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Application of gold catalysts to selective liquid phase oxidation

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Abstract

New applications of gold catalysts for selective oxidation of organic molecules are reported. All reactions investigated were performed using molecular oxygen in aqueous solution under mild conditions. Polyhydroxylated aliphatic molecules can be oxidised to monocarboxylates with high selectivity towards the primary alcoholic group in the presence of alkali, whereas the phenyl group enhances the reactivity of a benzylic alcoholic group as it limits the selectivity to mandelate starting from phenyl-1,2-ethanediol. α- and β-aminoalcohols react slowly with oxygen in the absence and quickly in the presence of alkali to produce the corresponding aminoacid derivatives. Aliphatic aldehydes and glucose are easily oxidised to free carboxylic acid. A comparison of gold catalysts and conventional Pd and Pt monometallic, bimetallic and tricomponent catalysts has, in some cases, been done. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Liquid phase; Selective oxidation; Carboxylic acids; Amino acids

1. Introduction

In the early 1990s our research group was interested in the selective oxidation of organic molecules, particularly hydroxylated compounds, using molecular oxygen under mild conditions in the presence of metal catalysts. Finely dispersed copper was quite active and good results in terms of advanced catalytic methodologies for the synthesis of organic molecules were obtained [1–4]. However for practical application, the dissolution of the catalyst in the reaction medium was a strong drawback.

Within group 11, Ag and Au show higher redox potentials than Cu, thus stabilising the metal form; we investigated the catalytic behaviour of these elements in order to assess them as possible substitutes for copper. In the first experiment the silver was scarcely active, but gold appeared as a promising candidate for the liquid phase oxidation of the alcoholic group.

At about the same time, the surprising activity of gold in promoting the low temperature oxidation of carbon monoxide was discovered [5], thus opening new perspectives for fascinating applications of this metal in catalysis. Since then many recent academic reports have been collected in a review; knowledge on the use of gold in homogeneous and heterogeneous catalysis has been extended [6]. In this paper we describe the application of gold catalyst to the liquid phase oxidation of organic molecules containing carbon oxygen bond.

2. Experimental

2.1. Materials

Gold sponge of 99.9999% purity from Fluka, γ-Al_2O_3 from La Roche (SA $= 180\,m^2\,g^{-1}$, PV $=$

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0.5 ml g^{-1}), TiO_2 from Degussa (P25, SA = 49 $m^2\,g^{-1}$, 80% anatase) and activated carbon from Carbosorb (MK, SA = 900–1100 $m^2\,g^{-1}$, PV = 1.5 ml g^{-1}, pH 9–10) were used. Commercial 5% Pd/C was supplied by Süd Chemie—M.T., 5% Pt/C by Engelhard, 1% Pt–4% Pd–5% Bi/C by Degussa.

All the reagents were of the highest purity from Fluka and were used without any further purification. NaOH was 99.9% pure from Merck. Gaseous oxygen from SIAD was 99.99% pure.

2.2. Catalyst preparation and characterisation

The catalysts were prepared as reported elsewhere by immobilisation of preformed gold sol [7]. The 5% Pd–5% Bi on carbon catalyst was prepared by using the impregnation method previously reported on commercial 5% Pd on carbon [8].

Electron micrographs of the samples were obtained by a Jeol 2000EX microscope equipped with polar piece and top entry stage. Before introduction into the instrument the samples, in powder form, were ultrasonically dispersed in isopropyl alcohol and a drop of the suspension was deposited on a copper grid covered with a lacey carbon film. Histograms of particle size distribution were obtained by counting onto the micrographs at least 300 particles, and the mean particle diameter (d_m) was calculated by using the formula $d_m = \Sigma d_i n_i / \Sigma n_i$, where n_i is the number of particles of diameter d_i.

2.3. Oxidation procedures

Reactions were carried out in a thermostated glass reactor (30 ml) provided with an electronically controlled magnetic stirrer connected to a large reservoir (5000 ml) containing oxygen at 300 kPa. The oxygen uptake was followed by a mass flow controller connected to a PC through an A/D board, plotting a flow/time diagram.

Glycol or alcohol (5 mmol), NaOH (as reported in tables) and the catalyst (reactant/metal = 1000) were mixed in distilled water (total volume: 10 ml). The reactor was pressurised at 300 kPa of O_2 and thermostated at the appropriate temperature. After an equilibration time of 15 min, the mixture was stirred for 1 h and the products analysed by HPLC on a Varian 9010 instrument equipped with a Varian 9050 UV (210 nm) and Waters 2410 R.I. detectors. An Alltech OA-1000 column (300 mm × 6.5 mm) was used with aqueous 0.01 M H_2SO_4 or alternatively 0.01 M H_3PO_4 (0.8 ml/min) as the eluent. Samples of reaction mixture (0.1 ml) were diluted (10 ml) by using the eluent after adding an internal standard.

For aldehyde oxidation, the same procedure was used except that NaOH was omitted.

All the experiments at controlled pH were carried out at atmospheric pressure bubbling dioxygen through the slurry (20 $Ncm^3\,min^{-1}$) and the control of the pH value (7, 8 and 9.5) was performed by using a 718 STAT Titrino (Metrohom) equipped with a 0.3 M NaOH reservoir. The products were identified and quantified by comparison with authentic samples by using HPLC and ^{13}C-NMR techniques. The total amount of acidic products was also determined from the added amount of NaOH for neutralisation or by titration (inverse).

Recycling tests were carried out by filtering off the catalyst used which was reused in the next run with a freshly prepared solution of reagent. After the appropriate number of runs the catalyst was filtered and washed several times with water until neutral pH of water. The metal content was determined by ICP analysis on a Jobin Yvon JY24.

3. Results and discussion

3.1. Catalyst design

Like many noble metals, supported gold shows a marked dependence of its catalytic activity upon the preparation method. Moreover, a high performance gold catalyst for the oxidation of the alcoholic group is not necessarily a good candidate for the oxidation of the aldehydic group. Therefore, a careful choice of the catalyst for each application is required. On comparing different preparation methods, we found that traditional procedures for gold deposition, namely adsorption and deposition–precipitation of the metal from chloroauric acid solution were unsatisfactory in the case of carbon. As an alternative, we used preformed colloidal metal particles of desired dimensions. The choice of the appropriate sol stabiliser for each support allowed gold particle deposition with maintenance of their original

Table 1
Dimensions of supported gold particles obtained by sol immobilisation

Support	Protecting agent	d_m (nm, HRTEM)
SiO_2	PVP	2.5–3.5
Al_2O_3	THPC	3.8–4.5
TiO_2	THPC	3.7–4.7
C	PVA	4–15

dimensions by avoiding aggregation. In particular, tetrakis(hydroxymethyl)phosphonium chloride, first employed to prepare gold catalysts for CO oxidation [9,10], produced small particles on TiO_2 and Al_2O_3, whereas it proved unsuitable for preparing active catalysts for liquid phase oxidation using carbon powder as support. In this latter case, polyvinylalcohol of average molecular weight of 10 000 Da was found to be the preferred stabiliser [7]. In Table 1 the dimensions of supported gold particles obtained by sol immobilisation on different supports are reported.

Basic correlations between morphology of the catalyst, nature of the support and activity have been derived by using HRTEM, XRD and XPS techniques in connection with a standardised procedure for the selective oxidation of ethylene glycol to glycolate [11]. From these studies, a linear dependence of gold particle size and activity has been found in the case of oxide supports, namely Al_2O_3 and TiO_2, the smaller particles being more active than the larger ones. In the case of carbon, a positive peak of activity has been found for gold particles of 7 nm diameter [12], while the distribution of gold between surface and bulk is influenced by the nature of the carbon [13].

3.2. Oxidation of the alcoholic group

The state of the art of selective oxidation of alcohols by using atmospheric oxygen, in aqueous solution, under mild conditions has recently been reviewed [14]. Platinum group metals, stabilised by Bi and Pb promoters, have for a long time been the most thoroughly investigated catalytic systems. Gold however shows promising applications in the gas phase oxidation of alcohols to aldehydes [15] and in the liquid phase oxidation of diols to monocarboxylates [16].

The special property of supported gold to catalyse the oxidation of alcohols to acids under mild conditions (1–3 atm of O_2, 50–70 °C) and only in alkali solution makes this metal different from conventional catalysts, which are more active under basic conditions, but can be used also in the absence of a base. This is probably due to a lower activity of gold in the initial step, the metal assisted hydrogen abstraction, which is favoured under basic conditions [14] (Scheme 1).

$$RCH_2OH_{sol} = RCH_2OH_{ads} = RCHO_{ads} + 2H_{ads}$$

$$RCHO_{ads} + H_2O = RCH(OH)_{2\,ads} = RCOOH_{ads} + 2H_{ads}$$

Scheme 1. Reaction pathway of alcohol oxidation: $RCH_2OH_{sol} = RCH_2OH_{ads} = RCHO_{ads} + 2H_{ads}$, $RCHO_{ads} + H_2O = RCH-(OH)_{2\,ads} = RCOOH_{ads} + 2H_{ads}$.

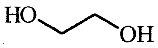
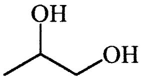
The production of carboxylates instead of carboxylic acids represents a limitation for gold. We have however found that gold is superior to palladium and platinum in many applications where selectivity and resistance are of primary importance.

In order to compare the activity and regioselectivity towards monooxidation, gold on carbon has been evaluated alongside commercial palladium and platinum on carbon catalysts using ethane-1,2-diol and propane-1,2-diol as substrates under similar experimental conditions [17] (Table 2).

Table 3 shows new results obtained in the oxidation of other interesting reagents, such as propane-1,3-diol, 2,2′-oxybisethanol (diethyleneglycol) and phenylethane-1,2-diol, using gold deposited on different supports. The data were obtained by optimising temperature and alkali concentration and represent a good compromise between activity and selectivity towards monooxidation to produce hydroxycarboxylates. In any case we observed a high selectivity with all aliphatic diols whereas the introduction of the phenyl group decreased the selectivity owing to the enhanced activation of the secondary carbon atom in a position (Scheme 2).

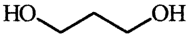
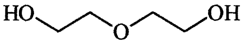
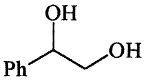
It has been experimentally demonstrated that benzoate is generated by phenylglyoxylate decarboxylation, whereas mandelate is stable under the working conditions. Therefore, favouring the base catalysed intramolecular Cannizzaro reaction (reaction f in Scheme 2), we can avoid the formation of a large amount of benzoate via phenylglyoxylate and, in fact, increasing alkali concentration and temperature we obtained a higher yield in mandelate (Table 4).

Table 2
Oxidation of ethane-1,2-diol to glycolate and propane-1,2-diol to lactate[a]

Substrate	Catalyst	TOF (h^{-1})	Selectivity (%)	Reference
	1% Au/C	1000	98	[16]
	5% Pd/C	500	77	
	5% Pt/C	475	71	
	1% Au/C	780	99	[17]
	5% Pd/C	720	90	
	5% Pt/C	650	89	

[a] Reaction conditions: substrate 0.4 M, substrate/Au = 1000, pO_2 = 3 atm, T = 343 K in the presence of alkali.

Table 3
Oxidation of propane-1,3-diol to 3-hydroxy-propanoate, 2,2′-oxy-bisethanol (diethyleneglycol) to 2-(2-hydroxyethoxy)-acetate and phenylethane-1,2-diol to mandelate[a]

Substrate	Catalyst	TOF (h^{-1})	Selectivity (%)
	Au/C	430	100
	Au/TiO_2	490	95
	Au/C	240	99
	Au/TiO_2	240	98
	Au/C	800	83

[a] Reaction conditions: substrate 0.4 M, substrate/Au = 1000, pO_2 = 3 atm, T = 343 K in the presence of alkali.

Table 4
Oxidation of phenylethane-1,2-diol to mandelate[a]

NaOH/PED	T (K)	Conversion (%)	Selectivity (%)
1	343	52	45
2	343	100	60
2	363	100	70
4	363	100	83

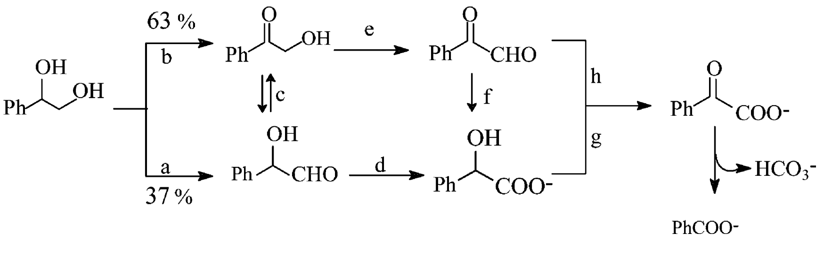
[a] Reaction conditions: substrate 0.4 M, catalyst = 1% Au/C, substrate/Au = 1000, pO_2 = 3 atm.

In some cases, the oxidation of both alcoholic groups in diols to produce a dicarboxylic acid is desirable. Considering the oxidation of diethyleneglycol with various gold catalysts we found that gold on carbon was always very selective towards monooxidation at higher (283 K), lower (90 K) temperatures and in the presence of different quantities of alkali. By using TiO_2 as support the oxidation can be forced to produce the diacid by increasing the NaOH:substrate ratio and increasing the temperature (Table 5).

3.3. Oxidation of aminoalcohols

The presence of the basic amino group in aminoalcohols suggests the possibility of oxidising the alcoholic group in the absence of added alkali by means of gold catalysts. However, it is known that aliphatic amines strongly interact with noble metals, resulting in their catalytic deactivation [18].

Therefore, it was of interest to compare the Au catalysts with Pd and Pt catalysts with a view to find a new convenient synthesis of aminoacids. The



Scheme 2. Oxidation pathway of phenylethanediol.

Table 5
Selectivity in diethyleneglycol oxidation[a]

Catalyst	NaOH/substrate	T (K)	t (h)	Conversion (%)	Monoacid (%)	Diacid (%)
1% Au/C	1	343	4	96	99	1
	2	343	4	80	97	3
		363	1	83	98	2
1% Au/TiO_2	1	343	4	95	98	2
		363	2	95	96	4
	2	343	3	94	70	30
		363	6	100	55	45

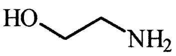
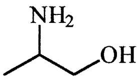
[a] Reaction conditions: substrate 0.4 M, substrate/Au = 1000, $pO_2 = 3$ atm.

actual interest in this application is well documented by academic and industrial research. In particular, a bimetallic Pt–Cu catalyst has been claimed to be active for the dehydrogenation of aminoalcohols [19] and Au/C has been claimed to catalyse the oxidation of ethanolamines to aminocarboxylates in aqueous NaOH [20].

Our results for the oxidation of 2-aminoethanol and 2-aminopropanol by using carbon supported Au, Pd and Pt catalysts under mild conditions, without added alkali, are reported in Table 6. It can be seen that the activity of Au/C catalyst in promoting the oxidation to aminoacid is very sensitive to the nature of substrate being very low in the case of 2-aminoethanol and higher with 2-aminopropanol. In both the cases, the Pd and Pt catalysts were inactive. By adding NaOH (1 equivalent) an improved conversion to aminocarboxylate can be obtained only in the case of Au/C, whereas the Pd and Pt catalysts remained inactive (Table 7).

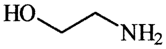
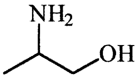
In order to improve the catalytic activity, we tested different supported gold catalysts: Au/Al_2O_3 in the presence of alkali produced the best yield with many substrates. Table 8 records the results obtained in the oxidation of α- and β-aminoalcohols. The selectivity towards aminocarboxylate is almost 100% in all cases except for 2-aminoethanol where a large part of the product was detected in the form of dimer.

Table 6
Oxidation of 2-aminoethanol to 2-aminoacetic acid (glycine) and 2-aminopropanol to 2-aminopropanoic acid (alanine) without alkali added[a]

Substrate	Catalyst	Conversion (%)
	1% Au/C	3
	5% Pd/C	0
	5% Pt/C	0
	1% Au/C	22
	5% Pd/C	0
	5% Pt/C	0

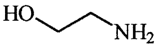
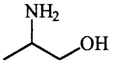
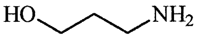
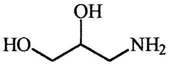
[a] Reaction conditions: substrate 0.4 M, substrate/M = 1000, $pO_2 = 3$ atm, $T = 343$ K, $t = 2$ h.

Table 7
Oxidation of 2-aminoethanol to 2-aminoacetate and 2-aminopropanol to 2-aminopropanoate[a]

Substrate	Catalyst	Conversion (%)
	1% Au/C	20
	5% Pd/C	0
	5% Pt/C	0
	1% Au/C	65
	5% Pd/C	0
	5% Pt/C	0

[a] Reaction conditions: substrate 0.4 M, substrate/M = 1000, substrate/NaOH = 1, $pO_2 = 3$ atm, $T = 343$ K, $t = 2$ h.

Table 8
Oxidation of various aminoalcohols to the sodium salt of the corresponding aminoacids with 1% Au/Al_2O_3[a]

Substrate	Conversion (%)
	23
	100
	27
	32

[a] Reaction conditions: substrate 0.4 M, substrate/M = 1000, substrate/NaOH = 1, $pO_2 = 3$ atm, $T = 343$ K, $t = 2$ h.

In conclusion, by using the appropriate catalyst under controlled conditions, we were able to obtain fully satisfactory results only in the oxidation of 2-aminopropanol to sodium alaninate. Owing to the strong influence of the substrate on catalyst activity, there is a need for more work in order to reach better results for other aminoalcohols.

3.4. Oxidation of the aldehydes

Aqueous solutions of nonactivated ketones are very stable towards aerobic oxidation in the presence of gold catalysts. On the contrary, aldehydes are smoothly oxidised to the corresponding acid in either the presence or absence of added alkali. This observation strengthens the previous hypothesis that dehydrogenation assisted by supported gold is the most energy-demanding step in the oxidation of alcohols in neutral solution. The scope of this study was to optimise the catalytic system for the selective oxidation of water soluble aldehydes and to make a comparison, under similar experimental conditions, between gold catalysts and commercial Pd and Pt catalysts, also in terms of poison resistance.

The results summarised in Table 9 indicate the performance of 1% Au deposited on three different supports: C, Al_2O_3 and TiO_2 in the oxidation of 1-propanal. The three catalysts, prepared starting from the same gold sol procedure and having similar particle dimensions, show different activity making the carbon the best support. In Table 10 the performance of carbon supported Au, Pd and Pt catalysts is compared in the 1-propanal oxidation.

In our experiments, gold was superior to unmodified Pd and Pt commercial catalysts with respect to the recycling test. It has been reported that catalyst overoxidation or surface modification can be responsible for Pd and Pt deactivation [21].

Table 9
Oxidation of 1-propanal to propanoic acid[a]

	1% Au/C	1% Au/TiO_2	1% Au/Al_2O_3
Conversion (%)	90	42	43
d_m (nm, HRTEM)	7.0	3.4	3.6

[a] Condition: propanal 0.23 M, solvent H_2O, $T = 363$ K, $P = 3$ atm, $t = 2$ h, selectivity >99%.

Table 10
Performances of metal on carbon in 1-propanal oxidation to propanoic acid[a]

Catalyst	Conversion (%)				
	Run I	Run II	Run III	Run IV	Run V
1% Au/C	90	93	89	89	91
5% Pd/C	81	81	80	68	62
5% Pt/C	89	51	45	49	45

[a] Conditions: propanal 0.23 M, solvent H_2O, $T = 363$ K, $P = 3$ atm, $t = 2$ h. The catalyst is washed with water and reused in wet form.

3.5. Oxidation of D-glucose

Gluconic acid and its salts are important industrial products as food additives and detergents. Actually biochemical oxidation of carbohydrates is the preferred method for its production despite many problems related to selectivity and disposal of waste water. A new route has been proposed recently which is based on the platinum–palladium–bismuth catalysed oxidation of glucose which shows not only high activity and selectivity but also problems related to the life-time [21].

Recently, we have applied supported gold catalysts to the oxidation of D-glucose in water solution under mild conditions [22] and made a direct comparison with monometallic [23], bimetallic [24] and trimetallic [25] catalysts claimed in previous studies.

In this research we found that 1% Au/C and platinum group metals are very selective to gluconate (99%). The gold catalyst works either in neutral or

Table 11
Oxidation of D-glucose to D-gluconic acid at controlled pH[a]

Entry	Catalyst	pH	TOF (h^{-1})
1	1% Au/C	9.5	500
2	5% Pt/C	9.5	220
3	5% Pd/C	9.5	7.5
4	5% Pd–5% Bi/C	9.5	450
5	1% Pt–4% Pd–5% Bi/C	9.5	480
6	1% Au/C	8	410
7	5% Pt/C	8	103
8	5% Pd/C	8	5
9	5% Pd–5% Bi/C	8	317
10	1% Pt–4% Pd–5% Bi/C	8	292

[a] Reaction conditions: glucose 10%, glucose/M = 1000, O_2 flow = 20 ml/min, $T = 323$ K. The pH was maintained at the indicated value by dropping 0.1 M NaOH.

basic solution but it is more effective in alkaline solution. Pd and Pt derivatives are almost inactive in neutral solution. In any case, the TOF values are always better for gold as shown by the data reported in Table 11. Also experiments on catalyst recycling have shown a better performance of gold catalyst.

The present results show that gold on carbon represents a valid alternative to the more complicated multimetallic catalysts for the liquid phase oxidation of D-glucose avoiding, in particular, the problem of bismuth leaching [26].

4. Conclusions

Suitable methods for catalyst preparation could enlarge the use of gold in the chemical industry for producing valuable, medium–large scale products according to clean technologies based on the use of gaseous oxygen, in aqueous solution under mild conditions.

From our studies the following applications seem to be encouraging in terms of catalyst activity, selectivity and durability:

1. Synthesis of glycolic acid (estimated world production 2000 t/year) via ethylene glycol as alternative to Du Pont processes via chloroacetic acid and via formaldehyde–carbon monoxide.
2. Synthesis of racemic lactic acid (total world production L + LD 50 000 t/year) via 1,2-propanediol as alternative to fermentation process and to acetaldehyde–hydrogen cyanide process.
3. Gluconic acid (estimated world production 60 000 t/year) via glucose as alternative to enzymatic oxidation.

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