Surfactant-protected gold particles: new challenge for gold-on-carbon catalysts

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N-dodecil-*N*,*N*-dimethyl-3-amino-1-propan sulphonate was used for stabilizing gold nanoparticles in water that afforded Au/C (SB-Au/C) when immobilized on activated carbon. Characterization by XPS revealed a high atomic percentage of superficial gold (% at. Au(4f)/C(2s)), compared with other Au/C catalysts prepared by the immobilization of different sols. The activity of the SB-Au/C catalyst was found to be superior to that observed in the liquid-phase oxidation of ethylene glycol using other gold-on-carbon catalysts.

KEY WORDS: gold on carbon; liquid-phase oxidation; gold catalyst preparation.

1. Introduction

Recently, it has been shown that the immobilization of gold sols represents a suitable method for producing gold catalysts characterized by good metal dispersion, a prerequisite for high catalytic activity [1–3]. In particular, when carbon is used as the support, the choice of the proper sol is fundamental to the maintenance of gold particle size during the immobilization step, being underlined that both steric and electrostatic stabilization are necessary to preserve particle dimension [4]. Although a high protecting agent/metal ratio prevents particle aggregation during sol immobilization [5], a marked amount of these bulky molecules has the drawback of shielding the metal particle, as shown in the liquid-phase oxidation of ethylene glycol catalyzed by gold on carbon [4,6]. Gold-on-carbon catalysts were very active and selective in liquid-phase oxidation [7–9] and during past studies we established that this activity is ruled by two factors: particle dimension and gold exposure on the carbon surface [10]. These two parameters are also connected to the nature of activated carbon where the chemical nature of the surface oxygenated groups probably plays an important role [11].

Our studies, focused on the design of an active gold-on-carbon catalyst for liquid-phase application, were aimed, operating a fine tuning of all the parameters involved in determining activity, to optimize gold-on-carbon preparation, keeping in mind that gold particle activity increases with decreasing particle size and increasing gold exposure. Throughout this work, we have used only one sol stabilizing agent, the *N*-dodecil-*N*,*N*-dimethyl-3-amino-1-propan sulphonate (SB), that provides both sterical and electrostatic stabilization, a condition we have already demonstrated as being necessary to preserve particle dimension when carbon is used as the support [4]. We generated different gold sols by varying the relative amount of reagents ($HAuCl_4$, SB, $NaBH_4$), the type of alkali and the temperature of the gold precursor reduction. Moreover, as we had recently evidenced that there is also a carbon effect [11], we employed only one active carbon to immobilize the sols.

2. Experimental

2.1. Materials

Gold of 99.9999 purity in sponge from Fluka and activated carbon from Carbosorb (MK; $SA = 900–1100\,m^2\,g^{-1}$; $PV = 1.5\,mL\,g^{-1}$; pH 9–10) were employed. Before use, the carbon was suspended in HCl 6M and left under stirring for 12 h, then washed several times with distilled water by decantation until the pH of the solution reached values of 6–6.5. At the end, the carbon was filtered off and dried for 5–6 h at 150 °C in air. The final water content was evaluated to be $< 3\%$.

$NaBH_4$ of purity $> 96\%$ from Fluka, polyvinylalcohol (PVA) (M 10 000) and *N*-dodecil-*N*,*N*-dimethyl-3-amino-1-propan sulphonate of $> 98\%$ from Aldrich were used. NaOH, LiOH, KOH, Na_2CO_3, Li_2CO_3, K_2CO_3, $(NH_4)_2CO_3$, $NaHCO_3$, $KHCO_3$, $(NH_4)HCO_3$, NaCl, $NaNO_3$, Na_2SO_4 and $SnCl_{2*}2H_2O$ were from Fluka of the highest purity available. Gaseous oxygen from SIAD was 99.99% pure.

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2.2. PVA-protected gold sol preparation

An aqueous $HAuCl_4$ solution of 100 μg/mL is prepared by dissolving gold (30 mg) in a minimum amount of HCl/HNO_3 3/1 v/v mixture and, after removing the HNO_3, it is diluted with distilled water. Maintaining the auric solution under vigorous stirring, the PVA 2 wt% solution (0.96 mL) is added; a 0.1 M freshly prepared solution of $NaBH_4$ (7.62 mL) is then added dropwise to yield a ruby red metallic sol.

2.3. SB-protected gold sol preparation

To an aqueous $HAuCl_4$ solution prepared as above ($Au = 0.3$ mg/mL), the SB and the base were added under stirring. The amount of the base was adjusted to $pH = 8$. Then 0.1 M of a freshly prepared solution of $NaBH_4$ was added to reduce the Au(III) to Au(0). The additions were made using three different procedures: in the "one pot" procedure, the total amount of $NaBH_4$ was added in one single step; in the "stepwise" procedure, $NaBH_4$ was added in portions as specified later in the discussion; in the third procedure, $NaBH_4$ was added dropwise throughout the whole period. The relative amounts of reagents are specified in table 3.

2.4. Catalyst preparation and characterization

Within a few minutes of sol generation, the sol is immobilized by adding activated carbon under vigorous stirring. The amount of support is calculated as having a final gold loading of 1 wt%. After 2 h, the slurry is filtered, the catalyst is washed thoroughly with distilled water and used in the wet form. The absorption of gold is checked by ICP analysis of the filtrate on a Jobin Yvon JY24. The water content is determined by drying the sample for 5 h at 150 °C in air.

X-ray diffraction experiments were performed on a Rigaku D III-MAX horizontal-scan powder diffractometer with Cu Kα radiation, equipped with a graphite monochromator in the diffracted beam. The crystallite sizes of the gold were estimated from peak half-widths by using Scherrer's equation with corrections for instrumental line broadening.

X-ray photoelectron spectroscopy (XPS) measurements were performed in an M-Probe Instrument (SSI) equipped with a monochromatic Al Kα source (1486.6 eV) with a spot size of $200 \times 750\,\mu$m and a pass energy of 25 eV, providing a resolution of 0.74 eV.

The accuracy of the binding energies (BE) was estimated to be ±0.2 eV. All the samples were in this range around the value for metallic gold (84.0 eV). The quantitative data were checked accurately and reproduced several times (at least 10 times for each sample).

2.5. 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 300 kPa. The oxygen uptake was followed by a mass flow controller connected to a PC through an A/D board, plotting a flow/time diagram.

Ethylene glycol (8 mmol), NaOH (8.25 mmol) and the Au/C catalyst (glycol/metal = 1000 mol/mol) were mixed in distilled water (total volume 10 mL). The reactor was pressurized at 300 kPa of O_2 and thermostatted at 70 °C. After an equilibration time of 15 min, the mixture was stirred for 60 min. Samples were taken every 15 min and analyzed by HPLC on a Varian 9010 instrument equipped with a Varian 9050 UV (210 nm) and a Waters RI detector in series. An Alltech OA-1000 column (300 mm × 6.5 mm) was used with aqueous H_2SO_4 0.01 M (pH 2.1) (0.8 mL/min) as the eluent. Samples of the reaction mixture (0.1 mL) were diluted (10 mL) using the eluent after adding the internal standard (propionic acid).

3. Results and discussion

Using MK Carbosorb as activated carbon in supporting PVA-protected gold particle, we have shown that the maximum activity in the liquid-phase oxidation of ethylene glycol was reached when the particle diameter was around 7 nm [10]. However, shielding owing to the support limited the reactivity of smaller particles that, in principle, should be more reactive, as evidenced on oxides. Thus, our aim was to generate gold particles as small as possible, but located on the external surface of the carbon to reduce the shielding effect.

Sols generated by reducing the auric solution with partially hydrolized tetrahydroxymethyl phosphonium chloride (THPC) result in a 2–3-nm-sized particle [12], but the protection provided by the phosphonium salt is unable to preserve the mean particle diameter when the sols are immobilized on carbon [4]. Also, the cationic polymer poly(diallyldimethylammonium chloride)(PDDA) used with $NaBH_4$ as a reductant suffers the same limitation; an enlargement of the metal particle is observed on passing from sol to the supported particle, an enlargement that depends on the PDDA/Au ratio [6]. Another interesting point is the role of the protective agent in the activity of an Au/C catalyst; for example, in the case of PDDA, it has been demonstrated that by using a 0.15, wt/wt PDDA/Au ratio instead of 0.30, the activity was three times higher (TOF 840 and 320 h^{-1} respectively) for similar mean size diameter (9 and 7 nm respectively).

Quite recently, *N*-dodecil-*N*,*N*-dimethyl-3-amino-1-propan sulphonate was used to prepare colloidal

Platinum Adams in the presence of lithium carbonate at water reflux temperature [13]. We employed the same procedure to obtain colloidal gold, and 1% Au/C catalysts were prepared by immobilizing the sols on carbon. The catalytic test for liquid-phase oxidation that we used (ethylene glycol, NaOH, O_2, 343 K) revealed poor activity (TOF = 103–107 h^{-1}), in agreement with the large mean diameter of the gold particle calculated from XRPD diffractograms (10–13 nm) (table 1, entries 1 and 2). By decreasing the temperature, we obtained supported gold particles that showed higher activity (TOF = 450–504 h^{-1}), although XRPD revealed almost the same mean diameter (9 versus 10 nm and 13 versus 13 nm). However, as shown in table 1, we again observed that the higher activity corresponds to a higher percentage of gold at the surface (% at. Au(4f)/C(2s) measured by XPS) (entry 1 compared to entry 3, and entry 2 to entry 4). We also observed that the mean dimensions of the gold particles appeared to be ruled by the gold dilution, whereas the surface exposure was influenced by temperature.

As we recently reported, the effect of the presence of an energy-reducing agent ($NaBH_4$) on the dimension and size distribution of the gold particle is very high, the decrease in particle size being correlated to an increased amount of $NaBH_4$ (i.e., increasing the rate of the reduction) [6]. Thus, operating at room temperature to enhance the percentage of gold at the surface, and introducing $NaBH_4$ in order to produce smaller particles, we were able to obtain, after immobilization of the sol on active carbon, a 1%Au/C catalyst extraordinarily more active than previous ones (entries 1 and 2, table 2). However, we suspect that the low activity of the first catalyst could be correlated to a not-total reduction of the gold(III)species in solution. Therefore, we treated the catalyst of entry 1—table 2 with $NaBH_4$ to ensure complete reduction; however, we observed a decreased activity (TOF = 331 h^{-1}), although the XPS and XRPD data of the catalyst remained practically constant. The explanation was found on measuring the Au content of the catalyst by ICP: we detected 13% metal leaching. The effect of the relative Au/$NaBH_4$ amounts was then studied in greater detail, and we found that by increasing the Au/$NaBH_4$ ratio the particle dimensions increased, probably through aggregation, with a consequent decrease in the TOF (table 2, entries 3–7). It is interesting to note that the same mean diameter, as in the absence of $NaBH_4$, was achieved by using a Au/$NaBH_4$ molar ratio of 0.5 (table 2, entries 1 and 3), the activity of the latter catalyst being, however, double that of the former (871 h^{-1} versus 449 h^{-1}). In our opinion, the slight increase in %at. Au(4f)/C(2s) detected by XPS is too small to justify this activity enhancement. Let us consider the trend shown in table 2: maximum activity occurs for an Au/$NaBH_4$ molar ratio of 0.15, and it can be seen that there is a constant decrease in activity on increasing the amount of $NaBH_4$, the highest activity corresponding to the lowest particle diameter and the greatest exposure.

As in these cases, the gold loading was constant (1%), and we had expected that increasing the $NaBH_4$ amount would have given us smaller particles, we hypothesized that an excess of reducing agent could damage, or modify, the sulphobetain protective double layer [14], creating a different gold particle protection. Thus, we compared the catalytic results of carbon-supported gold sols derived by stepwise reduction (table 3): four sols were prepared varying the Au/$NaBH_4$ ratio from 1 : 0.15 to 1 : 3, adding the reducing agent stepwise after an hour according to table 3 (entries 1–4). We ran catalytic tests and found that the obtained catalysts showed similar TOFs, in line with the similar XPS and XRPD parameters, allowing us to conclude that the ruling factor was not the total amount of $NaBH_4$ but the kinetics of metal sol formation. In fact, comparing entry 2 with entry 5, and entry 3 with entry 6 of table 3, it can be seen that the activities differ greatly, depending on the $NaBH_4$ addition methodology: in one step or in portions. We obtained larger particles, probably

Table 1
1%Au/C from SB/Li_2CO_3 sols without reducing agent[a]

Entry	[Au(III)] (mg/mL)	T(K)	% at. Au(4f)/C(2s) [XPS]	d (nm) [XRPD]	TOF (h^{-1})[b]
1	1	373	0.42	12.9	107
2	0.3	373	0.52	9.6	103
3	1	298	1.58	13.0	504
4	0.3	298	1.48	8.8	449

[a] Au/SB = 4 mol/mol; pH = 8.

[b] Catalytic test: catalytic test: ethylene glycol (8 mmol); NaOH (8.25 mmol); Au/C catalyst (glycol/metal = 1000 mol/mol); distilled water (total volume 10 mL); pO_2 = 300 kPa; T = 343 K. TOFs were calculated on total gold.

Table 2
1%Au/C from SB/Li_2CO_3/$NaBH_4$ sols[a]: influence of $NaBH_4$ amount

Entry	Au/$NaBH_4$ (mol/mol)	% at. Au(4f)/C(2s) [XPS]	d (nm) [XRPD]	TOF (h^{-1})[b]
1	–	1.48	8.8	449
2	1/0.15	3.26	5.5	1620
3	1/0.5	1.98	8.6	871
4	1/1	1.58	12.3	809
5	1/2	1.60	12.5	620
6	1/3.5	0.89	13.1	472
7	1/5	0.89	14.3	194

[a] Sol: [Au(III)] = 0.3 mg/mL; Au/SB = 4 mol/mol; $NaBH_4$ 0.1 M; pH = 8; T = 298 K.

[b] Catalytic test: catalytic test: ethylene glycol (8 mmol); NaOH (8.25 mmol); Au/C catalyst (glycol/metal = 1000 mol/mol); distilled water (total volume 10 mL); pO_2 = 300 kPa; T = 343 K. TOFs were calculated on total gold.

through an aggregation mechanism, and drastically lower activity when $NaBH_4$ was added in large quantities. Carrying out the reduction by adding the $NaBH_4$ solution dropwise gave us an extraordinarily active 1%Au/C (TOF = 3542 h^{-1}) (table 3, entries 8–9). The dropwise addition of $NaBH_4$ required at least a 0.5 ratio to reach higher activity, which was maintained for higher ratios. The dropwise addition of 0.15 mol of $NaBH_4$ per mol of gold did not substantially differ from the "one pot" addition (entries 1 and 7, table 3), in agreement with similar XPS and XRPD data. However, on comparing the XPS and XRPD data of the "one pot" addition with the XPS and XRPD data of the "dropwise" addition of a greater amount of reducing agent, it was found that the catalysts did not differ greatly from each other in terms of XPS and XRPD, but on considering the activity, there was a marked difference. Therefore, it can be concluded that the activity was not ruled only by the dimension and the exposure of gold. Figure 1 allows a direct comparison of the three reduction methodologies used.

By comparing the present results with those obtained using the PVA-protected sol as the precursor of 1% Au/C, it can be derived that the protective layer also plays an important role [10]. In fact, using the latter sol we produced gold-on-carbon catalyst that showed, in the same catalytic test as that actually used, lower TOFs (580 versus 3336 h^{-1}) for similar particle dimension (5.5 versus 5.0 nm) and exposure (2.51 versus 2.98% at. Au(4f)/C(2s)) (table 4, entry 2 versus table 3, entry 9). By carrying out "one pot" experiments using a Au/$NaBH_4$ ratio of 1/0.15 and varying the amount of SB, we concluded that the role of the protective agent was correlated to its nature and not to its amount, although a critical value was found (figure 2). In fact, after an Au/SB = 1 (mol/mol) had been reached, we observed almost constant particle dimension (6.1–6.5 nm) and activity in the catalytic test. The low activity observed for catalysts obtained using a ratio lower than 1 can be ascribed to the large diameter of the gold particle (16–22 nm).

Our screening then involved the role of the base employed: reducing the auric solution in the absence of $LiCO_3$ resulted in a very poorly active catalyst (TOF = 41 h^{-1}, d_m = 18 nm). In principle the role of the base should raise the pH value, favoring the hydrolysis of the chloroauric species. However, the base could also interfere with the zwitterionic nature of SB, modifying its conformation in solution and/or the double layer that is reported to be formed for metal particles stabilized this way [14]. Thus we expected that, in the presence of different bases, different salts of SB would be formed, and that their protective role would change depending on the strength of the ionic couples formed.

Table 5 shows the results of the XPS and XRPD characterization and the catalytic activities of the 1%Au/C obtained supporting different SB-Au/sols where we varied the added base, using carbonates and hydroxides with different cation counterparts (Li^+, Na^+, K^+ and $NH_4{}^+$). Note that it was necessary to vary the ionic strength of the solution to maintain a solution pH of around 8. This parameter will be dealt with later.

The ammonium salts (entries 4 and 8) produced catalysts characterized by large gold particles and, like the catalyst obtained in the absence of a base, they were poorly active. In the other cases, depending on the anion, we obtained almost the same gold particle dimension (5.4–5.9 nm for carbonates, 8.8–10 nm for hydroxides), but different gold exposure (entries 1–3 and entries 5–7 of table 5). Therefore it would seem that the

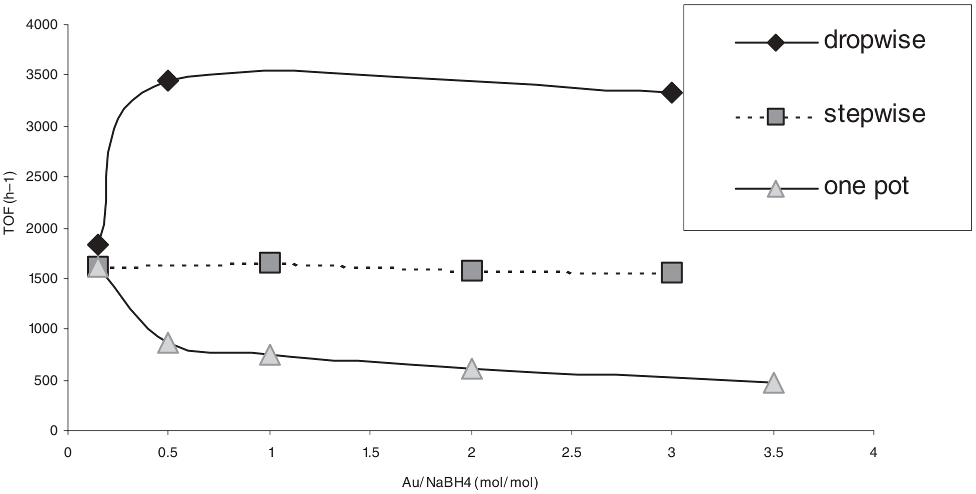

Figure 1. Influence of reductive methodology on activity of 1% SB-Au/C catalysts. (a) Sol: [Au(III)] = 0.3 mg/mL; Au/SB = 4 mol/mol; $NaBH_4$ 0.1 M; pH = 8; T = 298 K and (b) Catalytic test: catalytic test: ethylene glycol (8 mmol); NaOH (8.25 mmol); Au/C catalyst (glycol/metal = 1000 mol/mol); distilled water (total volume 10 mL); pO_2 = 300 kPa; T = 343 K. TOFs were calculated on total gold.

Table 3
1%Au/C from SB/Li_2CO_3/$NaBH_4$ sols[a]: influence of reducing methodology

Entry	$NaBH_4$ per mol of Au (mol)					% at. Au(4f)/C(2s) [XPS]	*d* (nm) [XRPD]	TOF $(h^{-1})^b$
	1st h	2nd h	3rd h	4th h	Total			
1	0.15	–	–	–	0.15	3.26	5.5	1620
2	0.15	0.85	–	–	1	3.20	5.9	1646
3	0.15	0.85	1.0	–	2	2.42	4.8	1586
4	0.15	0.85	1.0	1.0	3	2.36	4.9	1562
5	1.0	–	–	–	1	1.58	12.3	809
6	2.0	–	–	–	2	1.60	12.5	620
7	Dropwise				0.15	3.06	5.3	1842
8	Dropwise				0.5	3.15	5.7	3452
9	Dropwise				3	2.98	5.0	3336

[a] Sol : [Au(III)] = 0.3 mg/mL; Au/SB = 4 mol/mol; $NaBH_4$ 0.1 M; pH = 8; $T = 298$ K.
[b] Catalytic test: catalytic test: ethylene glycol (8 mmol); NaOH (8.25 mmol); Au/C catalyst (glycol/metal = 1000 mol/mol); distilled water (total volume 10 mL); $pO_2 = 300$ kPa; $T = 343$ K. TOFs were calculated on total gold.

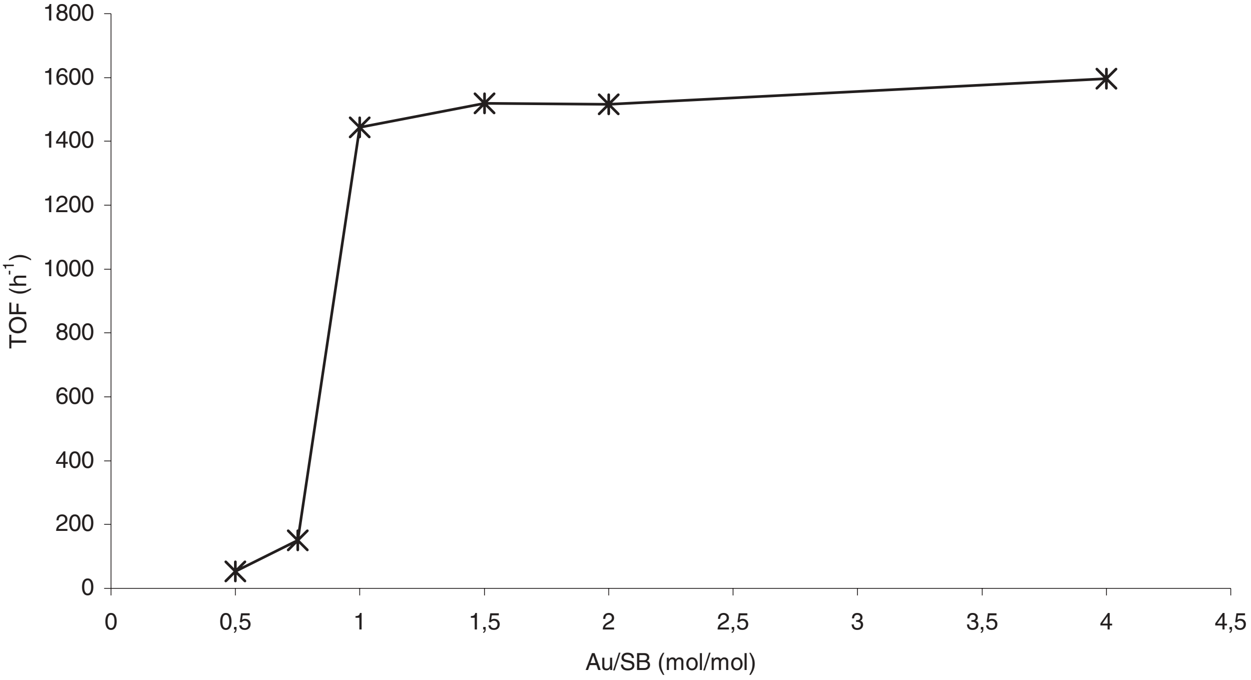

Figure 2. Influence of sulphobetaine amount on activity of 1% SB-Au/C catalysts. (a) Sol: [Au(III)] = 0.3 mg/mL; Au/$NaBH_4$ "one pot" = 1 : 0.15 (mol/mol) $NaBH_4$ 0.1 M; pH = 8; $T = 298$ K and (b) catalytic test: catalytic test: ethylene glycol (8 mmol); NaOH (8.25 mmol); Au/C catalyst (glycol/metal = 1000 mol/mol); distilled water (total volume 10 mL); $pO_2 = 300$ kPa; $T = 343$ K. TOFs were calculated on total gold.

anion is principally involved in determining particle dimension, while the cation determines its location. The activity of these catalysts followed, as expected, the trend in Au/C atomic percentage revealed by XPS [10]. In the carbonate series, the activity increased in the order $Na^+ > Li^+ > K^+$, whereas in the hydroxides, activity corresponding to Li^+ and Na^+ was reversed ($Li^+ > Na^+ > K^+$). This inversion, again in agreement with XPS data, can possibly be explained by the fact that the concentration of Li_2CO_3/Na_2CO_3 and LiOH/NaOH is also reversed (entries 1–2 and 5–6 of table 5), meaning that an increased sol ionic strength could favor an increased percentage of gold on the surface to which there corresponds higher activity.

Table 4
1%Au/C from PVA /$NaBH_4$ sols[a] [4]

Entry	% at. Au(4f)/C(2s) [XPS]	*d* (nm) [HRTEM]	TOF $(h^{-1})^b$
1	0.49	4.3	260
2	2.51	5.5	580
3	3.72	7.0	850

[a] Sol: [PVA] = 64 μg/mL; [$NaBH_4$]/[$HAuCl_4$] = 4 mol/mol; $HAuCl_4$ according to references [1] and [2].
[b] Catalytic test: catalytic test: ethylene glycol (8 mmol); NaOH (8.25 mmol); Au/C catalyst (glycol/metal = 1000 mol/mol); distilled water (total volume 10 mL); $pO_2 = 300$ kPa; T = 343 K. TOFs were calculated on total gold.

Table 5
1%Au/C from SB/Li_2CO_3/$NaBH_4$ sols[a]: influence of the base

Entry	Cation	Anion	Base concentration (mM)	% at. Au(4f)/C(2s) [XPS]	*d* (nm) [XRPD]	TOF (h^{-1})[b]
1	Li^+	CO_3^-	4.6	3.26	5.5	1620
2	Na^+		6.2	3.60	5.9	3004
3	K^+		1	2.20	5.4	1420
4	NH_4^+		17	0.30	17	22
5	Li^+	OH^-	5	2.78	8.8	1560
6	Na^+		2	1.28	10	1238
7	K^+		1	0.74	10	700
8	NH_4^+		3.6	0.23	16.1	30
9	Li^+[c]	CO_3^-, OH^-	6[e]	2.29	4.8	3324
10	Na^+[d]		4[e]	2.11	4.8	2840

[a] Sol : [Au(III)] = 0.3 mg/mL; Au/SB = 4 mol/mol; Au/$NaBH_4$ "one pot" = 1 : 0.15 (mol/mol); $NaBH_4$ 0.1 M; pH = 8; $T = 298$ K.
[b] Catalytic test: catalytic test: ethylene glycol (8 mmol); NaOH (8.25 mmol); Au/C catalyst (glycol/metal = 1000 mol/mol); distilled water (total volume 10 mL); $pO_2 = 300$ kPa; $T = 343$ K. TOFs were calculated on total gold.
[c] LiOH/Li_2CO_3 = 1 : 1 (mol/mol).
[d] NaOH/Na_2CO_3 = 1 : 0.5 (mol/mol).
[e] Based on cation.

By combining the effect of anion, cation and high ionic strength, we were able to obtain an extraordinarily active catalyst (3324 h^{-1}) characterized by 4.8-nm-sized particles with 2.29% at. Au(4f)/C(2s). On comparing this data with what is reported in table 4, entry 1 (260 h^{-1}, 4.3 nm and 0.49% at. Au(4f)/C(2s)) corresponding to the immobilization of a PVA-sol, we came to the conclusion that the SB-sol was more able than the PVA-sol to locate the gold particle externally, on the surface of the carbon, thus favoring gold particle activity in the liquid-phase oxidation.

4. Conclusions

We have demonstrated that gold-on-carbon catalysts can be prepared conveniently via metal sol immobilization [3,4], and that the activity of such catalysts depends on the particle dimension and carbon surface allocation [10] as well as on the chemical nature of the carbon support [11]. In the present study, we used a new sol generated in the presence of *N*-dodecil-*N*, *N*-dimethyl-3-amino-1-propan sulphonate as a protective agent, a base that provided the hydrolysis of chloroauric solution and

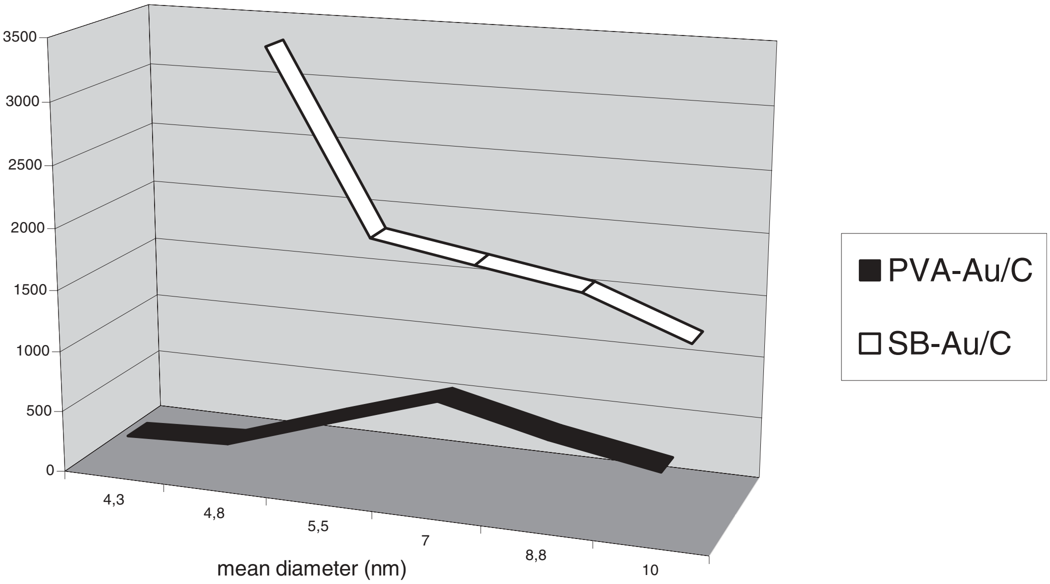

Figure 3. TOFs of 1% SB-Au/C catalysts related to gold mean size diameter. (a) Sol: [Au(III)] = 0.3 mg/mL; Au/SB = 4 mol/mol; Au/$NaBH_4$ "one pot" = 1 : 0.15 (mol/mol) $NaBH_4$ 0.1 M; pH = 8; $T = 298$ K and (b) Catalytic test: catalytic test: ethylene glycol (8 mmol); NaOH (8.25 mmol); Au/C catalyst (glycol/metal = 1000 mol/mol); distilled water (total volume 10 mL); $pO_2 = 300$ kPa; $T = 343$ K. TOFs were calculated on total gold.

$NaBH_4$ as reducing agent. These sols were adsorbed on the same carbon to afford Au/C (SB-Au/C) catalysts that differ from each other in particle dimension, the ionic species present deriving from the bases used and the by-products of the reducing agent.

Catalytic tests were carried out using the liquid-phase oxidation of ethylene glycol as the reference reaction; this allowed us to compare the catalytic behavior of the catalysts with that of the previously prepared immobilizing PVA-stabilized sols. The catalytic results were in agreement with the previous observations, that explained catalyst activity in terms of both gold crystallite mean dimension, provided by XRPD, and gold particle shielding, done by carbon and measured by XPS. Moreover, additional factors have now been revealed, e.g., the influence of both the protective layer and the presence of ions in determining particle location and dimension. These two parameters were obviously correlated as the presence of an ionic species could influence the protective layer conformation.

In an earlier paper, we reported that the maximum activity for 1%Au/C, generated from PVA-protected gold sol using the same presently employed carbon, was shown by gold particles of mean diameter centered at 7 nm [10]. However, using the sulphobetain protective agent we found extraordinary activity (3300–3400 h^{-1}) in catalysts characterized by a lower mean diameter (4.8–5.1 nm) but with a high atomic Au/C percentage at the surface. Moreover, the TOF trend in relation to mean diameter confirms our hypothesis that, if the gold particle activity is not limited by shielding effects, gold-on-carbon activity in liquid-phase oxidation should increase with decreasing particle dimension as observed in the case of oxides [10] (figure 3).

References

[1] J. Bond and D.T. Thompson, Catal. Rev.—Sci. Eng. 41 (1999) 319.

[2] J.-D. Grunwaldt, C. Kiener, C. Wögerbauer and A. Baiker, J. Catal. 181 (1999) 223.

[3] L. Prati and G. Martra, Gold Bull. 32 (1999) 96.

[4] F. Porta, L. Prati, M. Rossi, S. Coluccia and G. Martra, Catal. Today 61 (2000) 165.

[5] J.S. Bradley in *Cluster and Colloids*, G. Schimd (ed.), (VCH, Weinheim, 469 1994).

[6] F. Porta, L. Prati, M. Rossi and G. Scarì, J. Catal. 210 (2002) 464.

[7] L. Prati and M. Rossi, J. Catal. 176 (1998) 552.

[8] S. Biella, L. Prati and M. Rossi, J. Catal. 206 (2002) 242.

[9] S. Carrettin, P. McMorn, P. Johnston, K. Griffin and G.J. Huthchings, Chem. Commun. 696 (2002).

[10] C. Bianchi, F. Porta, L. Prati and M. Rossi, Top. Catal. 13 (2000) 231.

[11] C. Bianchi, S. Biella, A. Gervasini, L. Prati and M. Rossi, Catal. Lett. 55 (2003) 91.

[12] D.G. Duff, A. Baiker and P.P. Edwards, J. Chem. Soc., Chem. Commun. 96 (1993).

[13] M.T. Reetz and M.G. Koch, J. Am. Chem. Soc. 121 (1999) 7933.

[14] H. Bönnemann, R.M. Richards, Eur. J. Inorg. Chem. 2455 (2001).