Catalysis Letters, Vol. 115, Nos. 3–4, June 2007(© 2007)
DOI: 10.1007/s10562-007-9077-x

# Bimetallic gold/palladium catalysts for the selective liquid phase oxidation of glycerol

Alberto Villa, Claudio Campione, and Laura Prati*

*Dipartimento di Chimica Inorganica Metallorganica e Analitica e Centro CNR, Università degli Studi di Milano, Via Venezian 21, I-20133 Milano, Italy*

Received 20 February 2007; accepted 21 February 2007

A new methodology for the preparation of single phase bimetallic Au–Pd on activated carbon (AC) has been recently developed and now used for preparing Au/Pd catalysts at different atomic ratio. The bimetallic catalysts have been tested in the liquid phase oxidation on glycerol in water using oxygen as the oxidant and compared with monometallic Au and Pd catalysts. We observed that strong synergistic effect is present in a large range of Au/Pd ratio, being maximized for $Au_{90}$–$Pd_{10}$ composition. Gold-rich composition showed an increased durability compared to palladium-rich alloy.

**KEY WORDS:** bimetallic catalyst; selective oxidation; gold; palladium.

## 1. Introduction

Bimetallic catalysts are presently the subject of considerable interest in heterogeneous catalysis due to the fact that their catalytic properties can be superior to monometallic catalysts [1–6].

Gold is very useful as an alloying metal and it has been used with metal such as palladium [1–3, 6–13] and platinum [7, 10, 14–16] for various catalytic reactions. The interest for Au–Pd catalysts has been improved in recent years, as they were found to be superior to pure Pd and Au supported catalysts in various reactions as hydrogenation [17], hydrodechlorination [18, 19] and hydrodesulphuration [20]. Moreover, it has also been reported that they were more active than corresponding monometallic and selective in the liquid phase oxidation of alcohols [21, 22] and polyols [23, 24].

The use of preformed metallic sols as precursor of heterogeneous catalysts appeared to be one of the most tuneable methods for preparing bimetallic nano-particles. In fact, with this method core-shell or alloyed bimetallic particles have been prepared by reduction of metal salts [11, 18, 25–29] using different stabilizers, and reducing methods [16]. However, characterization of supported catalysts often revealed the presence of multiphase that could differently contribute to catalyst activity. We recently set up a two-step methodology allowing the preparation of single alloyed bimetallic $Au_{60}$–$Pd_{40}$ catalyst [12]. Comparing Au–Pd with Au and Pd catalysts in the liquid phase oxidation of glycerol, the high enhancement of activity could be univocally addressed to the presence of alloyed phase.

In this study we used the same preparation method for preparing Au–Pd on activated carbon (AC) catalysts at different atomic ratio in a range of 95:5–20:80. The liquid phase oxidation for glycerol has been carried out with the aim of establishing the contribution of each composition with respect to the catalytic activity.

## 2. Experimental section

### 2.1. Materials

$NaAuCl_4 \cdot 2H_2O$, $Na_2PdCl_4$ were from Aldrich (99.99% purity) and AC 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) (Mw = 13,000–23,000 87–89% hydrolysed,) from Aldrich were used. Gaseous oxygen from SIAD was 99.99% pure.

### 2.2. Catalyst preparation

### 2.2.1. Monometallic catalysts

*Au sol*: solid $NaAuCl_4 \cdot 2H_2O$ (0.043 mmol) and PVA solution (410 $\mu$L) was added to 130 mL of $H_2O$. After 3 min, $NaBH_4$ solution (1.3 ml) was added to the yellow solution under vigorous magnetic stirring. The ruby red

---

*To whom correspondence should be addressed.
E-mail: Laura.Prati@unimi.it

Au(0) sol was immediately formed. An UV-visible spectrum of the gold sol was recorded, showing complete reduction of Au (III) species.

*Pd sol*: $Na_2PdCl_4 \cdot 2H_2O$ (0.043 mmol) and PVA solution (880 $\mu$L) was added to 130 mL of $H_2O$. After 3 min, $NaBH_4$ solution (860 $\mu$L) was added to the yellow–brown solution under vigorous magnetic stirring. The brown Pd(0) sol was immediately formed. An UV-visible spectrum of the palladium sol was recorded for ensuring the complete reduction of Pd (II).

Within a few minutes of their generation, the colloids (acidified at pH 2, by sulphuric acid) were immobilised by adding carbon under vigorous stirring. The amount of support was calculated as having a final metal loading of 1%wt.

### 2.2.2. *Au/Pd bimetallic catalysts*

Bimetallic catalysts have been prepared following the procedure reported in [12]. As an example the preparation of $Au_{60}$–$Pd_{40}$ is reported. $NaAuCl_4 \cdot 2H_2O$ (0.072 mmol) was dissolved in water ($10^{-4}$ M) and PVA (2% w/w) was added (Au/PVA 1:1 wt/wt). The yellow solution was stirred for 3 min and 0.1 M $NaBH_4$ (Au/$NaBH_4$ 1:3 mol/mol) was added under vigorous magnetic stirring. The ruby red Au(0) sol was immediately formed. An UV-visible spectrum of the gold sol was recorded to check the complete $AuCl_4^-$ reduction and the formation of Plasmon peak. Within a few minutes of sol generation, the gold sol was immobilised by adding activated carbon (acidified until pH 2 by sulphuric acid) under vigorous stirring. The amount of support was calculated as having a gold loading of 0.73% wt when Au/Pd was prepared. After 2 h the slurry was filtered, the catalyst washed thoroughly with distilled water (neutral mother liquors). ICP analyses were performed on the filtrate using a Jobin Yvon JV24 to verify the total metal loading on carbon. The Au/AC was then dispersed in water; $Na_2PdCl_4$ (10%wt in Pd solution) (Pd final concentration $10^{-4}$ M) and PVA solution (Au/PVA 1:1 wt/wt) were added. $H_2$ was bubbled (50 mL/min) under atmospheric pressure and room temperature for 2 h. After additional 18 h, the slurry was filtered, the catalyst washed thoroughly with distilled water. ICP analyses were performed on the filtrate using a Jobin Yvon JV24 to verify the metal loading on carbon. 1% wt has been the total metal loading. For other composition relative quantities of Au(III) and Pd (II) salts have been varied according to table 1.

### 2.3. *Catalytic test*

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 3 atm. The oxygen uptake was followed by a mass flow controller connected to a PC through an A/D board, plotting a flow/time diagram. An aqueous solution of glycerol (0.3 M, 10 mL total volume) was prepared and mixed with the desired amount of NaOH and catalyst (glycerol/metal = 1000 mol/mol, NaOH/glycerol = 4 mol/mol). The reactor was pressurised at 300 kPa of $O_2$ and thermostatted at the appropriate temperature. Once the required temperature (50 °C) was reached, the gas supply was switched to oxygen and the monitoring of the reaction started. The reaction was initiated by stirring. 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 in terms of TOFs (based on total metal loading).

## 3. Results and discussion

Recently we have shown an extraordinary effect due to the presence of alloyed phase on catalytic performance of bimetallic $Au_{60}$–$Pd_{40}$/AC catalyst in glycerol oxidation [12]. On recycling, we observed an almost stable conversion up to the 4th run (less than 4% loss), then a decrease of about 6% (10% on initial conversion) after 6 cycles additionally. ICP analyses of collective filtrate evidenced a leaching of Pd of 4% after 10 recycles of the catalyst. No leaching of Au was detected. However, TEM-EDX measurements on used catalyst showed that the leaching of Pd differed from particle to particle, depending on particle size and leading to a multiphase catalyst. As catalytic activity did not follow the expected decrease on the basis of metal leaching, a different contribution to catalytic activity of different phases could be envisaged [13]. Therefore, in the present paper we reported on the preparation and the catalytic test of bimetallic Au–Pd of various Au/Pd ratio. We tested these catalysts in the selective oxidation of glycerol (0.3 M) solution, glycerol/NaOH = 4 mol/mol, glycerol/metal = 1000, $pO_2$ = 3 atm, T = 50 °C).

Using the same procedure reported in [12], that allowed us to prepare a single phase bimetallic catalyst for Au–Pd and also for Au–Pt [22], we prepared five catalysts varying the nominal Au/Pd molar ratio from 95/5 to 20/80.

Figure 1 reported the TOF data after 15 min versus of the Au/Pd molar ratio.All the bimetallic systems showed activity higher than the corresponding Au and Pd monometallic catalysts. Referring to system $Au_{60}$–$Pd_{40}$ tested under the same conditions, we observed that by increasing the gold content the activity increased, reaching a maximum value for $Au_{90}$–$Pd_{10}$. TOF in fact increased from 3482 $h^{-1}$ for $Au_{60}$–$Pd_{40}$ to 4400 $h^{-1}$ for $Au_{90}$–$Pd_{10}$ then it declined to 2962 $h^{-1}$ for $Au_{95}$–$Pd_5$

Table 1
Summary of different amount of precursors

| Au/Pd ratio | $NaAuCl_4 \cdot 2H_2O$ (mmol) | $Na_2PdCl_4$ (mmol) |
|---|---|---|
| $Au_{95}$–$Pd_5$ | 0.098 | 0.005 |
| $Au_{90}$–$Pd_{10}$ | 0.095 | 0.011 |
| $Au_{80}$–$Pd_{20}$ | 0.089 | 0.022 |
| $Au_{60}$–$Pd_{40}$ | 0.072 | 0.048 |
| $Au_{20}$–$Pd_{80}$ | 0.032 | 0.129 |

(volcano type behaviour). This latter value resulted similar to the $Au_{60}$–$Pd_{40}$system. On the contrary for higher Pd content than in $Au_{60}$–$Pd_{40}$, the activity drastically decreased and the TOF varied from 3482 $h^{-1}$ for $Au_{60}$–$Pd_{40}$ to 1241 $h^{-1}$ for $Au_{20}$–$Pd_{80}$, similar to the value showed by pure Pd (1000 $h^{-1}$) (figure 1). From these results it appeared that the highest activity corresponded to a rich Au system ($Au_{90}$–$Pd_{10}$). This result is in agreement to the previous observation that partial leaching of Pd revealed in the recycling of $Au_{60}$–$Pd_{40}$system can lead to Au-rich phases that, resulting more active than initial $Au_{60}$–$Pd_{40}$ phase, could reduce the expected decline of activity on recycling.

Figure 2 reported the profile of conversion versus time for all bimetallic and monometallic catalysts. Au and Pd behaved similarly in terms of initial activity (TOF about 1000 $h^{-1}$), but a fundamental difference between them can be derived, observing the conversion profiles. In fact Pd catalyst deactivated rapidly, whereas gold didn't show this phenomenon, according to previous result [30]. Looking at the conversion profiles for bimetallics, some other considerations can be underlined: $Au_{60}$–$Pd_{40}$ and $Au_{95}$–$Pd_5$ showed similar initial rate, and also similar conversion profile. Although $Au_{90}$–$Pd_{10}$showed the highest TOF, it behaved similarly to $Au_{80}$–$Pd_{20}$ reaching full conversion almost in the same time. On the contrary $Au_{20}$–$Pd_{80}$ presented a drastically lower activity than all the other Au/Pd ratio

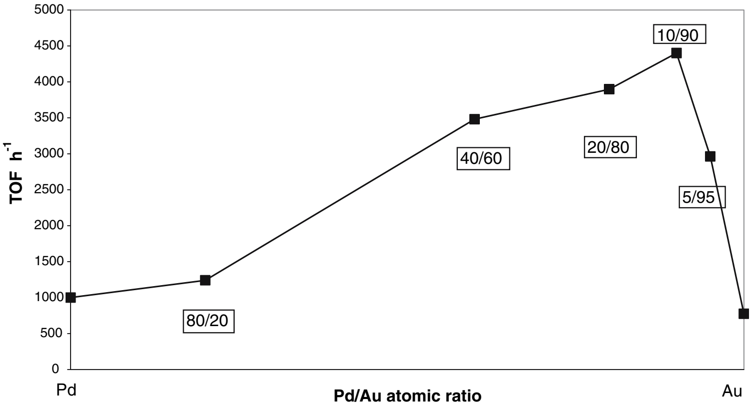

Figure 1. TOFs of $Au_xPd_y$ bimetallic catalysts in glycerol oxidation. Reaction conditions: glycerol 0.3 M, glycerol/NaOH = 4 mol/mol, glycerol/metal = 1000, $pO_2$ = 3 atm, T = 50 °C.

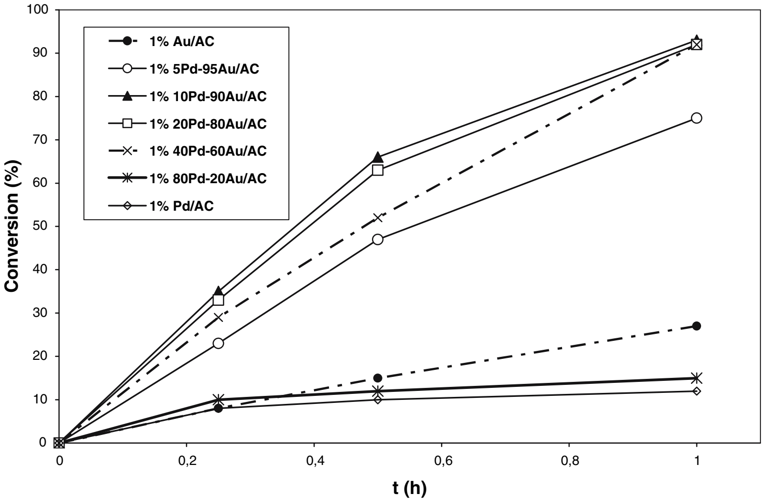

Figure 2. Glycerol oxidation using Au, Pd and $Au_x$–$Pd_y$ catalysts. Reaction conditions: glycerol 0.3 M, glycerol/NaOH = 4 mol/mol, glycerol/metal = 1000, $pO_2$ = 3 atm, T = 50 °C.

Table 2
Selectivity to glyceric and glycolic acids in glycerol oxidation[a]

| Catalyst | S90 Glycerate[b] | S90 Glycolate[c] |
|---|---|---|
| 1%Au/AC | 68 | 25 |
| 1%($Au_{95}$–$Pd_5$)/AC | 75 | 20 |
| 1%($Au_{90}$–$Pd_{10}$)/AC | 75 | 19 |
| 1%($Au_{80}$–$Pd_{20}$)/AC | 76 | 18 |
| 1%($Au_{60}$–$Pd_{40}$)/AC | 78 | 18 |
| 1%($Au_{20}$–$Pd_{80}$)/AC | 79[d] | 15[e] |
| 1%Pd/AC | 80[d] | 12[e] |

[a] Reaction conditions: glycerol 0.3 M, glycerol/NaOH = 4 mol/mol, glycerol/metal = 1000, $pO_2$ = 3 atm, T = 50 °C.
[b] Selectivity to glyceric acid 90% conversion.
[c] Selectivity to glycolic acid 90% conversion.
[d] Selectivity to glyceric acid at 50% conversion.
[e] Selectivity to glycolic acid at 50% conversion.

systems, even a higher TOF with respect to pure Au and Pd. However observing the conversion profile (figure 2) we highlighted a similar deactivation phenomenon as seen for pure Pd. In fact the conversion profile is the same as Pd/AC. Therefore after 1 h of reaction, pure Au resulted more active (figure 2). This latter observation could explain why a palladium-rich composition appeared to be less active than gold-rich alloy.

In table 2 the selectivity to glyceric acid and to the sum of glyceric and tartronic acids of mono and bimetallic systems at 90% conversion is reported (a part from Pd and $Au_{20}$–$Pd_{80}$ for which we reported selectivities at 50%, the 90% conversion being not reachable). In general, selectivities to glycerate appeared almost independent to Au/Pd ratio. It should be observed, however, that Pd content plays an important role in reducing oxidative C-C bond cleavage leading to glycolate, pure Au showing the highest S90 to glycolate [31].

## 4. Conclusions

By using a two step methodology useful for producing alloyed Au–Pd systems, we prepared a series of $Pd_x$–$Au_y$/AC and we tested them in the liquid phase oxidation of glycerol. All the bimetallic catalysts have an initial activity (TOF) higher than monometallics. However for Pd rich composition (Au/Pd = 20/80) we observed deactivation similarly to pure Pd. A first, important conclusion can then be stated: gold has a beneficial effect in terms of durability of the catalyst not only when is pure but also when alloyed with palladium. However there is a limit of composition that lies between a Au/Pd ratio of 20/80 and 60/40.

Investigating the Au/Pd different ratio from 95/5 to 20/80 we found that the activity increases with increasing gold loading up to $Au_{90}Pd_{10}$, thereafter it declines for higher gold content. This finding is in agreement with the observed high activity of recycled catalyst although it underwent to a partial Pd leaching [28]. Varying the Au-Pd molar ratio there is not an obvious change in selectivity to glyceric acid: all bimetallic systems and pure Pd are more selective than gold.

## References

[1] M.C. Daniel and D. Astruc, Chem.Rev. 104 (2004) 293.
[2] Toshima N., Wang Y. (1993) Chem. Lett. 1611.
[3] N. Toshima, M. Harada, Y. Yamazaki and K. Asakura, J. Phys. Chem. 96 (1992) 9927.
[4] A.F. Lee, C.J. Baddeley, C. Hardacre, R.M. Ormerod, R.M. Lambert, G. Schmid and H. West, J. Phys. Chem. 99 (1995) 6096.
[5] N. Toshima, M. Harada, T. Yonezawa, K. Kushihashi and K. Asakura, J. Phys. Chem. 95 (1991) 7448.
[6] T. Yonezawa and N. Toshima, J. Mol. Catal. 83 (1993) 167.
[7] J. Turkevich and G. Kim, Science 169 (1970) 873.
[8] Y. Mizukoshi, K. Okitsu, Y. Maeda, T.A. Yamamoto, R. Oshima and Y. Nagata, J. Phys. Chem. 101 (1997) 7033.
[9] Y. Mizukoshi, T. Fujimoto, Y. Nagata, R. Oshima and Y. Maeda, J. Phys. Chem. B 104 (2000) 6028.
[10] G. Schmid, A. Lehnert, J.-O. Malm and J.-O. Bovin, Angew. Chem. Int. Ed. Engl. 30 (1991) 874.
[11] V.I. Parvulescu, V. Parvulescu, U. Endurushat, G. Filoti, F.E. Wagner, C. Kubel and R. Richards, Chem. Eur. J. 12 (2006) 2343.
[12] D. Wang, A. Villa, F. Porta, D. Su and L. Prati, Chemm. Comm. 18 (2006) 1956.
[13] Prati L., Villa A., Porta F., Wang D., Su D. Catal. Today (2006) in press.
[14] C.J. Baddeley, D.A. Jefferson, R.M. Lambert, R.M. Ormerod, T. Rayment, G. Schmid and A.P. Walker, Mater. Res. Soc. Symp. Proc. 272 (1992) 85.
[15] L. Guczi, Catal. Today 101 (2005) 53.
[16] M. Harada, K. Asakura and N. Toshima, J. Phys. Chem. 97 (1993) 5103.
[17] G.C. Bond and A.E. Andrawle, J.Mol.Catal. A 109 (1996) 261.
[18] M. Bonarowska, J. Pielaskez, W. Juszczyk and Z. Karpinsky, J. Catal 195 (2000) 304.
[19] M. Bonarowska, A. Malinowsky, W. Juszczyk and Z. Karpinsky, Appl. Catal. B 30 (2001) 187.
[20] A.M. Venezia, V. La Parola, G. Deganello, B. Pawelec and J.L. Fierro, J. Catal. 215 (2003) 317.
[21] D.I. Enache, J.K. Edwards, P. Landon, B. Solsona-Espriu, A.F. Carley, A.A. Herzing, M. Watanabe, C.J. Kiely, D.W. Knight J. and G.J. Hutchings, Science 311 (2006) 362.
[22] N. Dimitratos, A. Villa, D. Wang, F. Porta, D. Su and L. Prati, J. Catal 244 (2006) 113.
[23] C.L. Bianchi, P. Canton, N. Dimitratos, F. Porta and L. Prati, Today Catal 102 (2005) 203.
[24] N. Dimitratos, F. Porta, L. Prati and A. Villa, Catal. Lett. 9 (2005) 181.
[25] T. Yonezawa and N. Toshima, J. Chem. Soc. Faraday Trans. 91 (1995) 4111.
[26] N. Toshima and T. Yonezawa, New J. Chem. 22 (1998) 1179.
[27] N. Toshima, M. Harada, Y. Yamazaki and K. Asakura, J. Phys. Chem. 96 (1992) 9927.
[28] H. Liu, G. Mao and M. Meng, J. Mol. Catal. 74 (1992) 2775.
[29] L. Guczi, A. Beck, A. Horvath, Z. Koppany, G. Stefler, K. Frey, I. Sajo, D. Bazin and J. Lynch, J. Mol. Catal. A Chem. 204-205 (2003) 545.
[30] M. Rossi and L. Prati, J. Catal. 176 (1998) 552.
[31] L. Prati and F. Porta, J.Catal. 224 (2004) 397.