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Catalytic oxidation of 1,2-diols to α-hydroxy-carboxylates with stabilized gold nanocolloids combined with a membrane-based catalyst separation

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Gold (Au) nanosols stabilized with poly(vinylalcohol) can be used as homogeneous oxidation catalysts, both in water and in a variety of alcoholic solvents. Under 0.5 MPa O_2 pressure, 1,2-diols with varying chain length, such as 1,2-propanediol or 1,2-octanediol, are oxidized to the corresponding α-hydroxy-carboxylates with total chemoselectivity. The activity of the sol is of the same order as previously reported for stabilized nanoparticles deposited on carbon supports. The stabilized sols retain their activity over extended periods. The Au metal colloids can efficiently be recycled by means of a nanofiltration, either from an aqueous reaction medium, or from an organic solvent. The most suitable membranes for the Au sol recuperation are cellulose acetate membranes for the aqueous filtration, and poly(dimethyl)siloxane membranes for the solvent resistant filtration. Recycling tests after nanofiltration show that catalytic activity is largely preserved in consecutive runs.

KEY WORDS: liquid phase oxidation; selective oxidation; gold nanoparticles; colloidal catalysts; membrane filtration; lactic acid.

1. Introduction

Catalysis by metallic or ionic gold (Au) is still in an early stage of development. Ionic Au catalyzes various reactions such as the oxygenation of methane [1,2] or additions to C≡C bonds [3]. Zerovalent Au only acquires catalytic activity when the metal clusters have nanometer dimensions [4,5]. Catalysis by supported Au clusters has found application in gas phase reactions, for example the low temperature oxidation of CO [6], the hydrochlorination of ethyne [7], the water–gas shift reaction [8], the reduction of CO_2 to methanol [9], the epoxidation of propylene [10] and the dehydrogenation of alcohols [11]. On the other hand, supported Au catalysts have been studied in detail for liquid phase redox reactions, such as the reduction of unsaturated ketones to allylic alcohols [12], the synthesis of H_2O_2 [13], or the oxidation of alcohols and aldehydes. Suitable substrates in the latter reactions are 1,2-diols [14–17], glucose [18,19], and aminoalcohols [20,21].

Innovative and reliable methods have recently been developed to synthesize Au nanocolloids. In the methodology pioneered by Rossi and his co-workers, a metal sol is generated by chemical reduction of a Au salt in the presence of protecting agents [22–25]. The sol may be stabilized by steric or by electrostatic effects. Deposition of this prereduced Au sol on carbon yielded superior catalysts in comparison with materials prepared via conventional methods, such as deposition–precipitation. Especially in selective oxidation of alcohols or aldehydes, such Au/C catalysts prove to be suitable alternatives for platinum group metal catalysts. In comparison with Pt and Pd, Au is more resistant to deactivation by chemical poisoning or overoxidation, and it displays a higher intrinsic chemoselectivity in the oxidation of 1,2-diols to 2-hydroxy-acids.

While supported Au clusters have received broad attention, the catalytic activity of Au sols as such has only received limited attention. In a recent publication, Rossi *et al.* show that the use of non-stabilized, ‘naked’ Au nanoclusters allows to reach extremely high turnover frequencies (TOF 18000 h^{-1}) in the oxidation of glucose [26]. While the sols as such are subject to rapid aggregation and deactivation, deposition of the sols on carbon allows to considerably increase the catalyst lifetime. This recent publication prompted us to publish our own results with catalytic Au sols, stabilized with poly(vinylalcohol). Obviously, the use of a sol demands a suitable recycling of the sol catalyst. A possible option is the recuperation of the catalyst via a membrane filtration. This approach has recently been explored for the recuperation of homogeneous catalysts, e.g. with solvent-resistant nanofiltration [27,28], but has yet to prove its value for metallic sols.

In this paper, we report on the use of stabilized Au sols in 1,2-diol oxidation. It is shown that these sols can be used either in water or in organic solvents, and this substantially widens the substrate scope of the diol oxidation to water-insoluble diols. It is also proven that the stabilized sols preserve a considerable catalytic

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activity, even upon long storage in ambient conditions. Finally, we report the first efficient recycling of such catalytically active nanoparticles by means of a membrane filtration, either from an aqueous or from an organic phase. The mild conditions of reaction and filtration make it possible to combine both steps in a hybrid oxidation process.

2. Experimental

2.1. Catalyst preparation

A standard stabilized Au sol was prepared by adding 1 mL of an aqueous 2.5 wt.% poly(vinylalcohol) solution (PVA, M_w 13,000–23,000, Aldrich) to 100 mL of a stirred aqueous 0.002 M $HAuCl_4$ solution. Next the Au solution was reduced at 50 °C by drop wise addition of 10 mL of a 0.1 M $NaBH_4$ solution.

The Au sols were characterized by UV–Vis absorption spectroscopy (Perkin Elmer Lambda 12) and transmission electron microscopy (Philips CM 20) after deposition on carbon grids.

2.2. Membrane preparation

For the aqueous filtrations, various membranes were prepared based on the immersion–precipitation phase inversion technique. Polyimide membranes (PI) were successfully prepared by immersing an organic polyimide solution film in water. 20.0 g of a solution containing 3.00 g polyimide (Matrimid® Ciba-Geigy 5218), 0.50 g H_2O, 12.38 g *N*-methyl-2-pyrrolidone and 4.12 g THF was coated on an inox plate using a casting knife with a 250 μm slit. After evaporation of the THF at room temperature, the polymer solution film was coagulated in a de-ionized water bath at room temperature for 3 h. After synthesis the membranes were kept in 2-propanol for 3 h, in a 2:2:1 mixture of toluene, 2-methyl-4-pentanone and mineral oil ÖLP3 (Pfeiffer) for 24 h, and dried for 1 h at 60 °C. For the synthesis of cellulose acetate (CA) membranes, a solution consisting of 3.00 g CA (Sigma, acetyl content 40%), 5.66 g formamide and 11.30 g acetone, was cast in 250 μm thickness, coagulated for 3 h in water at 5 °C, annealed for 10 min in water at 75 °C, and stored in a 5 wt.% formamide solution.

For the sol filtration in organic solvents, a solvent-resistant poly(dimethylsiloxane) (PDMS) membrane was selected. The membrane synthesis was based on Vankelecom *et al.* [29]. This membrane comprises a polyacrylonitrile/polyester support layer (VITO), covered by a PDMS layer which is prepared from vinyl-functionalized prepolymer RTV 615A and the silicon hydride cross-linker RTV 615B in a 10:1 ratio. In the preparation, a coating slope of 30° was applied, and an adhesion promotor was used (SS4155 from GE Bayer Silicones).

2.3. Oxidation experiments and analysis

A standard oxidation mixture contained the solvent, 4 mmol of the diol, 4 mmol NaOH and an aliquot (0.55 or 0.88 mL) of the Au colloidal solution, depending on the desired substrate:catalyst ratio (4000 or 2500, with 1 or 1.6 μmol Au, respectively). The total volume of the solvent and sol together was fixed at 5 mL. This mixture is pressurized to 0.5 MPa O_2, heated to 70 °C and stirred at 1000 rpm.

For GC analysis (CP-SIL-5 column, FID detector), the reaction mixture was acidified, the solvent was evaporated and the substrates and products were derivatized by silylation of the –OH groups with *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide (Avocado, >98%) in ether. As standards, commercial lactic acid, 2-hydroxy-hexanoic acid and 2-hydroxy-octanoic acid were employed. The identity of all derivatized products was confirmed by GC-MS.

The catalyst activity is expressed as the average turnover frequency (TOF, h^{-1}), i.e. the molar amount of substrate (S) converted per mole of Au catalyst (C), divided by the reaction time (h).

2.4. Filtration experiment

Filtrations were performed at room temperature with a 0.5 MPa N_2 driving force; the Au content of the starting solution and the filtrate were analyzed with ICP-AES (ICP-OES 3300DV). In order to investigate membrane fouling, the membrane was first used for a Au sol filtration, and then digested in aqua regia; the obtained solution was analyzed with ICP-AES.

3. Results and discussion

The standard PVA-stabilized Au sol was characterized in order to obtain information about the Au dispersion. The violet color of the colloidal solution, with an absorption maximum at $\lambda_{max} = 539$ nm, can be ascribed to the surface plasmon resonance phenomenon, and thus evidences the presence of zerovalent Au nanoparticles [30]. The characteristic particle dimensions, as determined by TEM, were 2–4 nm, with more than 60% of the total number of Au particles in this size range. In agreement with earlier observations, the use of a large $NaBH_4$:Au ratio (5:1) results in a fast reduction, with formation of small Au^0 nanoclusters [23].

Initial experiments indicated that the sols were active catalysts for oxidation of 1,2-propanediol in water, and for oxidation of 1,2-propanediol, 1,2-hexanediol or 1,2-octanediol in tBuOH. In all cases, the α-hydroxy-carboxylates were formed by applying the standard oxidation procedure. Regarding the chemoselectivity, GC analysis after derivatization showed that lactate, α-hydroxy-hexanoate and α-hydroxy-octanoate were the only oxidation products (selectivity >98%), confirming the excellent chemoselectivity of Au catalysts [14]. Other oxidation products or side products were not detected, neither in the aqueous oxidation nor in the organic media.

The effect of the solvent was investigated by comparing water with selected alcohols. The data in table 1 evidence that water is the solvent of choice for the oxidation of water-soluble 1,2-diols like 1,2-propanediol. In water, the average TOF over a reaction time of 3 h is 850 h^{-1} at 343 K. This value is of a similar order of magnitude as previously recorded for supported Au catalysts. Indeed, in the 1,2-propanediol oxidation, Carretin *et al.* [17] obtained a TOF of 373 h^{-1} at 333 K for 0.25 wt.% Au/graphite; Prati and Rossi [14] obtained a TOF value of 780 h^{-1} at a higher reaction temperature of 363 K for a 1 wt.% Au/C catalyst prepared via deposition–precipitation. It should be remarked that with other substrates, higher TOF values have been obtained. For instance, with 1,2-ethanediol and the same catalyst, Prati and Rossi [20] obtained 1000 h^{-1} as a TOF at a lower temperature of 343 K. Oxidation of a water-soluble aldehyde such as glucose can proceed even much faster. In their kinetic study, Claus and co-workers [19] obtained a rate of 1000 h^{-1} at 323 K with Au/C; for 'naked' Au clusters, a TOF of 18,000 h^{-1} at 303 K was found, albeit for just a short time span [26]. However, as it is well known that the first oxidation is the slowest step in the Au-catalyzed oxidation of diols [14], it can be expected that TOFs for alcohol oxidation are considerably lower than TOFs for glucose oxidation. For a water-soluble diol such as 1,2-propanediol, water is the best solvent, but acceptable activities are observed as well in tBuOH, with a TOF of 510 h^{-1}. In other, primary or secondary alcohols, lower rates were observed.

The suitability of tBuOH as a solvent enables the oxidation of diols that are much less water soluble than 1,2-propanediol, as demonstrated in table 2. Even if the TOF values gradually decrease as the carbon chain length is increased, the activity can be sustained over longer reaction times, and for 1,2-octanediol, a total of 1890 moles of product is formed per mole of Au over a 6 h period. This implies that the substrate scope of the Au catalyst is not limited to water soluble 1,2-diols, such as 1,2-ethanediol and 1,2-propanediol. The decreasing reactivity of the higher diols is in line with previous observations for 1,2-propanediol and 1,2-ethanediol [20].

Table 1
Solvent effect on 1,2-propanediol oxidation with the stabilized Au sol

Solvent	TOF (h^{-1})
Water	850
tert-Butanol	510
2-Propanol	285
Methanol	80

Conditions: Au-sol, 70 °C, 0.5 MPa O_2, S:C 4000, 3 h.

Table 2
Effect of 1,2-diol chain length on oxidation rate

Substrate	TOF (h^{-1})
1,2-Propanediol	460
1,2-Hexanediol	370
1,2-Octanediol	315

Conditions: Au-sol, *tert*-butanol, 70 °C, 0,5 MPa O_2, S:C 4000, 6 h.

Non-deposited sols have previously been observed to be sensitive to aggregation and deactivation, especially if they are not stabilized by protecting polymers [26]. In order to assess the stability of the present PVA-stabilized sols, catalysts were aged during various periods before use. In these experiments, the appropriate amount of the sol was diluted into the reaction solvent; the other compounds of the reaction mixture were either added immediately, or after a delay of 7 or 28 days. Meanwhile, the diluted Au^0 solution was kept at ambient conditions under air. Results for the reactions conducted with sols aged for 0, 7 or 28 days are given in table 3. From the data, it is clear that the catalysts excellently retain their performance, even after 28 days, proving that the polymer-protected sol has a high colloidal stability. For the sols diluted in different solvents, the decline of the activity was comparable. In all cases, at least 75% of the original activity was maintained after a catalyst ageing of 28 days. This proves that the nature and the amount of the protecting polymer offer an excellent compromise between catalytic activity and stability. It has indeed been proposed that too large amounts of protecting polymer decrease the catalyst activity by covering the active sites of the Au, while a too small amount leads to fast deactivation [31].

In view of the satisfactory stability of the sol catalysts, the possibility of recuperating the sols by nanofiltration was investigated. For the sol diluted with 2-propanol, a PDMS membrane was selected, based on earlier successful nanofiltrations of homogeneous catalysts with this membrane composition [32]. The PDMS membrane retained >99% of the Au species present in the filtration mixture (table 4). For water-diluted sols, both PI and CA membranes were effective, as well as a commercial Desal membrane. Based on both Au

Table 3
Effect of catalyst age on activity in 1,2-propanediol oxidation

Catalyst age	TOF (h^{-1})		
	Water[a]	*tert*-Butanol[b]	2-Propanol[b]
Fresh	480	570	310
7 days	450	540	265
28 days	405	475	230

Conditions
[a]Au-sol, 25 °C, 0,6 MPa O_2, S:C 2500, 6 h.
[b]Au-sol, 70 °C, 0,5 MPa O_2, S:C 4000, 3 h.

Table 4
Gold sol filtration over various membranes

Membrane	Flux_{eq} ($L\ m^{-2}\ h^{-1}$)	Au retention(%)	Fouling (%)
PI[a]	19.6	90.2	0.2
CA[a]	64.1	99.5	2.2
Desal-5 DK[a,b]	10.1	94.7	0.0
PDMS[c]	88.8	100.0	0.0

Conditions
[a] Au-sol, water, 25 °C, 0,5 MPa N_2.
[b] Desal-5 DK (Osmonics).
[c] Au-sol, 2-propanol, 25 °C, 0,5 MPa N_2.

retention and the fluxes, the CA membrane is to be preferred. In each case, membrane fouling was negligible, as determined by ICP-AES after membrane digestion.

Finally, the combination of Au sol catalysis and membrane-assisted catalyst recuperation was investigated (table 5). After each oxidation run, the major fraction of the reaction solution was removed by nanofiltration, and the solvent volume containing the catalyst was reduced to a minimum (0.5 mL). Next, fresh substrate and solvent were added, and the reaction was restarted. As evidenced by the data, at least 60% of the initial activity is preserved after three oxidation runs with intermediate filtrations. With the PDMS solvent-resistant nanofiltration membrane, even more than 85% of the initial activity is maintained after three runs. These encouraging results can be ascribed to the perfect Au retention of the PDMS membrane without fouling (table 4), combined with the long-term stability of the Au sol, as evidenced in table 3. In view of a comparison with the re-use of supported Au catalysts, we have been looking for numeric re-use data in the literature. Such detailed data seem hitherto only available for the glucose oxidation, which is a relatively facile reaction. In this reported example, the TOF decreases from 2600 h^{-1} in the first run, to 1050 h^{-1} in the third run [18], which corresponds to preservation of only 40% of the initial activity. The data of table 5 show that the nanofiltration results in high cumulative turnover numbers (TON), which range between 4420 and 6380 moles of product per mole of Au over three reaction runs. Since rate, as expressed in the TOF, and catalyst stability, as expressed in the TON, are both important parameters for a catalyst, it seems that the stabilized Au sol offers a reasonable compromise of both TOF and TON. Hence, re-use of a stabilized colloidal solution of Au via nanofiltration is an alternative that can be considered alongside recuperation of heterogenized catalysts.

Table 5
Recycling of the Au-sol catalyst by filtration over various membranes

Run	TOF (h^{-1})[a]			
	PDMS[b]	DESAL-5 DK[c]	PI[c]	CA[c]
1	530	435	450	380
2	480	310	330	290
3	465	300	280	265
TON (1 + 2 + 3)[d]	4420	6260	6380	5600

Conditions
[a] In the oxidation of 1,2-propanediol.
[b] *tert*-Butanol, 70 °C, 0,5 MPa O_2, S:C 4000, 3 h.
[c] Water,70 °C, 0,5 MPa O_2, S:C 2500, 6 h.
[d] Total turnover number (TON), i.e. moles of product per mole of Au over 3 cycles.

4. Conclusion

The data demonstrate following points:

(1) A well-stabilized Au sol displays a considerable activity and high selectivity in the oxidation of 1,2-diols to α-hydroxy-carboxylates;
(2) even water insoluble 1,2-diols can be oxidized when alcohol solvents are employed;
(3) the sols can efficiently be recovered by membrane filtration;
(4) the combination of Au sols as homogeneous catalysts with efficient recycling of the nanoparticles by a polymer membrane leads to a hybrid oxidation process.

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