Catalysis Letters Vol. 108, Nos. 3–4, May 2006 (© 2006)
DOI: 10.1007/s10562-006-0036-8

Effect of particle size on monometallic and bimetallic (Au,Pd)/C on the liquid phase oxidation of glycerol

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Received 15 October 2005; accepted 10 February 2006

The influence of metal particle size of monometallic and bimetallic supported catalysts (Au, Pd, Au–Pd)/C was studied using as a model reaction the liquid phase oxidation of glycerol. By tuning the metal particle size from 2 to 16 nm a progressive decrease of activity and simultaneously an increase in the selectivity to sodium glycerate was observed. Moreover, the influence of the temperature was studied and it was found that by increasing the temperature, only with a large particle size the formed glycerate was retained and not over-oxidized to tartronate.

KEY WORDS: glyceric acid; glycolic acid; tartronic acid; liquid-phase oxidation of glycerol; gold; palladium; particle size effect.

1. Introduction

A range of possible products (scheme 1) can be derived from the oxidation of glycerol. Thus, control of the selectivity to the desired product and of the over-oxidation is the crucial target. It has been shown that by using monometallic or bimetallic catalysts based on Au, Pd and Pt metals the selectivity could be tuned [1–7]. In general, Au and Pd catalysts are more selective towards glyceric and tartronic acids [4–6], whereas Pt [4, 7] towards hydroxypyruvic and glycolic acids. However, except from the choice of the metal, the temperature and the pH conditions are very crucial for the formation of the desired product. Thus, at alkaline conditions higher selectivity towards glyceric acid could be obtained using Au and Pd catalysts [4, 8], while under acidic conditions the formation of hydroxyacetone and hydroxypyruvic acid is favoured with Pd and Pt catalysts [2, 3]. One factor, which has been shown to play important role on the formation of the desired product, is the particle size of the metal. Hutchings *et al.* [9] and recently our group [8] have reported that a particle size more than 15 nm had a beneficial effect on the formation of glyceric acid using Au. In the case of Pd and Pt metals the particle size reported [5–7] was in the range 1–5 nm, so there is no systematic study on the effect of particle size in terms not only of selectivity but also in activity on glycerol oxidation. Since we had stated that on glycerol oxidation the dimensions of the particles affected the formation of the desired product, we decided to further investigate this matter by preparing a range of Au and Pd (mono and bimetallic) catalysts using the same general preparation method (immobilization method) as we have already reported [10]. The tuning of particle size was done by adjusting concentration of precursor, reducing agent or by choosing the appropriate reducing agent. In this paper we present preliminary results in the correlation between particle size and particular catalyst with respect to the activity and distribution of products.

2. Experimental

2.1. Materials

Na_2PdCl_4, K_2PtCl_4, $NaAuCl_4 \cdot H_2O$, $N_2H_4 \cdot 2HCl$ (purity $>99.0\%$) and PVA (MW = 13,000–23,000, 98% hydrolysed) were from Aldrich.

Stock aqueous solutions of Na_2PdCl_4 (10% w/w in Pd, $d = 1.32$ g mL^{-1}), PVA (1–2% w/w), $N_2H_4 \cdot 2HCl$ (0.1 M) and $NaBH_4$ (0.1 M) were freshly prepared. Activated carbon was from Camel (X40S; SA = 900–1100 m^2 g^{-1}; PV = 1.5 mL g^{-1}; pH 9–10). Gaseous oxygen from SIAD was 99.99% pure. Deionised water (Milli-Q purified) was used in all the experiments. Before use, the carbon was suspended in HCl 6 M 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 $<3\%$.

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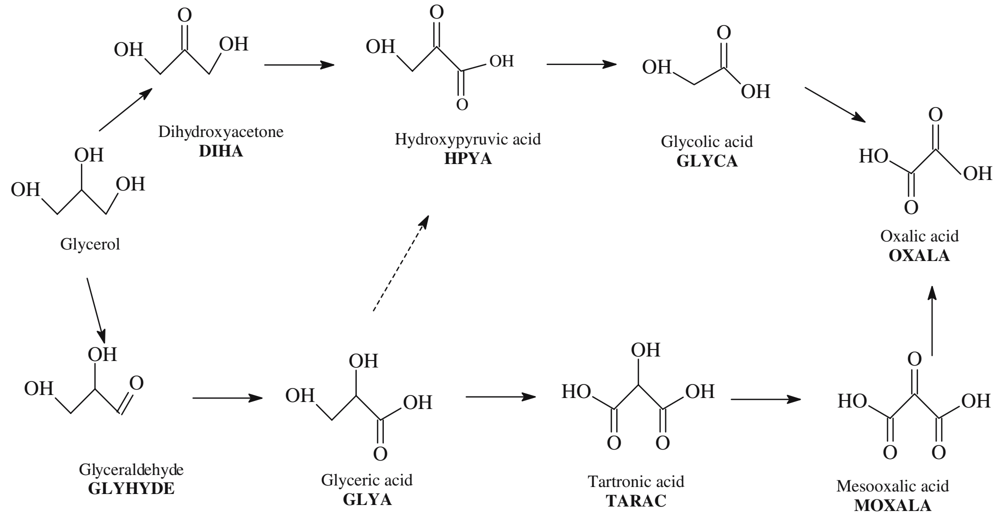

Scheme 1. General reaction pathways.

2.2. Catalyst preparation

2.2.1. Monometallic gold sols

(A) Solid $NaAuCl_4$ (200.58 mg, 0.50 mmol) was dissolved in water (270 mL) and 10 mL PVA (10 mL, 1% w/w) added under stirring. After 3 min $NaBH_4$ (15 mL) was added obtaining a red sol. It was reacted for 27 h.

(B) About 5 mL of a 2.96×10^{-2} M $NaAuCl_4$ stock solution (0.148 mmol) were added to 19.9 mL of water and PVA (2.4 mL, 1% w/w) added under stirring. After 3 min $NaBH_4$ (3.54 mL) was added obtaining a red sol. It was reacted for 19 h.

(C) Solid $NaAuCl_4$ (30.42 mg, 0.0765 mmol) was dissolved in water (230 mL) and PVA (1.4 ml, 1%w/w) under stirring After 3 min, $N_2H_4{\cdot}2HCl$ (1.52 mL) was added obtaining a blue sol. It was reacted for 10 min.

2.2.2. Monometallic palladium sols

(A) About 0.035 mL of Na_2PdCl_4 stock solution (0.20434 mmol), 10 mL of water and PVA (1.4 mL, 2% w/w) were mixed under stirring. After 3 min, $NaBH_4$ (0.8 mL) was added obtaining a brown sol. It was reacted for 30 min.

(B) About 0.074 mL of Na_2PdCl_4 stock solution (0.092 mmol), 276 mL of water and PVA (0.47 mL, 2% w/w) were mixed under stirring. After 3 min, $N_2H_4 \cdot 2HCl$ (1.8 mL) was added obtaining a brown sol. It was reacted for 3 min.

(C) About 0.228 mL of Na_2PdCl_4 stock solution (0.282 mmol), 50 mL of water, and PVA (1.4 ml, 2% w/w) were mixed under stirring. After 3 min, $NaBH_4$ (5.6 mL) was added obtaining a brown sol. It was reacted for 19 h.

2.2.3. Bimetallic Au–Pd sols (molar ratio 1:1)

For the synthesis of the bimetallic Au–Pd sols the modification of the same preparation method (C) (as reported in ref. [10]) happened, by changing reduction time using the same reducing agent ($NaBH_4$) and by using N_2H_4 instead of $NaBH_4$.

Basic preparation – $PdCl_4^{2-}$ stock aqueous solution (0.099 mmol), and PVA solution (1.8 mL PVA) were added to a solution of $NaAuCl_4{\cdot}2H_2O$ (0.095 mmol) in 290 mL of H_2O. The yellow-brown solution was stirred for 3 min and reducing agent was added under vigorous magnetic stirring.

(A) The (Au–Pd) sol was produced by reduction with $NaBH_4$. It was reacted for 6 h.

(B) The (Au–Pd) sol was produced by reduction with $NaBH_4$. It was reacted for 19 h.

(C) The (Au–Pd) sol was produced by reduction with $N_2H_4{\cdot}2HCl$. It was reacted for 10 min.

2.2.4. Immobilization method

Within a few minutes of sol generation, the colloid (acidified at pH 1, by sulphuric acid) was immobilized by adding activated carbon under vigorous stirring, The amount of support was calculated as having a final total metal loading of 1% wt. After 2 h the slurry was filtered, the catalyst washed thoroughly with distilled water (neutral mother liquors) and dried at 120 °C for 4 h. ICP analyses were performed on the filtrate using a Jobin Yvon JV24 to verify the metal loading on carbon.

2.3. Oxidation procedure

Glycerol oxidation was performed at a temperature range 50–70 °C, using a glass reactor (30 mL capacity), equipped with heater, mechanical stirrer, gas supply system and thermometer. The glycerol solution (0.3 M and NaOH/Glycerol ratio = 4, mol/mol) was added into the reactor and the desired amount of catalyst (Glycerol/metal ratio = 500, mol/mol) was suspended in the solution. The pressure of the oxygen was 3 atm. Once the required temperature (50 or 70 °C) was reached, the gas supply was switched to oxygen and the monitoring of the reaction started. Samples were removed periodically and analysed by high-performance chromatography (HPLC) using a column (Alltech OA-10308, 300 mm × 7.8 mm) with UV and refractive index (RI) detection in order to analyse the mixture of the samples. H_3PO_4 0.1% solution was used as the eluent. The identification of the possible products was done by comparison with the original samples. The activity of catalysts was reported based on TOF (calculated based on the total metal loading). The kinetic regime has been proved by subsequent experiments, changing the amount of catalyst.

2.4. Characterization

UV–visible spectra of sols were performed on HP8452 and HP8453 Hewlett-Packard spectrophotometers in H_2O between 190 and 1200 nm, in a quartz cuvette.

X-ray diffraction experiments were performed on a Rigaku D III-MAX horizontal-scan powder diffractometer with CuK_α 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 using a JEOL 1200FX 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 metal particle size distribution were obtained by the counting of at least 300 particles from the micrographs.

3. Results and discussion

In a previous work [8] we had reported the influence of different preparation methods with respect to the particle size dimension of Au metal and also on the catalytic performance in the liquid phase oxidation of glycerol. We found that by changing the preparation method the particle size and also the selectivity to GLYA were altering. In this work we used the same preparation method (immobilization method) while by changing reducing agent, concentration of Au precursor and time of sol reaction, the particle size is altered, thus, avoiding influence of preparation method. Moreover, the PVA/Metal ratio (table 1) was kept in a closed range (PVA/Au = 0.93–1.015; PVA/Pd = 0.93–1.28 for monometallics and PVA/Au = 0.96; PVA/Pd = 1.71 for bimetallics). In a previous work [11] we had demonstrated that activity of Au/C particles was not affected significantly by altering PVA/Au wt/wt ratio. Nevertheless, by keeping a similar range in the PVA/Metal ratio, we can hypothesize that the main contribution in the control of activity and selectivity will be due to the particle size effect and in a less extent due to the PVA amount.

3.1. Characterization of the catalysts

The reductions of the metals were followed by UV–visible spectroscopic analyses. The UV–visible spectra were recorded in H_2O in the 190–800 nm region.

For monometallic sols, in the case of Au, the transformation of $AuCl_4^-$ anion ($\lambda_{max} = 220$ nm) was shown, through the appearance of the plasmon resonance peak of Au(0) sol (490–520 nm), while in the case of Pd ([$PdCl_4^{2-}$]: $\lambda_{max} = 210$] and 238 nm), only the disappearance of precursor peaks were observed after reduction as Pd(0) sols did not present plasmon bands, in agreement with the literature reports [12].

For bimetallic sols, the preparation method consists in the simultaneous reduction of the $AuCl_4^-$ and $PdCl_4^{2-}$. In the bimetallic systems the spectra of Pd(0) sols are usually superimposed to the one of gold at the end of reduction and the plasmon resonance peak does not appear.

The particle size dimension (XRPD and TEM data) of the monometallic and bimetallic catalysts are presented in table 1. The mean diameter discrepancies observed between XRPD and HRTEM were not unexpected as the two techniques are based on different principles. We only can indicate that the two measurements come into agreement when metal particles are constituted by coherently scattering domains [8]. The correlation of particle size with respect to activity/

Table 1

Characteristics of mono (Au/C, Pd/C) and bimetallic (Au–Pd/C) catalysts in terms of particle size dimension (XRPD and TEM) and PVA/metal ratio

Catalysts	PVA/M[a] (*M* = Au,Pd)	*d*(nm)	
		XRPD	TEM
1% Au/C–A	1.01	4.2	6.4
1% Au/C–B	0.82	11.6	–
1% Au/C–C	0.93	16.2	–
1% Pd/C–A	1.28	<2	5.6
1% Pd/C–B	0.96	9.2	7.2
1% Pd/C–C	0.93	14.5	–
1% (Au–Pd)/C–A	Au = 0.96, Pd = 1.71	<2	–
1% (Au–Pd)/C–B	Au = 0.96, Pd = 1.71	2.0	6.1
1% (Au–Pd)/C–C	Au = 0.96, Pd = 1.71	6.1	8.5

[a] Wt/wt ratio.

selectivity was based on the values obtained from XRPD data.

3.2. Catalytic testing

The catalytic study in the liquid phase oxidation of glycerol under alkaline conditions was performed in the 50–70 °C temperature range at conditions described above. The major products were glycerate, tartronate and glycolate followed by small amounts of hydroxypyruvate and oxalate.

3.2.1. Au/C catalysts

The effect of particle size (XRPD or TEM values presented in table 1) in terms of selectivity to glycerate, glycolate and tartronate at 50 and 70 °C are summarized in figures 1 and 2 for Au/C catalysts. It is clear that increasing the particle size from 3 to 17 nm the selectivity to glycerate at 90% conversion was also increased significantly, as expected on our previous results [8]. It is interest to notice the trend in terms of selectivity of by-products as a function of temperature. At 70 °C by increasing the particle size selectivity to glycolate decreased as well as to tartronate. At 50 °C no influence of particle size was observed on the selectivity to glycolate, whereas to tartronate we observed a significant decrease (from 22% to 1%) comparable to that observed at 70 °C (from 11% to 3%). Having in mind the reaction scheme of glycerol oxidation (scheme 1), glycerol oxidation can follow two routes, one leading to

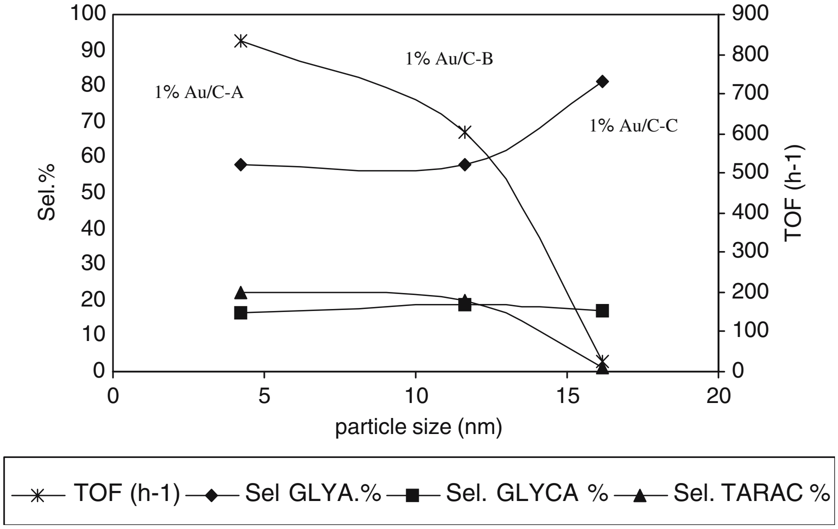

Figure 1. Selective oxidation of glycerol in the presence of 1% Au/C as a function of particle size (XRPD) at 90% conversion. Reaction conditions: water 10 mL, 0.3M glycerol, glycerol/M = 500, NaOH/glycerol = 4, T = 50°C, pO_2 = 3 atm.

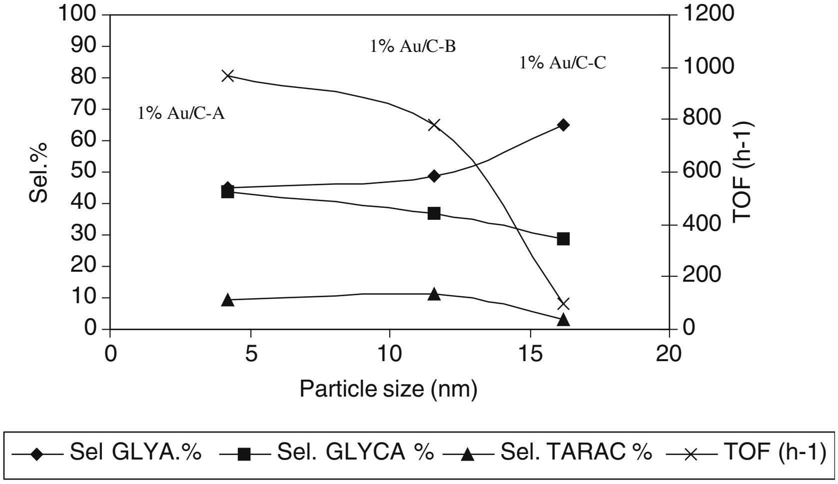

Figure 2. Selective oxidation of glycerol in the presence of 1% Au/C as a function of particle size (XRPD) at 90% conversion. Reaction conditions: water 10 mL, 0.3M glycerol, glycerol/M = 500, NaOH/Glycerol = 4, T = 70 °C, pO_2 = 3 atm.

C–C scission (glycolate), the other to glycerate and tartronate. By tuning the particle size we can almost suppress the consecutive oxidation of glycerate even at 50 °C but for reducing the formation of glycolate we had to increase the temperature to 70 °C.

In terms of catalyst activity (figures 1 and 2), increase of particle size led to significant decrease of the activity (TOF h^{-1}), as expected.

3.2.2. *Pd/C catalysts*

In the case of Pd/C catalysts the increase of particle size had the same effect as with Au/C catalysts, which is the enhancement in selectivity to glycerate and decrease of activity. However, glycolate and tartronate products (figure 3) were both reduced by increasing particle size (from 21% to 11% for tartronate and from 15% to 5% for glycolate).

3.2.3. *Comparison of Au/C and Pd/C catalysts*

For evaluation of the two monometallic systems it would be ideally if the comparison could be done at similar particle size. For this comparison is interesting to consider the "large" monometallic Au and Pd catalysts with particle dimension between 14–16 nm (figure 4). At the same reaction temperature (50 °C) both of the monometallic catalysts gave high and similar selectivity (at 90% conversion) to GLYA (79–81%). However, is it noteworthy to observe the distribution of the by-products. Thus, with Au/C the main by-product was glycolate, whereas with Pd/C was tartronate. Note also that only with Au/C catalysts the selectivity to tartronate (i.e. the consecutive oxidation of glycerate) diminished significantly, by increasing particle size. Nevertheless, with both catalysts a similar activity was observed (27–28 TOF h^{-1}). From these results we can derive that with a similar but large particle size, a similar activity and also similar selectivity to glycerate was obtained, with Au/C to inhibit mainly the over-oxidation of glycerate to tartronate, while with Pd/C to diminish significantly the formation of glycolate.

3.3. *Bimetallic catalysts (Au–Pd)/C*

Recently we have shown the synergistic effect of the incorporation of Au into Pd metal and the catalytic performance of bimetallic (Au–Pd)/C catalysts on glycerol oxidation [24]. As in the case of monometallic catalysts, the (Au–Pd)/C catalysts were of small particle size (2–3 nm), thus we decided to investigate the effect of particle size by varying the particle dimension. We used as a reference the catalysts prepared as we reported in [10] by preparation method C. The particle size of this catalyst resulted in the range 2–3 nm, thus we modified the preparation method in order to increase the mean diameter. By using N_2H_4 instead of $NaBH_4$ as the reducing agent produced this effect even in bimetallic system not only the diameter could be changed. Nevertheless, these results should be considered as preliminary. In table 2, the catalytic performance of different bimetallic (Au–Pd)/C on glycerol oxidation as function of temperature is shown. Increasing the reaction temperature an increase of activity was observed as expected but with a significant loss in the selectivity to glycerate. In figure 5 the effect of particle size at the same temperature (50 °C) on the distribution of the major products (glycerate, glycolate and tartronate) for (Au–Pd)/C is shown. It is noteworthy to observe, that by increasing the particle size a substantial decrease in the selectivity to tartronate happened, whereas for glycolate selectivity variation of particle size did not seem to affect it. This result is similar with the catalytic behaviour of the Au/C catalysts. Apparently, the synergistic effect of Au and Pd disappeared when particle diameter

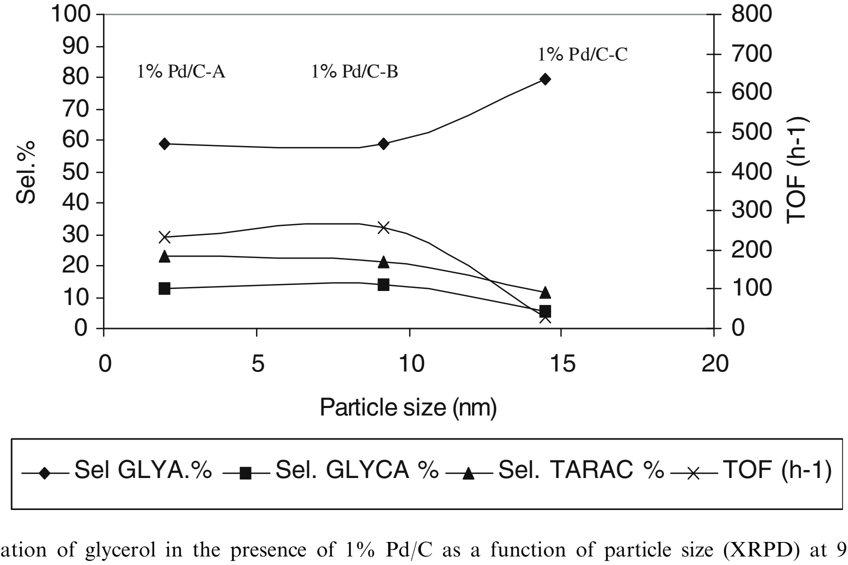

Figure 3. Selective oxidation of glycerol in the presence of 1% Pd/C as a function of particle size (XRPD) at 90% conversion. Reaction conditions: water 10 mL, 0.3M glycerol, glycerol/M = 500, NaOH/glycerol = 4, T = 50 °C, pO_2 = 3 atm.

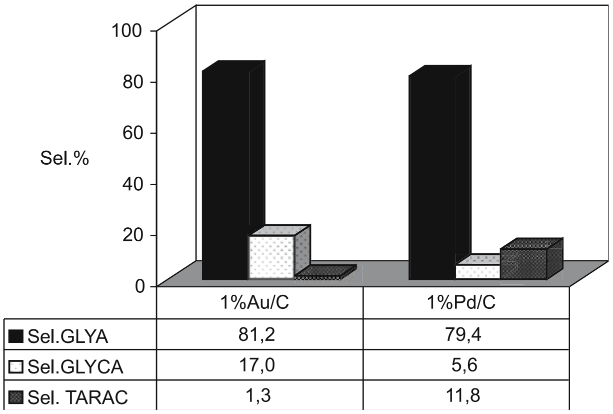

Figure 4. Comparison of 1%Au/C and 1%Pd/C on the selective oxidation of glycerol in the presence of 1% Pd/C with similar particle sizes (XRPD) at 90% conversion. Reaction conditions: water 10 mL, 0.3M glycerol, glycerol/M = 500, NaOH/glycerol = 4, T = 50 °C, $pO_2 = 3$ atm.

Table 2

Oxidation of glycerol using bimetallic catalysts[a]

Catalysts	50 °C		70 °C	
1% (Au–Pd)/C–A	S_{90}	TOF(h^{-1})[b]	S_{90}	TOF(h^{-1})[b]
	63	956	32	686
1% (Au–Pd)/C–B	S_{90}	TOF(h^{-1})[b]	S_{90}	TOF(h^{-1})[b]
	56	904	30	981
1%(Au–Pd)/C–C	S_{90}	TOF(h^{-1})[b]	S_{90}	TOF(h^{-1})[b]
	67	143	55	373

[a] Reaction conditions: water 10 mL, 0.3 M glycerol, Glycerol/M = 500, NaOH/Glycerol = 4, T = 50, 70 °C, $pO_2 = 3$ atm.

[b] Calculation of TOF (h^{-1}) after 0.5 h of reaction. TOF numbers were calculated on the basis of total loading of metals.

S_{90}indicate the selectivity observed at 90% conversion.

increases. Nevertheless, this important result has to clear out with a deep characterization of the catalysts.

3.4. Overview

Collectively, these results establish a distinct structure sensitivity [12] for the liquid phase oxidation of glycerol over carbon-supported gold and palladium catalysts. Recent work examining gold catalysts for hydrogenation reactions have also observed changes in activity and selectivity profiles as a function of gold particle size [13–15]. With reference to the seminal structural considerations of van Hardefeld and Hartog [16], it is assumed that certain planes of the Au crystallites favour certain branches of the glycerol oxidation reactions outlined in Scheme 1. Clearly, figures 1 and 2 show increasing particle size decreases overall activity but increases the selectivity to glyceric acid. Increasing particle size proportionally increases the density of (111) planes [29] and, therefore, it is tentatively assumed that (111) planes favour glyceric acid formation. However, this is mainly true for particle size not more than 4 nm. Similarly, from analogies to hydrogenation studies [15], the converse activity issue could be linked to oxygen supply, with small Au particles emphasizing particle edges, which could be associated with oxygen activation and hence TOF. Additional detailed structural studies are required to refine these concepts further. Nevertheless, this work clearly establishes that Au particle size can play a significant role in modifying yields in multi-step oxidation reactions.

4. Conclusions

These preliminary studies have shown that the catalytic performances of mono and bimetallic catalysts based on Au and Pd supported on carbon in liquid

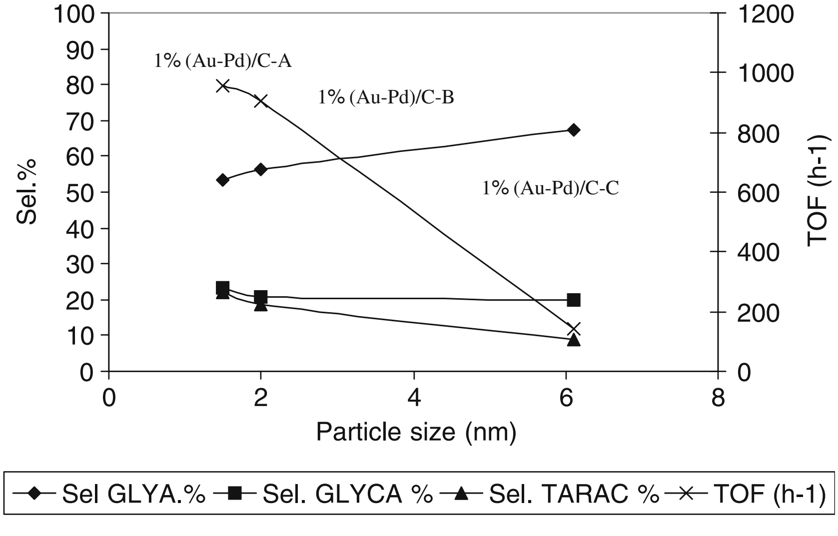

Figure 5. Selective oxidation of glycerol in the presence of 1% (Au–Pd/C as a function of particle size (XRPD) at 90% conversion. Reaction conditions: water 10 mL, 0.3M glycerol, glycerol/M = 500, NaOH/glycerol = 4, T = 50°C, $pO_2 = 3$ atm.

phase oxidation of glycerol, in terms of activity and selectivity, were affected significantly mainly due to the variation of the particle size of the metal and in a less extent due to PVA amount. Nevertheless, we can not exclude a possible role of PVA in the catalytic performance of the catalysts, for example blocking certain Au sites. However, this affect will influence in the same way the catalytic behaviour of the catalysts since the PVA variation was in a closed proximity. Thus, larger particle size leads to the decrease of activity and increase of the selectivity to glycerate. However, depending on the metal (Au or Pd) a different distribution of the by-products was observed. Hence, for Au/C catalysts at 50 °C, increase of the particle size resulted in the blockage of the consecutive oxidation of glycerate to tartronate without affecting significantly the selectivity of glycolate. In the case of Pd/C catalysts, a similar decrease as in the case of Au/C in the formation of tartronate was found, whereas glycolate formation was decreased with respect to Au/C. Moreover, in the case of (Au–Pd)/C, preliminary results show that they behave like Au/C where an increase of particle size leads to the blockage of the consecutive oxidation of glycerate to tartronate. Furthermore, the particle size seems to apparently affect the synergistic effect of Pd and Au when bimetallic systems are used. With similar particle size (XRPD values) and reaction temperature either Au/C or Pd/C catalysts gave almost the same value of selectivity to glycerate (80%) and similar activity (TOF). Finally, detailed HRTEM studies would be helpful for further investigating the topic of the of particle size effect particularly in the case of bimetallics.

Acknowledgment

The authors are grateful for financial support from the Auricat EU network (HPRN-CT-2002-00174).

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