

AperTO - Archivio Istituzionale Open Access dell'Università di Torino

## **Sol immobilization technique: a delicate balance between activity, selectivity and stability of gold catalysts**

### **This is the author's manuscript**

*Original Citation:*

*Availability:*

This version is available <http://hdl.handle.net/2318/141674> since 2016-09-07T15:13:06Z

*Published version:*

DOI:10.1039/c3cy00260h

*Terms of use:*

Open Access

Anyone can freely access the full text of works made available as "Open Access". Works made available under a Creative Commons license can be used according to the terms and conditions of said license. Use of all other works requires consent of the right holder (author or publisher) if not exempted from copyright protection by the applicable law.

(Article begins on next page)



# UNIVERSITÀ DEGLI STUDI DI TORINO

***This is an author version of the contribution published on:***

*Questa è la versione dell'autore dell'opera:*

A. Villa, D. Wang, G. M. Veith, F. Vindigni and L. Prati, Catal. Sci. Technol., 2013, 3, 3036–3041, DOI: 10.1039/c3cy00260h

***The definitive version is available at:***

*La versione definitiva è disponibile alla URL:*

<http://pubs.rsc.org/en/results?searchtext=DOI%3A%2010.1039%2Fc3cy00260h>

# Sol immobilization technique: a delicate balance between activity, selectivity and stability for gold catalyst

Alberto Villa,<sup>a</sup> Di Wang,<sup>b</sup> Gabriel M. Veith,<sup>c</sup> Floriana Vindigni,<sup>d</sup> and Laura Prati<sup>\*,a</sup>

<sup>5</sup> Received (in XXX, XXX) XthXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXXXX 20XX

Sol immobilization is a widely used method to prepare gold catalysts. The presence of the protective layer can have a significant influence on catalyst properties by mediating metal-support and reactant-metal interactions. This paper details the effect of a polyvinyl alcohol (PVA) protecting groups on the activity of a supported gold catalysts as well as its selectivity towards glycerol oxidation.

## 1. Introduction

Since the first attempts to produce gold catalysts it has become clear that the activities and/or the selectivity of gold catalysts are correlated with a lot of parameters; morphology, dispersion and interactions between gold particles and the support.<sup>1</sup> In addition, due to the low melting point of gold, traditional catalyst synthesis methods (e.g. incipient wetness, impregnation) often fail to producing high metal dispersion except few cases.<sup>2-5</sup> One way around this limitation is the immobilization of pre-formed metallic sol. This method produces highly dispersed metal catalysts whose sizes only partially depend on the support employed.<sup>3-7</sup>

The method is based on the preparation of Au nanoparticles in the presence of a stabilizing agent (polymer, surfactant, polar molecule, etc) and their subsequent immobilization on a support.<sup>8,9</sup> It should be noted that the crucial point for obtaining good metal dispersion in this technique is the immobilization step that depends on the surface properties and morphology of the support.<sup>10</sup> Normally the immobilisation is simply performed by dipping the support in the sol and metal particles resulted adsorbed from the solution. The kinetics of adsorption depends on sol stabilizer and on the IEP and surface area of the support.<sup>9</sup> As a general trend, it has been shown that metal dispersion increases by increasing the functionalities of the support.<sup>10</sup> Moreover, the nature and the relative amount of the protective agent are additional factors influencing the metal dispersion.<sup>11,12</sup>

It has been show that polyvinyl alcohol (PVA) represents a quite versatile protective agent that provides good metal dispersion regardless the support.<sup>2,9,13-16</sup> Moreover it has been shown that it can be removed by thermal decomposition (>300 °C) or under milder conditions by solvent washing.<sup>17</sup> This latter method has the advantage of limiting the coarsening of metallic nanoparticles that normally occurs during thermal treatment and to be applicable for not-refractory supports. However, it is unknown how this protecting group mediates catalyst activity and stability. In this paper we have investigated the impact of the PVA on activity and selectivity for the liquid phase oxidation of glycerol using gold catalysts.

## 2. Experimental

### 2.1 Material

<sup>55</sup> NaAuCl<sub>4</sub> • 2H<sub>2</sub>O, was from Aldrich (99.99% purity) and TiO<sub>2</sub> P25 from Degussa. NaBH<sub>4</sub> of purity > 96% from Fluka, polyvinylalcohol (PVA) (Mw = 13000–23000 87–89% hydrolysed,) from Aldrich were used. Gaseous oxygen (99.99%) from SIAD was used in the catalytic reactions.

### 2.2 Catalyst preparation

<sup>60</sup> 2.2.1 Au<sub>PVA</sub>/TiO<sub>2</sub> catalyst preparation: Solid NaAuCl<sub>4</sub>•2H<sub>2</sub>O (0.043 mmol) and PVA (Au/PVA= 1:1 wt/wt) solution were added to 130 ml of H<sub>2</sub>O. After 3 min, 0.1M NaBH<sub>4</sub> (Au/NaBH<sub>4</sub>= 1:4 mol/mol) solution was added to the yellow solution under vigorous magnetic stirring. A ruby red Au(0) sol was immediately formed. 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 catalysts were filtered, washed on the filter and dried at 80°C for 4h. Au<sub>PVA</sub>/TiO<sub>2</sub> catalysts containing different Au/PVA ratio (Au/PVA= 1:1, 1:0.5, 1:0.25, 1/0.125 wt/wt), were prepared. Au<sub>PVA</sub>/TiO<sub>2</sub> prepared using Au/PVA ratio 1:1 was poured into a large amount of water (100 ml/g of catalyst) at room temperature or in alternative at 60°C and stirred for 8h. The catalyst was then recovered by filtration and dried at 80°C for 4h.

<sup>70</sup> 2.2.2 Au<sub>DP</sub>/TiO<sub>2</sub> catalyst preparation: the support was dispersed in distilled water (approximately 10 ml/g of support) to which ammonia was added to raise the pH to a value between 9 and 10. 0.05M NaAuCl<sub>4</sub> solution (as having 1wt%) was added drop wise to the support under vigorous stirring. The catalyst was filtered and washed several times with water. The material was then suspended in distilled water and a freshly prepared solution of NaBH<sub>4</sub> (0.1 M) was added (NaBH<sub>4</sub>/Au (mol/mol) = 4) under vigorous stirring at room temperature. The sample was filtered, washed and dried at 80°C for 4 h. PVA has been added to Au<sub>DP</sub> catalyst by impregnation. A portion of the catalyst has been redispersed in water (10 ml/g of support) with the proper amount of PVA (Au/PVA= 1:1, and 1/0.125 wt/wt). After 1h the catalyst has been filtered and dried at 80°C for 4 h.

### 2.3 Catalyst characterization

X-ray photoelectron spectroscopy (XPS) data were collected using a PHI 3056 spectrometer with an Al anode source operated at 15KV and an applied power of 350 W with samples mounted on indium foil. Adventitious carbon was used to calibrate the binding energy shifts of the sample ( $C1s = 284.8$  eV). FEI Titan 80-300 aberration corrected electron microscope, operating at 80 kV was used for high-resolution TEM observation. Fourier transform – IR spectra were recorded with a Perkin Elmer 100 spectrometer using a mercury cadmium telluride (MCT) detector. Spectra with  $4\text{ cm}^{-1}$  resolution, 128 scans and a scan speed of  $0.50\text{ cm s}^{-1}$  were recorded at room temperature using CaF windows in the range  $5500 - 450\text{ cm}^{-1}$ . The powders (KBr and sample) were pressed at 10 MPa for 10 minutes. Adsorption experiments by FTIR spectroscopy were carried out on a Perkin-Elmer 2000 spectrometer (equipped with a MCT detector) with the samples in self supporting pellets introduced in cells allowing thermal treatments in controlled atmospheres and spectrum scanning at room temperature (r.t.) in vacuum or in the presence of probe gases. Prior to FTIR analysis, the catalysts were outgassed at  $120^\circ\text{C}$  for 1 h and cooled at r.t. Metal content on the solution was checked by ICP analysis on a Jobin Yvon JY24 verifying the quantitative loading of Au on the support for the sol procedure and 0.89%wt loading for the DP sample.

### 2.4 Catalytic test

Glycerol 0.3 M, and the catalyst (substrate/ total metal = 1000 mol/mol) were mixed in distilled water (total volume 10 mL) and 4 eq of NaOH. The reactor was pressurized at 300 kPa of nitrogen and the temperature set to  $50^\circ\text{C}$ . 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) using a column (Alltech OA- 10308, 300 mm\_7.8 mm) with UV and refractive index (RI) detectors. Aqueous  $\text{H}_3\text{PO}_4$  solution (0.1 wt%) was used as the eluent. Products were identified by comparison with original samples.

## 2. Results and discussion

Au sols were prepared using different Au/PVA wt/wt ratios (1:1 to 1:0.125). After immobilization of the metal nanoparticles (1 wt%) on the  $\text{TiO}_2$ , the Au/ $\text{TiO}_2$  catalysts were evaluated for the liquid phase oxidation of glycerol under standard conditions: glycerol 0.3M,  $50^\circ\text{C}$ , 3atm  $\text{O}_2$ , glycerol/Au 1000 mol/mol, NaOH/glycerol 4mol/mol. Figure 1 shows reaction profiles for these catalysts as a function of time. This data clearly indicates a correlation between the Au/PVA ratio and the activity of the catalysts. Indeed the activity decreased by increasing the relative amount of PVA. This behaviour is similar to what was reported for PVA stabilized Au nanoparticles supported on activated carbon.<sup>12</sup>

To confirm this trend these materials were characterized in greater detail. TEM data collected on the samples revealed that the mean size of Au particles is also affected by the Au/PVA ratio, Table 1. Reducing the PVA concentration resulted in a

slight increase in particle size, 3.5 –4.1 nm, and reduction in particle uniformity, Table 1.

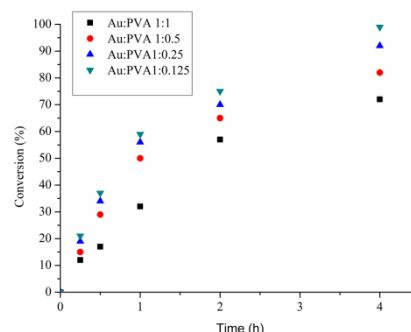


Figure 1. Glycerol oxidation profile with 1%wt Au/ $\text{TiO}_2$ . Glycerol 0.3M in water; 4eq of NaOH; metal/alcohol = 1/1000 mol/mol; 300kPa  $\text{O}_2$ ;  $T=50^\circ\text{C}$ ;

Table 1. Statistical median and standard deviation of particle size analysis for Au/ $\text{TiO}_2$  based catalysts

Catalyst <sup>a</sup>	Statistical median (nm)	Deviation standard ( $\sigma$ )
Au <sub>PVA</sub> (1:1)	3.5	0.7
Au <sub>PVA</sub> (1:0.5)	3.6	0.8
Au <sub>PVA</sub> (1:0.25)	3.9	1.1
Au <sub>PVA</sub> (1:0.125)	4.1	1.2
Au <sub>PVA</sub> (1:1) washed r.t	3.7	0.9
Au <sub>PVA</sub> (1:1) washed $60^\circ\text{C}$	4.9	1.4
AuDP	3.8	1.1
AuDP + PVA (1:1)	3.8	1.1
AuDP + PVA (1:0.125)	3.8	1.1

<sup>a</sup> Au loading was 1% in all cases except for Au<sub>DP</sub> where the actual loading was 0.89%

Correlating the activity data with the particle sizes revealed, surprisingly, that the largest particles, which should be expected the least active, were actually the most active. This may indicate that the PVA actively shields the reactive site. To explore this size-PVA concentration correlation we adopted a strategy gradually removal of the capping agent using a slightly modified procedure reported by Lopez-Sanchez et al.<sup>17</sup> A Au<sub>PVA</sub> (1:1) catalysts was subject to additional washes using deionized water at room temperature and  $60^\circ\text{C}$ . The removal of the PVA was followed by IR spectroscopy (Figure 2) looking at stretching bands of PVA C-O-C between  $1140-1220\text{ cm}^{-1}$ . Washing the as-prepare catalyst with water at ambient temperature resulted in the partial removal of PVA (dotted green line in Figure 2). A washing treatment at  $60^\circ\text{C}$  was effective at completely remove residual PVA (red line in Figure 2).

Table 2. Oxidation of glycerol using TiO<sub>2</sub> supported catalysts<sup>a</sup>

Catalyst	Activity $\frac{\text{mol (Au)}}{\text{mol}^{-1} \text{ h}^{-1} \text{ b}}$	Selectivity (%) <sup>c</sup>				
		Glyc	Gly	Tar	F	Lac
Au <sub>PVA</sub> (1:1)	236	81	3	5	2	9
Au <sub>PVA</sub> (1:0.5)	282	78	5	4	3	10
Au <sub>PVA</sub> (1:0.25)	356	75	4	5	5	11
Au <sub>PVA</sub> (1:0.125)	434	70	12	2	9	7
Au <sub>PVA</sub> (1:1) washed r.t	355	77	6	3	4	10
Au <sub>PVA</sub> (1:1) washed 60°C	138	68	14	3	7	8
AuDP	390	69	12	2	9	8
AuDP + PVA (1:1)	255	76	5	7	3	9
AuDP + PVA (1:0.125)	401	70	10	5	7	8

<sup>a</sup> Glycerol 0.3M in water; 4eq of NaOH; metal/alcohol = 1/1000 mol/mol; 300kPa O<sub>2</sub>; T=50°C;

<sup>b</sup> Mol of glycerol converted per hour per mol of metal, calculated after 15 min reaction

<sup>c</sup> Selectivity calculated at 90% conversion

Glyc=glycerate; Gly=glycolate; Tar=tartronate; F=formate;

Lac=Lactate

The gradual removal of PVA was also evidenced by HRTEM where the capping of the particle by the protective agent is clearly visible in the as-prepared sample (Figure 3a) whereas is much less prominent in the sample washed (Figure 3b).

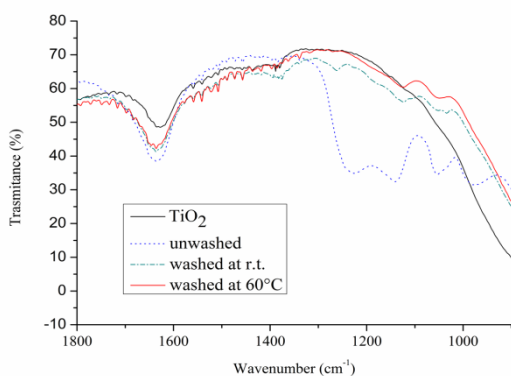
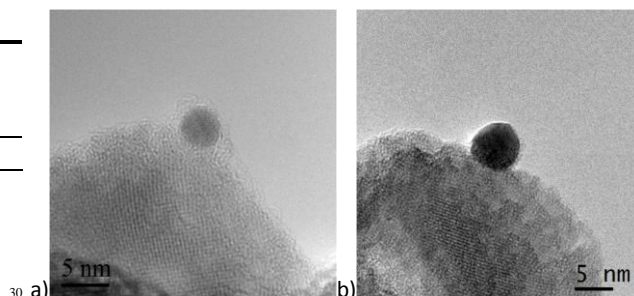


Figure 2. IR spectra of 1%Au/TiO<sub>2</sub> of 3.5nm mean size

HRTEM measurements also highlighted the negligible effect of washing treatment at room temperature on particle size and the slight growing at 60°C (from 3.5nm to 4.9nm).

Testing these three different catalysts under the same conditions as the previous experiments produced some unexpected results (Table 2, Figure 4). The partial removal of the PVA (by washing at RT) produced as expected a more active catalyst compared with the as-prepared sample. However the complete removal of PVA (by washing at 60°C) led to a

drastically drop of activity (Table 2 and Figure 4).



Figures 3. HRTEM representative images of a) PVA capped and b) partially covered by PVA.

This result is not completely justified by the relative increasing of particle size dimension especially considering the threefold activity obtained with the catalyst prepared with Au/PVA 1:0.125 wt/wt showing very similar particle size (Tables 1 and 2). We thus could infer that the role of PVA is not merely to shielding the AuNPs but can be considered as a useful component of the catalyst itself.

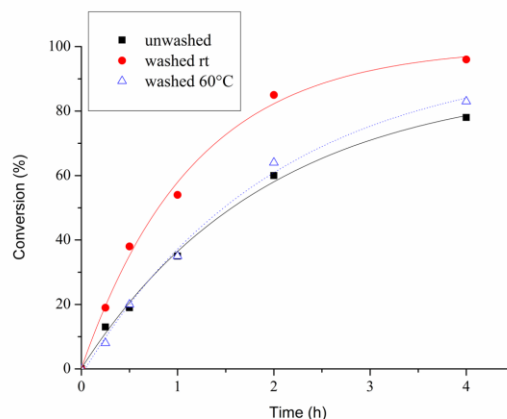


Figure 4. Glycerol oxidation profile with 1%wt Au/TiO<sub>2</sub> differently washed. Glycerol 0.3M in water; 4eq of NaOH; metal/alcohol = 1/1000 mol/mol; 300kPa O<sub>2</sub>; T=50°C;

To explore the usefulness of the PVA we investigated the recyclability of the catalyst. Not surprising we observed that the presence of PVA has a positive effect on the catalyst lifetime. Recycling experiments carried out just by filtering the catalyst and adding fresh solution of glycerol revealed a better resistance to recycling of the as-prepared sample with respect to the washed one (at 60°C) (Figure. 5) the activity of which declines very similarly to Au<sub>DP</sub> sample.

A second benefit incurred by the presence of PVA is a significant modification in catalyst selectivity, Table 2. Comparing all the samples we observed an increase in selectivity to glyceric (and tartronic acids) as the Au/PVA ratio increased (i.e. particle size decreases). However, the well-known dependence of selectivity from particle size in this reaction should lead at an opposite conclusion: we indeed expected that decreasing the particle size

we also decrease the glyceric and tartronic acid selectivities.

Therefore we should conclude that PVA has also a beneficial effect on the selectivity to glyceric and tartronic acids. This conclusion is supported by the fact that adding PVA to the  $\text{Au}_{\text{DP}}/\text{TiO}_2$  (Au/PVA 1:1wt/wt) leads to almost same catalytic properties as the pure  $\text{Au}_{\text{PVA}}/\text{TiO}_2$  1:1 (Table 2). It should be noted that 1%wt Au/TiO<sub>2</sub> prepared by deposition-precipitation showed the worst selectivity to glyceric/tartronic acids.<sup>18-22</sup> The selectivity did not significantly change with conversion during the reaction (within 1-2% difference) We assume this indicative that both the amount of PVA on the active site and the morphology of the Au particle did not change significantly during a single run. On the contrary variation on selectivity has been noted during the recycling tests. Indeed, the selectivity to glyceric acid for  $\text{Au}_{\text{PVA}}/\text{TiO}_2$  (1:1) unwashed decreased from 81% to 75% after the 6<sup>th</sup> run. In this case, a partial removal of PVA from the surface occurred (as evidenced by IR measurement). Conversely, the selectivity of  $\text{Au}_{\text{PVA}}/\text{TiO}_2$  (1:1) washed and  $\text{Au}_{\text{DP}}/\text{TiO}_2$  increased from 68% to 74% and from 69% to 76%, probably due to aggregation and/or increasing of the Au particles which is known to be more selective toward C3 products.<sup>19</sup>

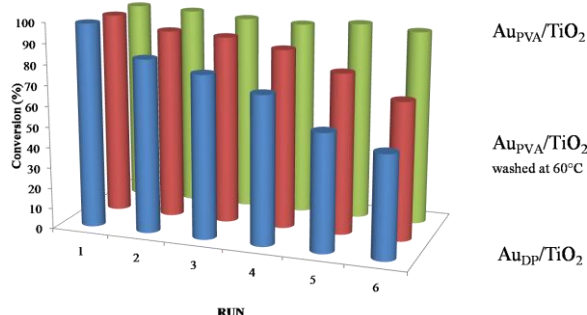


Figure 5. Recycling tests using  $\text{Au}_{\text{PVA}}/\text{TiO}_2$  and  $\text{Au}_{\text{DP}}/\text{TiO}_2$  catalysts. Glycerol 0.3M in water; 4eq of NaOH; metal/alcohol = 1/1000 mol/mol; 300kPa O<sub>2</sub>; T=50°C.

FTIR spectra of increasing coverage of glycerol were collected at room temperature, in order to study the different interaction of glycerol with Au/TiO<sub>2</sub> with or without PVA (Au:PVA 1:1 wt/wt). Before the glycerol inlet, the spectrum of  $\text{Au}_{\text{PVA}(1:1)}/\text{TiO}_2$  (fig 7, bold curve) shows the bands related to the presence of PVA. In particular, the peaks of CH<sub>2</sub> stretching (2928 and 2855 cm<sup>-1</sup>), C-OH deformation (1337 and 1289 cm<sup>-1</sup>) and C-O stretching (weak absorption at 1100-1200 cm<sup>-1</sup>) are present. The adsorption of increasing amounts of glycerol at room temperature (figure 7, fines and dotted curves) gives rise to a modification of the C-OH deformation band of PVA. A conversion of the component at 1337 cm<sup>-1</sup> into the 1278 cm<sup>-1</sup> band, well evident through an isosbestic point at 1298 cm<sup>-1</sup>, occurs. This feature points out that the glycerol interacts with PVA, by OH groups. This interaction is reversible at room temperature, as it is shown in Fig 7 (inset, solid curve) where the spectrum collected after 30' of outgassing exhibits again the component at 1337 cm<sup>-1</sup>.

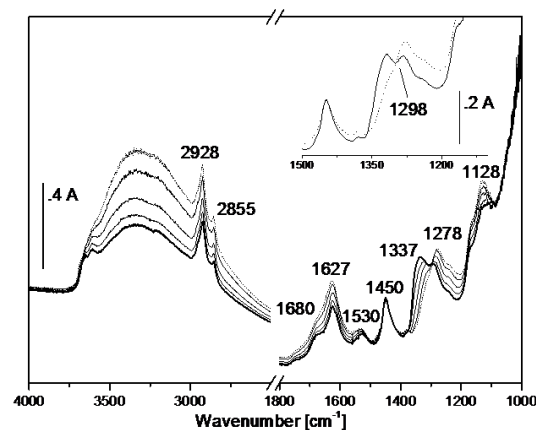


Figure 7. FTIR absorbance spectra of  $\text{Au}_{\text{PVA}(1:1)}/\text{TiO}_2$  before (bold curve) and after interaction with 0.01 mbar, 0.1 mbar, 0.15 mbar (fine curves) and 0.25 mbar (dotted curve) of glycerol at r.t.. Inset: FTIR absorbance spectra of  $\text{Au}_{\text{PVA}}/\text{TiO}_2$  with 0.25 mbar of adsorbed glycerol (dotted curve) and after prolonged outgassing at r.t. (30 min, solid curve).

On the contrary, the interaction between glycerol and  $\text{Au}_{\text{DP}}/\text{TiO}_2$  only slightly perturbs the surface species as signalled by no significant change in the FTIR spectra. Therefore a possible explanation of PVA effect on selectivity in glycerol oxidation could lie on the ability of PVA in directing the adsorption mode of glycerol as depicted in Figure 7. PVA arrangement on the surface of AuNP can create a sort of porous structure, interacting with the OH groups of glycerol, thus in turn directing the contact between the active site and OH functionality.

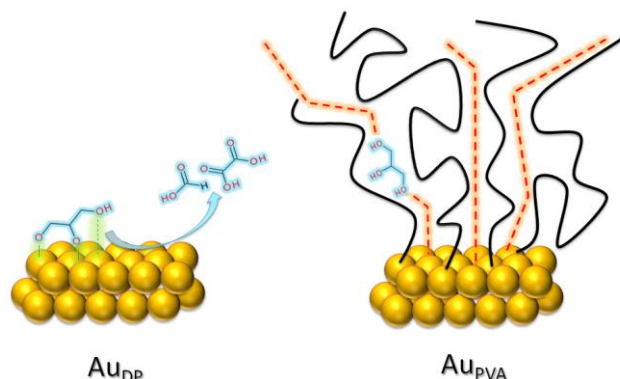


Figure 6. Model for glycerol adsorption a) in the presence of PVA, b) on free surface

Finally, we observed a decreasing of activity by increasing the relative amount of PVA (entries 1 and 2 Table 2 and Table 3). However, by considering activities of  $\text{Au}_{\text{PVA}}$  1:0.125 (showing a TOF of 434 h<sup>-1</sup> and a mean Au size of 4.1nm) and of  $\text{Au}_{\text{PVA}}$  washed at 60°C (showing a TOF of only 138 h<sup>-1</sup> and a mean Au size of 4.9 nm) it is clear that the presence of PVA likely has a promoting effect (Table 3). This finding can be also supported by comparing  $\text{Au}_{\text{DP}}$  samples treated with different amount of PVA. We observed in fact an increasing activity in the case of very



small addition of PVA (Au/PVA 1:0.125 wt/wt) with respect to bare Au<sub>DP</sub>. The activity however drastically declines by increasing the amount of PVA (Au/PVA 1:1 wt/wt) (Table 3).

Therefore, we can conclude that the absence of PVA (DP preparation) or its complete removal (Au/PVA 1:1 washed at 60°C) produced less active, less stable and less selective catalysts. On the contrary the presence of PVA enhanced the catalytic activity but only when the Au/PVA ratio is quite high (i.e. 1:0.125 wt/wt). For high PVA content (i.e. Au/PVA 1:1 wt/wt) the shielding effect of the capping agent prevails and the catalytic activity declines. Tsukuda et al. assessed the presence of an electronic effect in the case of PVP (poly N-vinyl-2-pyrrolidone) capping agent.<sup>23</sup> In that case they explained the increased activity of Au PVP protected particles with respect to PAA (polyallylamine) to an increased negative charge on the Au transferred to the adsorbed O<sub>2</sub> forming a superoxo- or peroxy-like species which can readily abstract a β-hydrogen atom from the alcohol to generate the corresponding aldehyde.

Table 3. Effect of PVA amount on activity of Au/TiO<sub>2</sub> in glycerol oxidation<sup>a</sup>

Au/PVA (wt/wt)	Catalyst	Statistical median (nm)	Activity mol mol <sup>-1</sup> h <sup>-1</sup> (Au mol) <sup>b</sup>
1:1	Au <sub>PVA</sub>	3.5	236
1:0.125	Au <sub>PVA</sub>	4.1	434
-	Au <sub>PVA</sub> washed	4.9	138
-	AuDP	3.8	390
1:1	AuDP + PVA	3.8	255
1:0.125	AuDP + PVA	3.8	401

<sup>a</sup> Glycerol 0.3M in water; 4eq of NaOH; metal/alcohol = 1/1000 mol/mol; 300kPa O<sub>2</sub>; T=50°C

<sup>b</sup> Mol of glycerol converted per hour per mol of metal, calculated after 15 min reaction

To explore the possibility of an electronic effect we performed XPS studies on Au<sub>PVA</sub>/TiO<sub>2</sub>, Au<sub>DP</sub>/TiO<sub>2</sub> and Au<sub>DP</sub>/TiO<sub>2</sub>+PVA in order to check a possible electron transfer from the capping agent to Au as a possible explanation of the enhanced activity due to the presence of PVA. As shown in Figures 7 there are no differences in the Au4f, C1s, O1s, or Ti2p signals in any of these three samples. This would likely exclude any electron transfer from PVA molecules and Au. Surprisingly, the only changes that were observed were to the C1s spectra collected for the Au<sub>DP</sub>/TiO<sub>2</sub>. This data revealed the presence of additional carbonates on the TiO<sub>2</sub> surface (289 eV). This likely originates from the basicity of the TiO<sub>2</sub> treated in NH<sub>4</sub>OH during DP. The PVA addition process may be dissolving this carbonate and acting to prevent the

readsorption of CO<sub>2</sub>. Given that the acid/base chemistry of catalyst supports directly mediate activity of gold catalysts the PVA may help mediate the surface acidity. Davis et al. reported this acid/base chemistry is a critical element in glycerol glycerol oxidation.<sup>24</sup> On the basis of DFT calculations and labelling tests, it was proposed that the role of the OH groups present on the support surface becomes fundamental in the second elementary step of the reaction, i.e. the hydration of aldehyde to acetal with the subsequent formation of the corresponding carboxylic acid.

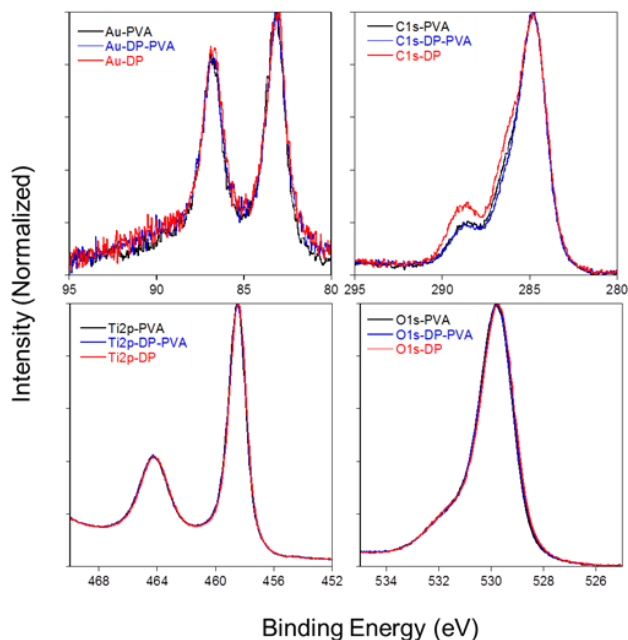


Figure 7. XPS spectra of AuPVA/TiO<sub>2</sub> (black line), AuDP/TiO<sub>2</sub> (red line) and AuDP/TiO<sub>2</sub>+PVA (blue line)

## Conclusions

We prepared Au/TiO<sub>2</sub> samples by PVA stabilized AuNP immobilisation. The presence of the capping agent modifies the activity and the selectivity in glycerol oxidation. In addition, the presence of PVA has been demonstrated to lower the activity of Au/TiO<sub>2</sub> catalysts but increase the stability of the catalyst on recycling prolonging considerably the catalyst-life. However these effects strictly depend on the amount of the protective agent. It has been indeed demonstrated that small amount of PVA (Au/PVA 1:0.125 mol/mol) enhance the activity of the catalyst. We checked a possible electron transfer from PVA molecule to Au particle to explain the higher activity obtained with the Au/TiO<sub>2</sub> catalyst with very low amount of PVA as revealed for PVP protected AuNPs.<sup>24</sup> However we didn't find any supporting XPS data for this electronic modification and thus conclude that the PVA effect could be related to a possible active role of PVA in the reaction mechanism. IR adsorption studies evidenced a direct interaction between PVA and the glycerol molecule which indeed could take active part in the oxidation reaction. This study evidenced different adsorption modes of glycerol on the active sites with or without PVA thus also contributing to explain the positive effect on the selectivity toward glyceric and tartronic acids of the presence of PVA.

## Notes and references

<sup>a</sup> Dipartimento di Chimica, Università degli Studi di Milano, via Golgi 19, 20133 Milano, Italy

Fax: +390250314405; Tel: +390250314357; E-mail: Laura.Prati@unimi.it

<sup>b</sup> Institute of Nanotechnology and Karlsruhe Nano Micro Facility, Karlsruhe institute of technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen (Germany)

<sup>c</sup> Materials Science and Technology Division, Oak Ridge National Laboratory Oak Ridge, TN 37831 (USA)

<sup>d</sup> Dipartimento di Chimica and NIS Centre of Excellence, Università di Torino, Via P.Giuria 7, 10125 Torino, Italy.

Acknowledgements: A portion of this work (GMV-XPS) was supported by the U.S. Department of Energy (DOE), Basic Energy Sciences (BES), Materials Sciences and Engineering Division. TEM characterization was carried out in KIT and sponsored by Euminafab.

† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See

DOI: 10.1039/b000000x/

- 1 M. Haruta, *Catal. Today*, 1997, **36**, 153.
- 2 L. Prati, G. Martra, *Gold Bull.* 1999, **32**, 96.
- 3 L. Prati and A. Villa, *Catalysts* 2012, **2**, 24.
- 4 C. Baatz, N. Decker, U. Prüße, *J Catal.* 2008, **258**, 165.
- 5 M. Sankar, Q. He, M. Morad, J. Pritchard, S. J. Freakley, J. K. Edwards, S. H. Taylor, D. J. Morgan, A. F. Carley, D. W. Knight, C. J. Kiely, and G. J. Hutchings, *ACS Nano*, 2012, **6**, 6600
- 6 D.G.Duff, A. Baiker, P.P. Edwards, *J. Chem. Soc. Chem. Commun.* 1993, 96.
- 7 M.-C. Daniel and D. Astruc, *Chem. Rev.* 2004, **104**, 293.
- 8 P. Zhao, N. Li, D. Astruc, *Coord. Chem. Rev.* 2013, 257, 638.
- 9 S. Coluccia, G. Martra, F. Porta, L. Prati, M. Rossi, *Catal. Today*, 2000, **61**, 165.
- 10 L. Prati, A. Villa, C. E. Chan-Thaw, R. Arrigo, D. Wang and D. S. Su, *Faraday Discuss.*, 2011, **152**, 353.
- 11 A. Villa, D. Wang, D. S. Su, and L. Prati, *ChemCatChem* 2009, **1**, 510.
- 12 A. Villa, D. Wang, D. Su, G. M. Veith and L. Prati, *Phys. Chem. Chem. Phys.*, 2010, **12**, 2183.
- 13 A. Villa, G. M. Veith, D. Ferri, A. Weidenkaff, K. A. Perry, S. Campisi and L. Prati, *Catal. Sci. Technol.*, 2013, **3**, 394.
- 14 E. G. Rodrigues, S. A.C. Carabineiro, J. J. Delgado, X. Chen, Manuel F.R. Pereira, J.M. Órfão, *J Catal.* 2012, **285**, 83
- 15 Nadia El Kolli, Laurent Delannoy, Catherine Louis, *J Catal.* 2013, **297**, 79
- 16 P. G. N. Mertens, M. Bulut, L. E. M. Gevers, I. F. J. Vankelecom, P. A. Jacobs and D. E. De Vos, *Catal. Lett.*, 2005, **102**, 57
- 17 J. A. Lopez-Sanchez, N. Dimitratos, C. Hammond, G. L. Brett, L. Kesavan, S. White, P. Miedziak, R. Tiruvalam, R. L. Jenkins, A. F. Carley, D. Knight, C. J. Kiely and G. J. Hutchings, *Nat. Chem.* 2011, **3**, 551.
- 18 S. Carrettin, P. McMorn, P. Johnston, K. Griffin, C. J. Kiely, G. J. Hutchings, *Phys. Chem. Chem. Phys.* 2003, **5**, 1329.
- 19 F. Porta, L. Prati, *J. Catal.* 2004, **224**, 397.
- 20 S. Demirel-Gülen, M. Lucas, P. Claus, *Catal. Today* 2005, **102** – **103**, 166.
- 21 N. Dimitratos, J. A. Lopez-Sanchez, D. Lennon, F. Porta, L. Prati, A. Villa, *Catal. Lett.* 2006, **108**, 147..
- 22 W. C. Ketchie, Y. Fang, M. S. Wong, M. Murayama, R. J. Davis, *J. Catal.* 2007, **250**, 94.
- 23 H. Tsunoyama, N. Ichikuni, H. Sakurai, and T. Tsukuda, *J. Am. Chem. Soc.* 2009, **131**, 7086.
- 24 B.N.Zope, D.D.Hibbits, M.Neurock, R.J.Davis, *Science*, 2010, **330**, 74