Catalysis Letters Vol. 99, Nos. 3–4, February 2005 (© 2005)
DOI: 10.1007/s10562-005-2114-8

Synergetic effect of platinum or palladium on gold catalyst in the selective oxidation of D-sorbitol

Nikolaos Dimitratos, Francesca Porta, Laura Prati* and Alberto Villa

Dipartimento di Chimica Inorganica Metallorganica e Analitica e INSTM Unit, Centre of Excellence CIMAINA, Auricat Programme Università di Milano, via Venezian 21, 20133 Milano, Italy

Received■; accepted■

Monometallic Au, Pt and Pd on carbon catalysts show poor activity in the liquid phase oxidation of D-sorbitol to gluconic/gulonic acids. However, by using bimetallic based catalysts (Au–Pt or Au–Pd) a great enhancement in the activity has been observed with respect to all the monometallic catalysts tested probably due to a synergetic effect between Au and Pt or Pd. In fact physical mixture of monometallic catalysts presented poor activity. Bimetallic showed a resistance to poisoning by dioxygen and by reaction products as high as gold monometallic catalyst, but also an improved selectivity toward monooxidation with respect to monometallic.

KEY WORDS: oxidation of polyols; sorbitol oxidation; bimetallic catalyst; gold/palladium; gold/platinum.

1. Introduction

Liquid phase oxidation of polyols like glycols [1], glycerol [2–4] and monosaccharides [5–7] represents a useful method to evaluate the use of renewable sources for the synthesis of fine chemicals [8]. However catalytic methods suffer deactivation due to sintering, leaching and irreversible adsorption of (by)-products [9]. This last phenomenon strongly depends on the nature of the products and, in turn, limits the catalytic oxidation of superior polyols because the chelating nature of the product can cause both sintering (Ostwald ripening) and leaching of the metallic active phase with a consequent decrease in catalyst activity. Moreover, classical Pd or Pt catalysts when dioxygen is used as the oxidant, often show deactivation due to overoxidation [8]. The use of gold catalyst greatly contributes to the development and use of oxidative catalytic method since its resistance to poisoning derives both from (by)products and overoxidation [1].

However, in the oxidation of alcohols and polyols it has been shown that the activity of gold catalyst normally is lower than that of Pd or Pt and is very sensitive to pH, being zero in the absence of a base probably able to abstract an hydride for initiating the process. Even in principle not necessary, the use of basic conditions are also suggested for Pt or Pd:in these cases the purpose of the base is to speed up the reaction and minimise the irreversible absorption of the carboxylic group allowing the catalyst to work [8].

In this paper we tested gold based catalysts in the liquid phase oxidation of a C6-polyols, the D-sorbitol, for studying catalyst performances in terms of activity in the presence of a chelating molecule and selectivity toward monooxidation.

2. Experimental

2.1. Materials

$NaAuCl_4 \cdot 2H_2O$, K_2PtCl_4, $NaPdCl_4$ Gold were from Aldrich (99.99% purity) and activated carbon from Camel (X40S; SA = 900–1100 m^2/g; PV = 1.5 ml/g; pH 9–10). 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 $< 3\%$.

$NaBH_4$ of purity >96% from Fluka, polyvinylalcohol (PVA) 87–89% hydrolysed, (M.W. 13,000–23,000) from Aldrich were used. NaOH was from Fluka of the highest purity available. Gaseous oxygen from SIAD was 99.99% pure.

2.2. Catalyst preparation

Catalysts were prepared by immobilisation sol technique [10].

Monometallic sol. A typical preparation is here reported. A PVA aqueous solution (42 mL, 2% w/w) was added to a solution of $NaAuCl_4$ (20.19 mg, 5.07 10^{-2} mmol, in 151.5 mL of H_2O) and magnetically stirred for 3 min. $NaBH_4$ 0.1 M (1.42 mL) was added and immediately a ruby red sol was formed. The vigorous stirring was maintained for 3 min and the reduction checked by recording UV–visible spectra.

---

*To whom correspondence should be addressed.
E-mail: laura.prati@unimi.it

The precursors $NaPdCl_4$ and K_2PtCl_4 under similar conditions gave Pd and Pt sols (brown and grey, respectively).

Bimetallic sols. A typical preparation is here reported. 35 μl of a Na_2PdCl_4 stock solution (0.043 mmol, Pd 10% w/w, d = 1.32 g/ml) and PVA (0.680 mL, 2% w/w) were added to 130 mL of H_2O. The brown solution was stirred for 3 min and $NaBH_4$ 0.1 M (0.89 mL) was added under vigorous magnetic stirring. The brown Pd(0) sol was immediately formed and the reduction checked by recording UV–visible spectra. After further 3 min, 1.0 mL of a stock solution of $NaAuCl_4.2H_2O$ (8.58 mg, 0.043 mmol) and $NaBH_4$ 0.1 M (1.33 mL) were added, obtaining after 3 min a dark brown sol. An UV–visible spectrum of the bimetallic sol was recorded. A similar preparation based on K_2PtCl_4 was used for Au–Pt sol.

Sol immobilisation on carbon. After 5 min the sol was immobilised 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 and used in the wet form. The absorption of gold was checked by ICP analysis of the filtrate on a Jobin Yvon JY24. The water content was determined by drying a sample for 5 h at 150 °C in air.

2.3. Catalytic test

Under pressure. 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. Sorbitol 0.3 M, NaOH (Sorbitol/NaOH = 1 mol/mol) and the catalyst (sorbitol/metal = 1000 mol/mol) were mixed in distilled water (total volume 10 ml). The reactor was pressurised at 300 kPa of O_2 and thermostatted at 50 °C. The reaction was started up by stirring.

Samples were taken every 15 min and analysed by HPLC on a Varian 9010 instrument equipped with a Varian 9050 UV (210 nm) and a Waters R.I. detector in series. An Alltech OA-10308 column (300 mm × 6.5 mm) was used with aqueous H_3PO_4 0.01 M (0.5 ml/min) as the eluent. Samples of the reaction mixture (0.5 ml) were diluted (5 ml) using the eluent.

Atmospheric pressure and controlled pH conditions. Sorbitol 0.3 M and the catalyst (sorbitol/metal = 1000 mol/mol) were mixed in distilled water (total volume 20 ml). NaOH 0.5 M was added until pH 11 was reached. The reactor was thermostatted at 50 °C and the reaction was started up by flowing O_2 at atmospheric pressure (25 ml/min). The pH was automatically controlled by Metrohom Titrino 718 and maintained by adding NaOH 0.5 M. Samples were taken every 15 min and the analyses of the products were performed on a Varian 9010 HPLC equipped with a Varian 9050 UV (210 nm) and a Waters R.I. detector in series.

Recycling test. Recycling tests have been performed by filtering the solution at the end of the reaction and reusing the catalyst under pressure with a freshly prepared 0.3 M sorbitol solution and a stoichiometric amount of NaOH.

3. Results and discussion

Triol, like glycerol, can be selectively oxidised by gold on carbon to α-hydroxy acid, like glyceric acid [2–4]. However, in this case the use of strong alkaline medium masks the real selectivity of the catalyst and what we measured represents an overall selectivity due to the merge of the preferencial oxidation of primary alcohol (–CHOH–CHO) and the base catalysed interconversion between $–CO–CH_2OH$ and –CHOH–CHO (Canizzaro reaction). D-sorbitol, on the contrary of glycerol, presents some other problems: (1) different chemoselectivity deriving from different OH groups; (2) chelating (by)products; (3) less resistance to basic conditions of the oxidation products.

Monometallic gold supported on active carbon, contrarily to Pd or Pt, has been found to be an active catalyst in the production of gluconic acid starting from D-glucose even in the absence of base [5], meaning that the effect of the chelating nature of C6 polyol oxidation product was negligible for gold catalyst. However, for oxidising alcohol instead of the aldehydic group [11] we have already reported that gold as the catalyst requires the presence of a base [1,12]. Therefore, to oxidise D-sorbitol using supported gold as the catalyst we should use basic conditions but, as gluconic/gulonic acid is base sensitive, we had to carry out the reaction carefully at controlled pH. We started by using reaction conditions where the pH was carefully tuned. d-sorbitol 0.3 M and the catalyst (sorbitol/metal = 1000 mol/mol) were mixed in distilled water (total volume 20 ml) and thermostatted at 50 °C. The pH was raised to 11 ± 0.1 using NaOH 0.5 M and the reaction started by flowing oxygen (25 ml/min) at atmospheric pressure. Figure 1 reports the results using 1% Au/C, 1% Pd/C and 1% Pt/C prepared by immobilizing PVA-stabilised metallic sols in 6 h tests. The reaction appeared very slow in all the cases (<40% conversion in 6 h) but, surprisingly, gold appeared more active than palladium and similar to platinum.

As in simple alcohol oxidation the trend of activity is Pt>Pd≫Au [12], the behaviour of monometallic catalysts in sorbitol oxidation could be ascribed to a poisoning effect of the product, this being stronger in the case of Pd than in that of Pt as in the case of D-Glucose oxidation [5]. In fact, prolonging the reaction time only with gold we were able to obtain full

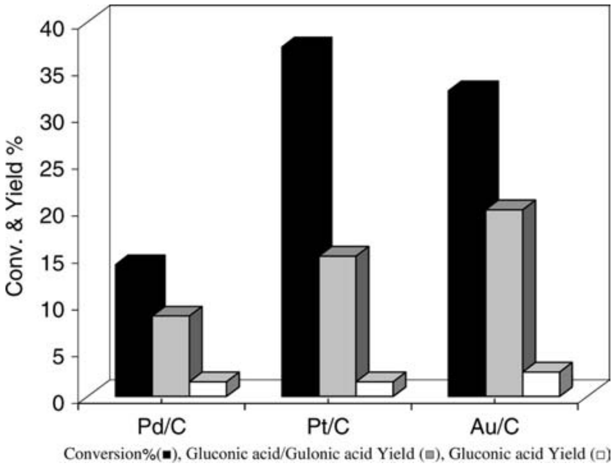

Figure 1. Activity comparison of 1% Au/C, 1% Pd/C and 1% Pt/C in the oxidation of D-sorbitol. Reaction conditions: Sorbitol (0.3 M), T (50 °C), pH 11, Sorbitol/metal = 1000, flowing O_2 at atmospheric pressure (25 ml/min). Conversion% (■), Gluconic acid/Gulonic acid Yield (▨), Gluconic acid Yield (□).

conversion even in an unacceptable long time (>40 h). With regard to selectivity, gold showed the best selectivity (60%) to mono-carboxylate (gluconate/gulonate), in agreement with what is known about the higher selectivity of gold toward primary OH with respect to Pt or Pd [1,12].

Focusing on gold, in order to speed up the reaction by increasing oxygen dissolution, we also tried to operate under pressure (3 atm of O_2) in a closed vessel. In fact gold, contrary to Pt or Pd, appears not to suffer from oxygen poisoning [1,9]. The compulsory presence of a base and the experimental necessity under pressure to use all the stechiometric amount of base at the beginning of the reaction, could be compatible with sorbitol but not with products. However, we considered that as the reaction proceeds the pH decreases, thus providing a less basic environment for gluconate/gulonate (final pH = 7–8). The result was impressive: Au/C allowed full conversion in 6 h, but the selectivity drastically decreased with respect to that obtained at atmospheric pressure controlling the pH (40% vs 60% at full conversion). Nevertheless we could correlate the decrease of selectivity principally to the subsequent oxidation of gluconate/gulonate to glucarate ($NaOOC(CHOH)_4COONa$) and not to the product instability under basic conditions. Table 1 shows the comparison of Au, Pt and Pd on carbon under these conditions. Au/C appeared to be the most active catalyst; this is not surprising as it is known that Pt and Pd suffer oxygen poisoning that probably deactivates the catalysts before full conversion has been reached.

Table 1
Activity comparison of 1%Au/C, 1% Pd/C and 1% Pt/C in the oxidation of D-sorbitol[a]

Catalyst	TOF (h^{-1})	S^b_{50}
1% Au/C	158	38
1% Pd/C	83	–
1% Pt/C	51	–

[a] Reaction condition: D-sorbitol (0.3 M) at 50 °C, pO_2 3 atm, Sorbitol/metal = 1000, sorbitol/NaOH = 1.

[b] Selectivity at 50% conversion.

Table 2
Activity comparison of 1% Au–Pd/C and 1% Au–Pt/C in the oxidation of D-sorbitol (0.3 M) under different conditions

Catalyst	TOF (h^{-1})	S^c_{50}
1% Au-Pd/C[a]	154	60
1% Au-Pt/C[a]	149	71
1% Au/C[a]	54	55
1% Pd/C[a]	23	60[d]
1% Pt/C[a]	62	40
1% Au-Pd/C[b]	333	57
1% Au-Pt/C[b]	266	58
1% Au/C[b]	158	38

[a] Reaction condition: D-sorbitol (0.3 M) at 50 °C, pH 11, Sorbitol/metal = 1000, flowing O_2 at atmospheric pressure (25 ml/min).

[b] Reaction condition: D-sorbitol (0.3 M) at 50 °C, pO_2 3 atm, Sorbitol/metal = 1000, sorbitol/NaOH = 1.

[c] Selectivity at 50% conversion.

[d] Selectivity at 20% conversion.

In order to merge the properties of gold (resistance) with these of Pd or Pt (activity) we prepared bimetallic catalysts using the sol immobilisation technique. A specific synthesis of bimetallic particle was set up in order to obtain alloyed metallic phase. The molar ratio Au/Pd or Pt was fixed to 1 (mol/mol) and the final total metal loading after adsorption of these sols on active carbon to 1% wt. We tested these catalysts in D-sorbitol oxidation, either using a stoichiometric amount of NaOH and under 3 atm O_2 pressure or controlling the pH at atmospheric pressure.

The results are reported in table 2. By comparing bimetallic (Au–Pd, Au–Pt) to monometallic (Au, Pt, Pd) catalysts in all cases the activity extraordinarily increased, full conversion being reached in 8–10 h at atmospheric pressure or in 3–4 h under pressure respectively. The second point of interest is that, under pressure, both bimetallic catalysts resulted able to reach full conversion whereas Pt or Pd on carbon rapidly deactivates. Moreover, as monometallic gold showed a considerably lower activity (TOF 158 h^{-1} for Au vs. 266–333 h^{-1} for Au–Pt, Au–Pd), this proves a synergetic effect between Au and Pd or Pt.

By operating at atmospheric pressure the rate enhancement resulted more evident (TOF 20–60 h^{-1} for monometallics vs. 150 h^{-1} for bimetallics) and we ascribed it to a beneficial effect of gold on the resistance of catalysts, as in the previous case.

Surprising as well are the results from the selectivity point of view. We noted a better selectivity to mono-carboxylate of bimetallics with respect to monometallics operating both under pressure and at atmospheric

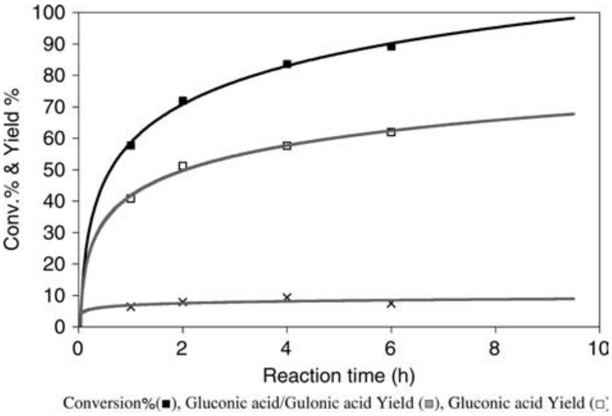

Figure 2. Activity of 1% Au–Pt/C in the oxidation of D-sorbitol. Reaction conditions: Sorbitol (0.3 M), T (50 °C), pH 11, Sorbitol/metal = 1000, flowing O_2 at atmospheric pressure (25 ml/min). Conversion% (■), Gluconic acid/Gulonic acid Yield (▨), Gluconic acid Yield (□).

pressure. Under pressure, as monometallic gold, produced a larger amount of glucarate (GLUCA.A) and the overall selectivity toward primary OH appeared similar by using Au–Pd or Au–Pt (about 60%). Operating at atmospheric pressure and controlling the pH we were able to differentiate the behaviour of Au–Pt and Au–Pd, generally obtaining better results with respect to operating under pressure. Figures 2 and 3 show the reaction profiles.

Although the activity of 1% Au–Pd/C is similar to 1% Au–Pt/C (TOF 154 and 149 h^{-1} respectively), the reaction profiles differ, the Au–Pt showing higher selectivity. In the case of Au–Pd (figure 3) we found a glucarate profile consistent with rapid gluconate/gulonate oxidation (as operating under pressure) but also with subsequent glucarate overoxidation. In this case the selectivity at full conversion to gluconate resulted 58%. On the contrary, Au–Pt (figure 2) produced monocarboxylate (gluconate/gulonate) that was oxidized more slowly to glucarate, the yield of which appearing almost constant. Thus, by using Au–Pt as the catalyst we were able to obtain 70% selectivity to monocarboxylate even at full conversion. The overall selectivity toward primary OH (gluconate/gulonate/glucarate) at full conversion reached 81%. Comparing selectivity data with those obtained with monometallic gold or platinum (table 2), we can conclude that the co-presence of Pt and Au increased both the activity and, most interestingly, the selectivity. Moreover a test using a physical mixture of the two monometallic catalysts revealed very low activity (comparable with monometallic) proving that a real synergetic effect between gold and platinum exists depending on the preparation method of the catalyst.

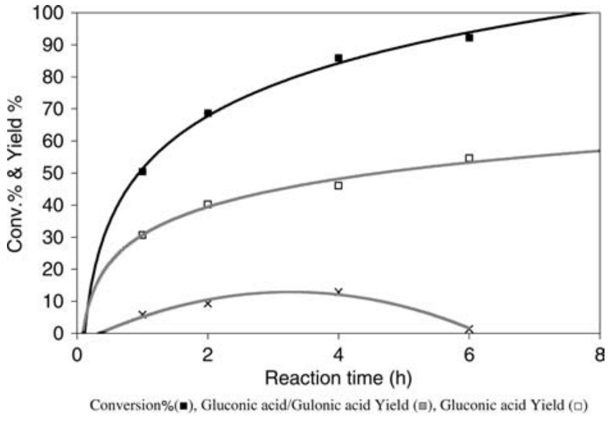

Figure 3. Activity of 1% Au–Pd/C in the oxidation of D-sorbitol. Reaction conditions:Sorbitol (0.3 M), T (50 °C), pH 11, Sorbitol/metal = 1000, flowing O_2 at atmospheric pressure (25 ml/min). Conversion% (■), Gluconic acid/Gulonic acid Yield (▨), Gluconic acid Yield (□).

Finally, we also tested the resistance (life-time) of the bimetallic Au–Pt catalyst carrying out some recycling experiments. We runned five times the catalyst under pressure without any washing. The loss of the activity per run (<5%) revealed a good catalyst resistance and ICP analyses showed that no leaching of the metal happened.

4. Conclusions

Sorbitol was oxidised with oxygen in the presence of palladium, platinum and gold on carbon as the catalyst. We used two different methodologies: the first bubbling O_2 at atmospheric pressure and controlling the pH; the second using O_2 under pressure and a stoichiometric amount of NaOH. At atmospheric pressure gold on carbon showed an activity as high as platinum, higher than palladium; under pressure however it was the only catalyst that allowed reaching full conversion. We ascribed this behaviour to the known higher resistance of gold to oxygen/product poisoning.

By studying the effect of palladium or platinum on gold catalyst we found an extraordinary effect in terms of both activity and selectivity. The activity increased but the most interesting point was that bimetallic catalysts (Pt–Au and Pd–Au) allowed to reach full conversion whereas monometallic rapidly deactivate.

Operating at atmospheric pressure and controlling the pH we stated a different behaviour of Pt–Au and Pd–Au catalysts in terms of selectivity, being the Pt–Au the one able to preserve the initial selectivity. The best result was 70% selectivity to monocarboxylic acid, being 81% the overall selectivity to glucarate.

The resistance to poisoning of this latter catalyst was proved by recycling experiments done under pressure revealing that the bimetallic catalyst, with respect to both monometallic (also physically mixed), showed increased activity and selectivity to gluconic/gulonic acid. Further investigations are in progress for preparation with different Au–Pd or Au–Pt molar ratios in order to optimise the synergetic effect of the two metals.

References

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

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

[3] S. Carrettin, P. McMorn, P. Johnston, K. Griffin, G.J. Huthchings and C. J. Kielly, Phys. Chem. Chem. Phys. 5 (2003) 1329.

[4] L. Prati and F. Porta, J. Catal. 224 (2004) 397.

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

[6] M. Besson, F. Lahmer, P. Gallezot, P. Fuertes and G. Flèche, J. Catal. 152 (1995) 116.

[7] O. Enea and J.P. Ango, Elect. Acta 34 (1989) 391.

[8] T. Mallat and A. Baiker, Catal. Today 19 (1994) 247 and reference cited therein.

[9] M. Besson and P. Gallezot, Catal. Today 81 (2003) 547.

[10] F. Porta, L. Prati, M. Rossi and G. Scarì, J. Catal. 211 (2002) 464.

[11] S. Biella, L. Prati and M. Rossi, J. Mol. Cat. A: General 197 (2003) 207.

[12] L. Prati and M. Rossi, Stud. Surf. Sci. Catal. 110 (1997) 509.