

Supported gold nanoparticles for aerobic, solventless oxidation of allylic alcohols*

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Abstract: After giving some general considerations about the specific properties of nanoparticles below 20 nm, procedures for size stabilization, and the importance of developing green alcohol oxidation reactions, catalytic data are presented showing that gold nanoparticles (3–7 nm) supported on nanoparticulated ceria (4 nm) are far more chemoselective than related palladium catalysts for the aerobic oxidation of allylic alcohols. Using palladium catalysts, in addition to minor oxidation of the alcohol functional group, we have also observed polymerization, 1–2 hydrogen shift, and hydrogenation. In contrast, ceria-supported gold nanoparticles exhibit a remarkable chemoselectivity (in many cases, almost complete) to the alcohol oxidation.

Keywords: gold nanoparticles; solventless reactions; green alcohol oxidation; chemoselectivity; allylic alcohols.

PROPERTIES AND PREPARATION OF NANOPARTICLES

The recent interest in using gold nanoparticles as catalysts derives from Haruta's ground-breaking contribution describing the fact that gold nanoparticles are able to promote efficiently the low-temperature CO oxidation and that the catalytic activity of gold decreases as the particle size increases until eventually this activity is lost beyond 20-nm size [1–4]. Thus, in contrast to the broad use of platinum, palladium, and other noble metals in catalysis for hydrogenation, oxidation, C–C couplings, etc., it was a general belief until very recently that gold was devoid of any significant catalytic activity. The current body of research has provided firm evidence that the catalytic properties of gold are observed only in the nanometric regime. A detailed chronology of gold catalysis and proper credit to precedents in gold catalysis (including homogeneous catalysis) has appeared recently in the literature [5].

The term “nanoparticle” refers to particles below 100-nm size. Typically, solid particles have sizes on the micrometric scale or beyond, owing to the instability of small particles in the nanometric domain and their spontaneous tendency to grow. But, as Hatura showed for the catalytic activity of gold, many properties of a given solid or element depend on the particle size and can disappear beyond a certain size [3]. Therefore, our perception of the properties of a substance is valid for common micrometric particles and misleading for particles of nanometric size of the same substance.

Due to the relative size among atoms, chemical bonds, and nanoparticles, these types of particles are constituted by tens to thousands of atoms. Thus, from the point of view of quantum mechanics, it is in this length scale in which a smooth transition between the defined energy levels characteristic of

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atomic orbitals to the continuous empty or occupied bands characteristic of solids is occurring. Smaller nanoparticles having tens of atoms should be more like conventional molecules with defined orbital levels, while the states of larger nanoparticles with thousands of atoms should be better described as bands. Needless to say, such dramatic variations in the orbital diagrams occurring in the nanometer scale are reflected by remarkable changes in the properties of the nanoparticles.

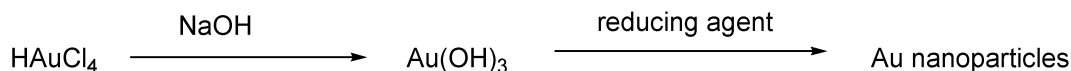
A different complementary consideration to rationalize the exceedingly high reactivity of nanoparticles is to realize the relative percentage of atoms located at the surface. While in conventional solids, the number of atoms at the surface is negligible with respect to the atoms occupying internal positions, in the case of the nanoparticles due to the small size, the proportion of external atoms is remarkably high. The smaller the size of the nanoparticle is, the higher is the percentage of external atoms of the nanoparticle (Table 1). Nanoparticles of 1 and 2 nm diameter have approximately 45 and 35 % of the atoms located on the external surface. Atoms on the external surface have their valence and coordination sphere not fully saturated, and, therefore, they are particularly reactive.

Table 1 Percentage of surface gold atoms as a function of the nanoparticle shells.

Dimensions (nm)	Number of full shells	Total number of atoms	Percentage of surface atoms
1	1	13	92
	2	55	76
	3	147	63
	4	309	52
2	5	561	45
	7	1415	35

One strategy to stabilize nanoparticles against their tendency to grow is to support nanoparticles on a solid surface. The surface of solids can interact with nanoparticles through van der Waals, hydrogen bond, and electrostatic forces. These interactions, generally described as *adsorption forces*, occur mainly with the part of external atoms of the nanoparticle in interfacial contact with the solid surface and reduce the mobility of the nanoparticle, making their aggregation more difficult.

Supported gold nanoparticles are generally prepared by the precipitation–deposition method (Scheme 1). This two-step procedure starts with a water-soluble gold salt, typically HAuCl_4 , and by adjusting the pH to nonacidic values, precipitation of $\text{Au}(\text{OH})_3$ on the solid surface takes place. Subsequently, the gold species are reduced on the surface under mild conditions to form gold metal nanoparticles. Among the reducing agents, alcohols (methanol and 1-phenylethanol), hydrazine, or metal hydrides are the most widely used.



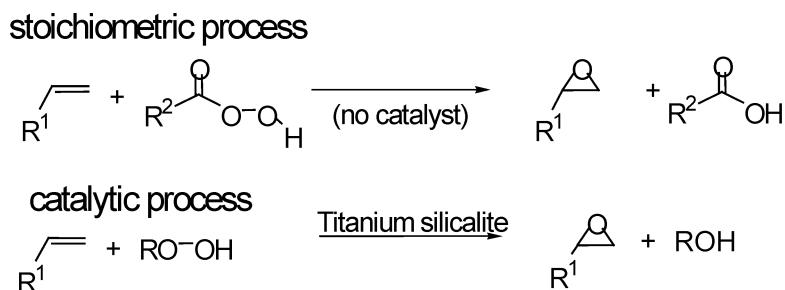
Scheme 1 Precipitation–deposition method to prepare gold metal nanoparticles on solid supports.

ALCOHOL OXIDATION AND GREEN CHEMISTRY

Alcohol oxidation to aldehydes, ketones, or carboxylic derivatives is one of the most important transformations in organic chemistry. Alcohols, being stable compounds and easy to handle and store, play a central role in the preparation of many other functional groups. Also, alcohols are involved as intermediates or products in many conventional C–C bond-forming reactions, such as the Grignard reaction.

In spite of this importance in organic chemistry, current alcohol oxidation procedures described in textbooks, although general in scope, are unsatisfactory from the green chemistry point of view [6]. Normally, they use stoichiometric amounts of transition-metal ions or oxides, oxoacids, or halogenated compounds. Also, in the Swern reaction, stoichiometric amounts of sulfides are formed [7]. All these processes do not conform to the principles of green chemistry, which require minimization of wastes and maximization of the atom efficiency [8].

In contrast to stoichiometric reactions in which no catalyst is needed, the use of other greener oxidizing reagents requires the development of suitable active and selective catalysts. A paradigmatic case is the selective epoxidation of C=C bonds. This reaction can be effected in a general way using organic peracids as stoichiometric reagents forming organic acids as side products [6]. Alternatively, a more recent process using titanium silicalite (TS1) as catalyst has been developed in which the oxidants can be environmentally friendly hydrogen peroxide or organic peroxides (Scheme 2) [9].



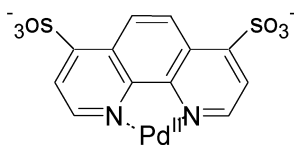
Scheme 2 Differences between a stoichiometric and a catalytic process for the selective epoxidation of C=C bonds.

The development of a catalytic process is particularly important for the aerobic oxidation of alcohols using molecular oxygen as oxidant [10]. One of the major conditions of the required catalyst is that it has to be general for any type of alcohol including primary, secondary, aliphatic, alicyclic, benzylic, allylic, etc. The ideal catalyst should also be selective in the oxidation of alcohols, leaving other functional groups such as multiple bonds, thioethers, heterocycles, etc. unaltered. In this contribution, we will present data indicating that we are close to reaching this goal by using gold-supported nanoparticles.

PRECEDENTS OF CATALYTIC AEROBIC OXIDATION OF ALCOHOLS

Sheldon and coworkers reported the use of a water-soluble palladium complex with bathophenanthroline (Scheme 3) as recoverable and reusable homogeneous catalyst for the aerobic oxidation of alcohols [11]. The main drawback of this simple and active system is the extreme water insolubility of some alcohols and the need for using autoclave and pressure for the oxidation of some alcohols.

In the search for heterogeneous catalysts, the use of ruthenium oxide supported on $\gamma\text{-Al}_2\text{O}_3$ as heterogeneous catalyst for the atmospheric-pressure, aerobic oxidation of alcohols represented a step forward [12,13]. Even air at atmospheric pressure can be used to effect the alcohol oxidation [12,13]. It has to be noted that from the point of view of safety, heating a mixture of organic compound and oxygen at high pressure in the presence of a catalyst can be extremely hazardous due to the possibility of



Scheme 3 Structure of water-soluble palladium bathophenanthroline complex.

overcoming the flash point and the risk of vigorous explosions. However, RuO_2 has several disadvantages, including limitations in the nature of alcohol and the sensitivity to water.

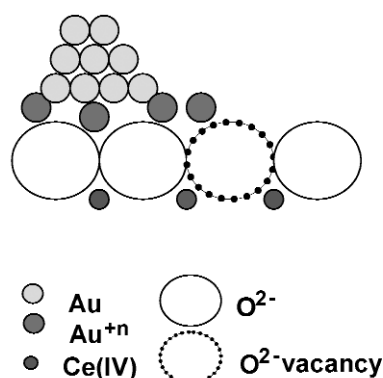
Kaneda and coworkers reported that palladium nanoparticles supported on hydroxyapatite are an extremely active and reusable catalyst for the aerobic oxidation of alcohols [14]. The turnover number obtained for the oxidation of 1-phenylethanol is remarkable high, and this material constitutes a benchmark catalyst for comparing the activity of any other solid.

Concerning the aerobic oxidation of alcohols by gold, the work carried out in this field can be considered as a logical extension of the remarkable catalytic activity of gold nanoparticles for the low-temperature CO oxidation. For this reason, most of the solids that have been tested for the aerobic oxidation of alcohols are those that have been found to be the most active for the CO oxidation, including P-25 TiO_2 and Fe_2O_3 , silicas being considered as inadequate supports. Italian workers and Hutchings' group have been very active in this field and have reported the aerobic oxidation of diols, polyols, and amino alcohols in water under strong basic conditions using supported gold nanoparticles [15–20,21]. Under these conditions, besides conventional oxides as supports, naked gold nanoparticles and supported on activated carbon have been found to be extremely active and selective catalysts.

COOPERATIVE EFFECT BETWEEN GOLD NANOPARTICLES AND CERIA NANOPARTICLES

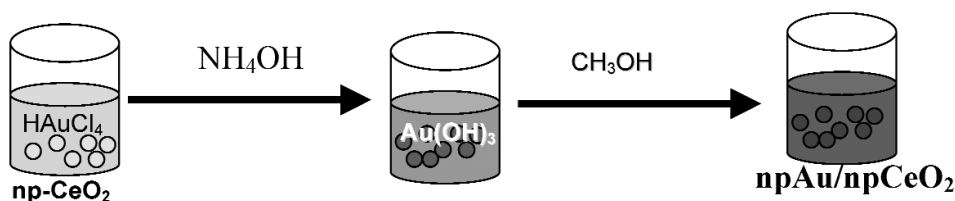
The aim of the present report is to provide reactivity data showing the superior chemoselectivity of supported gold nanoparticles for the aerobic oxidation of allylic alcohols as compared to analogous palladium catalysts. Related work from our group describing the activity of ceria-supported gold nanoparticles has been published recently [22–24]. As commented earlier, palladium on hydroxyapatite exhibits a high catalytic activity and is considered a reference system [14]. Thus, it is of interest to determine if gold nanoparticles exhibit lower or higher activity and chemoselectivity than palladium for allylic alcohols.

In this context, it has been reported that the activity of supported gold catalysts is strongly dependent on the support. It has been found that one of the most highly active aerobic catalyst for gold is that in which gold is supported on nanoparticulated ceria [22]. The reason for this suitability of ceria nanoparticles as support as compared to bulk, micrometric ceria or any other support is the creation of oxygen vacancies and the increase in the population of Ce^{III} vs. Ce^{IV} ions. Gold-supporting nanoparticles may even increase these structural defects on ceria, making these metal oxide nanoparticles specially suited to act in the aerobic oxidation by physisorption of molecular oxygen and strong interaction with positive gold atoms (Scheme 4). Positive gold atoms will act as Lewis sites reacting with alcohol molecules forming gold alcoholates.



Scheme 4 Illustration of the interphase between gold and ceria nanoparticles showing the presence of lattice oxygen defects.

Gold nanoparticles supported on nanoparticulated ceria can be prepared by the standard precipitation–reduction method generally used for other solid supports. The result is a material (npAu/npCeO₂) in which there is a distribution of gold nanoparticles between 3–7 nm with the mode of 4 nm deposited on nanoparticles of ceria of about 5-nm size (Scheme 5).



Scheme 5 Preparation procedure for npAu/npCeO₂.

The catalytic activity of this npAu/npCeO₂ (0.44 wt % Au) has been compared with related palladium catalysts, including palladium nanoparticles supported on hydroxyapatite [Pd/Ca(OH)PO₄] (0.18 wt % Pd) and supported on ceria nanoparticles (npPd/npCeO₂) (0.2 wt % Pd). We also included in our study a titania-supported gold (core)/palladium (shell) [(Au)Pd/TiO₂] (2.5 wt % of Pd and 2.5 wt % Au) catalyst that has been recently reported by Hutchings and coworkers as highly active and selective for the aerobic oxidation of primary alcohols to aldehydes [25].

The results obtained for the aerobic oxidation of allylic alcohols with the series of metal-supported catalysts are summarized in Table 2.

As can be seen in Table 2, there are several products that have been detected in the aerobic oxidation of allylic alcohols catalyzed by gold or palladium nanoparticles. Scheme 6 shows the products observed and the corresponding process in which they are formed. Thus, in addition to the corresponding α,β -unsaturated carbonylic compound arising from the chemoselective oxidation of the alcohol group, there are several other processes that can take place in various proportions depending on the substrate and the catalyst.

Although C=C bond epoxidation was not observed in any of the catalysts, palladium catalysts were especially active in promoting the 1,3-hydrogen shift from the hydroxy carbon to the β carbon of the double bond. After keto-enol tautomerization, the corresponding saturated ketone is formed as the resulting product. Other observed processes were C=C hydrogenation to give rise to the saturated alcohol and C=C polymerization.

Table 2 Results for the solventless aerobic oxidation of allylic alcohols using a series of gold- and palladium-supported catalysts. Reaction conditions: PO₂ 1 atm, O₂ flow through the vessel 35 ml min⁻¹, reaction temperature 120 °C, alcohol 12.5 mmol. For the amount of noble metal, see footnotes a–d. Blank controls using CeO₂, TiO₂, and Ca(OH)PO₄ in the absence of metal particles do not lead to the unsaturated ketone under the experimental conditions.

Substrate	Catalyst	Conversion (%) (time, h)	TOF ^a (h ⁻¹)	Unsaturat. carbonyl ^b (%)	Isomer ^c (%)	Hydrog. ^d (%)	Polym. ^e (%)
1-Octen-3-ol	npAu/npCeO ₂ ^f	>99 (5)	2198	99	–	–	–
	Pd/Ca(OH)PO ₄ ^f	>99 (0.7)	14 976	49	49	2	–
	(Au)Pd/TiO ₂ ^f	>99 (0.3)	29 408	26	73	1	–
1-Hepten-3-ol	npAu/npCeO ₂ ^f	>99 (14)	720	93	–	–	–
	npPd/npCeO ₂ ^f	>99 (2)	6204	24	74	2	–
	(Au)Pd/TiO ₂ ^f	>99 (2)	11 765	12	77	1	–
<i>Trans</i> -carveol	npAu/npCeO ₂ ^g	91 (21)	405	98	–	–	–
	Pd/Ca(OH)PO ₄ ^g	98 (6)	608	40	–	–	59
3-Octen-2-ol	npAu/npCeO ₂ ^h	96 (21)	1767	92	–	–	–
	Pd/Ca(OH)PO ₄ ^h	98 (0.5)	9815	19	45	–	36
2-Octen-1-ol	npAu/npCeO ₂ ^{i,j}	56 (1)	1032	72	–	–	25
	Pd/Ca(OH)PO ₄ ^{i,k}	67 (1)	3393	32	–	–	76

^aTOF defined as mol substrate reacted divided per mol of metal and per hour.

^bMol % of α,β -unsaturated carbonylic compound arising from the oxidation of the alcohol group.

^cMol % of isomerization product (see Scheme 6).

^dMol % of hydrogenation product (see Scheme 6).

^eMol % of polymeric material product.

^f0.01 mol % metal.

^g0.05 mol % metal.

^h0.02 mol % metal.

ⁱCarboxylic acid and ester were formed as minor secondary products.

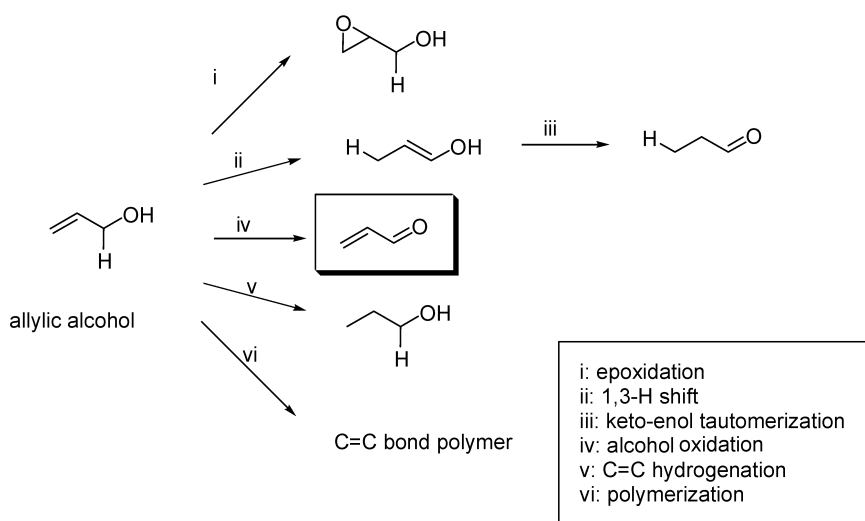
^j0.1 mol % metal.

^k1.44 wt % Pd/Ca(OH)PO₄.

From Table 2, it can be concluded that gold-supported catalysts are far more selective than palladium catalysts to promote under the conditions used the solventless oxidation of allylic alcohols to the corresponding α,β -unsaturated carbonylic compound. The results of Table 2 point out that with palladium catalysts the corresponding saturated carbonylic compound arising from 1,3-hydrogen shift or polymeric materials arising from C=C bond addition are very frequently the major products. Thus, in conclusion, the reactivity data from Table 2 show the superior chemoselectivity of npAu/npCeO₂ compared with the most active, state-of-the-art palladium catalysts.

To rationalize the difference in chemoselectivity, it is of interest to note that from the mechanistic point of view the isomerization of allylic alcohol to the saturated carbonylic compound (process ii in Scheme 6) and C=C bond hydrogenation (process v in Scheme 6) may have as common intermediates the corresponding metal hydride formed in the oxidation by hydride abstraction of the hydrogen bonded to the carbon bearing the hydroxy group. Therefore, a possible rationalization is that under solventless conditions, the concentration and reactivity of palladium hydride is higher than that of gold-hydride. The presence of reactive metal hydride would be highly detrimental for the chemoselectivity of the oxidation since this species can promote also the 1,3-hydrogen shift leading to the saturated carbonylic compound and the C=C bond hydrogenation.

To determine experimentally the relative tendency of palladium and gold to form metal hydride and their relative reactivity, we performed a simple catalytic test consisting in submitting to 1-octen-3-ol in the absence of oxygen to a certain pressure of hydrogen in the presence of palladium and gold catalysts. The results are shown in Table 3.



Scheme 6 Possible competing chemical processes occurring in the catalytic aerobic oxidation of allylic alcohols in the presence of gold or palladium catalysts. For the actual product distribution depending on the substrate, see Table 2.

Table 3 Comparative catalytic activity of npAu/npCeO₂ and Pd/Ca(OH)PO₄ and (Au)-Pd/TiO₂ to promote C=C double-bond isomerization of 1-octen-3-ol in a N₂/H₂ (90/10) atmosphere.^a

Catalyst	TOF ^b (h ⁻¹) isomerization	TOF ^c (h ⁻¹) hydrogenation
(Au)-Pd/TiO ₂	2423	269
Pd/Ca(OH)PO ₄	4906	551
npAu/npCeO ₂	621	182

^aSolventless, magnetic stirring (2000 rpm), *T*^a 393 K, metal/substrate molar ratio 10⁻⁴, 1.1·10⁵ Pa pressure (10 % H₂ in N₂).

^bTOF related to mol of double-bond isomerization compound formed and measured by GC using undecane as internal standard after first 0.5 h of reaction.

^cTOF related to mol of double bond hydrogenation compound formed and measured after first 0.5 h of reaction.

From the data obtained, it can be concluded that palladium metal has either a larger tendency than gold to form the corresponding hydrides, or these hydrides are more reactive in the case of palladium than in gold, or there is a contribution of both factors. In any case, the results of Table 3 serve to justify the superior chemoselectivity of gold catalysts for the allylic oxidation of palladium under the same conditions. Thus, as the aerobic alcohol oxidation progresses, metal hydrides are being formed. Apparently, these palladium hydrides are more efficient to interact with the C=C double bond promoting side reactions than those of gold.

Supplementary information concerning preparation and characterization of the gold catalysts as well as the reaction procedure is available at <http://www.iupac.org/publications/pac/2007/pdf/7911x1847_s.pdf>.

CONCLUSIONS

Green chemistry requires the development of environmentally benign, novel processes. The previous data illustrate that oxidation of allylic alcohols can be performed selectively at moderate temperatures using oxygen as oxidant and gold-supported nanoparticles as catalyst. This process is almost ideal from the green chemistry point of view and particularly fulfills three green chemistry principles: (i) replacement of stoichiometric by catalytic processes, (ii) avoidance of noxious reagents and reagents, and (iii) minimization of hazards. Although higher catalytic activity is always desirable, the crucial point now is to show the general applicability of these gold catalysts for a broad range of alcohols bearing different functional groups. Therefore, the current situation is close for making available a general catalyst for the green, solventless, atmospheric-pressure air oxidation of alcohols.

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