Gold Based Bimetallic Catalysts for Liquid Phase Applications

Nikolaos Dimitratos and Laura Prati*
Dipartimento di Chimica Inorganica Metallorganica e
Analitica e Centro C.N.R., AURICAT Programme,
Centre of Excellence CIMAINA Unit, Università di
Milano, via Venezian 21, 20133 Milano, Italy

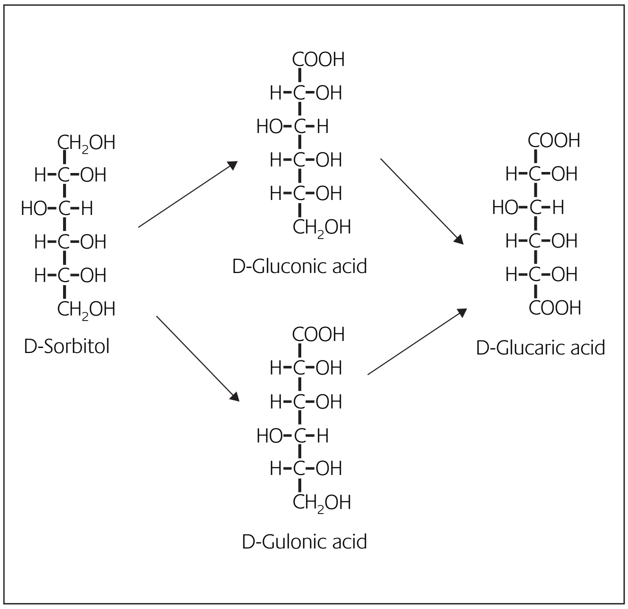
Abstract

The liquid phase oxidation of D-Sorbitol has been carried out in water using oxygen as the oxidant in the presence of gold based catalyst. Au/C, Pt/C and Pd/C monometallic systems were compared to bimetallic Au/Pd and Au/Pt on carbon. A strong synergistic effect was observed producing a significant increase of reaction rate. Moreover, the addition of gold to Pd or Pt catalyst produced a system more resistant to oxygen poisoning allowing it to work also under a moderate pressure. The effect of varying the molar ratio of the metals has also been studied.

1 Introduction

Over the last ten years, gold catalysts have been recognized as being active materials in oxidation reactions [1-8] and all the studies until now have revealed the strong dependence of gold catalyst activity on the type of support and the preparation method [9-13]. In liquid phase oxidation, gold catalysts have been shown as a good alternative for classical Pd and Pt based catalysts in terms of both selectivity and resistance to poisoning. This traditionally represents a strong limitation to industrial application of those Pd and Pt based materials [14-16].

During recent studies [17-18] we demonstrated the importance of the addition of gold to palladium/platinum metals in terms of their catalytic performance compared to the single metal catalysts. We found that a significant increase not only of the activity but also of the selectivity occurred when gold was added. Moreover, the resistance to poisoning (oxygen or by-product poisoning) using bimetallic catalysts was improved considerably. Particularly in the case of the oxidation of D-Sorbitol, we have also studied the effect of reaction conditions by changing the pressure of oxygen and pH conditions. The use of bimetallic systems allowed by increasing the oxygen pressure to be increased from 1 to 3 Atm (increasing oxygen solubility), without observing any poisoning due to over-oxidation and observing a significant increase in the reaction rate. Unfortunately a drawback of this experimental procedure low yield of monocarboxylate (gluconate/gulonate) due to the consecutive reactions. In this paper we have focused on the preparation of bimetallic systems using three different preparation methods (based on the sequence of metal addition and reduction) and also altering the molar ratio of the metals. As a model reaction we chose the selective oxidation of D-Sorbitol, (Scheme 1).



Scheme 1

2 Experimental

2.1 Materials

Na_2PdCl_4, K_2PtCl_4, $NaAuCl_4.2H_2O$ (purity > 99.0%) and PVA (Mw=13000-23000, 98% hydrolysed) were sourced from Aldrich.

Stock aqueous solutions of Na_2PdCl_4 ([Pd]= 0.449 M), K_2PtCl_4 ([Pt] = 0.038 M), $NaAuCl_4.2H_2O$ ([Au] =0.036 M), PVA (1% w/w) and $NaBH_4$ (0.1M) were prepared. The solutions of PVA and $NaBH_4$ were freshly prepared. Activated carbon was sourced from Camel (X40S; SA=900-1100 m^2 g^{-1}; PV=1.5 ml g^{-1}; pH 9-10). Gaseous oxygen sourced 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 6M and left under stirring for 12h, then washed several times with distilled water by decantation until the pH of the solution reached values of 6-6.5. Finally 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%.

2.2 Catalyst preparation

2.2.1 Au-M bimetallic sols (M = Pd, Pt, 1:1 molar ratio)

Preparation method 1 – solid $NaAuCl_4.2H_2O$ (0.095 mmol) was dissolved in 290 ml of H_2O and PVA solution added (M = Pd, 1.8 ml PVA; M = Pt, 3.3 ml PVA). After 3 min, $NaBH_4$ solution (2.9 ml) was added under vigorous magnetic stirring. The red Au(0) sol was immediately formed. After further 3 min, stock aqueous solution of MCl_4^- (0.099 mmol) and $NaBH_4$ solution (2.0 ml) were added, obtaining a dark brown sol.

Preparation method 2 – MCl_4^- stock aqueous solution (0.099 mmol) and PVA solution (M = Pd, 1.8 ml PVA; M = Pt, 3.3 ml PVA) were added to 290 ml of H_2O. After 3 min, $NaBH_4$ solution (2.0 ml) was added under vigorous magnetic stirring. The dark brown Pd(0) sol was immediately formed. After 3 min, an aqueous solution of $NaAuCl_4.2H_2O$ (0.095 mmol) and $NaBH_4$ solution (2.9 ml) were added, obtaining a dark-brown sol.

Preparation method 3 – MCl_4^- stock aqueous solution (0.099 mmol), and PVA solution (M = Pd, 1.8 ml PVA; M = Pt, 3.3 ml PVA) were added to a solution of $NaAuCl_4.2H_2O$ (0.095 mmol) in 290 ml of H_2O. The yellow-brown solution was stirred for 3 min and $NaBH_4$ solution (4.9 ml) was added under vigorous magnetic stirring, obtaining a dark-brown sol.

2.2.2 Au/Pd catalysts with different molar ratio (1:8 to 8:1)

The synthesis of the Au/Pd catalysts with different molar ratio utilized preparation method 3, by changing the amounts of gold and Pd precursor to the desired stoichiometry.

2.2.3 Immobilization method

Within a few minutes of sol generation, the colloid (acidified at pH 1, by sulfuric acid) was immobilized by adding activated carbon under vigorous stirring, The amount of support was calculated as having a total final 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 4h. ICP analyses were performed on the filtrate using a Jobin Yvon JV24 to verify the metal loading on carbon.

2.3 Catalytic test

a) Atmospheric pressure and controlled pH conditions: D-Sorbitol 0.3 M and the catalyst (D-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 thermostatically controlled at 50°C and the reaction was commenced by flowing O_2 at atmospheric pressure (25 ml min^{-1}). The pH was automatically controlled by Metrohom Titrino 718 and maintained by adding NaOH 0.5 M. Samples were taken every 15-30 minutes 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.

b) Under pressure: the reactions were carried out in a thermostatically controlled glass reactor (30 ml) with an electronically controlled magnetic stirrer connected to a large reservoir (5,000 ml) containing oxygen at 300 kPa. The oxygen uptake was monitored by a mass flow controller connected to a PC through an A/D board, plotting a flow/time diagram. D-Sorbitol 0.3 M, NaOH (D-Sorbitol/NaOH=1 mol/mol) and the catalyst (D-Sorbitol/metal = 1000 mol/mol) were mixed in distilled water (total volume 10 ml). The reactor was pressurized at 300 kPa of O_2 and thermostatically controlled at 50°C. The reaction was commenced by stirring.

Samples were taken every 15-30 minutes and analyzed 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 x 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.

3 Results and discussion

3.1 Bimetallic catalysts based on Au/Pd and Au/Pt (1 to 1 atomic ratio)

Three preparation methods were employed for the synthesis of bimetallic catalysts (Au/Pd and Au/Pt). With preparation method 1 the Au precursor was added and reduced prior to the addition of the Pd precursor, whereas with preparation method 2 the opposite was utilized and finally, preparation method 3 the simultaneous addition of the metal precursors occurred before the reduction step. In this way, we can determine from a catalytic point of view if the sequence of addition of the metal precursors is important.

The effect of using different preparation methods on the catalytic performance of the bimetallic catalysts is shown in

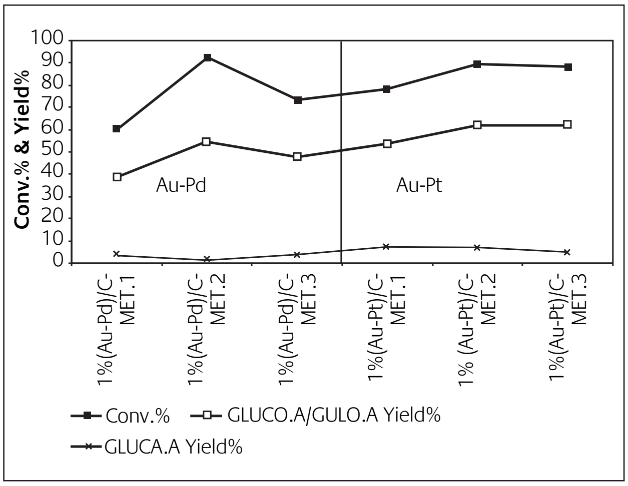


Figure 1

Comparison of (Au-Pd)/C versus (Au-Pt)/C for D-Sorbitol oxidation at atmospheric pressure and pH (11) controlled conditions

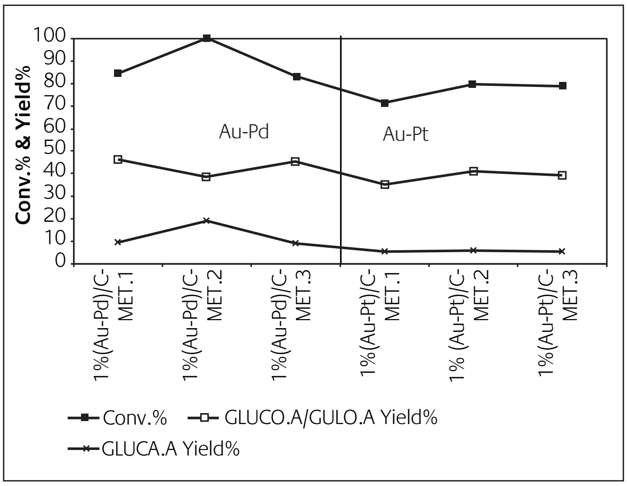


Figure 2

Comparison of (Au-Pd)/C versus (Au-Pt)/C for D-Sorbitol oxidation under pressure and alkaline conditions

Figures 1 and 2. In Figure 1 the catalytic performance of the Au/Pd and Au/Pt catalysts using pH controlled conditions (pH=11) at atmospheric pressure is illustrated. With preparation method 2 the highest conversion and yield to gluconate/gulonate was observed either using Au/Pd or Au/Pt catalysts. In the case of using alkaline conditions under pressure (Figure 2) we found again a similar catalytic behavior in terms of activity. However, the yield to gluconate/gulonate was lowered due to the over-oxidation to glucarate. Thus, in both cases the bimetallic catalysts prepared by method 2 were the most active, whereas yield of the product depended on the reaction conditions used. The order of activity for the different preparation methods was as follows: Method 2> Method 3> Method 1. These results suggest that addition of Au after the former addition and reduction of Pd/Pt metal resulted in the most active system, whereas the opposite was found (less reactive system) when Pd/Pt was added after the prior addition and reduction of Au. Simultaneous addition and reduction of the two precursors resulted in intermediate activity.

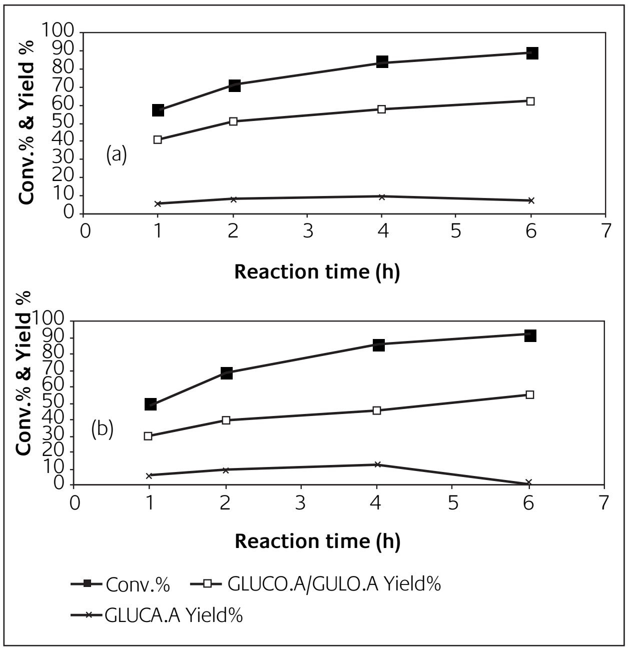


Figure 3

(a) D-Sorbitol oxidation on (Au-Pt)/C-MET.2 at 50°C-controlled pH (11) conditions

(b) D-Sorbitol oxidation on (Au-Pd)/C-MET.2 at 50°C-controlled pH (11) conditions

Table 1

Catalytic data for bimetallic catalysts at 50ºC for sorbitol oxidation after 3h of reaction under alkaline conditions

1%(Au-M)/C	S_{80}	TOF(h^{-1})^a
	GLUCO.A/GULO.A	
1%(Au-Pd)/C-MET.1	54.7	415.2
1%(Au-Pd)/C-MET.2	50.7	463.2
1%(Au-Pd)/C-MET.3	57.4	401.7
1% (Au-Pt)/C-MET.1	48.2	404.3
1%(Au-Pt)/C-MET.2	52.0	403.6
1%(Au-Pt)/C-MET.3	49.9	377.0

[a] Calculation of TOF (h^{-1}) after 1 hour of reaction

Comparison of the two bimetallic systems (Au/Pd versus Au/Pt) at the same reaction conditions (atmospheric pressure-pH=11 versus under pressure-3 Atm of O_2 and alkaline conditions) showed that under atmospheric pressure and pH controlled conditions the Au/Pt systems performed better than Au/Pd systems in terms of activity/yield. As an example, the reaction profile of the Au/Pd and Au/Pt catalysts synthesized by method 2 is shown, (Figure 3). With the Au/Pd catalyst a lower yield to monocarboxylate (54%) was obtained than Au/Pt catalyst (62%). As it can be seen from the reaction profiles of the two catalysts an over-oxidation of gluconate/gulonate occurred using the Au/Pd catalyst. However, changing the reaction conditions and working under pressure at alkaline conditions, Au/Pd were more active than Au/Pt, which could be a result of the increased amount of oxygen on the Au-Pt

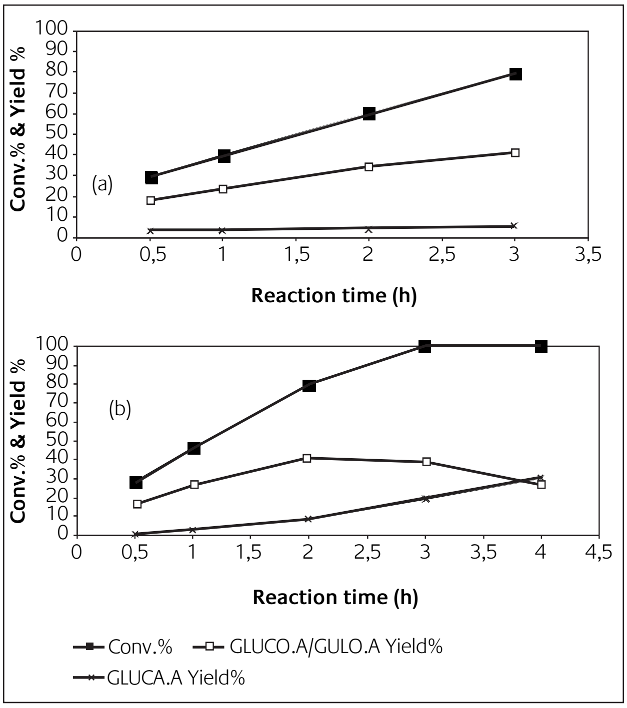


Figure 4

(a) D-Sorbitol oxidation on (Au-Pt)/C-MET.2 at 50°C-under pressure at alkaline conditions

(b) D-Sorbitol oxidation on (Au-Pd)/C-MET.2 at 50°C- under pressure at alkaline conditions

surface, (Table 1). By taking into consideration the reaction profiles of the Au/Pd and Au/Pt synthesized by method 2 (Figure 4), increase of conversion was accompanied with decrease of yield to gluconate/gulonate for the Au/Pd catalyst at the expense of glucarate, whereas for Au/Pt catalyst a steady increase of the yield to monocarboxylate was found and yield of glucarate was almost constant.

3.2 Bimetallic catalysts (Au/Pd) based on different atomic ratio

Since we had observed that bimetallic systems are more active and selective than the monometallic systems we focused on the preparation of bimetallic systems with different atomic ratio in order to evaluate if by altering the atomic ratio we could influence the activity/yield. Thus, we synthesized Au/Pd catalysts with varying atomic ratios from 1/8 to 8/1 using preparation method 3. Figure 5 illustrates the results of the Au/Pd catalysts when the reaction was performed under pressure and alkaline conditions. It can be seen that by increasing the gold concentration a simultaneous increase of the conversion occured (conversion increase from 67 to 80% when the molar ratio increased from 1:8 to 6:4). This increase of activity reached a maximum value when the molar ratio of the Au/Pd was 6:4 and then declined (volcano type behavior). In terms of yield similar values were obtained when the molar ratio was between 1:3 to 3:1 and only for 1:8 and 8:1 the lowest yields were obtained. It is interesting to note that even in the presence of a minor amount of Au (in the case of 1:8) a significant increase of the catalytic activity was achieved i.e. conversion increased from 15% to 67%, indicating the importance of the addition of Au for obtaining an active bimetallic system. The reaction profile of the Au_6Pd_4 catalyst is shown in graph 6 as an example of the Au_xPd_y catalysts. The major product was gluconate/gulonate with substantial amount of glucarate as in the case of the Au/Pd systems.

Table 2

Comparison of 1%(Au_xPd_y)/C at iso-conversion for D-Sorbitol oxidation after 3h of reaction under alkaline conditions at 50ºC

1%(Au_xPd_y)/C	S_{70}	TOF(h^{-1})[a]
	GLUCO.A/GULO.A	
1%(Au_1Pd_8)/C	54.9	609.9
1%(Au_1Pd_3)/C	58.1	712.4
1%(Au_1Pd_1)/C	53.0	704.9
1%(Au_6Pd_4)C	50.6	752.1
1%(Au_3Pd_1)/C	53.2	696.2
1%(Au_8Pd_1)/C	49.2	622.9

[a] Calculation of TOF (h^{-1}) after 1 hour of reaction

Comparison at iso-conversion will reveal which bimetallic

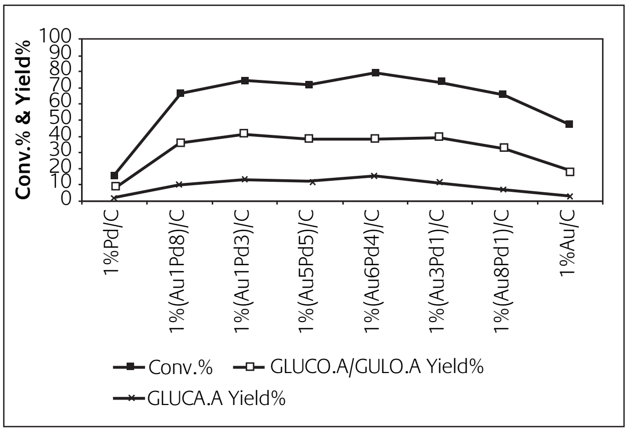


Figure 5

Comparison of (Au_xPd_y)/C-MET.3 for D-Sorbitol oxidation at 50°C-under pressure at alkaline conditions

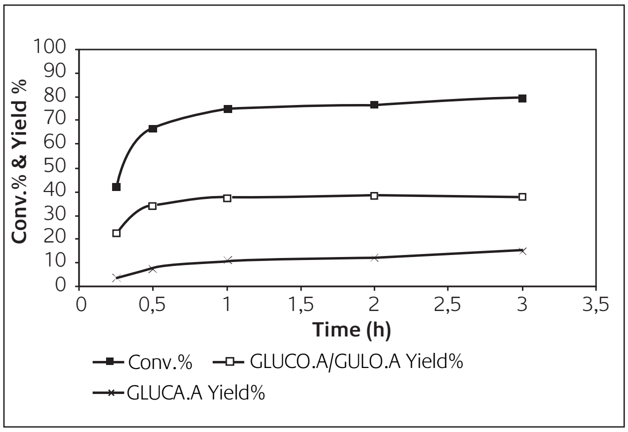


Figure 6

D-Sorbitol oxidation on (Au_6Pd_4)/C-MET.3 at 50°C-under pressure at alkaline conditions

Au_xPd_y catalyst is the most selective for the formation of the monocarboxylate. Table 2 shows the results obtained at 70% conversion. In general higher selectivities to monocarboxylate (53-58%) were obtained when the catalysts were in excess in Pd concentration, whereas with higher Au concentration lower values were obtained (50-53%). However, there is little difference between the values obtained among Au-rich or Pd-rich samples.

These results show that by changing the molar ratio of the bimetallic Au/Pd system it is possible to tune the activity/yield of the Au/Pd catalysts. Moreover, an optimum value in terms of activity for Au/Pd molar ratio exists, which is 6:4. Recently, it has been reported that a 10:7 Au/Pd molar ratio is the optimum for the formation of hydrogen peroxide (19).

Conclusions

Three methodologies were used for the preparation of the bimetallic systems, depending on the sequence of addition of the metal precursor. We found that for the selective oxidation of D-Sorbitol the sequence of addition of the metal precursor had a strong influence on the catalytic results in terms of activity/yield. Moreover, adding Au after the prior addition and reduction of the Pd or Pt metal resulted in the most active catalytic system irrespective of the reaction conditions used. However, yield of desired product was significantly influenced by the presence of the secondary metal (Pd or Pt) and the reaction conditions. Thus, by using atmospheric pressure and conrolled pH conditions, we obtained with Au/Pt catalyst synthesized by method 2 the highest yield to gluconate/gulonate (62%).

The effect of atomic ratio for the Au_xPd_y system was investigated and it was found that a volcano type diagram exists, with Au_6Pd_4 to be the most active catalyst. Moreover, even in the presence of small amounts of the one metal in the presence of the other seems to be enough in order to create an active bimetallic system, more active than the individual metal component catalysts.

About the Authors

LAURA PRATI is presently an Associate Professor in Inorganic Chemistry at the University of Milan. She is a graduate in Chemistry (1983), received her specialisation in “Tecniche Analitiche per la Chimica Organica Fine” from the Politecnico of Milan in 1985 and was awarded a PhD in Industrial Chemistry in 1988. Her main interest deals with catalytic hydrogenation and oxidation reactions and she was involved in gold catalytic application since 1996. Particular experience she had acquired in the field of preparation of gold on carbon and its use in liquid phase oxidation.

Nikolaos Dimitratos works as a Postdoc researcher in the Inorganic chemistry department at the University of Milan for the Auricat project (Catalysis by Gold) funded by E.U. He graduated in chemistry (1998) and he received his PhD from Liverpool University in the field of Heterogeneous catalysis. His research is in the field of liquid and gas phase oxidation.

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