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Gold catalyzed oxidation of aldehydes in liquid phase

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Abstract

Gold on carbon oxidizes aldehydes to carboxylic acids in water solution under mild conditions without loss of activity on recycling, as does not occur for platinum on carbon. Also scarcely soluble aldehydes can be oxidized but the reaction rate is slower. Experiments carried out in an organic solvent such as CCl_4 show a speed up of the reaction, in this solvent being recyclable both Au/C and Pt/C. Another explored possibility was represented by carrying out the reaction in the absence of solvent. However, for solid aldehydes like *p*- and *o*-OH-PhCHO the water solvent represent the unique alternative.
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1. Introduction

The oxidation of aldehydes with O_2 as the oxidant is actually performed in the liquid phase using homogeneous catalytic systems based on salts of copper, iron, cobalt, manganese, etc. [1]. However, the use of heterogeneous systems would be advantageous as metal recovery is easier and more efficient than in homogeneous systems and, furthermore, far less damaging from an environmental point of view.

From the industrial point of view, gas phase oxidation is more attractive as the absence of solvent facilitates product collection, but limitations due to high boiling points or thermal instability sometimes preclude this choice.

Liquid phase catalytic oxidation can normally be carried out under milder conditions than the gas phase and, by employing O_2 as the oxidant, the choice of solvent determines the active mechanism, organic solvents favoring the radical pathway [2], whereas water privileges the ionic pathway [3]. Moreover, water is a safe and environmentally compatible solvent, and is favored from the industrial point of view. However, in liquid aqueous phase oxidation the classical heterogeneous catalysts based on platinum-group metals suffer deactivation when O_2 is the oxidant, thus catalyst lifetime is compromised [3,4].

In order to meet both environmental (liquid aqueous phase and heterogeneous system) and industrial requirements (safety and high productivity), we turned our attention to gold based catalytic systems, gold having been reported as being much more resistant to poisoning in liquid phase oxidation where O_2 is the oxidant than platinum metal based catalysts [5].

This paper deals with the use of gold catalysts in the oxidation of aldehydes in the liquid phase, extending promising results from the oxidation of D-glucose to gluconic acid [6]. We also compared catalyst activity and catalyst lifetime in different solvent systems (pure water, organic solvent and mixture of both), evaluating the differences in reactions using platinum catalyst as a function of reagent and solvent employed.

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2. Experimental

2.1. Materials

Gold of 99.9999 purity in sponge from Fluka and activated carbon from Carbosorb (MK; SA = 900–1100 m^2/g; PV = 1.5 ml/g; pH 9–10) were used. $NaBH_4$ of purity >96% from Fluka and polyvinylalcohol (PVA) (M = 10,000 Da) from Aldrich were used. Gaseous oxygen from SIAD was 99.99% pure. Aldehydes of the maximum purity grade (>98%) were from Fluka and used without any further purification.

Pt/C (5%) commercial catalyst was from Engelhard (Escat 21, water content 54%).

2.2. Gold sol preparation

The procedure has been reported elsewhere [7,8]. An aqueous $HAuCl_4$ solution of 100 μg/ml is prepared by dissolving gold (30 mg) in a minimum amount of HCl/HNO_3 3/1 (v/v) mixture and, after removing the HNO_3, it is diluted with distilled water. Maintaining the auric solution under vigorous stirring the PVA 2 wt.% solution (0.96 ml) is added; a 0.1 M freshly prepared solution of $NaBH_4$ (7.62 ml) is then added dropwise to yield to a ruby red metallic sol.

2.3. Catalyst preparation

Within a few minutes of sol generation, the sol is immobilized by adding activated carbon under vigorous stirring. The amount of support is calculated as having a final gold loading of 1 wt.%. After 2 h the slurry is filtered, the catalyst washed thoroughly with distilled water and used in the wet form. The absorption of gold is checked by ICP analysis of the filtrate. The water content is determined by drying a sample for 5 h at 150 °C in air.

2.4. Oxidation procedures

The 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.

The aldehyde (5 mmol) and the catalyst (reagent/metal = 1000 mol/mol) were mixed in the solvent (total volume 10 ml). The reactor was pressurised at 300 kPa of O_2 and thermostated at the appropriate temperature depending on the solvent employed. After an equilibration time of 15 min, the mixture was stirred for 2 h. Also the work up of the reaction depended on solvent:

(a) when the solvent was water or water/CH_3CN and the aldehyde was in solution, HPLC analysis of products was carried out directly on the solution after filtering-off the catalyst and diluting the sample with the eluent;
(b) when the solvent was water but the aldehyde was unsoluble, solubilization was achieved by adding CH_3CN; the solution was filtered to remove the catalyst, diluted with the eluent and analyzed;
(c) when CCl_4 was used as solvent and the aldehyde was insoluble in water the reaction mixture was evaporated under reduced pressure and the products dissolved in the minimum amount of CH_3CN, HPLC analysis of the products was carried out after removing the catalyst by filtration and diluting the sample with the eluent;
(d) when CCl_4 was used as solvent and the aldehyde was soluble in water, the reaction mixture was diluted with the solvent, filtered and extracted with water, HPLC analysis of the products was carried out on the aqueous phase.

Solvent-less experiments were carried out in a stainless steel autoclave under an air pressure of 1500 kPa with a reagent/metal molar ratio of 20,000. The autoclave was thermostated by an electronically controlled furnace. HPLC analysis of the products was carried out after diluting the sample at the appropriate concentration with the eluent and removing the catalyst by filtration.

2.5. Analyses of products

Products were analyzed by HPLC on a Varian 9010 instrument equipped with a Varian 9050 UV (210 nm) and a Waters RI detectors in series.

An Alltech OA-1000 column (300 mm × 6.5 mm) with aqueous H_2SO_4 0.01 M (pH 2.1) (0.8 ml/min) as the eluent was used for water-soluble aldehydes whereas a Merck-Lichrocart 125-3 column (Purospher RP-18) with H_2O/CH_3CN (4/6 to 6/4)

(0.5–0.7 ml/min) as the eluent was used for water insoluble aldehydes.

2.6. Recycling tests

After the first run, the catalyst was filtered-off and reused in the next run with a freshly prepared solution of aldehyde. To check for metal leaching the filtrate underwent ICP analysis on a Jobin Yvon JY24.

3. Results and discussion

We recently reported that gold on carbon was able to oxidize D-glucose (an emiacetal) to gluconic acid, even in the absence of a base that neutralized the acid formed [6]. Contrarily to the reaction carried out in the presence of a base, we noted a slow deactivation process of the catalyst that we ascribed to metal leaching and sintering of gold particles. Comparing gold to PGM-based catalysts, however, we evidenced a better resistance of gold to poisoning at low pH.

In this research, we have considered aldehyde oxidation in greater detail with the aim of proposing supported gold as a catalyst for wider applications.

We first considered aqueous soluble aldehydes, such as *n*-propanal, *n*-butanal and 2-methyl-propanal.

Table 1
Water-soluble aldehydes oxidized in water

Reagent	Conversion (%)[a]	
	1% Au/C	5% Pt/C
n-Propanal	90	89
n-Butanal	92	86
2-Methyl-propanal	86	84

[a] Reaction conditions: [aldehyde] = 0.23 M in water; metal/aldehyde = 1000 mol/mol; $T = 363$ K; $p(O_2) = 300$ kPa; $t = 2$ h.

Table 1 shows the results for oxidation in water under 300 kPa of O_2 pressure at 363 K for 2 h. We were not surprised to find that gold on carbon is as active as platinum on carbon, converting about 90% of the substrate in 2 h, as we had already observed in our previous studies on gold catalyzed oxidation of glucose that the reaction rate using gold or platinum on carbon is similar [5,6].

Focusing our attention on *n*-propanal we carried out recycling experiments. Fig. 1 clearly shows that the behavior of gold on carbon differs from that of platinum on carbon, maintaining its activity for five runs whereas platinum loses 40% of its activity after the second cycle. This surprised us as in glucose oxidation we detected, under similar conditions, gold leach-

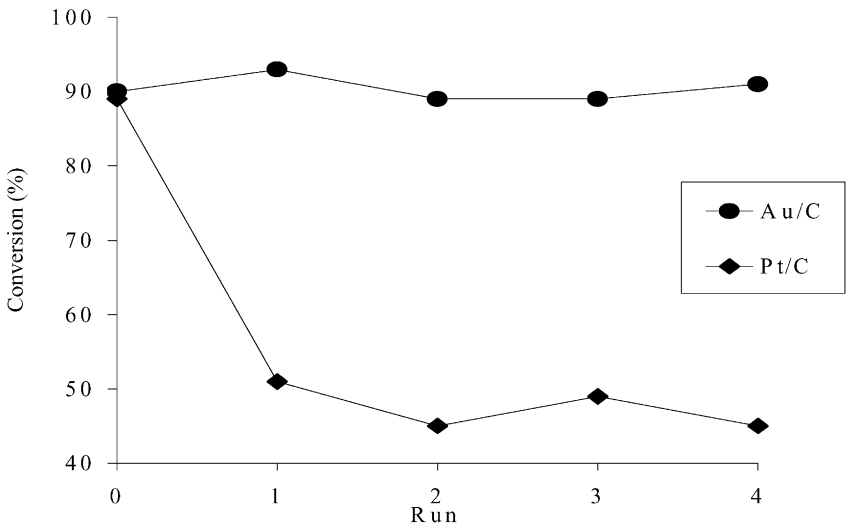

Fig. 1. Conversion on recycling of *n*-propanal in water. Reaction conditions: [*n*-propanal] = 0.23 M in water; $T = 363$ K; $p(O_2) = 300$ kPa; $t = 2$ h. After the first run, the catalyst was filtered-off, thoroughly washed with water and used in the next run with a freshly prepared solution of aldehyde.

Table 2
Oxidation of water-unsoluble aldehydes

Reagent	Conversion (%)[a]			
	Water		Water/acetonitrile (9/1 (v/v))	
	1% Au/C	5% Pt/C	1% Au/C	5% Pt/C
p-Me-PhCHO	8	6	3	2
PhCHO	24	20	5	5
p-F-PhCHO	24	21	4	5
n-$C_6H_{13}CHO$	9	9	4	3
n-C_2H_5CHO	90	81	25	41

[a] Reaction conditions: [aldehyde] = 0.23 M in water; metal/aldehyde = 1000 mol/mol; $T = 363$ K; $p(O_2) = 300$ kPa; $t = 2$ h.

ing with a consequent decrease in conversion on recycling [6]. The maintenance of activity and the total retention of the metal loading in unsubstituted aldehyde oxidation means that for glucose oxidation it is not the experimental conditions that are responsible for metal leaching, but, most probably, the chelating nature of the reagent, though a different mechanism cannot be excluded as glucose is a particular form of aldehyde. Moreover, the recycling results have highlighted gold's resistance to the typical deactivation suffered by PGM-based catalysts when oxygen is the oxidant in liquid phase.

In order to generalize the positive result found above, we extended our test to superior aldehydes, that resulted poorly soluble in water. Table 2 shows the results obtained using Au/C and Pt/C. In water slurry, both catalysts show very poor activity compared with the activity using a soluble reagent as propanal. Therefore, we carried out oxidation in the presence of a solvent able to dissolve aldehydes, like acetonitrile. Surprisingly, we observed, with both catalysts, a drastic drop off in conversion despite the complete dissolution of the aldehydes. Suspecting a direct interference by the solvent we oxidized *n*-propanal, which is smoothly oxidized in water, using acetonitrile or even a mixture of water/acetonitrile (9:1 (v/v)) as the solvent. Again, we observed a marked decrease in activity with respect to that in water, more evident for gold than for platinum meaning that the poor activity of the catalysts in the presence of acetonitrile was due to the solvent.

In order to overcome this limitation, we carried out some experiments dissolving various aldehydes in an organic solvent; for safety reason we focused our attention on CCl_4. By carrying out the reactions in this solvent, we observed a high activity (Table 3) regardless of the nature of the substrate. Note that by using CCl_4 instead of water we were obliged to decrease the reaction temperature, from 363 (in water) to 343 K (in CCl_4). Therefore, the conversion enhancement observed in CCl_4 for the same time as for water was more pronounced than the numbers show. Also the oxidation of *n*-propanal, representative of a water-soluble aldehyde, was more rapid in CCl_4 than in water, but, on adding to the CCl_4 solution a few drops of CH_3CN we again observed a decrease in the reaction rate.

Table 3
Comparison of oxidations in different solvent

Reagent	Conversion (%)[a]			
	H_2O[b]		CCl_4[c]	
	1% Au/C	5% Pt/C	1% Au/C	5% Pt/C
p-Me-PhCHO	8	6	76	69
n-$C_6H_{13}CHO$	9	9	99	99
n-C_2H_5CHO	90	81	96	95

[a] Reaction conditions: [aldehyde] = 0.23 M in water; metal/aldehyde = 1000 mol/mol; $p(O_2) = 300$ kPa; $t = 2$ h.
[b] $T = 363$ K.
[c] $T = 343$ K.

We observed a particular behavior for *o*- and *p*-hydroxybenzaldehyde that were slowly oxidized in water (Table 4) but were unreactive in CCl_4. Thus, probably, also a different mechanism of oxidation was active in water and in CCl_4.

As shown in Fig. 2, we observed that recycling experiments in CCl_4 showed good performances for Pt/C as well as for Au/C.

Table 4
Oxidations using gold on carbon

Reagent	Conversion (%)[a]		
	H_2O[b]	H_2O/CH_3CN[c]	CCl_4[d]
p-Me-PhCHO	8	3	88
PhCHO	24	5	96
n-$C_6H_{13}CHO$	9	4	96
n-C_2H_5CHO	90	25	96
p-OH-PhCHO	10	9	0
o-OH-PhCHO	19	21	0

[a] Reaction conditions: [aldehyde] = 0.23 M in solvent; metal/aldehyde = 1000 mol/mol; $p(O_2) = 300$ kPa; $t = 2$ h.
[b] $T = 363$ K.
[c] $H_2O/CH_3CN = 9/1$ (v/v); $T = 363$ K.
[d] $T = 343$ K.

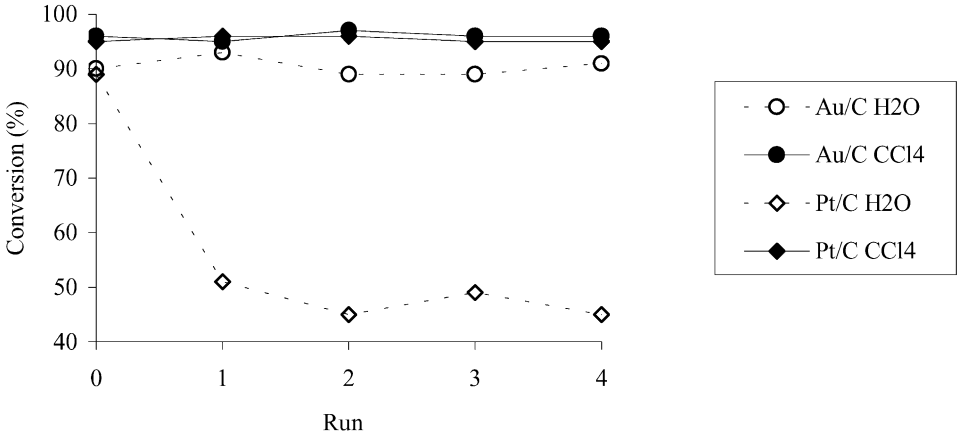

Fig. 2. Conversion on recycling of *n*-propanal in CCl_4. Reaction conditions: [*n*-propanal] = 0.23 M in CCl_4; $T = 343$ K; $p(O_2) = 300$ kPa; $t = 2$ h. After the first run, the catalyst was filtered-off, thoroughly washed with the solvent and used in the next run with a freshly prepared solution of aldehyde.

Table 5
Oxidation with air of aldehydes with gold on carbon in the absence of solvent

Reagent	Conversion (%)[a]	
	70 °C	25 °C
2-Methyl-propanal	75	40
n-$C_6H_{13}CHO$	68	–

[a] Reaction conditions: aldehyde/metal = 20,000 (mol/mol); p(air) = 1500 kPa; $t = 2$ h.

A third typology of reaction, i.e. operating in the absence of solvent, was carried out on liquid aldehyde such as 2-methyl-propanal and *n*-eptanal. In these cases, security constrains led to use air instead of pure oxygen. Surprisingly, we observed that the oxidation took place smoothly also at room temperature with TOF ranging from 7500 to 4000 h^{-1} depending on the temperature (Table 5). Recycling experiments of the catalyst showed that also in this case gold on carbon can be used several times without any loss of activity.

4. Conclusion

Gold on carbon showed good activity in oxidizing aldehydes in water solution and, contrary to Pt/C, there was no deactivation of the catalyst on recycling. In water solvent, almost all the tested aldehydes are oxidized, the reaction rate depending on the nature of substrate. Scarcely soluble reagents show a slower reaction rate. Using organic solvents we highlighted the worst behavior of CH_3CN whereas CCl_4 produced an enhancement of the reaction rate in most cases. An alternative for liquid aldehydes is represented by the absence of solvent; neat aldehydes in fact were rapidly and smoothly oxidized also at room temperature. In all cases, gold on carbon can be profitably recycled.

We found that there are some cases where the use of water was the unique alternative, as in the cases of hydroxy benzaldehydes, being the reaction rate in organic solvent nil.

From an environmental point of view, the use of water is always auspicable, such a solvent fulfilling both environmental and safety requirements. Thus, gold on carbon can be used profitably in the liquid phase oxidation of aldehydes as an alternative to heterogeneous Pt/C, that deactivates rapidly, and to homogeneous systems having high environment impact.

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