



Au–Pd/AC as catalysts for alcohol oxidation: Effect of reaction parameters on catalytic activity and selectivity

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Abstract

The oxidation of different alcohols with molecular oxygen in water has been investigated using a range of activated carbon-supported Au-Pd bimetallic catalysts. The effect of the Au-Pd ratio on the conversion and selectivity was observed and a synergistic effect is present in a large range of the Au-Pd ratio, being maximized for Au₈₀-Pd₂₀ composition instead of Au₉₀-Pd₁₀ shown in glycerol oxidation [1]. Moreover the enhancement of conversion observed by adding a base resulted greater for gold-rich catalysts rather than for palladium-rich ones.

The effect of the alcohol concentration and the metal/substrate ratio in the presence or the absence of the base was also studied revealing substantial differences in terms of both activity and selectivity. At 1 M concentration under biphasic conditions benzyl alcohol has been selectively oxidized to benzaldehyde (S₉₀=98%) even in the presence of NaOH with a TOF of 18000h⁻¹ using Au₆₀-Pd₄₀/AC as the catalyst.

Keywords: Gold – Palladium alloy, Alcohol oxidation

1. Introduction

The catalytic oxidation of alcohols with molecular oxygen/air or hydrogen peroxide instead of stoichiometric amounts of inorganic or organic oxidants is a crucial process for the synthesis of fine chemicals [2, 3]. The advantage of using such oxidants lies in the formation of water as the sole co-product and the low cost of the oxygen/air.

Different catalysts (homogeneous and heterogeneous) have been investigated in the alcohol oxidation using molecular oxygen or hydrogen peroxide in the liquid phase [4-15].

Supported gold has been demonstrated to be an active catalyst for oxidizing alcohols and polyols in the presence of O₂ [16-21] showing higher resistance to poisoning than Pt or Pd. In particular different groups showed that adding Au to Pd and Pt catalysts improves not only the catalytic activity and selectivity to the desired product [22],

but also the resistance to the deactivation appears to be enhanced [23-25]. We recently set up a two step methodology allowing the preparation of a single phase alloyed bimetallic Au₆₀-Pd₄₀ catalyst [26]. Comparing Au₆₀-Pd₄₀ with Au and Pd catalysts in the liquid phase oxidation of glycerol and alcohols [26, 27], the high enhancement of the activity could be univocally addressed to the presence of alloyed phase and in some cases the use of the base could be avoided (ie. benzyl, cinnamyl .. [27]). Furthermore with the same preparation method we prepared Au-Pd catalysts at different atomic ratio in the range of 90:10-20:80 [1, 28]. We showed that with this technique it's possible to obtain a single alloyed phase only in determinate range of Au-Pd ratio (6/4 to 9/1) and that the catalyst structure can be unambiguously correlated with the catalytic performance [28]. In fact any segregation or inhomogeneity weakens the synergistic effects of bimetallic catalysts.

In this paper we examine the effect of the Au-Pd ratio in Au-Pd/AC catalysts on the catalytic performance in the liquid phase oxidation of alcohols (allylic, benzylic or aliphatic) extending our previous study on the oxidation of glycerol [1, 28]. We studied the role and the effect of the base on activity and selectivity. In fact the role of the base is still a matter of study: it seems to be involved in the first step of the oxidative process, the hydride abstraction, and promoting the formation of the corresponding carboxylate by the hydration of the aldehyde intermediate [29].

Recently two different mechanisms of Au and Pd supported nanoparticles (NPS) in the alcohol oxidation have been highlighted [30-34]. The most relevant difference is that in the case of Pd the rate determining step is represented by the transfer of H-atom to the β -carbon of the adsorbed alkoxide forming the aldehyde and a Pd-hydride species, whereas with Au the rate determining step involves the H-atom abstraction by a superoxo-like oxygen species adsorbed on Au. Thus the effect of the base is expected to be different in the two cases. Moreover, this difference can be used to clarify the mechanism of bimetallic Au-Pd systems.

The effect of the alcohol concentration and the metal/substrate ratio in the presence or the absence of the base was also studied revealing substantial differences in terms of both activity and selectivity.

2. Experimental Section

2.1. Materials

$\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$, Na_2PdCl_4 were from Aldrich (99.99% purity) and the activated carbon from Camel (X40S; SA = 900–1100 m²/g; PV = 1.5 ml/g; pH 9–10). Before being used 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 by subsequent heating step (4 hours at 150°C) to be < 3%. NaBH_4 of purity > 96% from Fluka, polyvinylalcohol (PVA) (Mw = 13,000–23,000 87–89% hydrolyzed,) from Aldrich were used. Gaseous oxygen from SIAD was 99.99% pure.

2.2. Catalyst preparation

2.2.1. Monometallic catalysts

Au sol: Solid $\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$ (0.043 mmol) and 410 μl PVA solution were added to 130 ml of H_2O . After 3 min, 1.3 ml of 0.1M NaBH_4 solution was added to the yellow solution under vigorous magnetic stirring. The ruby red Au(0) sol was immediately formed. An UV-visible spec-

trum of the gold sol was recorded, showing a complete reduction of Au (III) species.

Pd sol: Solid Na_2PdCl_4 (0.043 mmol) and 880 μl PVA solution (2% w/w) (Pd/PVA 1:1 wt/wt) were added to 130 ml of H_2O . After 3 min, 860 μl of 0.1M NaBH_4 solution 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 few minutes from their generation, the colloids (acidified at pH 2, by sulphuric acid) were immobilized by adding carbon under vigorous stirring. The amount of support was calculated in order to obtain a final metal loading of 1%wt (on the basis of quantitative loading of the metal on the support).

2.2.2. Au/Pd Bimetallic catalysts

Bimetallic catalysts have been prepared following the procedure reported in [28].

The preparation of $\text{Au}_{60}\text{-Pd}_{40}$ is reported as an example. Solid $\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$ (0.072 mmol) was dissolved in 140ml of water (final 10^{-4}M) and 0.706 ml of PVA (2% w/w) was added (Au/PVA 1:1 wt/wt). The yellow solution was stirred for 3 minutes and 2.9 ml of 0.1 M NaBH_4 (0.285 mol, 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 the plasmon peak. Within a few minutes of sol generation, the gold sol was immobilized 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. After 2 h the slurry was filtered, the catalyst was thoroughly washed 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 0.73% wt Au/C prepared was then dispersed in 140 ml of water; Na_2PdCl_4 (0.048mol) and 0.225 ml of PVA solution (0.2% w/w) (Au/PVA 1:1 wt/wt) were added. H_2 has been bubbled (50 ml/min) under atmospheric pressure and room temperature for 2 h. After additional 18 h, the slurry was filtered, the catalyst was thoroughly washed with distilled water. ICP analyses were performed on the filtrate using a Jobin Yvon JV24 to verify the quantitative metal loading on carbon. The final total metal loading was 1% wt. For the other compositions relative quantities of Au(III) and Pd (II) salts have been varied according to the values reported in Table 1.

Table 1: Summary of different amount of precursors

Au/Pd ratio	NaAuCl ₄ ·2H ₂ O (mmol)	Na ₂ PdCl ₄ (mmol)
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

2.3. Catalytic test

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 1.5 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. Alcohol (0,15 -1 M) and the catalyst (substrate/ metal = from 500 up to 40000 mol/mol) were mixed in distilled water (total volume 10 ml) with/without the addition of the appropriate amount of NaOH (alcohol/NaOH = 1 mol/mol). The reactor was pressurized at the desired pressure of O₂ and thermostatted at 60°C. The reaction does not start during the heating up as verified by sampling when the reaction temperature was reached without stirring (t=0). The reaction was initiated by stirring. After the end of reaction the catalyst was filtered off and the product mixture was extracted with toluene. Recoveries were always 98%±3 with this procedure. For the identification and analysis of the products a GC-MS and GC (a Dani 86.10 HT Gas Chromatograph equipped with a capillary column, BP21 30m x 0.53mm, 0.5 µm Film, made by SGE) were used. Comparison with authentic samples was used. For the quantification of the reactant-products the calibration method using an external standard was employed

2.4. Catalyst characterisation

The metal content was checked by ICP analysis of the filtrate or alternatively directly on catalyst after burning off the carbon, on a Jobin Yvon JY24.

Morphology and microstructures of the catalysts are characterized by TEM. The powder samples of the catalysts were ultrasonically dispersed in ethanol and mounted onto copper grids covered with holey carbon film. A Philips CM200 FEG electron microscope, operating at 200 kV and equipped with a Gatan Tridiem imaging filter, was used for TEM observation. EDX analysis was performed in the same microscope using a DX4 analyzer system (EDAX).

3. Result and discussion

Recently we have shown an extraordinary synergistic effect, due to the presence of the alloyed phase, on the catalytic performance of bimetallic Au₆₀-Pd₄₀/AC catalyst in the liquid phase oxidation of glycerol [26] and alcohols [27]. Furthermore with the same procedure we prepared

Table 2: Statistical Median and Standard Deviation of particle size analysis for Au, Pd and Au/Pd catalysts

	Au	Au:Pd ^a				Pd
		90:10	80:20	60:40	20:80	
Statistical median (nm)	2.98	2.90	2.89	3.45	3.72	3.94
Standard deviation (σ)	1.31	1.30	1.28	1.40	1.36	1.15

a)→from [ref 28]

Au-Pd with varying Au/Pd ratios [1, 28]. A full characterization of these catalysts has been already reported elsewhere [28]. The statistical median value of particle size and the standard deviation for all the catalysts are listed in Table 2. All the catalysts show almost the same particles size distribution as the TEM image reported in Figure 1. We found that the three catalysts with Au:Pd ratios of 9:1, 8:2 and 6:4 consist of a single phase alloy whereas the Au:Pd = 2:8 catalyst showed inhomogeneity of the structure and Pd segregation was detected. In Figure 2 the left half represents a typical morphology of this catalyst and the right half represents the Pd segregation that was observed from time to time. The segregation of Pd was confirmed by the EDX spectrum from this region and the segregated Pd formed irregularly shaped big particles, in contrast to the small and spherical Au-rich alloy particles.

The catalytic test was performed using different alcohols under mild conditions (60°C, 1.5atm O₂, 0.3 M solution) in water with and without NaOH.

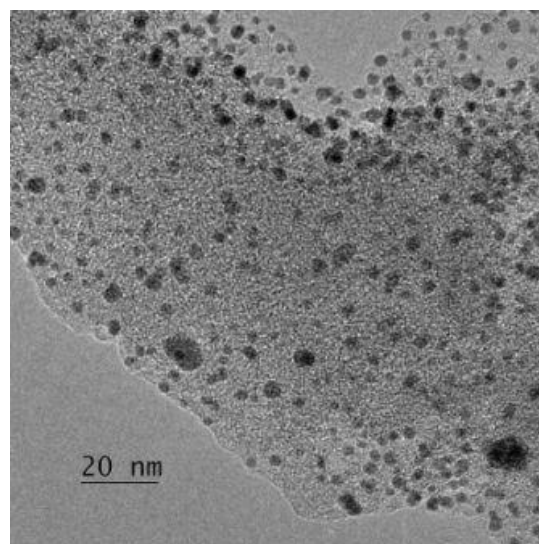


Fig. 1: A representative TEM image of the well alloyed Au_x-Pd_y/AC bimetallic catalysts.

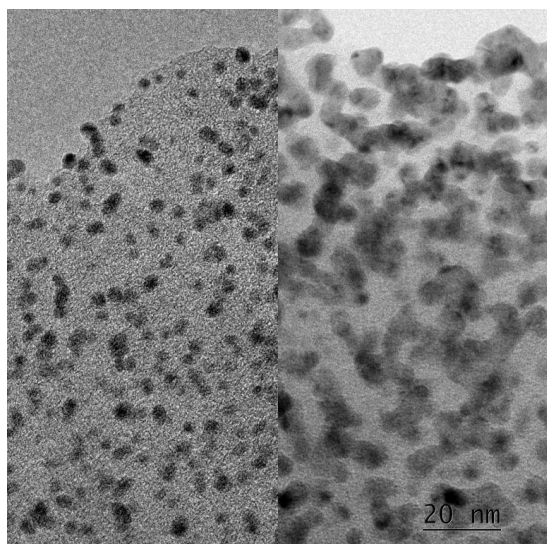


Fig. 2: The electron micrographs showing typical morphology (left) and Pd segregation (right) in the Pd₈₀@Au₂₀/AC catalyst.

3.1. Effect of the base

3.1.1. Benzyl alcohol

Benzyl alcohol was used as a model for aromatic activated alcohol. Table 3 reported the TOF data (calculated at 15 min) versus Au/Pd molar ratio with/without NaOH; the selectivity data are also reported.

All the bimetallic systems showed activity higher than that corresponding to Au and Pd monometallic catalysts. Those latter catalysts showed a really poor activity. Comparing the TOF for pure Au (2 h⁻¹) and Pd (15 h⁻¹) it is clear that as expected the Pd is more active than pure Au, which when supported on carbon, is not able to extract the hydride from the alcoholic function. In fact the presence of the base (NaOH) slightly increased the catalyst activity only in the case of Au/AC. Referring to system Au₆₀-Pd₄₀ tested under the same conditions [27], we observed that by increasing the gold content the activity increased, reaching a maximum value for Au₈₀-Pd₂₀. TOF in fact increased from 985 h⁻¹ for Au₆₀-Pd₄₀ to 1021 h⁻¹ for Au₈₀-Pd₂₀, and then it declined to 780 h⁻¹ for Au₉₀-Pd₁₀. For higher Pd content than in Au₆₀-Pd₄₀, the activity decreased and the TOF varied from 985 h⁻¹ for Au₆₀-Pd₄₀ to 716 h⁻¹ for Au₂₀-Pd₈₀. The selectivity to benzaldehyde in the absence of NaOH is always >99 and appeared to be independent from both the nature of the metal and the Au/Pd ratio.

Under the basic conditions we observed a general increasing of the activities of all bimetallic catalysts. However, considering the per cent increment we observed the highest effect for gold rich composition (46% for Au₉₀-Pd₁₀, 16% Au₈₀-Pd₂₀, 9% Au₆₀-Pd₄₀ and 8% for Au₂₀-Pd₈₀) (Figure 3). Moreover, in basic media the selectivity to aldehyde drastically decreases with the formation of carboxylate: in fact, the base promotes the overoxidation of the aldehyde to carboxylate. In agreement with the effect of the

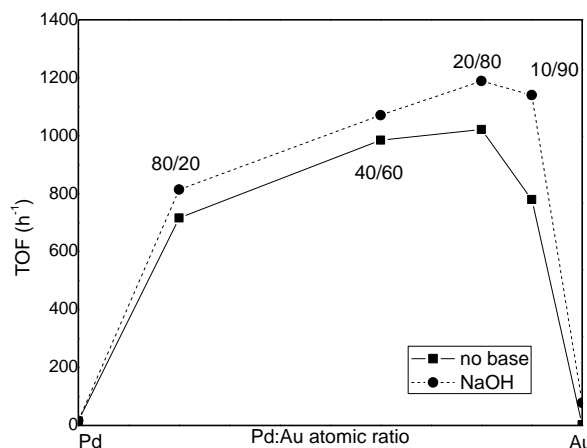


Fig. 3: TOF vs Au_x-Pd_y bimetallic catalysts in benzyl alcohol oxidation (without base and with NaOH)

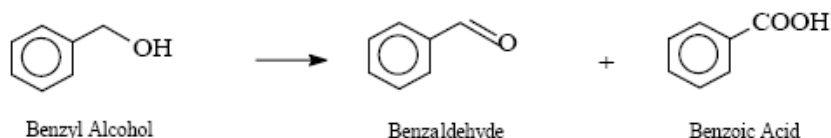
base on the activity, also the selectivity to benzaldehyde and benzoic acid appeared strongly dependent on the Au/Pd ratio, the higher the gold content the more important the overoxidation of benzaldehyde appeared. Au₉₀-Pd₁₀ showed a similar selectivity to aldehyde as that of pure gold, whereas Au₂₀-Pd₈₀ similar as pure palladium catalyst.

3.1.2. Cinnamyl alcohol

The oxidation of cinnamyl alcohol is often used as a model reaction for alcohol oxidation. Baiker et al. [33] demonstrated the existence of a complex reaction network. In fact, apart from the oxidation pathway, side reactions due to hydrogen transfer, hydrogenolysis and decarbonylation can be possible, depending on the reaction conditions and the catalyst used. In the presence of a base the formation of the ester has also been detected.

The behaviour of the tested catalysts using cinnamyl alcohol as the reactant (Table 4) followed the same trend as it was observed in the benzyl alcohol oxidation: all the bimetallic catalysts resulted more active than the corresponding monometallic ones either in the presence or in the absence of the base. In the absence of a base the activity of the mono metallic Au was negligible whereas Pd showed a poor but not negligible TOF. As in the case of benzyl alcohol, the NaOH addition enhanced drastically the activity of Au/AC but had almost no effect on that of Pd/AC. Moreover the effect of the base resulted more evident in gold-rich composition being the highest for the Au₉₀-Pd₁₀ composition (Figure 4). Thus the activity of the most active catalyst in the absence of NaOH (Au₈₀-Pd₂₀ TOF = 630 h⁻¹) became comparable to that of Au₉₀-Pd₁₀ when the reaction was carried out under basic condition (TOFs 858 and 861 h⁻¹ respectively). Gold rich catalysts are more selective to cinnamaldehyde compared to palladium rich catalysts (80% of selectivity to benzaldehyde for Au vs 70% for Pd) which promoted the hydrogen transfer (3-phenyl-propanol).

Table 3: Oxidation of benzyl alcohol^a



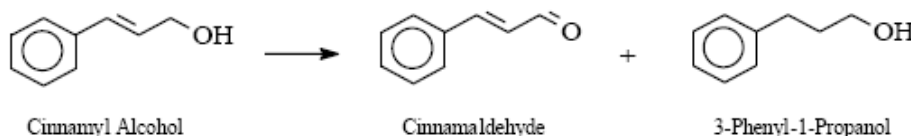
	base	TOF (h ⁻¹) ^b	Selectivity at 90% conversion		
			benzaldehyde	benzoic acid	benzyl benzoate
1% Au/AC	-	2	>99 ^c	-	-
1% Pd ₁₀ @Au ₉₀ /AC	-	780	>99	-	-
1% Pd ₂₀ @Au ₈₀ /AC	-	1021	>99	-	-
1% Pd ₄₀ @Au ₆₀ /AC	-	985	>99	-	-
1% Pd ₈₀ @Au ₂₀ /AC	-	716	>99	-	-
1% Pd/AC	-	15	>99 ^c	-	-
1% Au/AC	1 eq NaOH	78	26 ^c	41	33
1% Pd ₁₀ @Au ₉₀ /AC	1 eq NaOH	1140	28	40	32
1% Pd ₂₀ @Au ₈₀ /AC	1 eq NaOH	1189	46	32	22
1% Pd ₄₀ @Au ₆₀ /AC	1 eq NaOH	1071	45	31	24
1% Pd ₈₀ @Au ₂₀ /AC	1 eq NaOH	776	50	26	24
1% Pd/AC	1 eq NaOH	16	58 ^c	28	18

^a Catalytic test : benzyl alcohol 0.3M, benzyl alcohol/metal 1/500 (mol/mol), T = 60°C, O₂=1.5 atm; stirring rate 1250 rpm

^b TOF calculated after 15 min of reaction

^c selectivity at 50% conversion

Table 4: Oxidation of cinnamyl alcohol^a



	base	TOF (h ⁻¹) ^b	Selectivity at 90% conversion		
			cinnamaldehyde	3-P-P ^c	ester + acid
1% Au/AC	-	25	80 ^d	18 ^d	-
1% Pd ₁₀ @Au ₉₀ /AC	-	520	77	22	-
1% Pd ₂₀ @Au ₈₀ /AC	-	630	75	24	-
1% Pd ₄₀ @Au ₆₀ /AC	-	539	75	24	-
1% Pd ₈₀ @Au ₂₀ /AC	-	394	74	25	-
1% Pd/AC	-	120	70	28	-
1% Au/AC	1 eq NaOH	470	27	10	63
1% Pd ₁₀ @Au ₉₀ /AC	1 eq NaOH	858	28	16	56
1% Pd ₂₀ @Au ₈₀ /AC	1 eq NaOH	861	32	21	47
1% Pd ₄₀ @Au ₆₀ /AC	1 eq NaOH	669	50	24	26
1% Pd ₈₀ @Au ₂₀ /AC	1 eq NaOH	480	58	23	19
1% Pd/AC	1 eq NaOH	143	62	25	13

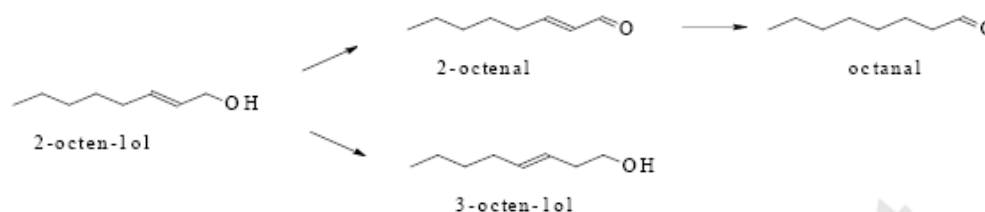
^a Catalytic test : Cinnamyl alcohol 0.3M, cinnamyl alcohol/metal 1/500 (mol/mol), T = 60°C, pO₂=1.5 atm; stirring rate 1250 rpm

^b TOF calculated after 15 min of reaction

^c 3-P-P = 3-phenyl-1-propanol

^d selectivity at 50% conversion

Table 5: Oxidation of 2-octen-1-ol



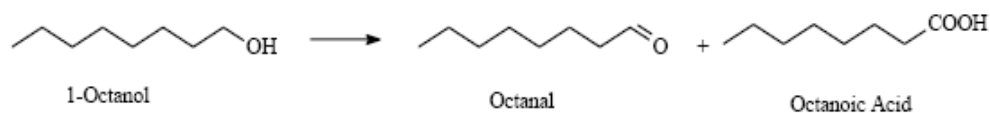
	base	TOF (h ⁻¹) ^b	Selectivity at 90% conversion		
			2-octenal	3-octen-1-ol	octanal
1% Au/AC	-	41	26 ^c	54 ^c	15 ^c
1% Pd ₁₀ @Au ₉₀ /AC	-	537	27	45	22
1% Pd ₂₀ @Au ₈₀ /AC	-	596	28	44	23
1% Pd ₄₀ @Au ₆₀ /AC	-	660	26	43	25
1% Pd ₈₀ @Au ₂₀ /AC	-	553	25	42	27
1% Pd/AC	-	234	23	38	30
With NaOH					
1% Au/AC	1 eq NaOH	810	16	68	8
1% Pd ₁₀ @Au ₉₀ /AC	1 eq NaOH	2523	17	60	10
1% Pd ₂₀ @Au ₈₀ /AC	1 eq NaOH	2577	16	57	12
1% Pd ₄₀ @Au ₆₀ /AC	1 eq NaOH	2080	15	56	14
1% Pd ₈₀ @Au ₂₀ /AC	1 eq NaOH	892	14	52	14
1% Pd/AC	1 eq NaOH	331	14	49	15

^a Catalytic test : 2-octen-1-ol 0.3M, 2-octen-1-ol/metal 1/500 (mol/mol), T = 60°C, pO₂=1.5 atm; stirring rate 1250 rpm

^b TOF calculated after 15 min of reaction

^c selectivity at 50% conversion

Table 6: Oxidation of 1-octanol



^a Catalytic test : 1-octanol 0.3M, 1-octanol/metal 1/500 (mol/mol), T = 60°C, pO₂=1.5

	base	TOF (h ⁻¹) ^b	Selectivity at 20% conversion	
			octanal	octanoic acid
1% Au/AC	-	1	-	-
1% Pd ₁₀ @Au ₉₀ /AC	-	27	43	33
1% Pd ₂₀ @Au ₈₀ /AC	-	27	44	30
1% Pd ₄₀ @Au ₆₀ /AC	-	28	45	30
1% Pd ₈₀ @Au ₂₀ /AC	-	24	45	29
1% Pd/AC	-	7	45	29
Selectivity at 90% conversion				
1% Au/AC	1 eq NaOH	30	-	87
1% Pd ₁₀ @Au ₉₀ /AC	1 eq NaOH	241	-	82
1% Pd ₂₀ @Au ₈₀ /AC	1 eq NaOH	235	5	72
1% Pd ₄₀ @Au ₆₀ /AC	1 eq NaOH	181	7	68
1% Pd ₈₀ @Au ₂₀ /AC	1 eq NaOH	104	8	64
1% Pd/AC	1 eq NaOH	22	9	60

atm; stirring rate 1250 rpm

^b TOF calculated after 1h of reaction

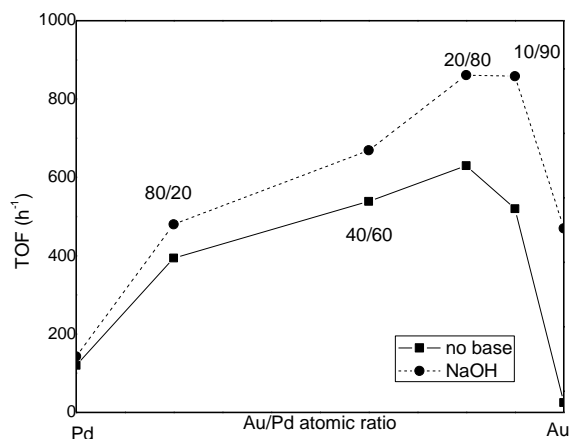


Fig. 4: TOF vs Au_x-Pd_y bimetallic catalysts in cinnamyl alcohol oxidation (without base and with NaOH)

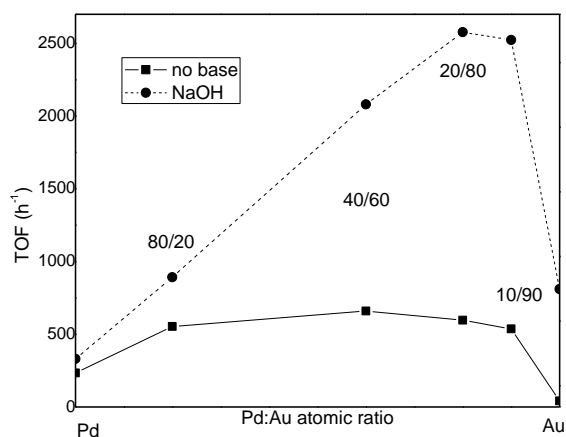


Fig. 5: TOF vs Au_x-Pd_y bimetallic catalysts in 2-octen-1-ol oxidation (without base and with NaOH)

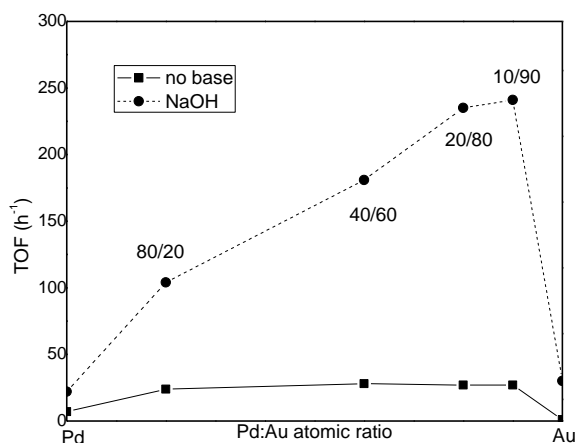


Fig. 6: TOF vs Au_x-Pd_y bimetallic catalysts in 1-octanol oxidation (without base and with NaOH)

This trend was maintained also in the presence of NaOH. Under basic conditions even Au rich composition promoted the overoxidation of the aldehyde to the carboxylate whereas the data (Table 4) showed an increasing of the hydrogenated alcohol (3-P-P) by increasing the catalyst palladium content.

3.1.3. 2-octen-1-ol and n-octanol

2-octen-1-ol is used as a model for oxidation of the activated aliphatic substrate. Reaction pathway resulted in very complex, as the presence of the double bond in the allylic position makes the isomerisation and the hydrogen transfer to be possible. 2-octenal, n-octanal and 3-octen-1-ol were in fact detected as products (Table 5).

Au/AC and Pd/AC were more active in this reaction than in the previous ones, Pd/AC being quite active (TOF 234 h⁻¹). However, the effect of the NaOH remained extraordinary as a 20 fold increase of TOF was observed in the case of Au/AC (TOF 41 vs. 810 h⁻¹ without and with NaOH respectively).

The TOF data for reactions done without and with NaOH showed a “volcano behaviour” with Au₆₀-Pd₄₀ catalyst resulting as the most active catalyst in the absence of NaOH and Au₈₀-Pd₂₀ in the presence of NaOH (TOF of 660 h⁻¹ and 2577 h⁻¹ respectively) (Figure 5). The trend of the activity data highlighted a slight difference for the bimetallic catalyst in the range of composition Au₉₀-Pd₁₀ and Au₆₀-Pd₄₀. However, the effect of the added base on the activity was extraordinary for Au₉₀-Pd₁₀ (about 370% of increasing) decreasing in the case of the more rich Pd composition (Figure 5). The main effect of NaOH on selectivity was to improve the isomerisation product (3-octen-1-ol) especially for Au rich composition. Conversely saturated octanal was decreased.

Using a more demanding reactant with similar structure as 1-octanol, we could highlight the effect of the double bond. Screening the same series of monometallic and Au/Pd bimetallic catalysts, we were not surprised to observe in general a very poor catalytic activity (Table 6 and Figure 6). This trend was in line with our previous observation in that when water was used as solvent in absence of a base, two different factors played a detrimental effect on catalytic activity: 1) a four-phase system that limits the contact between active sites and reactants; 2) a deactivating effect due to the formation of carboxylic acid instead of aldehyde [33]. This latter effect appeared not relevant for 2-octen-1-ol as no free acid was detected. Thus the comparison between these two reactants is difficult. However, when we added a base, octanoate became the main product for the oxidation of 1-octanol (Table 6) and the deactivating effect was negligible as shown by the conversion profile of Au₈₀-Pd₂₀ reported in Figure 7. Thus a comparison between octan-1-ol and 2-octen-1-ol under basic conditions allowed determining the effect of the double bond on the activity.

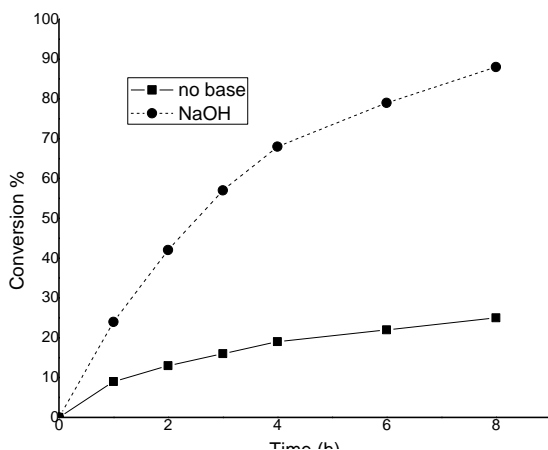


Fig. 7: Oxidation of 1-octanol in the presence of Au₈₀-Pd₂₀ in water with and without NaOH

As expected, in 1-octanol oxidation the addition of NaOH produced a significant increase of the activity of gold base catalyst (Table 6), considerably higher than the increase observed by adding NaOH in the oxidation of 2-octen-1-ol. However, considering the TOF values in Tables 5 and 6, it is evident that the double bond promotes the reaction rate of order one of magnitude. In both cases gold rich composition as Au₈₀-Pd₂₀ and Au₉₀-Pd₁₀ resulted in the most active catalysts.

3.1.4. Mechanistic considerations

For catalysts with Au-Pd ratio varying from 90:10 to 60:40 similar structures, particle distributions were observed and the presence of an alloy was confirmed [28]. Thus, excluding the particle size effect, it can be established that the nature of the metal and the Au-Pd ratio play the main role in determining the catalytic activity. In particular the bimetallic catalysts where the TEM evidenced uniform alloyed bimetallic particles (Au:Pd ratio = 90:10, 80:20, 60:40) showed a higher activity with respect to Au₂₀-Pd₈₀ where inhomogeneity in the structure is present. The addition of base enhanced the activity of all the catalysts, being the effect on Pd and Pd rich catalyst considerably lower than for gold and gold-rich composition (Figures 3-6).

It has been reported that in Au-Pd catalyst, Au acted as promoter to isolate Pd monomer [34] and that Au-Pd could create bifunctional site [26]. Moreover we observed a different effect of the base as a function of Au-Pd ratio, being negligible for pure Pd. Consequently we could suppose that different alloy composition worked differently: in the gold-rich composition a gold-type mechanism prevails where the rate determining step is represented by the H-abstraction (highest effect of NaOH) whereas in the palladium-rich composition the rate determining step is repre-

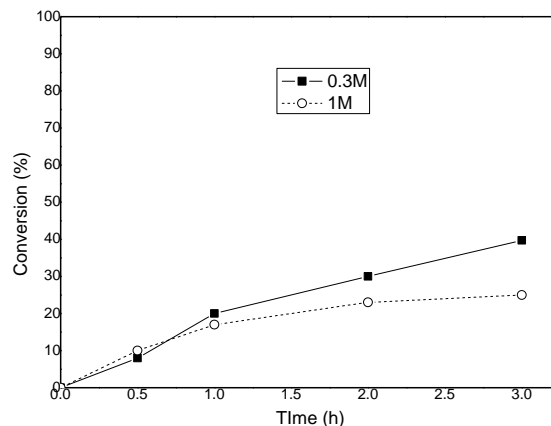


Fig. 8: Conversion profile for benzyl alcohol oxidation with Au₆₀-Pd₄₀/AC

sented by the H-transfer from Pd-H specie (negligible effect of the NaOH).

3.2. Effect of alcohol concentration and alcohol/metal ratio

We used Au₂₀-Pd₈₀ and Au₆₀-Pd₄₀ as representative of a Pd-rich composition and Au-rich composition respectively for studying the effect of alcohol concentration and the alcohol/metal ratio on activity and selectivity. The benzyl alcohol oxidation was used as a test reaction.

By varying the concentration of benzyl alcohol from 0.15 to 1 M we observed that in the absence of NaOH in both cases a negligible difference in TOFs was obtained carrying out the reaction at different alcohol/metal ratio (500- 1000 -3000). A slight increase of TOF values was observed by operating at higher concentration. Therefore the reaction proceeds under kinetic control using either Pd or Au rich catalyst at each of the tested concentrations (TOF= 1000 h⁻¹ for Au₆₀-Pd₄₀/AC and 700 h⁻¹ for Au₂₀-Pd₈₀/AC). Also the selectivity to aldehyde appeared almost independent from the concentration and the substrate/metal ratio, being always >98% for Au₆₀-Pd₄₀/AC and >92% for Au₂₀-Pd₈₀/AC. However by increasing the concentration, limitation due to catalyst deactivation occurred. Figure 8 reported for comparative purpose the reaction profile corresponding to 0.3 and 1M concentration at alcohol/metal ratio 3000 mol/mol of Au₆₀-Pd₄₀/AC. Clearly it can be noted that a strong catalyst deactivation occurred during the oxidation of the 1M benzyl alcohol. In the case of Au₂₀-Pd₈₀/AC deactivation can be noted also at lower concentration (0.3M).

A completely different situation was highlighted when the reaction was carried out in the presence of NaOH. The activity of both catalysts increased considerably but the effect of the basic environment differs for Au-rich or Pd-

Table 7: Oxidation of benzyl alcohol with Au₆₀-Pd₄₀/AC^{a)}

Alcohol concentration (M)	Alcohol/metal (mol/mol)	TOF ^{b)} (h ⁻¹)	S50 ^{c)} (%)
0.15	500	1000	14
	1000	1700	25
	3000	3700	48
0.30	500	1100	15
	1000	1500	31
	3000	3500	57
0.6	500	700	70
	1000	1200	76
	3000	3000	82
1.0	500	700	74
	1000	1000	77
	3000	2200	88

^{a)} Catalytic test : Alcohol/NaOH= 1 mol/mol; T = 60°C, O₂=1.5 atm; stirring rate 1250 rpm

^{b)} TOF calculated after 30 min of reaction

^{c)} selectivity to benzaldehyde at 50% conversion

Table 8: Oxidation of 1M benzyl alcohol with Au₆₀-Pd₄₀/AC

Alcohol/metal (mol/mol)	TOF ^{b)} (h ⁻¹)	S50 ^{c)} (%)
500	700	74
1000	1000	77
3000	2200	88
6000	4146	91
12000	5517	93
20000	7000	88
40000	8300	71

rich catalysts. For Au₂₀-Pd₈₀/AC, the activity (TOFs) remains constant (Kinetic regime) up to a 0.6M concentration by varying the alcohol/metal ratio from 500 to 3000 mol/mol (TOF=1500 h⁻¹ and 1600 h⁻¹ for 0.3 and 0.6 M respectively). By increasing the concentration to 1M, however, mass transfer limitation occurred. At this latter concentration in fact the TOF value increased from 750 to 2700 h⁻¹ by increasing the alcohol/metal ratio from 1000 to

3000 mol/mol. Surprisingly operating at 1M concentration the selectivity to aldehyde increased from 40 to 85%, even in the presence of NaOH that should in principle promote the carboxylate formation.

In the case of Au₆₀-Pd₄₀/AC mass transfer limitation occurred at any concentration (0.15 – 0.3 – 0.6 – 1.0 M) (Table 7) and increasing of selectivity to aldehyde was observed as before apparently ruled by the concentration. In fact benzoate represented the main product regardless the alcohol/metal ratio when an initial benzyl alcohol concentration of 0.15 and 0.3 M was used. Starting from a 0.6M solution, benzaldehyde was produced as the major product, its formation being enhanced by increasing the concentration and the alcohol/metal ratio (S50 = 88% at 1M and benzyl/metal=3000 mol/mol – Table 7).

In order to investigate more in detail this aspect we carried out tests using higher alcohol/metal ratio at 1M concentration (Table 8), following also the kinetic profile (Figure 9).

The Au₆₀-Pd₄₀/AC catalyst appeared extraordinarily active under these conditions and we reached a kinetic regime only over a benzyl/metal ratio of 40000. However,

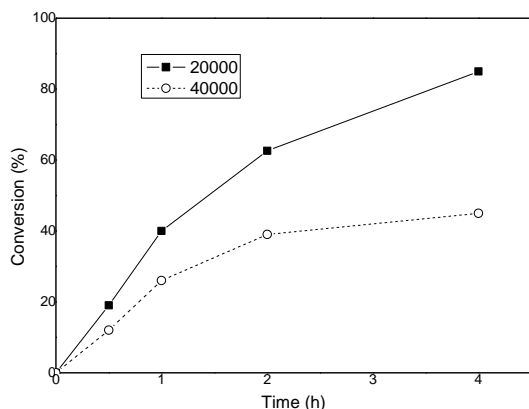


Fig. 9: Conversion profile for benzyl alcohol oxidation with Au₆₀-Pd₄₀/AC

when a 40000 benzyl/metal ratio was used deactivation of the catalyst was observed (Figure 9). Moreover, benzaldehyde always represented the major product but its selectivity was >88% for a alcohol/metal ratio between 3000 and 20000 mol/mol and under these conditions full conversion can be easily reached (Figure 9).

We have previously observed that the effect of the concentration was negligible on TOF at the same alcohol/metal ratio (Table 7). Nevertheless the effect on selectivity was strong. Thus in order to investigate this parameter, we also carried out a test at 5M concentration and solventless using a 20000 mol/mol alcohol/metal ratio. We observed that in both cases the conversion after 1 h was really poor (<2% for solventless and 4% for the 5M concentration). A possible explanation of the concentration effect on selectivity could be found in the poor solubility of benzyl alcohol in water which can limit the subsequent oxidation of benzaldehyde. A test carried out using a biphasic system (cyclohexane/water and NaOH) appeared to confirm this hypothesis: a 1 M solution of benzyl alcohol in cyclohexane in the presence of 1M solution of aqueous NaOH and a 20000 alcohol/metal molar ratio provided a TOF of 18000 h⁻¹ and a selectivity to benzaldehyde at 90% conversion of 89% .

4. Conclusion

Using a sequential deposition of Au and Pd we prepared a series of Au_x-Pd_y catalysts. TEM characterization established uniform alloyed bimetallic nanoparticles only in the range 90:10 to 60:40 of Au-Pd composition. These catalysts resulted very active in the liquid phase oxidation of alcohols such as benzylic, cinnamyl, octenol and octanol confirming the high synergistic effect of the alloy. The addition of a base increases the activity of all the catalysts, the extent of which depending on the nature of the alcohol to be oxidized and on gold/palladium ratio. The greatest effect was observed for aliphatic alcohols and for gold-rich composition. This latter observation possibly suggested the existence of different reaction mechanism for bimetallic systems depending on Au/Pd ratio as highlighted for Au/C and Pd/C.

The beneficial effect of NaOH addition is also in terms of durability of the catalyst, but normally the basic environment promotes the over-oxidation of aldehyde to carboxylate. However, in the case of benzyl alcohol the valuable benzaldehyde can be obtained in high yield even in the presence of NaOH, by increasing the initial alcohol concentration, thus merging the target of having a highly active catalyst with the one of maximizing the benzaldehyde selectivity. Using the Au₆₀-Pd₄₀/AC catalyst the best compromise between activity and selectivity was reached for 1M concentration and 20000 mol/mol benzyl alcohol/metal ratio. We ascribed the enhanced selectivity to aldehyde with the concentration to the formation of a biphasic system that limits the accessibility of benzaldehyde to the active site of the catalyst thus limiting its subsequent oxidation to benzoate. Using an organic solvent such as cyclohexane in the presence of 1M aqueous NaOH and an alcohol/metal ratio of 20000, we obtained a considerable enhancement of catalyst activity reaching a TOF of 18000 h⁻¹ and maintaining a high selectivity to benzaldehyde (S90 = 89%).

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