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# Metal sols as a useful tool for heterogeneous gold catalyst preparation: reinvestigation of a liquid phase oxidation

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## Abstract

Differently stabilised metal sols have been used as precursors in the preparation of heterogeneous gold catalysts for liquid phase oxidation in water solution. The methodology of sols generation appears to be fundamental to obtaining nanoparticles; the support, instead, plays an important role in maintaining particle dimension and morphology.

Three different materials ($\gamma$-$Al_2O_3$, $SiO_2$ and activated carbon) have been used as the supporting agents for different gold sols that were obtained by reducing $HAuCl_4$ with $NaBH_4$ in the presence of polyvinylalcohol (PVA) or polyvinylpirrolidone (PVP) and with the tetrakis(hydroxymethyl)phosphonium chloride (THPC)/NaOH system. During the immobilisation step, the maintenance of the particle dimension observed in solution depends on both the support and the type of sol. The gold particle mean size of the colloidal suspension is more easily maintained on oxidic supports than on carbon, the latter apparently needing both steric and polar stabilisation of the gold particle.

Comparison of Au/$\gamma$-$Al_2O_3$ and Au/C catalyst activity in the liquid phase oxidation of ethylene glycol to glycolate highlighted the peculiarity of gold on carbon catalysts; in fact, the normally observed trend of reactivity is partially reversed, medium sized gold particle being the most active. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Metal sols; Heterogeneous gold catalyst; Liquid phase oxidation

## 1. Introduction

The importance of gold based catalysts in environmental and synthesis fields is now well established [1–3]. The activity of these catalysts has been shown to depend strongly on both preparative method and the support [4], and this has prompted a search for preparative methods alternative to deposition–precipitation, first proposed by Haruta [5].

The use of metallic sols has been proposed to tailor the size of the supported gold particle [6] and this possibility is particularly attractive in the case of supports like carbon, where aggregation occurs with the deposition–precipitation method [7].

Gold colloids have been known since ancient times, but for catalytic purposes the gold particle diameter has to be $<10$ nm [4]. The classical standard reduction by citrate ions provides gold sols with a mean diameter of 20 nm and with a quite wide distribution. Thus, the reduction of chloroauric solution with tetrakis(hydroxymethyl)phosphonium chloride (THPC)/NaOH system [8] or sodiumborohydride in the presence of protective molecules [9–11], is a more suitable procedure as a smaller particle with a narrower distribution is obtained.

The former procedure was recently used to prepare gold on $TiO_2$ and $ZrO_2$ [6] with the advantage, with respect to other methods, of predetermining the

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size of the gold particle that is maintained during the immobilisation step. The second procedure is useful in preparing gold on carbon using polyvinylalcohol (PVA) as the protecting agent [7].

Here we report the extension of these preparative methodologies to activated carbon and oxide ($SiO_2$, $Al_2O_3$) supported catalysts; the different sols were compared to asses their ability to maintain particle dimension when supported. The catalysts obtained in this way were then tested in the liquid phase oxidation of ethylene glycol to evaluate their catalytic activity that highlighted the role of the support and the particle dimension, more accurately than was shown in previous reports [3,12].

## 2. Experimental

### 2.1. Materials

Gold of 99.9999% purity in sponge from Fluka, $\gamma$-$Al_2O_3$ from La Roche (SA=180 $m^2 g^{-1}$; PV=0.5 $ml g^{-1}$), $SiO_2$ from Grace (SA=419 $m^2 g^{-1}$; PV=2 $ml g^{-1}$) and activated carbon from Carbosorb (MK; SA=900–1100 $m^2 g^{-1}$; PV=1.5 $ml g^{-1}$; pH 9–10) were used. Ethylene glycol was of the highest purity from Fluka and was used without any further purification. NaOH was 99.9% pure from Merck and stored under nitrogen. Gaseous oxygen from SIAD was 99.99% pure. Gold powder was of the highest purity grade from Fluka.

### 2.2. Gold sols preparation

For sols stabilised by PVA or polyvinylpirrolidone (PVP) the following procedure was run: an aqueous $HAuCl_4$ solution of the desired concentration was prepared. To this was added, under vigorous stirring, the PVA or PVP 2 wt.% solution. Then, dropwise, a 0.1 M freshly prepared solution of $NaBH_4$. Tables 1–3 show the reagent amounts.

Sols generated in the presence of the THPC/NaOH system were prepared as reported elsewhere [8] and used as such. The relative amount of $HAuCl_4$ and NaOH 0.1 M or THPC 0.05 M aqueous solution is varied (Table 4).

### 2.3. Catalyst preparation

The different sols were immobilised by simply dipping the support in the metal dispersion. The amount of support was calculated as having a final gold load-

Table 1
Carbon supported gold from PVA stabilised sol

| Entry | Sol properties | | | Supported gold | | | |
|---|---|---|---|---|---|---|---|
| | [PVA] (μg/ml) | [Au] (μg/ml) | PVA/Au (wt/wt) | Support | Conversion (%)[a] | $d_m$ (nm) | |
| | | | | | | XRPD | HRTEM |
| 1 | 64 | 100 | 0.64 | C | 100 | 8 | 7.5 |
| 2 | 100 | 100 | 1 | C | 78 | 6 | 6.2 |
| 3 | 50 | 50 | 1 | C | 58 | 5 | 5.5 |
| 4 | 10 | 10 | 1 | C | 28 | 4.2 | 4.0 |

[a] Catalytic test: [EG]=0.5 M, EG/Au=1000, EG/NaOH=1, $pO_2$=2 atm, $T$=70°C, r.t.=1 h, EG=ethylene glycol.

Table 2
One percent Au on $SiO_2$ from PVP stabilised sol

| Entry | Sol properties | | | | Supported gold, $d_m$ (nm) | |
|---|---|---|---|---|---|---|
| | [PVP] (μg/ml) | [Au] (μg/ml) | PVP/Au (wt/wt) | $d_m$ (nm) HRTEM | XRPD | HRTEM |
| 1 | 960 | 394 | 2.44 | 2.7 | 3.8 | 3.7 |
| 2 | 960 | 276 | 3.57 | 3.0 | 3.2 | 3.5 |
| 3 | 1500 | 276 | 5.43 | 2.2 | 2.5 | 2.6 |

Table 3
Carbon supported gold from PVP stabilised sol

| Entry | Sol properties | | | | Supported gold | | | |
|---|---|---|---|---|---|---|---|---|
| | [PVP] (μg/ml) | [Au] (μg/ml) | PVP/Au (wt/wt) | $d_m$ (nm) HETEM | Support | Conversion (%)[a] | $d_m$ (nm) | |
| | | | | | | | XRPD | HRTEM |
| 1 | 64 | 100 | 0.64 | 6 | C | 84 | 7.14 | 6.9 |
| 2 | 500 | 394 | 1.27 | 2.9 | C | 76 | 10.2 | 8.6 |
| 3 | 100 | 394 | 0.25 | n.d. | C | 75 | 11.2 | 9.0 |
| 4 | 50 | 394 | 0.13 | n.d. | C | 58 | 15 | 13 |

[a] Catalytic test: [EG]=0.5 M, EG/Au=1000, EG/NaOH=1, $pO_2$=2 atm, $T$=70°C, r.t.=1 h, EG=ethylene glycol.

ing of 1 wt.% After 1 h the slurry was filtered and the total absorption of gold was checked by ICP analysis of the filtrate.

Before use, the catalysts were thoroughly washed with distilled water. Oxide materials were dried at 70°C for 5 h, whereas carbons were used in the wet form. In the latter the water content was determined by drying a 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–K$\alpha$ radiation, equipped with a graphite monochromator in the diffracted beam. The crystallite sizes of gold were estimated from peak half-widths by using Scherrer's equation with corrections for instrumental line broadening.

Electron micrographs of the samples were obtained by a Jeol 2000EX microscope equipped with polar piece and top entry stage. Before introduction into the instrument, the samples, in powder form, were ultrasonically dispersed in isopropyl alcohol, and a drop of the suspension was deposited on a copper grid covered with a lacey carbon film. Histograms of particle size distribution were obtained by counting on the micrographs at least 300 particles, and the mean particle diameter ($d_m \pm 0.25$ nm) was calculated by using the formula $d_m = \Sigma d_i n_i / \Sigma n_i$, where $n_i$ was the number of particles of diameter $d_i$.

### 2.4. Oxidation procedures

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 catalyst (reactant/metal=1000) were mixed in distilled water (total volume 10 ml). The reactor was

Table 4
Supported gold from THPC sol[a]

| Entry | Sol properties | | | Supported gold | | | |
|---|---|---|---|---|---|---|---|
| | [Au] ($10^{-3}$ M) | THPC/Au (mol/mol) | $d_m$ (mn) HRTEM | Support | Conversion (%)[b] | $d_m$ (nm) | |
| | | | | | | XRPD | HRTEM |
| 1 | 1 | 1 | 3.5 | C | 88 | 4.0 | 8.16 |
| | | | | $Al_2O_3$ | 100 | – | 3.80 |
| 2 | 0.5 | 2 | 2.9 | C | 26 | 3.1 | 4.26 |
| | | | | $Al_2O_3$ | 51 | – | 4.16 |
| 3 | 1.4 | 0.7 | 4.3 | C | 73 | 5.5 | 8.65 |
| | | | | $Al_2O_3$ | 50 | – | 4.20 |

[a] [THPC]=$10^{-3}$ M, [NaOH]=$6\times10^{-3}$ M.

[b] Catalytic test: [EG]=0.5 M, EG/Au=1000, EG/NaOH=1, $pO_2$=2 atm, $T$=70°C, r.t.=1 h, EG=ethylene glycol.

pressurised at 300 kPa of $O_2$ and thermostatted at 70°C. After an equilibration time of 15 min, the mixture was stirred for 1 h and the products analysed by HPLC on a Varian 9010 instrument equipped with a Varian 9050 UV (210 nm) and Varian RI detectors. 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 reaction mixture (0.1 ml) were diluted (10 ml) by using the eluent after adding the standard (propionic acid).

## 3. Results and discussion

We have recently reported that gold on carbon prepared via metallic sol stabilised with PVA, shows a greatly enhanced activity in the liquid phase oxidation of ethylene glycol compared to gold on carbon prepared via classical deposition–precipitation procedure [7]. As evidenced by high resolution transmission microscopy (HRTEM) analyses, the principal advantage of using pre-reduced metal as gold precursor lies in avoiding the growth of aggregates on the carbon surface.

Recently, Baiker and co-workers [6] reported that gold sol generated by reduction of $HAuCl_4$ with partially hydrolysed THPC is easily immobilised on $TiO_2$ and $ZrO_2$ at pH 2.5. Thus in the present work we compared these two systems to prepare gold on both carbon and oxides ($\gamma$-$Al_2O_3$, $SiO_2$).

### *3.1. $HAuCl_4$/PVA or PVP/$NaBH_4$ systems*

PVA stabilised sols are smoothly absorbed on carbon and, as Fig. 1 shows, we found good agreement between the XRPD and HRTEM measurements of mean gold particle size. However, an anomalous trend of reactivity in the liquid phase oxidation of ethylene glycol, was highlighted. In fact, we observed maximum of activity for $d_m$=7.5 nm, whereas smaller particles showed less (Table 1). Having previously demonstrated that this trend could not be ascribable to different amounts of the polymer [7], we concluded that this effect had to be related to interaction between the carbon surface and gold particle.

We tried to highlight this point by applying the same methodology to other supports like $\gamma$-$Al_2O_3$ and $SiO_2$. Unfortunately our efforts to immobilise the Au/PVA sol on $\gamma$-$Al_2O_3$ and also on $SiO_2$ failed. The principal problem encountered in using PVA sol on oxides was that the immobilising time and efficiency depend on the concentration of gold, the more dilute solutions being absorbed with greater difficulty. Thus, we changed the protective agent from PVA to PVP, reported to

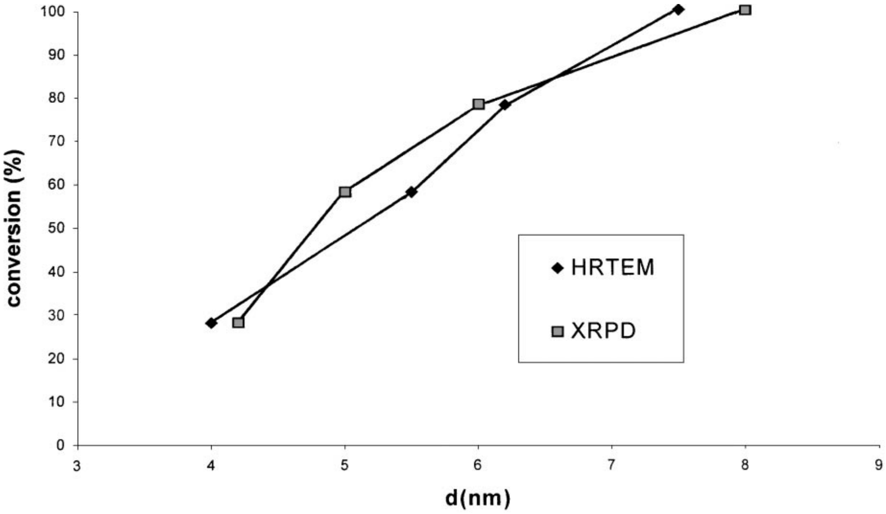

Fig. 1. Activity of Au/C as a function of mean diameter of gold particles. Catalytic test: [EG]=0.5 M; EG/Au=1000; EG/NaOH=1, $pO_2$=2 atm, $T$=70°C, r.t.=1 h; EG=ethylene glycol.

stabilise metal particles by steric effects alone [13], with the hope of overcoming this problem and making the procedure useful for gold on carbon as well on oxides. However, even the absorption of this new sol depends strongly on the PVP/Au ratio: only silica quantitatively adsorbs the sol even at high PVP/Au ratio and the mean size dimension of gold particle in the sol is maintained when immobilised (Table 2).

On carbon quantitative absorption began around a PVP/Au ratio of 1.5. Surprisingly, we found that unlike PVA, the PVP molecule was not able to impede the collapsing of the gold particle. In fact, even the XRPD measurements (Table 3) highlighted a mean metal particle dimension higher than in solution, confirmed by HRTEM data. Probably in protecting gold particle on carbon, the steric and polar stabilisation made by PVA was more efficient than only the steric made by PVP.

From a catalytic point of view, an important result was that similar particles, generated differently (7.14 nm, entry 1, Table 3; and 8 nm, entry 1, Table 1) show similar reactivity, confirming the negligible influence of the protective molecule on the activity of the catalyst in the liquid phase oxidation of ethylene glycol.

Alumina adsorbs the PVP sols only partly and at a low PVP/Au ratio (<1) which corresponds to quite large gold particles. In addition, the interaction between the support and the gold particles was very weak as gold was leached under the catalytic test conditions.

### 3.2. $HAuCl_4$/THPC/NaOH system

The reduction of the chloroauric solution by partially hydrolysed THPC has been reported to generate gold particles of mean diameter in the range 1.5–3 nm [8], and this system has been recently used to prepare gold on $TiO_2$ or $ZrO_2$ supports [6]. The immobilisation of the sol at pH 2.5 probably involves negatively charged gold particles that interact with a positively charged surface, the pH being lower than the point of zero charge (PZC) of $TiO_2$ and $ZrO_2$. However, we found that this sol can be easily immobilised on carbon, as well as on $Al_2O_3$, independently of the pH of the sol.

In Table 4, the conditions reported in entry 1 correspond to reagent concentrations in the literature [6]. By diluting the initial auric solution, i.e. increasing the THPC/Au ratio, we were able to decrease the mean particle size (Table 4), but the final dimension of the

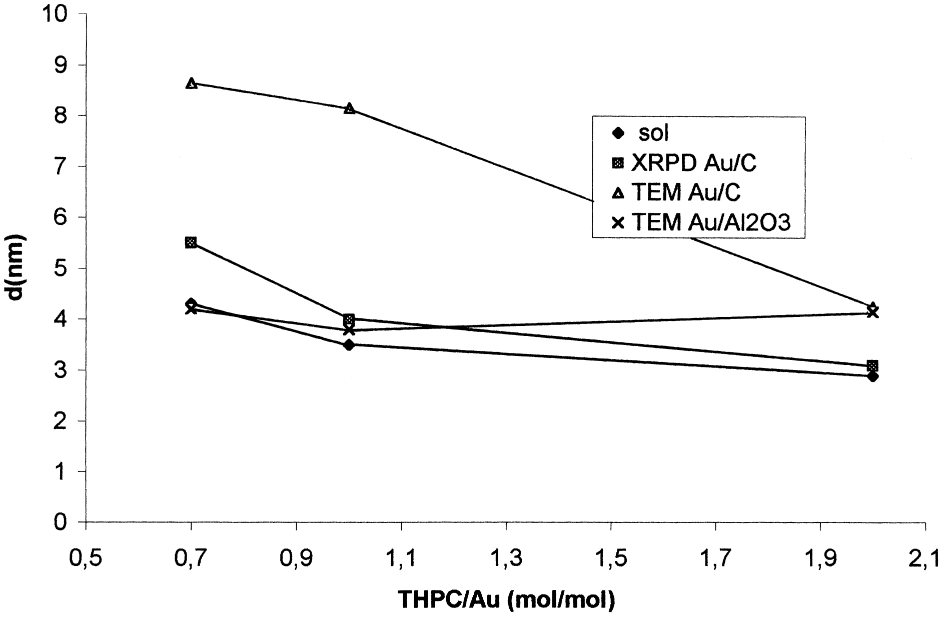

Fig. 2. Mean diameter of gold particles as a function of THPC/Au ratio.

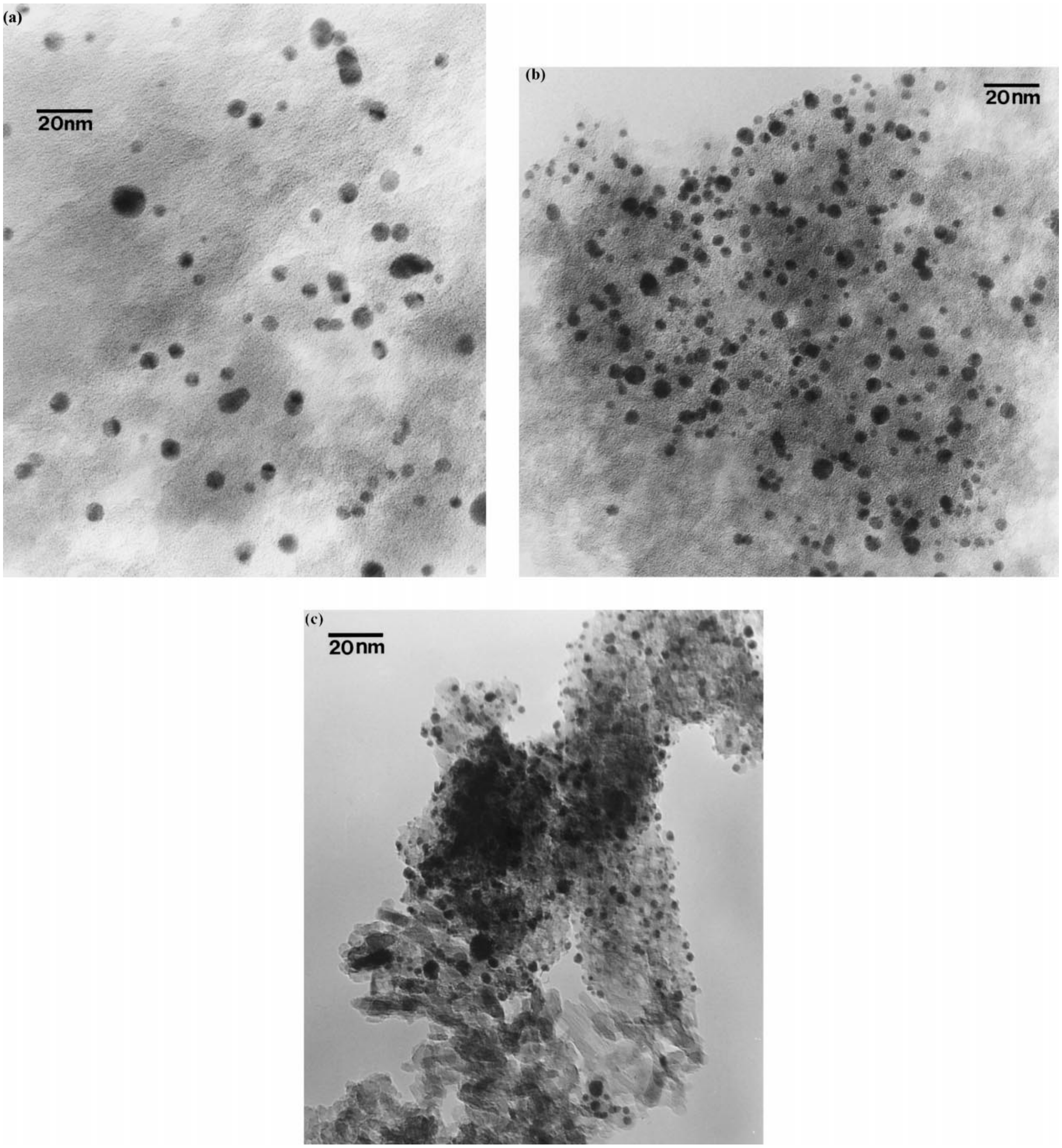

Fig. 3. HRTEM of supported gold catalysts from THPC system: (a) on carbon (conditions of Table 4, entry 1); (b) on carbon (conditions of Table 4, entry 2); (c) on alumina (conditions of Table 4, entry 1).

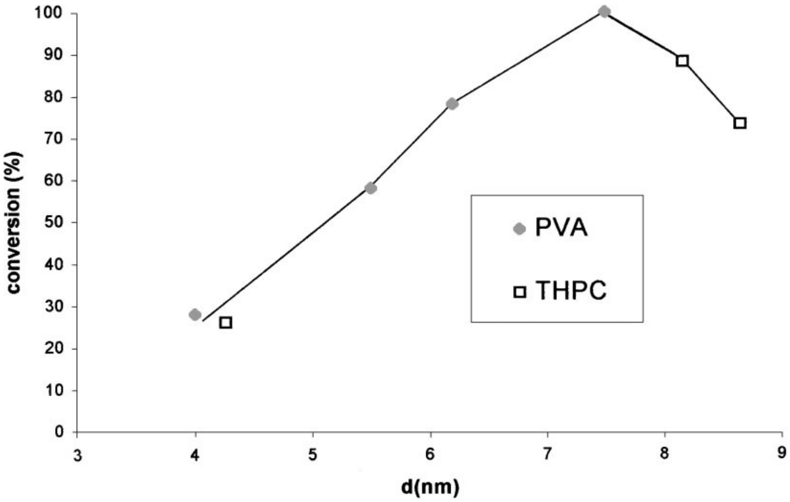

Fig. 4. Activity of Au/C from different sols as a function of mean diameter of gold particles.

immobilised metallic particle was drastically affected by the nature of the support. Fig. 2 shows the mean dimension of gold particles in the sol and supported on the various materials in relation to the THPC/Au ratio. The greatest differences were detected for carbon, especially for low THPC/Au ratio. However, in these cases if we consider the mean dimension of crystallites emerging from Scherrer equation using XRPD data, we find values very similar to that obtained from HRTEM analyses of the sols. As XRPD refers to coherently scattering domains whereas HRTEM refers to particle dimensions [14], and as XRPD analyses of metallic particle on carbon overestimate the dimension of gold particle [15], we concluded that the gold particles revealed by HRTEM were constituted by aggregation of the metal particle generated in solution (Fig. 3a). The HRTEM and XRPD measurements matched only for a THPC/Au ratio of 2 (Fig. 3b). On the contrary alumina almost maintained the particle dimension for a THPC/Au ratio $<2$ (Fig. 3c), whereas there was a discrepancy in the measurements for solution and support for a THPC/Au ratio of 2 where gold particle aggregation was observed.

On testing all the catalysts in the liquid phase oxidation of ethylene glycol we were able to differentiate between the behaviour of gold on alumina and on carbon. Gold on alumina showed a reactivity that follows the gold particle dimension, the smaller being more active than the larger one (Table 4). On the contrary, in the case of gold on carbon, as observed using the PVA sol, the activity of the catalysts apparently rose with increasing particle dimension (Table 4). Fig. 4 shows the data relative to PVA and THPC systems on carbon. By comparing entry 2 of Table 2 and entry 4 of Table 1, we noted that particles of similar dimension show almost the same activity. Thus, admitting that the influence of protective agents in both cases is negligible with regard to catalyst activity (they only influence the immobilising step and the maintenance of particle identity), the data can be considered all together. Thus a maximum of activity around 7.5 nm (HRTEM) is observed, regardless of the crystallographic disorder (XRPD) of the particles, whereas smaller and larger particles showed lower activity. A possible explanation of this anomalous trend could be connected, as previously mentioned, to the nature of the carbon surface: the smallest particles probably enter in micropores, consequently being shielded with respect to the reagents. Conversely, when particle dimension does not allow the particle to fit in such pores, the gold particle reactivity really depends on dimension and larger particles are found to be less reactive than smaller ones. On the contrary, Au/C, Au/$Al_2O_3$ shows the expected trend of reactivity, smaller particles being more reactive than larger ones (Table 4).

## 4. Conclusions

Three different gold sols have been used as precursors of heterogeneous gold catalysts. The particular nature of carbon as a support drastically influences the choice of the sol for maintaining, once supported, the gold particle dimension observed in solution. In fact, only doubly protected (steric and polar stabilisation) gold particles, as in the case of PVA-sol, show a constant dimension in both solution and on carbon. On alumina only THPC-sol is easily absorbed and the gold dimensions are almost maintained in the immobilising step, although an anomalous little enlargement of the supported particles was noted increasing the THPC/Au ratio with respect to 1 (i.e. by diluting gold concentration).

In both cases, Au/C and Au/$Al_2O_3$, catalytic tests of liquid phase oxidation confirmed that the effect of the protector on catalyst activity is negligible, similar-sized particles showing the same activity although differently generated. The high catalytic activity obtained by carefully choosing the sol precursor make this preparation of great interest for preparing gold supported catalysts with high metallic dispersion.

Smaller gold particles on alumina present higher reactivity than larger ones, but we observed an opposite trend on carbon until a mean dimension of 7.5 nm was reached. We have explained this anomalous trend by considering that with decreasing dimension, the gold particles can be easily fixed on the internal surface of carbon, consequently being less accessible to reagents than gold particles on the external surface. For particles of higher dimension than 7.5 nm, the reactivity follows the normal trend, explainable with the decreasing of the catalytically active metal surface.

Future studies will be aimed at assessing the influence of the carbon nature on the reactivity of gold particles of different dimensions.

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