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Effect of gold addition on Pt and Pd catalysts in liquid phase oxidations

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Single phase Au–Pd and Au–Pt on carbon catalysts have been compared in the liquid phase oxidation of glycerol (representative for polyols) and *n*-octanol (representative for long chain aliphatic alcohol). The observed overall enhancement of catalytic activity appeared to be function of support, substrate and reaction conditions. Effect of substrate structure has been disentangled: synergistic effect between Au and Pt was maximized when polyol-like substrates were oxidized whereas Au–Pd based catalyst showed a more general match.

1. Introduction

Gold as an active catalyst has been extensively studied in the last twenties and research appeared to be still active searching for new applications and also for investigating reaction mechanisms not yet clarified [1–10]. Initial main interest for gold was the complete CO oxidation. Presently a list of reactions of industrial interest has been added [3].

Selective oxidation, particularly in liquid phase, has found in gold metal a great candidate for substituting (or at least improving) Pt or Pd based catalysts that historically represented the most used catalysts for such an application. In fact the big advantage of using gold instead of Pt or Pd metals lies in the enhanced resistance to poisoning of gold with respect to Pd or Pt when O_2 is used as the oxidant [11]. However, gold suffers from a lower activity often related to preparation methods, most of them producing large particle size (diameter over 10 nm).

Carbons (activated carbon, graphite, carbon black) are very appreciable supports from an industrial point of view: they are stable in both acidic and basic environments, and allow an easy recovery of precious metals by burning off when catalyst deactivated. The most useful method to obtain high dispersion of gold on carbons is represented by the metal sol immobilisation [12,13].

Moreover, gold-containing bimetallic catalysts have found relevance in reactions with potential for industrial applications [14] such as vinyl acetate monomer from ethene and acetic acid [15,16], glyoxalic acid from glyoxal [17], glyceric acid from glycerol [18,19], gluconic acid from glucose [20], hydrodesulfurisation of benzothiophene [21] and hydrodechlorination of trichloroethene [22], synthesis of hydrogen peroxide from H_2 and O_2 [23–25], formation of aldehydes from alcohols [25,27], of cyclohexanol/hexanone from cyclohexane [28] and water in fuel cells applications [29].

Potential use of bimetallics are still growing due to a virtually enormous number of different catalysts even if based on a single couple of metals, because of different ratios and preparation methodologies. The main task of bimetallic studies is the correlation between surface and catalytic activity allowing a future design of appropriate catalysts. However, bimetallic catalysts can be relatively non-uniform and can show variations in morphology and particle composition making any correlation difficult and often not reliable.

Therefore, a complete study of bimetallic catalysts involves not only the test of catalytic activity but also a careful study of the preparation method for producing catalyst of definite composition. Moreover, a careful characterization is needed. Very recently we reported on a new preparation of Au–Pd and Au–Pt on carbon catalysts. These two catalysts were fully characterized [19,30] and have been demonstrated to be constituted by a single alloyed phase. Thus they represent two perfectly designed materials for studying the effect of gold on Pd and Pt properties. In this paper we report the application of these two catalysts to the liquid phase of alcohols comparing their catalytic behaviour to the corresponding monometallic. Concerns about the nature of substrate and the reaction conditions in the liquid phase oxidation of alcohols will be presented.

2. Experimental

2.1. Materials

Na_2PdCl_4, K_2PtCl_4, $NaAuCl_4 \cdot 2H_2O$ (purity > 99.0%) and PVA (Mw = 13,000–23,000, 98% hydro-

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lysed) were from Aldrich. Stock aqueous solutions of Na_2PdCl_4 ([Pd] = 0.449 M), K_2PtCl_4 ([Pt] = 0.038 M) were 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 and hydrogen from SIAD was 99.99% pure. Glycerol (88 wt.% solution), *n*-octanol (99.5%) and all the intermediates were from Fluka and *trans* 2-octen-1-ol (97%) from Aldrich. 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%.

2.2. Catalyst preparation

2.2.1. Monometallic sol

Au sol: Solid $NaAuCl_4 \cdot 2H_2O$ (0.043 mmoL) and PVA (2%wt) solution (1.64 mL) were added to 130 mL of H_2O. After 3 min, $NaBH_4$ (0.1 M) solution (1.3 mL) was added to the yellow solution under vigorous magnetic stirring. The ruby red Au(0) sol was immediately formed.

Pd sol: Na_2PdCl_4 stock aqueous solution (0.043 mmoL) and PVA (2%wt) solution (880 mL) were added to 130 mL of H_2O, obtaining a yellow-brown solution. After 3 min, $NaBH_4$ (0.1 M) solution (860 mL) was added under vigorous magnetic stirring. The brown Pd(0) sol was immediately formed.

Pt sol: Solid K_2PtCl_4 (0.051 mmoL) and PVA (2%wt) solution (1.9 mL) were added to 150 mL of H_2O. After 3 min, $NaBH_4$ (0.1 M) solution (1 mL) was added to the colourless solution under vigorous magnetic stirring. The light-grey Pt(0) sol was formed after 30 min.

2.2.2. Immobilisation

Within a few minutes of sol generation, the colloid (acidified at pH 1, by sulphuric acid) was immobilised 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 4 h. ICP analyses were performed on the filtrate using a Jobin Yvon JV24 to verify the metal loading on carbon.

2.2.3. Bimetallic catalysts M–Au on carbon (M = Pd, Pt)

$NaAuCl_4 \cdot 2H_2O$ (0.072 mmoL) was dissolved in 140 mL of H_2O and PVA (2% w/w) was added (0.706 mL). The yellow solution was stirred for 3 min and 0.1 M $NaBH_4$ (2.15 mL) 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 1 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 or 0.60% wt in the case of Au/Pt. 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/C was then dispersed in 140 ml of water; Na_2PdCl_4 (10%wt in Pd solution) (0.0386 mL) or K_2PtCl_4 (6.1×10^{-2} M solution) (0.850 mL) and PVA (2%wt) solution (0.225 mL) 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. One percent wt has been the total metal loading. Catalysts prepared by this procedure have been labelled as 1% M@Au/C.

2.3. Alcohol oxidation

Alcohol oxidations were performed at 50 °C using a glass reactor (30 mL capacity), equipped with heater, mechanical stirrer, gas supply system and thermometer. The solution (0.3 M with or without NaOH/alcohol ratio = 4, moL/moL) was added into the reactor and the catalyst (alcohol/total metal ratio = 1000, moL/moL) was suspended in the solution. The pressure of the oxygen was 3 atm. Once the required temperature (50 °C) was reached, the gas supply was switched to oxygen and the monitoring of the reaction started. Samples were removed periodically.

For glycerol analyses were performed by using HPLC using a column (Alltech OA- 10308, 300 mm × 7.8 mm) with UV and refractive index (RI) detection in serie. 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.

For octanol and octenol a GC-MS and GC (a Dani 86.10 HT Gas Chromatograph equipped with a capillary column, BP21 30 m × 0.53 mm, 0.5 μm Film, made by SGE), were used. Products and by-products were identified by comparison with authentic samples. For the quantification of the reactant/products the external calibration method was used. The activities of the catalysts were reported based on TOF (based on total metal loading).

3. Results and discussion

Palladium and Platinum when modified by gold have often shown a strong enhancement of their activity [31–33]. However, the support and the reaction itself have to be considered as a part of this effect. In fact, we normally explain the sometime unexpected catalytic activity of bimetallics by means of electronic and geometric modifications occurring between metals [30,34], interacting themselves with the support. Moreover, the overall catalytic result depends on the match between the above effects and reaction requirements. Thus, conflicting results could be obtained using the same catalyst in different reactions or under different conditions. As an example we recently reported on the different behaviour of Au-Pd metal particles supported on organic resins and active carbon in n-butanol oxidation [35] being the effect positive when carbon is used as the support and negative when a resin was used. Moreover, supported on carbon, Au–Pt nanoparticles showed opposite synergistic effect in oxidizing different substrate, being the effect positive in sorbitol [36] and negative in benzyl or cinnamyl alcohols [30] oxidations.

We prepared bimetallic catalysts following a procedure that ensures the formation of a single alloyed phase and a good metal dispersion for both Au–Pd and Au–Pt couples [19,30]. Pd or Pt metallic sol was generated in the presence of Au/C using H_2 as reducing agent instead of $NaBH_4$. Slowing down the reduction rate of the second metal represented the key for avoiding segregation of Pd or Pt, thus producing single alloyed phase catalysts. Therefore, the catalytic testing of these catalysts can be used as a probe for correlating the activity and the active surface species. By varying the substrate and the reaction conditions we could also be able to get some new findings in the activity of the Au, Pd, Pt and Au–Pd or Au–Pt catalysts in the liquid phase oxidation of alcohol using oxygen as the oxidant.

Catalysts were 1%wt loaded of total metal and presented similar particle distribution (centred at 2.5–3.5 nm) and an alloyed phase of similar composition (M_6Au_4, M = Pd,Pt). Glycerol was used as representative for polyol molecules and *n*-octanol as long chain aliphatic alcohols. Oxidations have been carried out using the following experimental conditions: 0.3 M solution, 50 °C, 3 atm O_2, substrate/total metal ratio = 1000 moL/moL. Note that especially using octanol as the substrate the ratio substrate/metal = 1000 moL/moL represents a quite high value compared with normally reported values in the literature, but we were not actually interested in productivity but to highlight any possible deactivation phenomena as already found in this reaction [30].

Under the above conditions glycerol did not undergo oxidation neither in the presence of mono- nor bimetallic catalysts. *N*-octanol showed poor conversions, (table 1). As expected gold was inactive in the absence of a base; whereas monometallic Pd was as active as monometallic Pt. Considering bimetallics, 1% Pd@Au/C and 1% Pt@Au/C did not show relevant differences, being a slight positive synergistic effect detected with respect to monometallic Pd or Pt catalysts. This result was however unexpected as our previous study [30] showed similar activity of mono and bimetallic catalysts in n-octanol oxidation. A possible explanation could be based on the use of different experimental conditions. Thus we performed some experiments by varying the oxygen partial pressure (1.5, 3 atm) and the temperature (50, 60 °C) (table 2). From these results we could conclude that the influence of pO_2 is negligible in terms of activity and have slight effect in reducing selectivity to aldehyde. On the contrary a strong effect was observed considering the temperature: beside the expected increase of activity, carrying out the reaction at 60 °C instead of at 50 °C, the high selectivity to aldehyde was lost, at the benefit of carboxylic acid formation. Interestingly the main by-product at 50 °C was represented by ester whereas at 60 °C by carboxylic acid. Following conversion versus time (4 and 8 h), operating at 60 °C and 1.5 atm the subsequent oxidation of aldehyde to carboxylic acid appeared to take place and catalyst progressively deactivated (conversion after 4 h = 19% and after 8 h = 28%). Thus, the beneficial effect of increasing the temperature in terms of activity has been lost in term of selectivity and, most importantly, overall activity has been reduced due to deactivation caused by irreversible octanoic acid adsorption [30]. Therefore, by lowering the temperature (from 60 °C to 50 °C) and increasing the substrate/metal ratio (from 500 to 1000 moL/moL) we were able to highlight that poor activities of Au–Pt and Au–Pd catalysts in oxidizing *n*-octanol in aqueous phase is principally due to an intrinsic poor activity toward this molecule. Deactivation by irreversible product adsorption could also occur under certain conditions (higher temperature and lower substrate/metal ratio). For stressing these two factors we also tested the catalysts with a similar but more activated substrate as 2-octen-1-ol. Results are showed in table 3. Reaction pathway here resulted more complex as the presence of a double bond in allylic position makes isomerisation and hydrogen transfer reactions to be possible. In fact, beside 2-octenal, n-octanal and 3-octen-1-ol were detected as products. Monometallic Pd and Pt behaved similarly showing very poor activities and considerations on selectivity could not be derived, as a variety of products were present. The comparison between Au–Pd and Au–Pt catalysts was more interesting. Isomerisation product (3-octen-1-ol) was the main product in all the cases but saturated octanal was present only when Au–Pd catalyst was used. Activity of 1%Pt@Au/C resulted considerably lower than that obtained with 1%Pd@Au/C catalyst, even if positive synergistic effect was revealed in both cases.

For Au–Pd system it is worth noting that Au acted as promoter to isolate Pd monomer sites [33] thus also limiting oxygen coverage [31]. This means that in the case of palladium we could expect an enhanced resistance to oxygen poisoning by alloying Pd with gold. Gold is also reported to reduce Pt self-poisoning [37,38].

Table 1
Catalytic data for 1-Octanol oxidation

Catalyst	Conversion[a]	Selectivity octanal[b]	TOF[c] (h^{-1})
1% Au/C	–	–	–
1% Pd/C	2	70	8
1% Pt/C	2	> 99	10
1% Pd@Au/C	17	70	15
1% Pt@Au/C	20	75	22

[a] Reaction conditions: 1-Octanol 0.3 M, (substrate/metal = 1000 moL/moL), pO_2 = 3 atm, T = 50 °C, reaction time = 8 h.
[b] Ester present as secondary product.
[c] TOF calculated on the basis of total metal.

Table 3
Catalytic data for 2-Octen-1-ol oxidation

Catalyst	Conversion[a]	Selectivity			TOF[b] (h^{-1})
		2-Octenal	3-Octen–1-ol	Octanal	
1% Au/C	–	–	–	–	–
1% Pd/C	3	–	–	–	24
1% Pt/C	1	–	–	–	5
1% Pd@Au/C	97	20	58	20	552
1% Pt@Au/C	8	10	90	–	39

[a] Reaction conditions: 2-Octen-1-ol 0.3 M, (substrate/metal = 1000 moL/moL), pO_2 = 3 atm, T = 50 °C, reaction time = 2 h.
[b] TOF calculated on the basis of total metal.

In consequence, in both cases we could exclude poisoning of the catalyst due to the use of oxygen. Excluding also irreversible adsorption of carboxylic acids that could deactivate the catalyst because of the high selectivity to aldehyde, we could ascribe the activity shown by the two catalysts to their intrinsic activity. Using *n*-octanol as the substrate, 1%Pd@Au/C and 1%Pt@Au/C showed strong differences. We observed an extraordinary enhancement of activity by using Au–Pd whereas the effect of adding gold to Pt resulted in only a poor increasing of activity. Synergistic effects are normally explained by electronic and geometric modification occurring in metal particles, but the results obtained indicated that substrate requirements represent an important factor. A possible mismatch between electronic/geometric effects obtained by adding gold to Pt and the octanol-like skeleton molecule requirements could occur, limiting the overall effect on the catalytic activity.

On this basis we supposed that also the specific reaction conditions could play an important role especially if they have been able to modify electronic constrains of the reaction. Hence, we tested the catalysts under basic conditions knowing that the accepted mechanism for metal catalyzed dehydrogenation process in aqueous solution involves hydride abstraction and subsequent oxidation by O_2 [39].

Under these conditions glycerol as well as *n*-octanol underwent oxidation (tables 4 and 5). Monometallic gold became active showing similar activity in glycerol and *n*-octanol oxidation. Also Pd/C behaved similarly in the two cases but activity was very low. On the contrary Pt/C appeared more active than gold when glycerol was used as substrate, whereas less active when octanol was oxidized. A positive, strong synergistic effect was observed with both substrate using either 1%Pd@Au/C or 1%Pt@Au/C, the most active catalyst resulting Au–Pt in glycerol oxidation whereas Au–Pd in *n*-octanol oxidation. As already observed in glycerol oxidation differences in selectivity were observed: Au–Pt based catalyst showed a higher selectivity to glycolate (C–C bond scission) whereas Au–Pd toward glycerate. It should also be noted that under basic condition *n*-octanol produced as main product octanoate. The formation of Na-salt prevented the irreversible adsorption of organic acid thus avoiding deactivation.

These results confirmed that the overall catalytic effect observed when gold was alloyed to Pd or Pt not only depends on the support and the substrate but also on the specific reaction conditions. The final activity of the catalyst is the result of the matching of all the effects involved.

Beneficial effect of using basic conditions was also found using 2-octen-1-ol (table 6) as the substrate. 1%Pd@Au/C resulted extraordinary active but we observed a positive synergistic effect also for 1%Pt@Au/C.

Table 2
Influence of reaction parameters in *n*-octanol oxidation using 1% Pt@Au/C

pO_2 (atm)	Temperature (°C)	Time (h)	Conversion[a]	Selectivity octanal	Selectivity octanoic acid
3	50	4	13	70	–
		8	20	75	–
3	60	4	20	38	31
1.5	50	4	10	85	–
1.5	60	4	19	25	34
		8[b]	28	28	31

[a] Reaction conditions: 1-Octanol 0.3 M, Octanol/metal ratio = 1000 moL/moL.
[b] From ref. 30.

Table 4
Catalytic data for glycerol oxidation/NaOH

Catalyst	Conv[a]	Selectivity					TOF[b] (h^{-1})
		Glyceric acid	Glycolic acid	Oxalic acid	Tartronic acid	Hydroxy pyruvic acid	
1% Au/C	21	66	24	2	8	0	845
1% Pd/C	3	–	–	–	–	–	61
1% Pt/C	42	48	46	2	4	0	1688
1% Pd@Au/C	79	71	11	2	13	3	3261
1% Pt@Au/C	88	61	23	2	14	0	3455

[a] Reaction conditions: glycerol 0.3 M, NaOH 4 eq, (substrate/metal = 1000 moL/moL), pO_2 = 3 atm, T = 50 °C, reaction time 15 min.
[b] Calculation of TOF (h^{-1}) based on total metal.

Table 5
Catalytic data for 1-Octanol/NaOH oxidation

Catalyst	Conversion[a]	Selectivity octanoic acid	TOF[b] (h^{-1})
1% Au/C	23	96	58
1% Pd/C	2	97	8
1% Pt/C	4	90	10
1% Pd@Au/C	93	98	413
1% Pt@Au/C	62	78	210

[a] Reaction conditions: 1-Octanol 0.3 M, NaOH 4 eq, (substrate/metal = 1000 moL/moL), pO_2 = 3 atm, T = 50 °C, reaction time = 4 h.
[b] Calculation of TOF (h^{-1}) based on total metal.

Table 6
Catalytic data for 3-Octen-1-ol/NaOH oxidation

catalyst	Conversion[a]	Selectivity 2-Octenal	TOF[c] (h^{-1})
1% Au/C	1	–	–
1% Pd/C	–	–	–
1% Pt/C	–	–	–
1% Pd@Au/C	98[b]	–	11741
1% Pt@Au/C	16	16	800

[a] Reaction conditions: 2-Octen-1-ol 0.3 M, NaOH 4 eq, (substrate/metal = 1000 moL/moL), pO_2 = 3 atm, T = 50 °C, reaction time 15 min.
[b] Reaction time 5 min.
[c] Calculation of TOF (h^{-1}) based on total metal.

4. Conclusion

We prepared single alloyed phase catalysts for studying the effect of gold on Pt or Pd on carbon catalysts in the liquid phase of alcohols using oxygen as the oxidant. Glycerol, *n*-octanol and 2-octen-1-ol have been used as substrates. Au–Pd and Au–Pt catalysts have shown different behaviour depending on reaction conditions and substrate. When non-basic conditions were used Au–Pd and Au–Pt behaved differently, being the synergistic effect more evident for Au-Pd with activated alcohol (2-octen-1-ol). Glycerol did not undergo oxidation.

On the contrary by operating under basic conditions (NaOH) we observed a general enhancement of activity using all the substrate. Strong positive synergistic effect was present between gold and Pt or Pd in the case of glycerol confirming that Au–Pt system is a very active catalyst in oxidizing polyols as shown for sorbitol [36]. Conversely, by using octanol-skeletal molecule Au–Pd resulted more active than Au–Pt. Excluding deactivation phenomena as poisoning by oxygen or products, we addressed the observed activity to the match between the substrate structure and electronic/geometric modifications caused by alloying gold to Pd or Pt.

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