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Pd and Pt catalysts modified by alloying with Au in the selective oxidation of alcohols

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Abstract

The use of gold on promoting PGM (platinum group metal) catalysts for the selective oxidation of various primary alcohols under mild conditions was investigated. Au/Pd and Au/Pt catalysts showing a single alloyed phase were prepared. It was found that using these bimetallic catalysts instead of monometallic ones caused a significant change in activity in the liquid-phase oxidation of alcohols. Au/Pd catalyst showed a positive synergistic effect; Au/Pt, a negative one. By using aqueous solvent instead of organic solvent (toluene), activity was enhanced for both Au/Pd and Au/Pt catalysts, with some changes in selectivity as well.

Keywords: Alcohol oxidation; Gold-based catalyst; Gold/palladium catalyst; Gold/platinum catalyst; Alloyed catalyst

1. Introduction

The oxidation of alcohols to carbonyl compounds is an important task in the fine chemicals industry. Traditional methods for the oxidation of alcohols are based on using stoichiometric amounts of either inorganic oxidants (such as chromate) or organic oxidants (such as DMSO) [1–3]. These methods lead to environmental and consequently economical problems due to large amounts of byproducts [4–7]. An alternative, more environmentally friendly method involves the use molecular oxygen or hydrogen peroxide [8,9] in the presence of a catalyst, being water as the main co-product.

Different catalysts (homogeneous and heterogeneous) have been already investigated for alcohol oxidation with molecular oxygen or hydrogen peroxide in the liquid phase. In the case of homogeneous catalysts, efficient catalysts based on cobalt [10,11], copper [12], palladium [13–18], ruthenium [19,20], and tungsten [21–24] have been reported. For heterogeneous catalysts, various different catalytic systems able to oxidize alcohols have been reported. Thus, catalysts based on heteropoly-acids [25,26], hydrotalcites [27–30], molecular sieves [31–33], and mixed oxides [34–37] have been reported to be active in the liquid-phase oxidation of alcohols. Research has historically focused on the use of Pt/C or Pd/C catalysts [38–42]; however, a drawback to using Pd or Pt catalysts in the liquid phase with oxygen as the oxidant is the sensitivity in deactivation due to overoxidation and poisoning from (by)products [43]. Recently, many groups have been demonstrated that using a secondary metal component, such as Bi or Pb, is advantageous in terms of activity/selectivity of various reactions, and, moreover, a beneficial effect in terms of durability (lifetime) of the catalyst has been noted [41,44]. Recently, gold has been demonstrated to be an active catalyst for oxidizing alcohol in the presence of O_2 [45]. In particular, our group demonstrated that adding Au to Pd or Pt catalysts in the liquid-phase oxidation of polyols (sorbitol and glycerol) under mild conditions ($<60\,^{\circ}C$ and <4 atm) not only improves catalytic activity and selectivity to the desired product, but also enhances the resistance to poisoning [46,47].

Using a specific methodology, we recently prepared a single-phase Au–Pd catalyst [48] and found that it showed extraordinary high activity in the selective oxidation of glycerol. Thus we thought to extend this same technique to prepare an analo-

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gous Au–Pt catalyst and tested it with a broad range of alcohols, because active catalysts still represent a goal for practical application.

In this paper we report a detailed study of the oxidation of alcohols (allylic, benzylic, or aliphatic) using Au–Pd and Au–Pt catalysts. For a proper comparison, we used monometallic Au, Pd and Pt on carbon prepared using a similar methodology on the same carbon as reference catalysts. Moreover, we also tested commercial Pd (Engelhard Escat 10) and Pt (Degussa) catalysts under the same conditions.

2. Experimental

2.1. Materials

$NaAuCl_4{\cdot}2H_2O$, K_2PtCl_4, Na_2PdCl_4 were obtained from Aldrich (99.99% purity), and activated carbon was obtained 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 stirred for 12 h, then washed several times with distilled water by decantation until the pH of the solution reached values of 6–6.5. After this, the end the carbon was filtered off and dried for 5–6 h at 150 °C in air. The final water content was evaluated as <3%. $NaBH_4$ of purity >96% from Fluka and polyvinylalcohol (PVA) (Mw = 13,000–23,000, 87–89% hydrolyzed) from Aldrich were used. Gaseous oxygen and hydrogen from SIAD was 99.99% pure. Stock aqueous solutions of PVA (2%, w/w) and $NaBH_4$ (0.1 M) were prepared.

2.2. Catalyst preparation

2.2.1. Monometallic catalysts

Au sol Solid $NaAuCl_4{\cdot}2H_2O$ (0.043 mmol) and PVA solution (410 μl) were 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 Au(0) sol was formed immediately.

Pd sol $Na_2PdCl_4{\cdot}2H_2O$ (0.043 mmol) and PVA solution (880 μl) were added to 130 ml of H_2O. After 3 min, $NaBH_4$ solution (860 μl) was added to the yellow-brown solution under vigorous magnetic stirring. The brown Pd(0) sol was formed immediately.

Pt sol Solid $K_2PtCl_4{\cdot}2H_2O$ (0.051 mmol) and PVA solution (1.9 ml) were added to 150 ml of H_2O. After 3 min, $NaBH_4$ solution (1 ml) was added to the colorless solution under vigorous magnetic stirring. The light-gray Pt(0) sol was formed immediately.

UV–visible spectra of sols were recorded. Within a few minutes after their generation, sols were immobilized by adding carbon (acidified at pH 2 by sulphuric acid) under vigorous stirring. The amount of support was calculated as having a final metal loading of 1 wt%.

2.2.2. Bimetallic catalysts

$NaAuCl_4{\cdot}2H_2O$ (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, after which 0.1 M $NaBH_4$ (2.15 ml) was added under vigorous magnetic stirring. The ruby-red Au(0) sol was formed immediately. A UV–visible spectrum of the gold sol was recorded to check the complete $AuCl_4^-$ reduction and the formation of a plasmon peak. Within a few minutes of sol generation, the gold sol was immobilized by adding activated carbon (acidified to 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 or 0.60 wt% when Au/Pt was prepared. After 2 h, the slurry was filtered and the catalyst washed thoroughly with distilled water (neutral mother liquors).

ICP analyses were performed on the filtrate using a Jobin Yvon JV24 instrument to verify the total metal loading on carbon. The Au/C was dispersed in 140 ml of water, with 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 solution (0.225 ml) added. H_2 was bubbled (50 ml/min) under atmospheric pressure and room temperature for 2 h. After an additional 18 h, the slurry was filtered and the catalyst washed thoroughly with distilled water. ICP analyses were performed on the filtrate using a Jobin Yvon JV24 instrument to verify the metal loading on carbon. The total metal loading was 1 wt%.

2.3. Catalytic test

The reactions were carried out in a thermostatted glass reactor (30 ml) equipped 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 (0.3 M) and the catalyst (metal/alcohol = 1/500 mol/mol) were mixed in distilled water or toluene (total volume, 10 ml). The reactor was pressurized at a specified pressure of O_2 and thermostatted at 60 °C. The reaction was initiated by stirring. When using the organic solvent, periodic removal of samples from the reactor was performed, whereas in the case of water solvent, at the end of reaction, the product mixture was extracted with toluene. Recovery was always 98 ± 3% with this procedure. Identification and analysis of the products were done by GC-MS and GC using a Dani 86.10 HT gas chromatograph equipped with a capillary column (BP21 30 m × 0.53 mm, 0.5 μm film; SGE) by comparison with the authentic samples. Quantification of the reactant products was done by the external calibration method.

2.4. Characterization

2.4.1. Sol characterization

UV–visible spectra of sols were performed on Hewlett-Packard HP8452 and HP8453 spectrophotometers in H_2O at 190–1200 nm in a quartz cuvette.

2.4.2. Catalyst characterization

The metal content was checked by ICP analysis of the filtrate or, alternatively, directly on the catalyst after the carbon was

burned off, using a Jobin Yvon JY24 instrument. Catalyst morphology and microstructure were 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 GIF100 imaging filter, was used for TEM observation. EDX analysis was performed using the same microscope with a DX4 analyzer system (EDAX).

3. Results and discussion

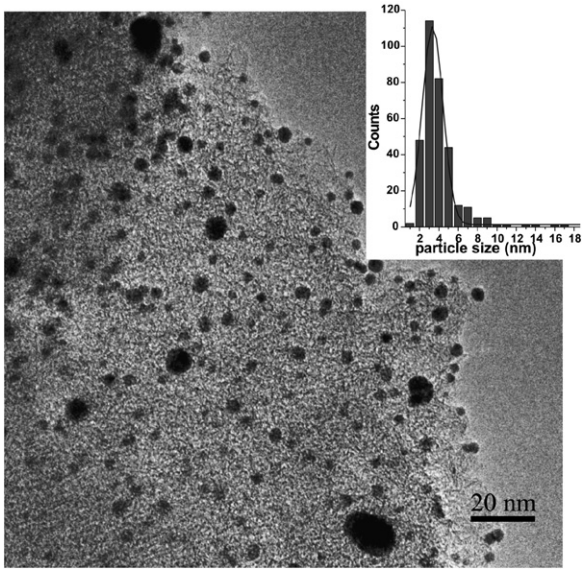
We focused our attention on preparing various catalysts based on a previously reported methodology, which allowed us to obtain a single phase in the case of Au/Pd catalyst [48]. We were confident that Au/Pt also can form a single alloyed phase when nanoparticles are formed, in contrast to bulk metals that exhibit a miscibility gap, as shown by Zhong et al. [49].

3.1. Catalyst characterization

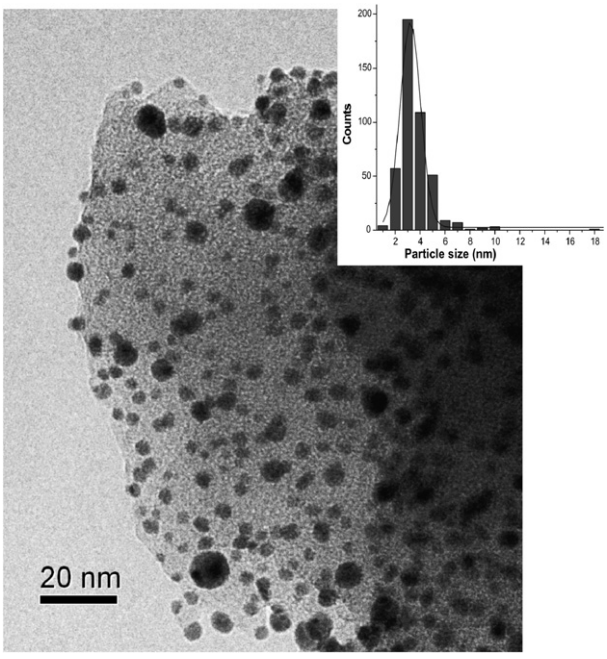
Electron micrographs of the Au–Pd and Au–Pt catalysts (Figs. 1a and 1b) show that the nanoparticles in both catalysts are evenly distributed on the activated carbon. The histogram of particle size distribution shows that the two catalysts have similar morphology, with most particles smaller than 10 nm. The size distribution can be fitted approximately by a Gaussian function centered at 3.4 nm for Au–Pd/AC and 3.2 nm for Au–Pt/AC. In addition, only about 2% of the particles were 10–30 nm in size.

Because Au and Pd may form alloy at almost any ratio while maintaining the fcc structure, examining whether the metal compositions in individual particles coincide with "single phase" is essential. With the electron beam converged to nanometer size, X-ray photons emitted from the very local area could be detected in the microscope. In this way, EDX spectra were acquired from single particles and compared with the overall spectrum. The single-particle EDX acquisition was repeated on more than 50 particles of different sizes. The overall spectrum and a representative spectrum for an individual single particle from the Au–Pd/AC are shown in Fig. 2a. The ratios of Pd to Au are almost unchanged for all of the examined single particles, regardless of the particle size, and are also similar to that of the overall spectrum. This indicates that the examined single particles are representative of the whole sample, with no segregation of Pd or Au. Similarly, the Au–Pt/AC catalyst also exhibits uniform distribution of Au and Pt. As shown in Fig. 2b, Pt L edges appear as small shoulders at the low-energy side of the Au L edges. The representative spectrum from the single particle has a similar Au to Pt ratio as the overall spectrum. The EDX results indicate that for both catalysts, all of the particles were formed into bimetallic alloy with an almost uniform Au:M ratio. EDX confirmed the nominal 6:4 molar ratio in the case of Au:Pd, whereas the ratio for Au–Pt was affected by some uncertainness due to the overlapping of Au and Pt signals (Fig. 2b).

High-resolution imaging was performed on the particles of various sizes. Representatively, the HRTEM images of small particles close to the average size from the Au–Pd/AC and Au–Pt/AC catalysts are shown in Figs. 3a and 3b, respectively. Fast Fourier transform (FFT) analysis [48], as was done for the two parts on each side of the twin boundary in Fig. 3a, shows that most of the particles are of a decahedral multiply twinned structure, with each twinned part maintaining the fcc structure. Fig. 3b shows two of the twin boundaries of a multiply twinned particle in the Au–Pt catalyst. Metal particles with such a multiply twinned structure are very common in colloidal chemistry and are also seen in materials synthesized by chemical vapor deposition [51,52]. The measured typical lattice spacings of the (111) plane are between Au (2.35 Å) and Pd (2.25 Å) or Pt (2.26 Å) for the corresponding bimetallic particles. Most im-



(a)



(b)

Fig. 1. Electron micrographs of (a) the Au–Pd and (b) the Au–Pt catalysts. The histogram of particle size distribution is inserted respectively.

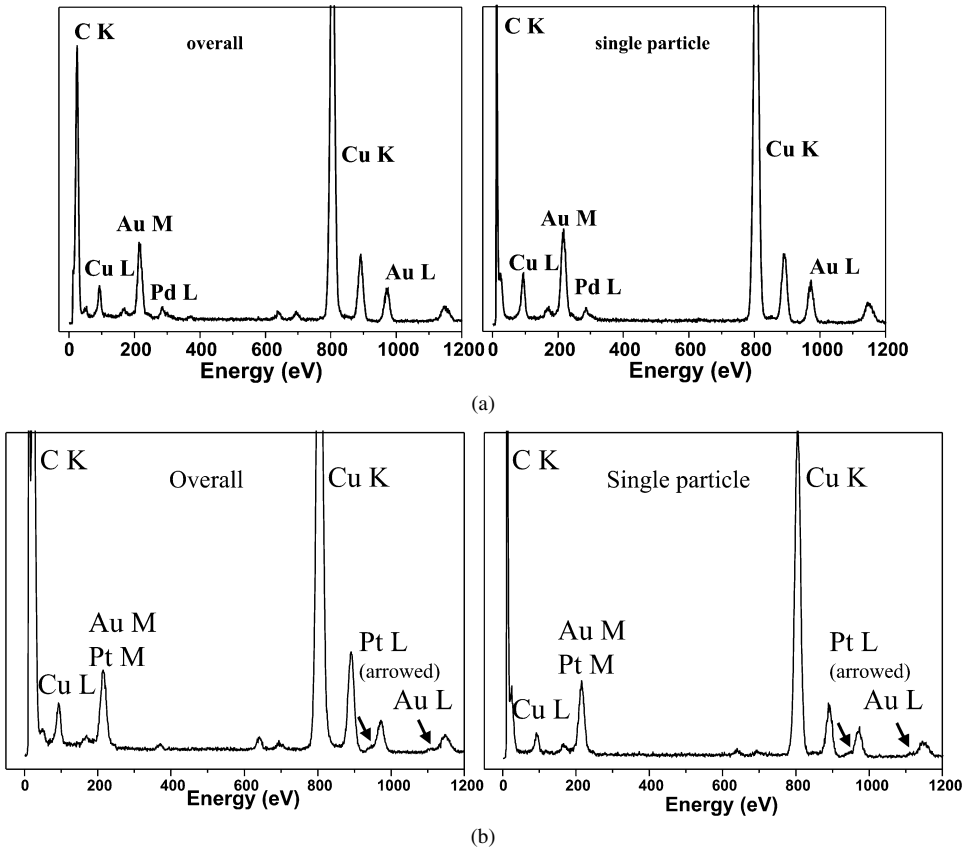


Fig. 2. The overall EDX spectrum and the representative one for individual single particle from (a) the Au–Pd/AC and (b) the Au–Pt/AC.

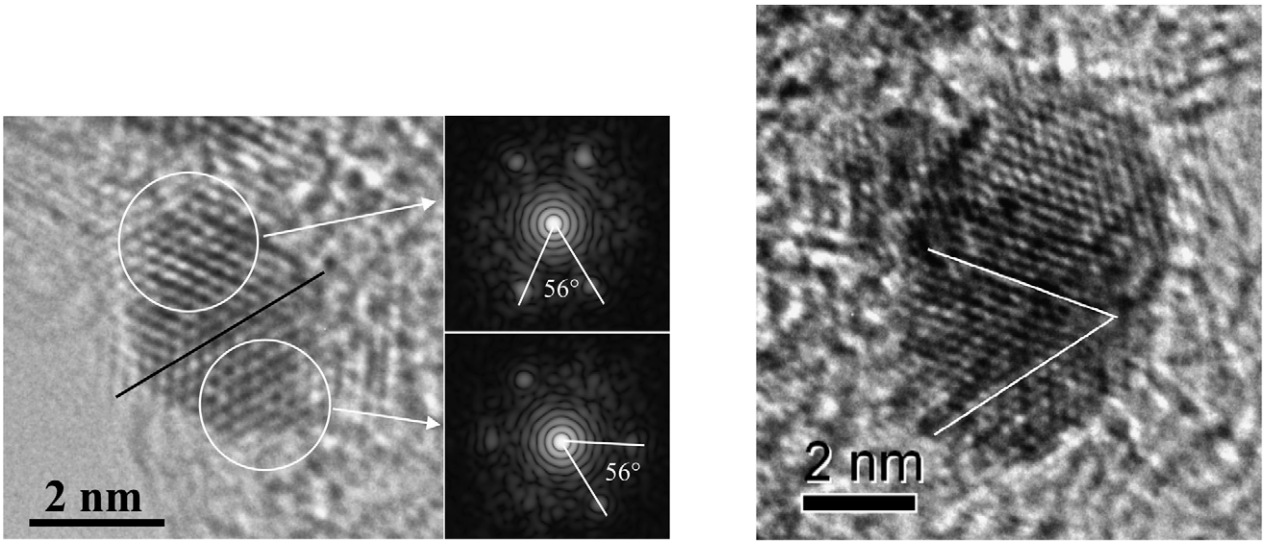


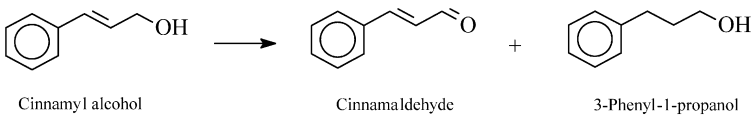
Fig. 3. The representative HRTEM images of small particles close to the average size from (a) the Au–Pd/AC and (b) the Au–Pt/AC catalysts, both exhibiting the multiply twinned structure.

portantly, no core-shell structure or any structural incoherency is observed in the HRTEM images for both catalysts.

3.2. Alcohol oxidation

Catalytic testing was performed with different alcohols using mild conditions (60 °C, 1.5 atm O_2, 0.3 M solution) in both organic (toluene) and aqueous solvent. The choice to use a reduced O_2 pressure rather than that normally used in water (3 atm) was due to safety problems associated with using oxygen and an organic solvent. Even the solubility of oxygen differs greatly in toluene and in water; thus, from a practical standpoint, the two solvents should be compared under the same conditions. Also note that the mechanism of alcohol oxi-

Table 1
Oxidation of cinnamyl alcohol[a]



Cinnamyl alcohol Cinnamaldehyde 3-Phenyl-1-propanol

Catalyst	Solvent	Conv. (%)	Sel. aldehyde (%)	Sel. 3-P-P[b] (%)	TOF (h^{-1})
0.73% Au–0.27% Pd	Toluene	72	85	13	180
0.6% Au–0.4% Pt	Toluene	5	100	0	12
1% Au	Toluene	0	0	0	0
1% Pd	Toluene	24	86	14	61
0.3% Pd	Toluene	26	86	14	66
1% Pt	Toluene	15	100	0	38
0.4% Pt	Toluene	15	100	0	38
Engelhard Escat 10 5% Pd	Toluene	19	88	9	48
Degussa 5% Pt	Toluene	16	100	0	41
0.73% Au–0.27% Pd	H_2O	95	83	17	237
0.6% Au–0.4% Pt	H_2O	18	100	0	45
1% Au	H_2O	0	0	0	0
1% Pd	H_2O	36	86	14	90
0.3% Pd	H_2O	34	88	9	89
1% Pt	H_2O	27	100	0	67
0.4% Pt	H_2O	22	100	0	60
Engelhard Escat 10 5% Pd	H_2O	21	89	10	53
Degussa 5% Pt	H_2O	30	100	0	76

[a] Catalytic test: Cinnamyl alcohol 0.3 M, cinnamyl alcohol/metal 1/500 (mol/mol), $T = 60\,^{\circ}C$, $pO_2 = 1.5$ atm; time of reaction = 2 h, stirring rate 1250 rpm.
[b] 3-P-P = 3-phenyl-1-propanol.

dation is known to differ in organic and aqueous phases, basing on what is known using Pd or Pt catalysts. Although no specific study has been done on gold catalyst, a similar mechanism has been attributed to this metal [50].

The choice to use bimetallic Au–Pd and Au–Pt was made so as to avoid using a base that is in compulsory when monometallic gold catalyst is used as a catalyst in a water/oxygen system. The enhanced properties of Au/Pd single-phase alloy recently displayed in glycerol oxidation [48] also could have been seen in simple alcohol oxidation. Moreover, we extended our study using a similar Au/Pt alloyed catalyst to determine whether gold acts similarly with Pt as with Pd.

3.2.1. Cinnamyl alcohol

The oxidation of cinnamyl alcohol is often used as a model reaction for alcohol oxidation. Baiker et al. [53] demonstrated the existence of a complex reaction network. The target product is cinnamaldehyde; however, side reactions due to transfer hydrogenation, hydrogenolysis and decarbonylation also can be possible, depending on the reaction conditions and metal catalyst used.

The catalytic data are given in Table 1. It was not surprising that the (Au–Pd)/AC catalyst showed a higher activity with respect to both the corresponding monometallic. We expected a similar result for (Au–Pt)/AC as well, because the monometallic Pt/AC did not differ much from the Pd/AC catalyst. However, in this case we observed a negative effect of adding Au to Pt, and monometallic Pt/AC catalyst was more active than (Au–Pt)/AC; Au/C was inactive. Both commercial catalysts behaved similarly to Pd and Pt prepared by sol methods. It seems that Pd-containing catalysts promote the hydrogen transfer more than Pt, resulting in decreased selectivity to cinnamaldehyde with respect to Pt-based catalysts. These results clearly indicate that the nature of the metal is significant for the oxidation of cinnamyl alcohol.

In general, catalyst activity (based on TOF calculation) was higher with water used as the solvent instead of toluene. The difference was particularly noteworthy for the bimetallics; TOF increased from 180 to 237 h^{-1} for (Au–Pd)/AC and from 12 to 45 h^{-1} for (Au–Pt)/AC. The Pd/AC from Engelhard showed less sensitivity to the solvent effect.

It has been speculated that the presence of water in the reaction media can have two effects [50]. Because water is a weak base, it can facilitate H abstraction from alcohol, thus promoting reactivity. Moreover, it can react with the aldehyde to form an aldehyde hydrate, which further reacts with oxygen to form the carboxylic acid.

The catalytic behavior of (Pd–Au)/AC in water, toluene, and CH_3CN solvent is compared in Fig. 4. Using toluene, higher conversion (by up to 2 orders of magnitude) was achieved in comparison to CH_3CN. Selectivity was also much higher with toluene than with CH_3CN (85% vs 58%). When water was used as the solvent, the highest reactivity was found compared to organic solvents despite the fact that selectivity remained largely unaffected.

3.2.2. Benzyl alcohol

Benzyl alcohol was used as a model for aromatic activated alcohol; in this case, Pt/AC appears to be more active than Pd/AC, as shown in Table 2. However, when Au was

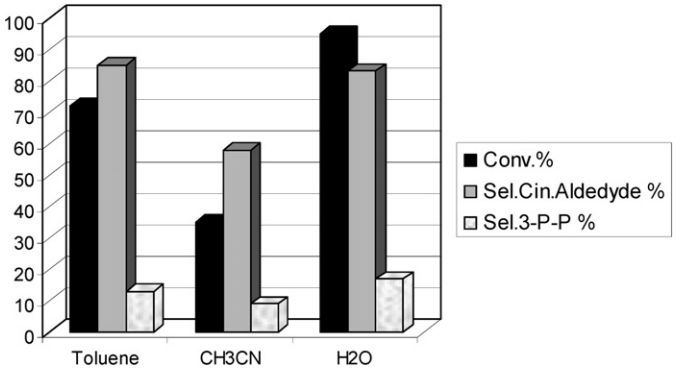


Fig. 4. Catalytic test in different solvent under same conditions (cinnamyl alcohol). Reaction conditions: Cinnamyl alcohol 0.3 M, cinnamyl alcohol/metal 1/500 (mol/mol), $T = 60\,^{\circ}C$, $pO_2 = 1.5$ atm; time of reaction = 2 h, stirring rate 1250 rpm.

added, a positive synergistic effect was observed only for Pd. In fact, (Au–Pd)/AC was more active not only than monometallic Pd/AC, but also than Pt/AC and (Au–Pt)/AC. In contrast, (Au–Pt)/AC had lower activity than monometallic Pt/AC (TOF 15 vs 30 h^{-1}). As in the previous case, commercial catalysts were as active as the corresponding catalysts prepared via the sol method.

As was the case for cinnamyl alcohol, all of the catalysts were more active in water than in toluene. The synergistic effect observed when gold was added was evident in water: positive in the case of Pd (increase in TOF from 30 to 160 h^{-1}), and negative in the case of Pt (decrease in TOF from 98 to 55 h^{-1}). The results clearly show that the catalyst was superior to all of the others only when Pd was present together with Au.

3.2.3. Octanol

Octanol was used as a model for linear, long-chain, aliphatic alcohol. Screening the same series of monometallic and bimetallic catalysts, we observed generally very poor catalytic performance (<12% conversion) when toluene was used as the solvent (Table 3). It has been reported [54] that the oxidation of octanol is much more difficult than the oxidation of cinnamyl and benzyl alcohol; thus, octanol is a more demanding substrate. Aldehyde and acid were not the only products of the reaction; the main byproduct was the ester.

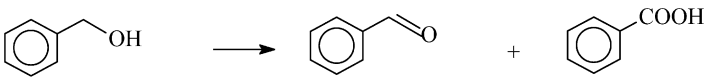
In contrast, in water, even with the presence of triphasic system, increased activity was seen. However, all of the catalysts behaved similarly; only a slight effect resulted from adding gold to Pd or Pt catalyst. As in previous cases, a positive effect occurred with Pd and a negative effect with Pt.

Based on our experience, we also carried out some experiments aimed at improving activity under basic conditions. A beneficial effect was evident for the Au–Pd catalyst, as shown in Fig. 5. The most interesting aspect was the almost linear conversion versus time occurring in the presence of NaOH, indicating the absence of any deactivation phenomena. Also note that, as expected, the presence of a base favors carboxylate formation.

3.3. Discussion

In general, all of the catalysts tested appeared to be more active when water was used as a solvent even with a barely soluble substrate. This result can be used as a basis for further investigation into different mechanisms in organic versus aqueous solvents.

Table 2
Oxidation of benzyl alcohol[a]

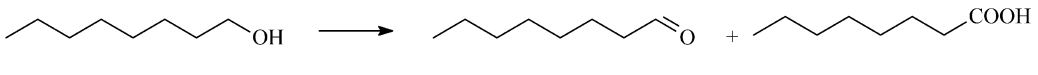


Benzyl alcohol Benzaldehyde Benzoic acid

Catalyst	Solvent	Conv. (%)	Sel. aldehyde (%)	Sel. acid (%)	TOF (h^{-1})
1% Au	Toluene	0	0	0	0
1% Pd	Toluene	3	94	0	5
0.3% Pd	Toluene	4	94	0	5
1% Pt	Toluene	18	95	0	30
0.4% Pt	Toluene	19	95	0	30
0.73% Au–0.27% Pd	Toluene	32	94	0	54
0.6% Au–0.4% Pt	Toluene	9	92	8	15
Engelhard Escat 10 5% Pd	Toluene	3	95	0	5
Degussa 5% Pt	Toluene	24	96	0	40
1% Au	H_2O	0	0	0	0
1% Pd	H_2O	18	91	0	30
0.3% Pd	H_2O	20	93	1	29
1% Pt	H_2O	49	79	8	98
0.4% Pt	H_2O	50	80	6	98
0.73% Au–0.27% Pd	H_2O	96	94	6	160
0.6% Au–0.4% Pt	H_2O	33	95	0	55
Engelhard Escat 10 5% Pd	H_2O	20	96	3	33
Degussa 5% Pt	H_2O	43	97	1	72

[a] Catalytic test: benzyl alcohol 0.3 M, benzyl alcohol/metal 1/500 (mol/mol), $T = 333$ K, time of reaction = 3 h, $pO_2 = 1.5$ atm; stirring rate 1250 rpm.

Table 3
Oxidation of 1-octanol[a]



1-Octanol Octanal Octanoic acid

Catalyst	Solvent	Conv. (%)	Sel. aldehyde (%)	Sel. acid (%)	TOF (h^{-1})
1% Au	Toluene	0	0	0	0
1% Pd	Toluene	2	97	0	1
0.3% Pd	Toluene	3	97	0	1
1% Pt	Toluene	6	98	0	4
0.4% Pt	Toluene	6	98	0	4
0.73% Au–0.27% Pd	Toluene	6	70	12	4
0.6% Au–0.4% Pt	Toluene	2	94	0	1
Engelhard Escat 10 5% Pd	Toluene	3	98	0	1
Degussa 5% Pt	Toluene	8	100	0	5
1% Au	H_2O	0	0	0	0
1% Pd	H_2O	34	30	24	22
0.3% Pd	H_2O	38	33	21	24
1% Pt	H_2O	32	31	25	20
0.4% Pt	H_2O	29	30	27	22
0.73% Au–0.27% Pd	H_2O	45	29	34	28
0.6% Au–0.4% Pt	H_2O	28	28	31	17
Engelhard Escat 10 5% Pd	H_2O	35	30	26	23
Degussa 5% Pt	H_2O	31	35	34	20

[a] Catalytic test: 1-octanol 0.3 M, 1-octanol/metal 1/500 (mol/mol), $T = 333$ K, $pO_2 = 1.5$ atm; time of reaction = 8 h, stirring rate 1250 rpm.

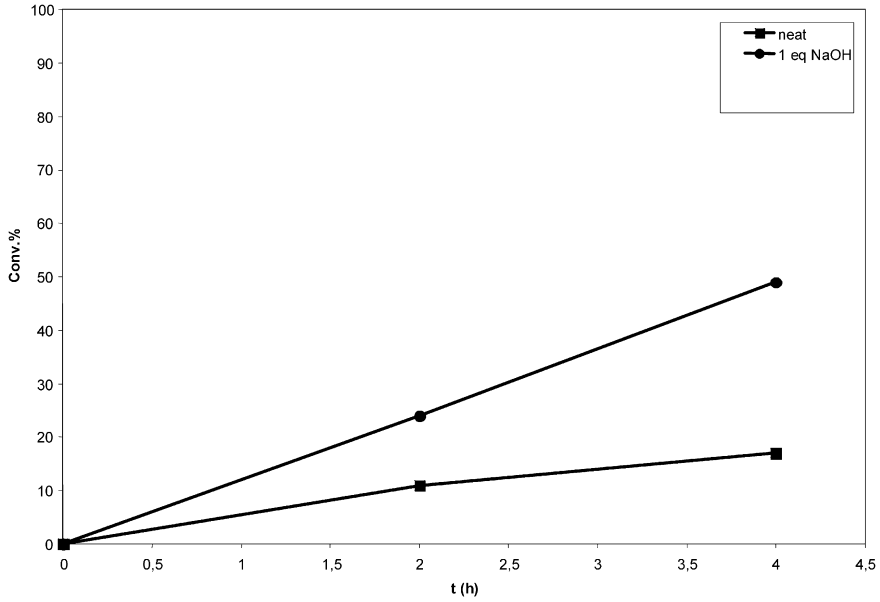


Fig. 5. Oxidation of *n*-octanol in the presence of Au–Pd/AC in water with and without NaOH.

Considering aliphatic substrates, such as *n*-octanol, catalyst activity was disappointing; all of the catalysts were poorly active in both toluene and water. However, the choice of solvent appeared to be crucial in terms of selectivity, with water promoting carboxylic acid formation.

In contrast to the other two substrates (cinnamyl and benzyl), in *n*-octanol the alcohol group demonstrated no electronic activation. Pd and Pt monometallic systems were as active as bimetallics (Au/Pd and Au/Pt); however, Au/AC itself was inactive, indicating that gold in any case improves Pd or Pt activity.

Following a kinetic profile, the rate of O_2 absorption rapidly decreased, indicating sequential catalyst deactivation, because no leaching of metals was observed. We attribute this phenomenon to carboxylate formation, because we observed no deactivation with cinnamyl or benzyl alcohol, in which the main product was aldehyde. Moreover, by carrying out *n*-octanol oxidation in the presence of a base, the activity of all catalysts was enhanced. As previously envisaged, NaOH should facilitate the first step of oxidation (H abstraction) that gold itself is unable to perform, and, based on these results, could play an additional

role as well. In fact, in water NaOH can favor the formation of Na-carboxylate, which is more stable than M-carboxylate, allowing desorption of products and making the metal centre able to continue the catalyst cycle. Thus the higher activity observed with benzyl and cinnamyl alcohols can be related to the nature of the reaction product, with carbonyl desorbing more readily than carboxylate, allowing the catalyst cycle to continue. We can conclude that the beneficial effect of gold in prolonging catalyst life is related mostly to enhancing the resistance to oxygen poisoning. Moreover, gold can be affected by poisoning by (by)products; this depends strictly on the nature of the substrate.

Interesting results were obtained when using benzylic and cinnamyl alcohols (which are similar from an electronic standpoint) as substrates. These alcohols exhibited no deactivation problems due to product formation.

We obtained similar results in terms of trend of synergistic effect, with a positive effect seen with Au on Pd (greater in water than in toluene) and a negative effect seen on Pt. Au/Pd on activated carbon was superior to Au/Pt.

Selectivity profiles appeared almost stable when bimetallics were used, indicating a negligible presence of consecutive reactions. Moreover, Au had almost no influence on overall selectivity, similar to monometallic Pd or Pt. Pt was more selective to aldehyde in cinnamyl alcohol oxidation, whereas Pd was more selective to aldehyde in benzyl alcohol oxidation.

Pd and Pt catalysts suffer from oxygen poisoning in liquid-phase oxidation [39], and Au can act as a diluent, reducing oxygen coverage and thereby enhancing the activity (durability) of Pd or Pt catalysts [56]. However, this cannot explain the observed negative effect of gold on Pt. Characterization of single-phase bimetallic Au/Pd and Au/Pt catalysts revealed that all of the nanoparticles were random alloy with similar Au–M ratios, with lattice parameters of the alloy between those of Au and of Pd or Pt. Such modifications also cause changes in surface interatomic distances and thus in the electronic structure [48,55]. Based on this, we can speculate that activity may be attributed to the Au–M bifunctional sites.

Modifications in the chemical properties of bimetallic systems are caused by electronic interaction between the components, as well as geometric effects due to changes in lattice constants. It is very difficult to disentangle these two effects experimentally, but, depending on the direction of these two effects, we can obtain two different types of bimetallic systems. If the qualitative effects in the two systems were in the same direction, we would expect superior properties compared with monometallic systems. Conversely, if the directions of electronic and geometric effects were opposite, we would not predict any properties; the catalyst could exhibit new and unexpected properties. Based on our results, Au–Pd and Au–Pt likely represent the two cases. Au–Pd showed a strong, positive effect; Au–Pt, an unexpected negative effect.

4. Conclusion

Using sequential deposition of gold and Pd or Pt, we were able to obtain Au–Pd and Au–Pt single-phase catalysts that presented only alloyed phases of a single composition. Testing these catalysts in the liquid-phase oxidation of alcohols, we were able to univocally establish the role of Au when alloyed with Pd or Pt. Using different substrates, we established that gold promotes the resistance of Pt and Pd to deactivation by oxygen but is affected by product poisoning. In fact, when octanol was used as a substrate, carboxylic acid production was enhanced, and strong deactivation of the catalyst was observed. Adding NaOH preserved the catalytic activity.

The presence of Pd or Pt should avoid using a base which, on the contrary, is required when gold is used as the catalyst in water/O_2 system. This occurred when benzylic or cinnamyl alcohols were used as substrates, indicating that principal role of the base in octanol oxidation is to preserve catalyst surface. The presence of a synergistic effect between the two metals was found in most of the catalytic tests, being positive with Pd and negative with Pt in most cases.

The characterization of prepared Au–Pd and Au–Pt catalysts revealed changes in surface interatomic distances and thus in the electronic structure. We attributed catalyst activity to Au–M bifunctional sites and ascribed the different behavior to a different balance between electronic and geometric effects. A cooperative effect makes the Au–Pd catalyst the most active with all the substrates tested.

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