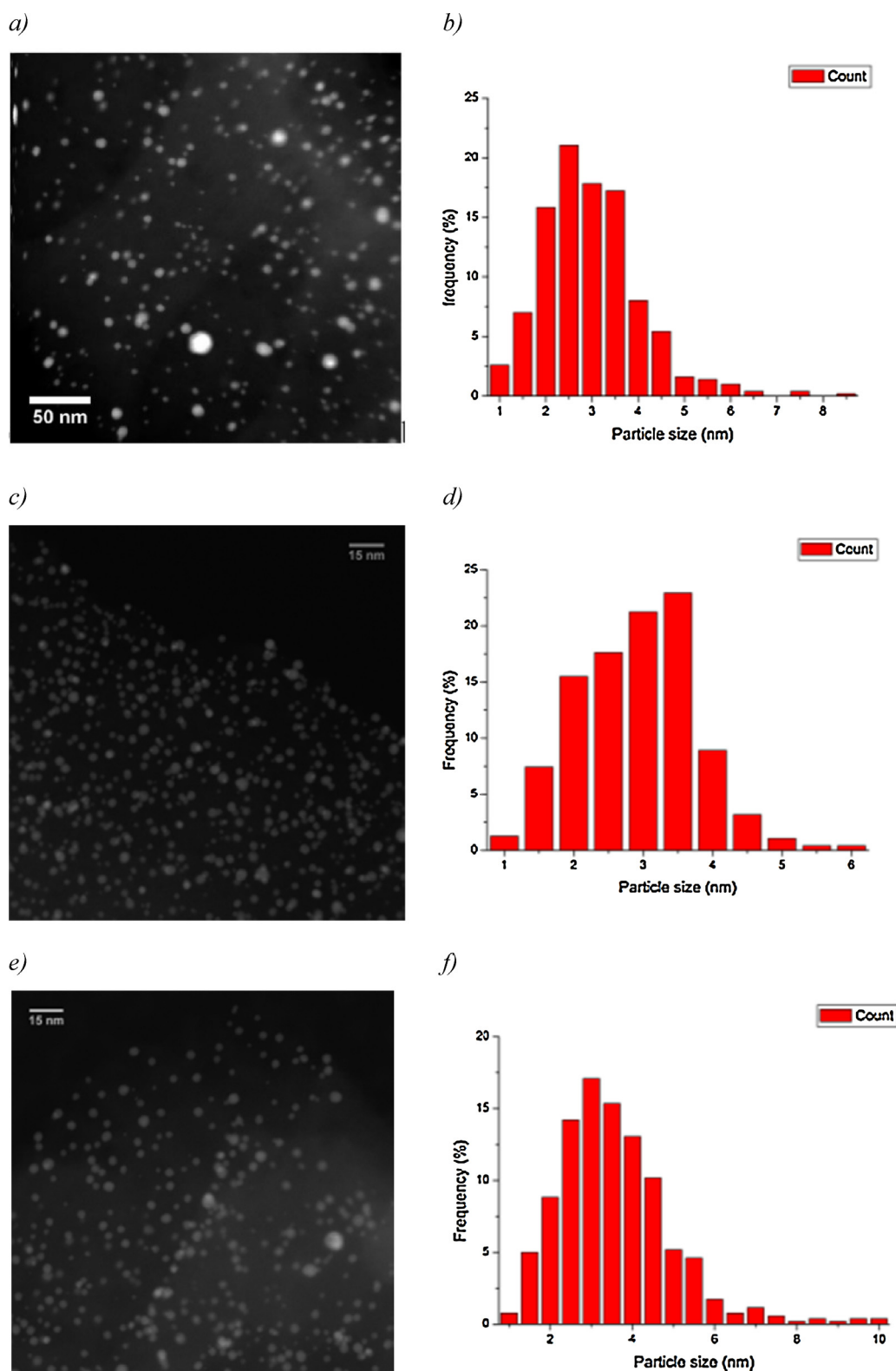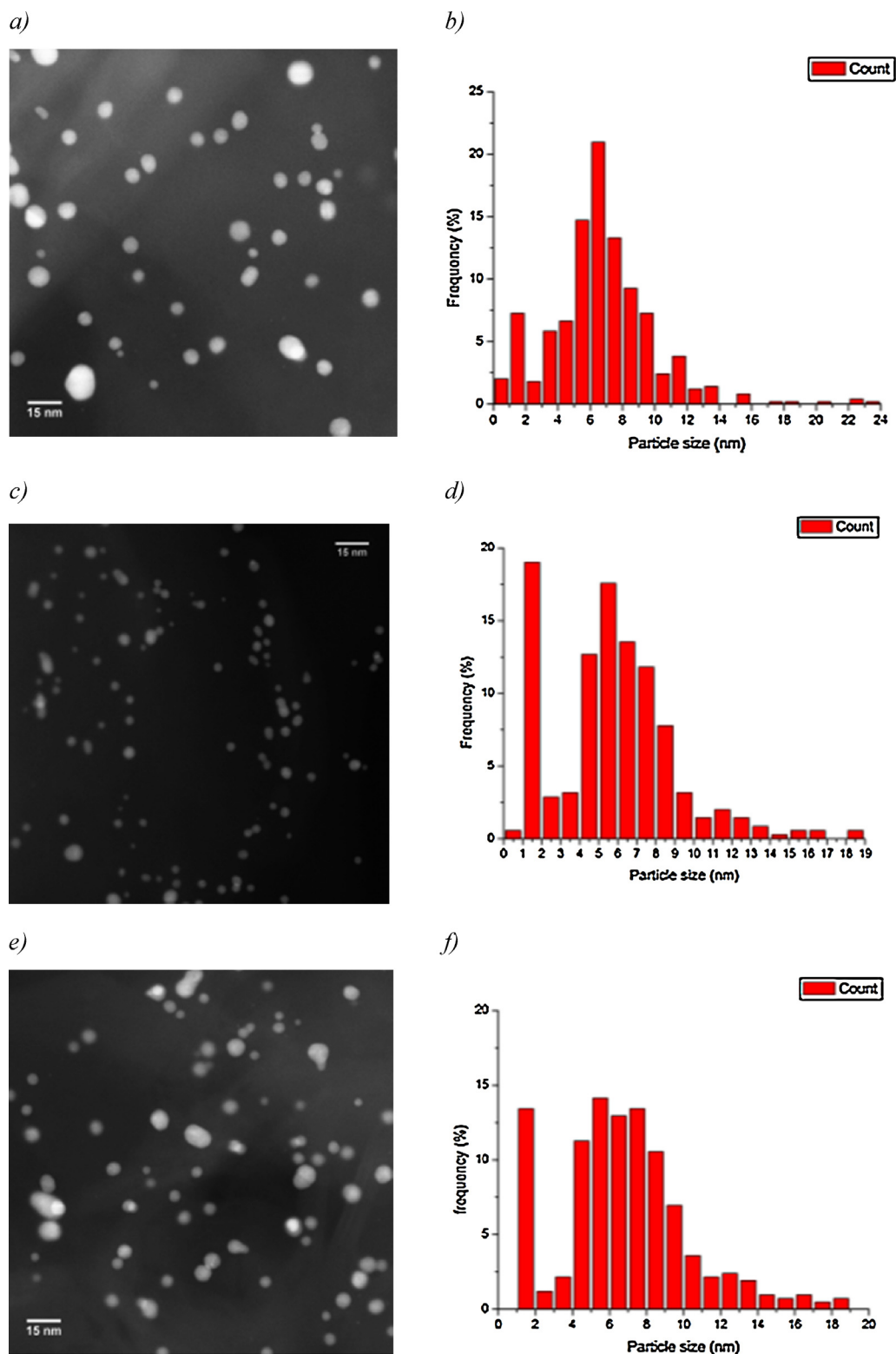
Fig. 1. STEM images and particle size distributions of 1%Au/AC unwashed (a and b), 1%Au/AC washed at r.t. (c and d) and 1%Au/AC washed at 60 °C (e and f).

3.2. Catalytic glycerol oxidation

Catalytic performances of untreated and treated catalysts were evaluated in the liquid phase oxidation of glycerol under standard conditions: glycerol 0.3 M, 50 °C, 3 atm O_2, glycerol/Au 1000 mol mol^{-1}, NaOH/glycerol 4 mol mol^{-1}. Fig. 4 shows reaction profiles for Au based catalysts as plot of conversion versus time. As a general consideration, graphite supported catalysts seem to be more prone to deactivate compared to carbon supported ones. On the basis of reaction profiles (Fig. 4a and b) in the case of 1%Au/AC the washing treatment at room temperature results in almost the same activities despite the washing treatment. The activity

a)

b)

c)

d)

e)

f)

Fig. 2. STEM images and particle size distributions of 1%Au/Graph. unwashed (a and b), 1%Au/Graph. washed at r.t. (c and d) and 1%Au/Graph. washed at 60 °C (e snd f).

trend revealed with 1%Au/AC greatly differs from the results previously obtained with 1%Au/TiO$_2$, where an increase of activity was observed after partial PVA removal while a drop in activity was observed for the sample washed at 60 °C due to a noticeable increase of the particles size. This dissimilarity can be ascribed to the different nature of supports. In fact activated carbon is a highly functionalized and defective support able to provide a

greater amount of anchoring sites than TiO$_2$. This in turn stabilized the metal nanoparticles against coarsening but operated a similar shielding effect as PVA. This hypothesis is supported by the observation that, after washing at 60 °C, an higher amount of amorphous carbon was observed on the surface of Au nanoparticles (Fig. 3c) with respect to the RT treatment (Fig. 2b). In other words, most probably, the high coordinating effect of active carbon replaced the
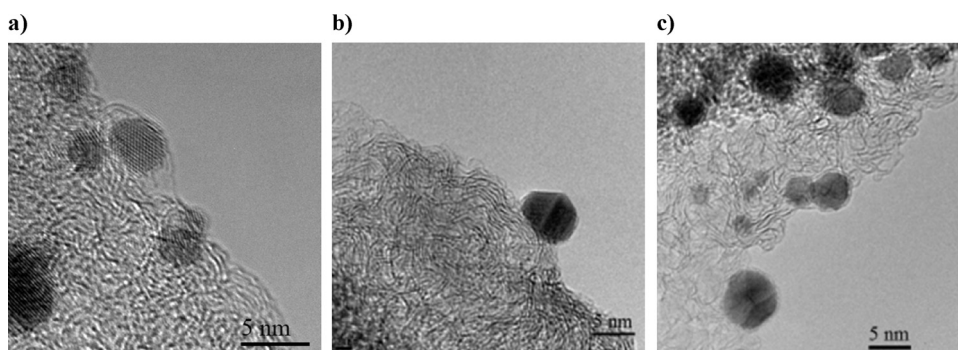
Fig. 3. HRTEM images for 1%Au/AC (a) unwashed; (b) washed at r.t. and (c) washed at 60 °C.
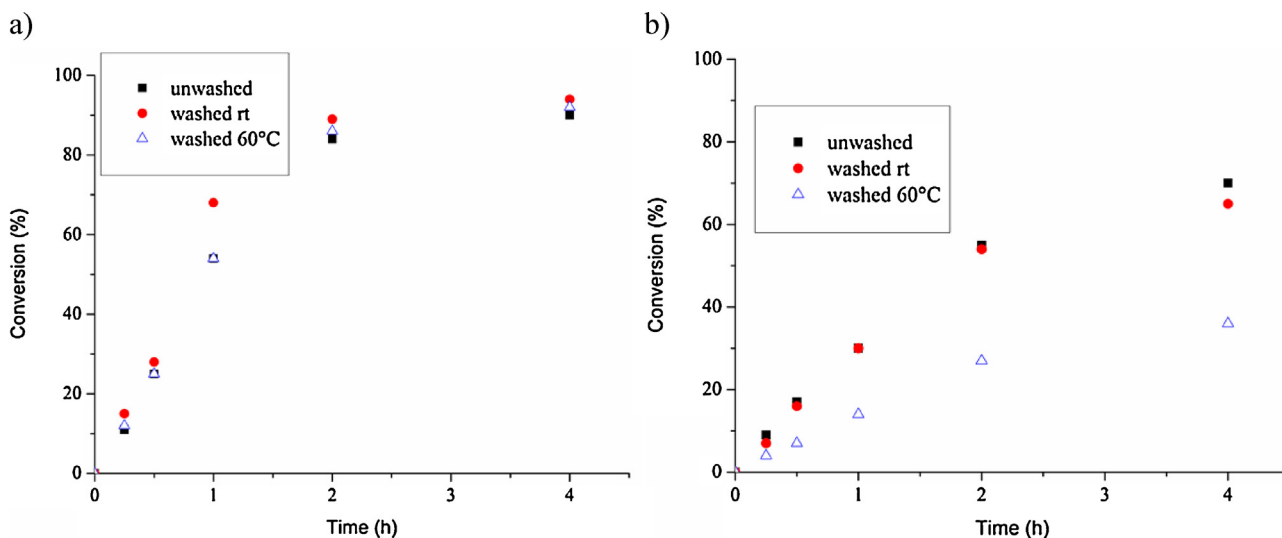

Fig. 4. Reaction profiles for untreated and treated 1%Au/AC (a) and 1%Au/graphite (b) catalysts.

PVA effect on the surface of the nanoparticles producing a similar effect.

Therefore, AC stabilizes more effectively Au nanoparticles after the protective agent removal thus preventing their aggregation. Au on graphite catalysts under the same conditions (Fig. 4b) behaved differently. Analogously to Au/TiO₂, when gold nanoparticles are supported on crystalline graphite the complete removal of PVA through washing at 60 °C leads to a less active catalyst, as a consequence of the particle size increase (Table 1). However, the sample washed at room temperature shows a similar activity as the as-prepared catalyst and, surprisingly, a smaller particle mean size. Keeping in mind the low density of surface groups in crystalline graphite, we could attribute the peculiar performances of graphite supported nanoparticles to the possible presence of small clusters in the as-prepared catalyst, not detectable by the microscope used. Indeed, it has been demonstrated that small gold clusters are significantly active [25]. Decreasing the amount of PVA, these clusters are not stable and incline to agglomerate forming less active nanoparticles than the previous clusters.

The presence of PVA is known to also influence the selectivity of glycerol oxidation [21]. With all tested catalysts, glyceric acid is the main product (Table 2). However the selectivity to this compound is altered by the relative amount of PVA and by the Au particle size. According to the literature [26,27], the selectivity to glyceric acid increases concomitantly with the growth of the Au mean particle size and the amount of PVA. Such a statement is highlighted in the case of Au/AC catalysts, where the lowest selectivity to glyceric acid is obtained with the sample washed at room temperature (65%),

Table 2
Oxidation of glycerol using AC supported and graphite supported gold catalysts[a].

	Catalyst	Selectivity at 70% conversion				
		GLYA	TA	GLYCA	OXA	FA
(i)	Au/AC not washed	68	2	25	5	10
(ii)	Au/AC washed rt	65	1	27	6	11
(iii)	Au/AC washed 60 °C	74	–	20	2	4
(iv)	Au/graph. not washed	72	10	8	5	5
(v)	Au/graph. washed rt	76	2	10	4	8
(vi)	Au/graph. washed 60 °C[b]	82	1	6	4	7

GLYA = glyceric acid; TA = tartronic acid, GLYCA = glycolic acid; OXA = oxalic acid; FA = formic acid.

[a] Glycerol 0.3 M in water; 4 eq. of NaOH; metal/alcohol = 1/1000 mol mol⁻¹; 300 kPa O₂; T = 50 °C.

[b] Selectivity at 30% conversion.

presenting a lower amount of PVA compared to the unwashed counterpart and smaller particles than the sample washed at 60 °C. Conversely, a different trend in the selectivity to glyceric acid can be emphasized in the case of Au/graphite. Indeed, in the latter case the lowest selectivity to glyceric acid is obtained with unwashed catalyst (72%), which also promotes the formation of tartronic acid (10%) (Table 2). These results are in agreement with the hypothesis of the presence of small gold clusters in the unwashed sample, which have been reported to be more selective to tartronic acid [25].

4. Conclusions

PVA protected Au nanoparticles were immobilized on activated carbon and graphite. A gradual removal of PVA was achieved by washing the as-prepared catalysts with water at room temperature and at 60 °C. We demonstrated that the morphology of the support plays an important role in determining metal particle sizes and in stabilizing nanoparticle under protective agent removal. In particular, it has been shown that activated carbon is able to efficiently stabilize gold nanoparticles compared to crystalline graphite, probably due to a different distribution of the anchoring sites. Therefore active carbon as support is able to act as stabilizing agent as well as PVA while crystalline graphite has an amount of functional groups too low to efficiently anchor the metal nanoparticle thus do not avoid the coarsening process during the PVA removal.

Conflict of interest

The authors declare no competing financial interests.

Acknowledgements

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