

# Selective oxidation of glycerol to sodium glycerate with gold-on-carbon catalyst: an insight into reaction selectivity

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## Abstract

Glycerol was oxidised with oxygen in the presence of gold on carbon as the catalyst. Two types of catalysts were identified: one, characterised by well-dispersed nanoparticles with a mean diameter centred at 6 nm, did not maintain the initial selectivity of the oxidation at full conversion; the other, characterised by larger particles (> 20 nm), showed constant selectivity from the beginning to the end of the reaction. The experimental conditions were studied to optimise glycerate production with selected catalysts, with particular regard to the effect of the NaOH/glycerol ratio, glycerol concentration, temperature, and glycerol/catalyst ratio. The best result was 92% selectivity to glycerate at full conversion, obtained by oxidising glycerol at 30 °C, with a NaOH/glycerol ratio of 4, a glycerol/Au = 500, and 0.3 M concentration.

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**Keywords:** Gold on carbon; Liquid-phase oxidation; Glyceric acid; Glycerol oxidation

## 1. Introduction

Glycerol has attracted attention as a usable starting material because of its easy availability (bio-sustainable sources) and its high functionalisation. Given its high boiling point, the selective oxidation of glycerol with air/oxygen is always carried out in the liquid phase using water as the solvent. Classical oxidation catalysts for liquid-phase oxidation such as platinum or palladium on carbon have been tested [1–3] and, depending on the nature of the metal and the pH at which the reaction is carried out, afford glyceric acid with quite good selectivity: 70% selectivity at full conversion using Pd on carbon catalyst at pH 11 is the best result reported [3]. It has also been reported that doping a Pt/C catalyst with Bi can orient the selectivity toward the oxidation of the secondary alcoholic group, reaching 50% selectivity to dihydroxyacetone (DHA) at 70% conversion [4]. This appears to depend on the method employed: a batch reactor working at pH 11 appears to produce more DHA than a fixed-bed reactor [2].

However, it should be noted that catalysts based on the platinum group metal suffer oxygen poisoning [4] propor-

tional to oxygen partial pressure [5]. This is the principal reason why, when using this type of catalyst, a low partial pressure of oxygen (air at atmospheric pressure as the oxidant) must be used to limit oxygen dissolution. Gold catalysts appear to be more resistant to oxygen poisoning than platinum-based ones [6], allowing a higher oxygen partial pressure. In fact, oxidation in the liquid phase, using gold on carbon as the catalyst, can be carried out using pure oxygen at 300 kPa pressure [7,8]. Under these conditions, gold on carbon is very selective toward primary alcohol, though the obligatory presence of a base [6] leads to intermediate product interconversion that can mask the true selectivity of the catalyst. Hutchings et al. recently reported that the selective oxidation of glycerol can be carried out using gold on carbon as the catalyst [9,10]. In a batch reactor at 60 °C under 3–6 atm of O<sub>2</sub>, the selectivity of the reaction toward glyceric acid appears to depend on the conversion, decreasing from 100% at half conversion to 86% at 72% conversion. In the present work we focused our attention on the productivity of glycerate, optimising the selectivity at high conversion by operating a fine tuning between catalyst design and reaction conditions.

We started from the consideration that the selectivity observed under alkaline conditions was due to the combination of the nature of the catalyst (metal [6], particle dimen-

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sions [11,12], support [13]), that determines the intrinsic selectivity of the catalyst, and the experimental parameters such as temperature and base concentration, that determine the stability of the intermediates and their interconversion.

## 2. Experimental

### 2.1. Materials

Gold of 99.9999 purity in sponge from Fluka, activated carbon from Camel (X40S; SA = 1100–1200 m<sup>2</sup> g; pH 8–9) or VulcanXC72R (graphitised carbon) and Graphite HSAG 300 (AS = 430 m<sup>2</sup> g) from Lonza S.p.A. were employed. Before use, the carbon was suspended in HCl 6 M and left under stirring for 12 h and 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%.

Sodium citrate and NaBH<sub>4</sub> of purity > 96% from Fluka and polyvinylalcohol (PVA) (M 10,000) and tetrakis(hydroxypropyl)phosphonium chloride (98% solution) from Aldrich were used. NaOH of the highest purity available was from Fluka. Gaseous oxygen from SIAD was 99.99% pure.

Glycerol (88 wt% solution), glyceric acid, and all the intermediates were from Fluka.

### 2.2. Catalyst preparation

#### 2.2.1. From metallic sol

**2.2.1.1. PVA-protected gold sol preparation** An aqueous HAuCl<sub>4</sub> solution of 100 µg/ml was prepared by dissolving gold (30 mg) in a minimum amount of HCl/HNO<sub>3</sub> 3/1 v/v mixture and, after removing the HNO<sub>3</sub>, it was diluted with distilled water. Maintaining the auric solution under vigorous stirring, PVA 2 wt% solution (0.96 ml) was added; a 0.1 M freshly prepared solution of NaBH<sub>4</sub> (7.62 ml) was then added dropwise to yield a ruby red metallic sol [14].

**2.2.1.2. Citrate-protected gold sol preparation** Sols generated in the presence of citrate were prepared by modifying the procedure reported elsewhere [15]. To an aqueous HAuCl<sub>4</sub> solution 2.36 × 10<sup>-4</sup> M (300 ml) thermostated at 65 °C, we added a sodium citrate solution 0.296 M (1.63 ml). After a reaction time of 1 h the yellow solution turned violet in colour, changing to ruby red after 3 h of reaction.

**2.2.1.3. THPC-protected sol** Sols generated in the presence of the THPC/NaOH system were prepared as reported elsewhere [16] and used as such. A freshly prepared solution 0.05 M of THPC was added to a NaOH solution 10<sup>-3</sup> M. After a few minutes HAuCl<sub>4</sub> 10<sup>-3</sup> M was added dropwise, yielding a brown metallic sol.

Within a few minutes of sol generation, the sol was immobilised by adding activated carbon under vigorous stirring.

The amount of support was calculated as having a final gold loading of 1% wt. After 2 h the slurry was filtered and the catalyst washed thoroughly with distilled water; it was then used in the wet form. ICP analyses were performed on the filtrate using a Jobin Yvon JY24 to verify the gold loading on carbon.

#### 2.2.2. Incipient wetness preparation

HAuCl<sub>4</sub> solution was prepared by dissolving gold (20 mg) in a minimum amount of HCl/HNO<sub>3</sub> 3/1 v/v mixture and, after removing the HNO<sub>3</sub>, it was diluted with distilled water (total volume 3.0 ml).

The solution was added rapidly to activated carbon (2 g) and mixed with a glass rod for at least 15 min. The carbon was then dried at 100 °C in air for 4 h. When the catalysts were calcined (150 °C, 6 h, air) the CALC abbreviation was added to the catalyst name.

#### 2.2.3. Impregnation

Two catalysts were prepared as reported elsewhere [9,10] using X40S active carbon or, alternatively, graphite as the support. A slurry of carbon was prepared using 10 g of carbon in 100 ml of water. A solution of HAuCl<sub>4</sub> (5 ml, 20 mg Au/ml) was added and refluxed for 2 h. HCHO 37% wt (3 ml) was added after cooling the slurry and then refluxed again for 2 h. The gold on carbon was then filtered, washed with water, dried, and calcined at 150 °C for 6 h.

### 2.3. Catalyst characterisation

The symbol for each catalyst indicates the preparation method (PVA, CIT, THPC for sols; IW for incipient wetness; I for impregnation) and the type of support (X40S, graphite, Vulcan XC72R).

The gold content was checked by ICP analysis of the filtrate, or directly on the catalyst after burning off the carbon, on a Jobin Yvon JY24. The water content was determined by drying a sample at 150 °C in air for 5 h.

X-ray diffraction experiments were performed on a Rigaku D III-MAX horizontal-scan powder diffractometer with Cu-K<sub>α</sub> radiation, equipped with a graphite monochromator in the diffracted beam. The crystallite sizes of the gold were estimated from peak half-widths 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 dispersed ultrasonically 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 onto the micrographs at least 300 particles, and the mean particle diameter ( $d_m$ ) was calculated using the formula  $d_m = \sum d_i n_i / \sum n_i$ , where  $n_i$  was the number of particles of diameter  $d_i$ .

XPS measurements were performed in an M-Probe Instrument (SSI) equipped with a monochromatic Al-K $\alpha$  source (1486.6 eV) with a spot size of 200 × 750  $\mu\text{m}$  and a pass energy of 25 eV, providing a resolution for 0.74 eV.

The accuracy of the reported binding energies (BE) can be estimated to be  $\pm 0.2$  eV. The quantitative data were checked accurately and reproduced several times (at least 10 times for each sample).

#### 2.4. Oxidation experiments

The reactions were carried out in a thermostated 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.

Glycerol, NaOH, and the Au catalyst (glycol/metal = 500 mol/mol) were mixed in distilled water (total volume 10 ml). If not otherwise specified, a 0.3 M solution was used. The reactor was pressurised at 300 kPa of O $_2$  and thermostated at the appropriate temperature. After an equilibration time of 10 min, the reaction was initiated by stirring and samples were taken every 30 min and analysed by HPLC.

#### 2.5. Analysis of products

Analyses were performed on a Varian 9010 HPLC equipped with a Varian 9050 UV (210 nm) and a Waters R.I. detector in series. An Alltech OA-1000 column (300 × 6.5 mm) was used with aqueous H $_3$ PO $_4$  0.1% wt/wt M (0.5 ml/min) as the eluent. Samples of the reaction mixture (0.5 ml) were diluted (5 ml) using the eluent. Products were recognised by comparison with authentic samples.

### 3. Results and discussion

#### 3.1. Selectivity of the reaction

As the reference catalyst we prepared 1% Au/C as reported by Hutchings and co-workers [9,10], using graphite (Lonza HSAG300) and active carbon (Camel X40S) as the support. Using similar experimental conditions (60 °C, 10% wt of glycerol, NaOH/glycerol = 1 mol/mol, glycerol/Au = 500 mol/mol) we obtained the product distribution reported in Fig. 1. There was an unexpected by-product, glycolate, whose formation can be explained by the oxidative degradation of hydroxypyruvic acid (Scheme 1). During the reaction we did not detect mesooxalate but only a small amount of oxalate (< 0.5%). From the general reaction scheme (Scheme 1) it can be seen that this oxalate could, in principle, derive from either the mesooxalate (through oxidative degradation) or the glycolate (through subsequent oxidation). Although glycolate has been found to be stable under oxidative conditions [6], we again tested its stability

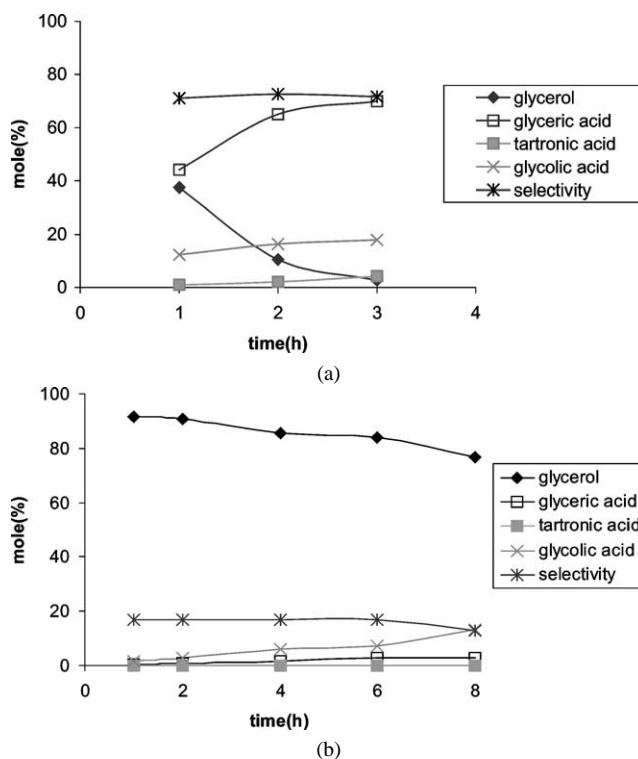


Fig. 1. Selective oxidation of glycerol in the presence of supported 1% Au prepared by impregnation of (a) active carbon X40S [I] and (b) graphite [I-graph]. Reaction conditions: glycerol 10% wt; glycerol/Au = 500; glycerol/NaOH = 1;  $T = 60$  °C;  $p_{\text{O}_2} = 3$  atm.

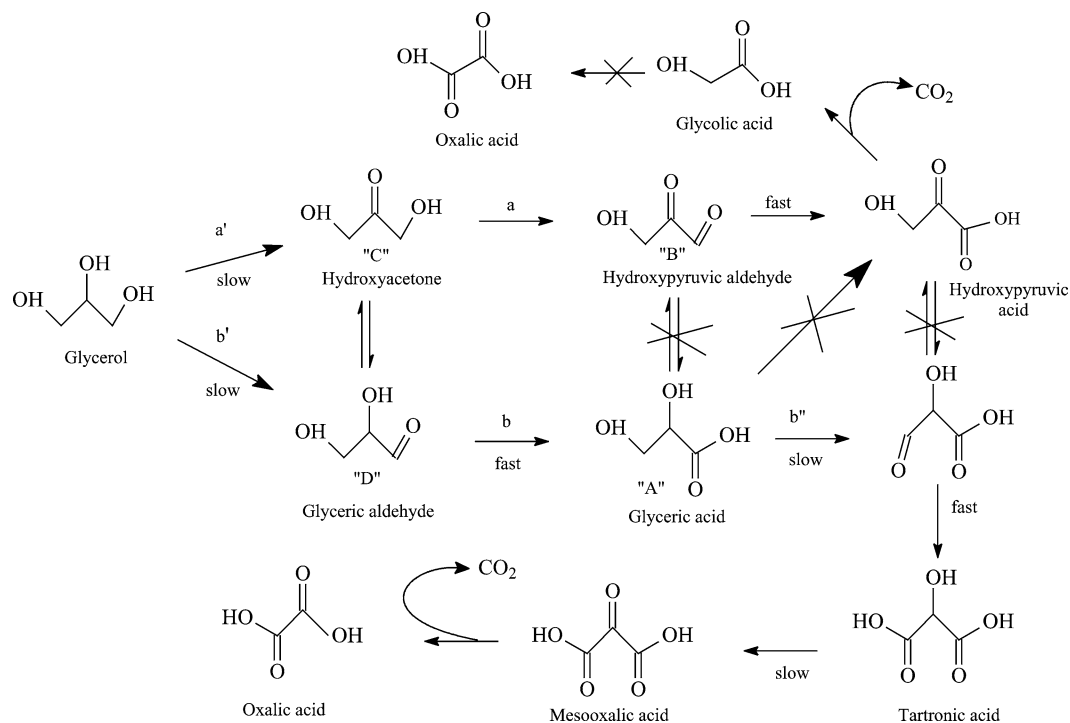
in the presence of the used catalyst. We found it to be stable and so assumed that the oxalate came from the mesooxalate. The product distribution revealed that:

1. Au on active carbon was more active than Au on graphite;
2. After total glycerol consumption (full conversion) the glycolate amount was almost stable, while the tartronate amount increased and the glycerate decreased slowly. However the total amount of glycerate plus tartronate remained stable.

This meant that the glycolate did not come from the glycerate, thus excluding a base-catalysed transformation of glycerate (A) to hydroxypyruvate aldehyde (B). On the other hand, as we had established that the total amount of glycerate plus tartronate was stable, the reverse reaction could be excluded, thus excluding the A and B interconversion in Scheme 1.

Thus in Scheme 1, the glycolate amount could be considered a probe of path a, whereas glycerate and tartronate were both probes of path b.

However these conclusions are not easily correlatable with the real selectivity of the gold catalyst toward the oxidation of the primary alcoholic group. In fact, under basic conditions dihydroxyacetone and glyceraldehyde can interconvert and the oxidation of the aldehydic group is faster than



Scheme 1. General reaction pathways.

the oxidation of the OH group. This could possibly enhance the observed overall selectivity to glyceric acid with respect to the first step selectivity (intrinsic selectivity of the catalyst). Thus the glycolate amount did not reflect the selectivity of the catalyst toward the secondary group, just as the glycerate does not reflect the selectivity toward the primary one.

Our experience in the oxidation of propan-1,2-diol [6] (100% selectivity) and phenyl-1,2-ethane diol (83% selectivity) [12] prompted us to consider the glycerol case as being more similar to phenyl-1,2-ethane diol than to propane-1,2-diol, as phenyls like the hydroxyl groups can activate the secondary position. Thus we could expect reduced selectivity toward the primary alcohol. This led us to conclude that the reaction selectivity is the result of the combination of two factors: one is obviously the nature of the catalyst, that determines the starting amounts of hydroxyacetone and glycerinaldehyde (these interconvert and are expected to be oxidized at different rates); the other, the experimental conditions, allows interconversion and contributes to single step kinetics. In principle, high overall selectivity can be achieved by using either a catalyst that is highly selective in producing glycerinaldehyde, or a less selective catalyst under basic conditions that favour dihydroxyacetone and glycerinaldehyde interconversion. In the former case the rapid oxidation of the glycerinaldehyde (kinetic control) favours the production of glyceric acid instead of dihydroxyacetic acid.

### 3.2. On the catalyst

Before studying the effect of the experimental parameters on the overall selectivity of the reaction let us look a mo-

Table 1  
1% Au/C characteristics

Method	Support	<i>d</i> (nm)		% at Au(4f)/C(1s) (XPS)
		XRPD	HRTEM	
Impregnation (I)	X40S	10	18.5	0.4
Incipient wetness (IW)	X40S	16.3	14.8 [50]	3.51
Sol (PVA)	X40S	3	5	2.34
Sol (THPC)	X40S	5.7	15	0.67
Sol (citrate)	X40S	7.4	21	0.98
Sol (citrate)	Graphite	8.7	nd	nd
Sol (citrate)	Vulcan	8.7	nd	nd
	XC72R			
IW-CALC	X40S	22.2	Large aggregate	0.16
Sol (citrate)-CALC	X40S	8	30	n.d.

ment at the gold catalyst itself. Fig. 1 shows how different gold catalysts (although nominally always 1% Au/C) differ in activity and selectivity. Thus we tested different catalysts, prepared tuning particle dimensions, exposition [11], and support [13] to maximise glyceric acid production. We used different preparation methods (incipient wetness, impregnation, sol immobilization) and different supports (active carbon, graphite, carbon black), determining the mean particle dimension (XRPD and HRTEM) and the surface exposition (XPS) for each catalyst. Table 1 shows the characteristics of all these catalysts.

The mean diameter discrepancies found between XRPD and HRTEM were not surprising as the two techniques are based on different principles. We only highlight that the greater the particle crystallinity, the more the two measure-

Table 2  
Glycerol oxidation with 1% Au/C<sup>a</sup> at 60 °C: Effect of preparation method and support

Entry	Catalyst <sup>b</sup>	S50 <sup>c</sup>	S90 <sup>d</sup>
1 <sup>e</sup>	I	71	70
2 <sup>e</sup>	I-Graph	20 <sup>f</sup>	–
3	IW	80	78
4	IW-CALC	83	83
5	PVA	47	35
6	THPC	52	45
7	CIT	75	75
8	CIT-Graph	nd <sup>g</sup>	–
9	CIT-Vulcan	60	61
10	CIT-CALC	90	89
11	CIT-Vulcan-CALC	81	81

<sup>a</sup> Reaction conditions: glycerol 10% wt; glycerol/Au = 500; glycerol/NaOH = 1;  $T = 60$  °C;  $p_{O_2} = 3$  atm.

<sup>b</sup> All the catalysts are 1% Au: I, impregnation method on X40S; I-Graph, impregnation method on graphite; IW, incipient wetness method on X40S (CALC, calcined); PVA, PVA sol immobilisation on X40S; THPC, THPC sol immobilisation on X40S; CIT, citrate sol immobilisation on X40S (CALC = calcined); CIT-Graph, citrate sol immobilisation on graphite; CIT-Vulcan citrate sol immobilisation on VulcanXC72R (CALC = calcined).

<sup>c</sup> Selectivity at 50% conversion.

<sup>d</sup> Selectivity at 90% conversion.

<sup>e</sup> Figs. 1a and 1b show the different selectivity/conversion path using I or I-graph under the reaction conditions reported in (a).

<sup>f</sup> Selectivity at 25% conversion.

<sup>g</sup> No conversion was observed.

ments come into agreement. From a catalytic point of view the more useful data are those of HRTEM.

We tested the catalysts in glycerol oxidation under the usual conditions (60 °C, 3 atm of O<sub>2</sub>, glycerol/Au = 500; glycerol/NaOH = 1) evaluating selectivity at 50% conversion (S50) and 90% conversion (S90).

On comparing S50 and S90 (Table 2) we observed that the catalysts formed two categories: one with S50 > S90, the other with S50 ≈ S90. The S50 > S90 class contains catalysts prepared via sol immobilisation (PVA, THPC), typically constituted by 4–5 nm of well-dispersed gold nanoparticles; these catalysts show the highest activity (lowest reaction time) (Table 2, entries 5 and 6). Instead the catalysts in the second category were prepared using more classical procedures (incipient wetness and impregnation) (Table 2, entries 1–4). A rough characterisation of the two catalyst classes highlights that those of the first class have smaller particle size and are characterised by good surface exposition, with corresponding higher activity. This activity determines, in turn, lower selectivity, due to the subsequent oxidation of the intermediates (i.e., glycerate). The catalysts belonging to the second class have larger particle size ( $d > 10$  nm). Therefore, when designing an optimal catalyst for the selective oxidation of glycerol to glycerate it would seem that the larger particle ( $d > 10$  nm) is preferable. To confirm this point we prepared other catalysts by a method that ensured a narrow distribution of large particles ≈ 20 nm: gold sol immobilisation via citrate reduction

Table 3  
Effect of glycerol/NaOH ratio and temperature using IW-CALC<sup>a</sup> as the catalyst in glycerol oxidation

$T$ (°C)	S/NaOH (mol/mol) S50 <sup>b</sup>			S/NaOH (mol/mol) S90 <sup>c</sup>		
	1	2	4	1	2	4
30	85	84	86	85	85	83
60	83	85	82	83	81	79
90	66	57	70	58	53	62

<sup>a</sup> Reaction conditions: glycerol 10% wt; glycerol/Au = 500;  $p_{O_2} = 3$  atm. IW-CALC = 1% Au/C prepared by incipient wetness on X40S and then calcined at 150 °C for 6 h.

<sup>b</sup> Selectivity at 50% conversion.

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

of HAuCl<sub>4</sub> [15]. As expected, the selectivity was enhanced with respect to catalysts prepared via immobilisation of different sols (Table 2, entry 7 versus entries 5 and 6), consistent with an increase in average particle size from 4 to 5 to 20 nm.

The same sol was supported on different carbons (X40S, graphite, Vulcan XC72R) to evaluate the support effect already observed in the liquid-phase oxidation of ethane-1,2-diol [13]. Also in this case we observed that the support drastically affected the catalyst activity, gold on graphite being inactive whereas on active carbon X40S or Vulcan XC72R it was active (Table 2, entries 7, 8, and 9). However, by calcinating both CIT/X40S and CIT/XC72R to increase particle dimension, we obtained a considerable enhancement in selectivity to glycerate (75 to 90 and 60 to 81%, respectively) (Table 2, entries 10 and 11), although activity decreased.

### 3.3. Optimisation of reaction conditions

In order to optimise glyceric acid production we tested different reaction conditions, keeping in mind that the gold catalyst screening had highlighted the fundamental property for a catalyst to have high selectivity, i.e., particle mean diameter > 20 nm. The reaction conditions evaluated were temperature, reagent concentrations and S/NaOH ratio.

Table 3 shows the results, using 1% Au supported on X40S by incipient wetness and then calcined (IW-CALC) as catalyst, of varying the temperature in the 30–90 °C range, and the S/NaOH ratio from 1 to 4 (mol/mol).

Our previous papers [6,12,17,18] have already reported that the rate-determining step in alcohol oxidation in the liquid phase, catalysed by gold, is the C–OH → CHO base-demanding transformation followed by the more rapid oxidation CHO → COOH not requiring the base. Thus increasing the base amount, starting from the 1/1 S/NaOH ratio, should not change the selectivity to glycerate (path b) as the equilibrium DHA ↔ Glald is soon reached. The only variations involved would be the oxidation kinetics and, possibly, the stability of the intermediate. Table 3 shows how, at 60 °C, using a 1/2, or 1/4, S/NaOH ratio instead of 1/1, the selectivity to glycerate remains almost constant, although there is increased reaction rate. The stability of the products, particularly glyceric acid, was not affected by the increased amount

Table 4  
Glycerol oxidation with 1% Au/C<sup>a</sup> at 30 °C: Effect of preparation method and support

Entry	Catalyst <sup>b</sup>	S50 <sup>c</sup>	S90 <sup>d</sup>
1	I	72	71
2	IW	81	80
3	IW-CALC	85	85
4	CIT	78	77
5 <sup>e</sup>	CIT-CALC	95	92
6	CIT-Vulcan	67	65
7	CIT-Vulcan-CALC	83	83

<sup>a</sup> Reaction conditions: glycerol 10% wt; glycerol/Au = 500; glycerol/NaOH = 1;  $T = 30\text{ °C}$ ;  $p_{\text{O}_2} = 3\text{ atm}$ .

<sup>b</sup> All the catalysts are 1% Au: I impregnation method on X40S; I-Graph impregnation method on graphite; IW incipient wetness method on X40S (CALC = calcined); CIT citrate sol immobilisation on X40S (CALC = calcined); CIT-Vulcan citrate sol immobilisation on VulcanXC72R (CALC = calcined).

<sup>c</sup> Selectivity at 50% conversion.

<sup>d</sup> Selectivity at 90% conversion.

<sup>e</sup> Fig. 2 reports selectivity as a function of conversion.

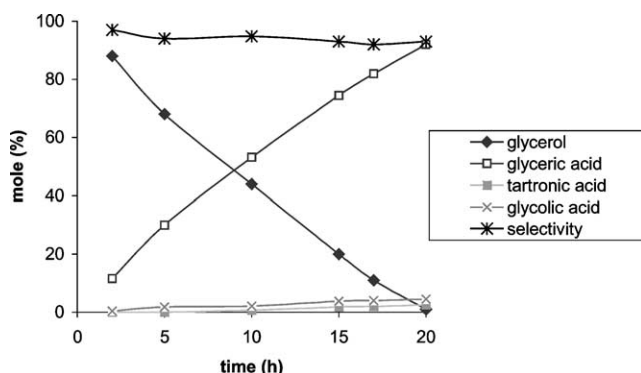


Fig. 2. Selective oxidation of glycerol in the presence of 1% Au/C [CIT-CALC]. Reaction conditions: glycerol 10% wt; glycerol/Au = 500; glycerol/NaOH = 1;  $T = 30\text{ °C}$ ;  $p_{\text{O}_2} = 3\text{ atm}$ .

of base. In fact the selectivities at 50% conversion (S50) and 90% (S90) were comparable, only a slight change being observed when a 1/4 S/NaOH ratio was used.

Concerning temperature (30 °C and 90 °C), increasing the temperature led to an expected decrease in selectivity. We also found that increasing the temperature resulted in S50 being higher than S90, meaning that glyceric acid is easily oxidised at the higher temperature. However, we noted from the product distribution that the total amount of glyceric and tartronic acid remained stable; this means that temperature promotes only the oxidation of glyceric acid to tartronic.

From Table 3 we selected the most promising reaction conditions, and retested some catalysts (Table 4) at 30 °C. Table 4 allows comparison with results obtained at 60 °C. All the tested catalysts showed better selectivity at 30 °C than at 60 °C, the highest enhancement being shown by 1% Au on X40S, prepared by immobilising citrate-protected sol and then calcined (CIT-CALC), as the catalyst (Table 4, entry 4). Fig. 2 shows the product distribution obtained with

this catalyst. The highest selectivity to glycerate (92%) was probably due to there being hardly any tartronic acid present, that means a quite good stability of glyceric acid. However the reaction rate was rather low (17 h for 89% conversion); thus, as we had already tested the influence of increasing the NaOH/S ratio to speed up the reaction, we increased the amount of NaOH (NaOH/S = 4) and reached 90% conversion in 6 h, maintaining almost constant selectivity to glycerate (93%).

#### 4. Conclusions

Glycerol was oxidised with oxygen in the presence of gold on carbon as the catalyst. Two types of catalysts were recognised: the first, characterised by well-dispersed nanoparticles with a mean diameter centred at 6 nm, that did not maintain the initial selectivity of the oxidation through to full conversion; the second, characterised by larger particles (> 20 nm), that, on the contrary, maintained constant selectivity from the beginning to the reaction end.

It thus became apparent that it is not only particle dimension that fulfils an important role but also the preparation method, sol immobilisation appearing better than the impregnation or incipient wetness methods.

The overall selectivity of the reaction derives from the combination of factors such as initial selectivity of the catalyst, base-catalysed interconversion, and stability of the products. We noted that interconversion between the hydroaldehyde and hydroxyketone occurs very rapidly and despite the product stability that should favour hydroxyketone, the subsequent rapid oxidation of the hydroxyaldehyde favours glyceric acid production (kinetic control). Also temperature plays an important role in determining product stability, increasing the temperature promotes the oxidation of glyceric acid to tartronic acid. By optimising the reaction conditions (30 °C, S/NaOH = 4) and the gold catalyst (CIT-CALC), we obtained 92% selectivity to sodium glycerate at full conversion.

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