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Efficient chemoselective alcohol oxidation using oxygen as oxidant. Superior performance of gold over palladium catalysts

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Abstract—Gold nanoparticles supported on nanocrystalline ceria (Au/CeO_2) is a general, air- and moisture-stable, commercial catalyst for the atmospheric pressure, solventless oxidation of aromatic, primary and secondary alcohols to the corresponding benzaldehyde or ketone compound. Aliphatic primary alcohols are oxidized to the corresponding alkyl ester and aliphatic secondary alcohols are oxidized to ketones. Conversions and product yields are in most of the cases excellent. The oxidizing reagent and the experimental conditions are almost ideal from the environmental point of view. Comparison with analogous ceria supported and hydroxyapatite-supported palladium catalysts, Au/CeO_2 clearly shows the superior performance of Au/CeO_2 in terms of higher chemoselectivity. In contrast to palladium catalysts that promote C=C double isomerization, Au/CeO_2 oxidizes selectively allylic alcohols to conjugated ketones.

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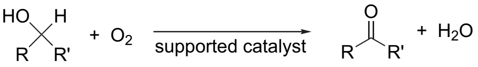
1. Introduction

Oxidation of alcohols to carbonyl compounds is one of the simplest and most useful transformations in Organic Chemistry that is at the core of many synthetic routes. This essential reaction has attracted the attention of considerable fundamental and applied research since the beginning of Organic Chemistry as a Science. However, in spite of this intensive research effort, alcohol oxidation processes are still far from being ideal from the environmental point of view and requires much improvement. The use of conventional transition metal or halogen oxo, salts such as permanganate, chromate, bromate or other stoichiometric oxidants generates an intolerably high amount of (toxic) wastes and violates at least three of the Green Chemistry principles.[1] Other alternative processes, like the Swern or Meerwein–Verley–Pondorf oxidations, also use noxious reagents, Lewis acid catalysts and organic solvents, producing a large amount of waste.[2,3] As a summary of the present status, it can be said that most of the currently used alcohol oxidation processes are not sustainable and suitable green alternatives need to be developed. The processes to be developed have to be general in scope for aliphatic primary and secondary alcohols, selective towards the corresponding carbonylic compound and compatible with the presence of other functional groups in the molecule, particularly allylic C=C double bonds.

There is no doubt that from the *green* point of view molecular dioxygen is the ideal oxidizing reagent, water being the only by-product of the process (Eq. 1). The use of oxygen as oxidant is very challenging from the catalytic point of view, since the general problem of thermal or photochemical oxygen oxidations is their lack of selectivity with the formation of complex reaction mixtures. Also, explosion hazard has to be taken into account when alcohols in organic solvents are mixed with oxygen under high pressure. For safety and experimental reasons, it would be convenient to use oxygen at atmospheric pressure when performing alcohol oxidations.

 (1)

Aerobic oxidation of alcohols

The problem of atmospheric pressure, oxygen oxidations was that until a few years ago, no active and general catalysts were known. This situation is about to change drastically, since recently highly active metallic catalysts have been reported to produce the aerobic, atmospheric-pressure oxidation of alcohols with high-turnover numbers, selectivity, and reusability. Currently there is a concurrence between ruthenium, platinum, palladium, and gold catalysts to become the most active and general catalyst for the aerobic oxidation of alcohols.[4–7]

As a continuation of our on-going work in the finding of oxygen-based oxidation catalysts,[8,9] we report here that

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ceria-supported gold catalyst exhibits a superior performance than analogous palladium catalysts for this process, approaching almost the status of being the perfect catalyst for aerobic alcohol oxidation. We will show that the supported gold catalyst is quite general for aliphatic and aryl alcohols and the process is chemoselective for allylic hydroxyl groups.

2. Results and discussion

2.1. Catalysts

The activity of a series of three supported palladium and gold catalysts for the oxidation of alcohols has been compared in the present work. Two of them used ceria nanoparticles as support. Ceria nanoparticles were obtained following a reported procedure consisting in the controlled aging in acid aqueous media of $Ce(NO_3)_3$. It is known that particle size reduced down to 3–8 nm makes considerable defects on ceria. These defects consist in the presence of lattice oxygen defective sites and in the presence of a considerable population of Ce(III) sites in addition to the normal Ce(IV) sites. These special defective properties are only encountered when sufficiently small particles are obtained and arise from the high external versus total atomic ratio characteristic of nanoparticles.

These ceria nanoparticles were prepared and used as support to deposit palladium and gold nanoparticles.[10] Gold supported on ceria (Au/CeO_2) was obtained by stirring a colloidal suspension of ceria nanoparticles in water containing a soluble gold(III) salt and adjusting the pH to 10. Under these basic conditions, gold hydroxides precipitate over the ceria. The preparation of palladium supported on ceria (Pd/CeO_2) follows an analogous procedure to that reported by Kaneda and co-workers for hydroxyapatite-supported palladium (Pd/apatite). Basically the procedure consists of dissolving in an organic solvent a soluble palladium complex and adsorbing it on the inorganic support by stirring the suspension. From these solids, the active form of these catalysts was obtained by reducing them to form noble metal particles. In contrast to the rest of noble metals such as platinum, palladium, etc., gold was considered until recently as not exhibiting interesting catalytic properties. However, Haruta reported that when the particle size is sufficiently small in the nanometer scale, gold can exhibit exceedingly good catalytic properties for the aerobic oxidation of CO.[11] Then gold on supported catalyst has shown to be active for different oxidation, reduction, and C–C forming bond reactions.[12–17]

The particle size distribution, the noble metal and ceria domains, and the particle morphology can be observed by transmission electron microscopy. Figures 1–4 show selected images and particle size distribution for the supported catalysts used in this work. As it can be seen there, the particle size of the noble metal is about 1–10 nm and the colloidal ceria particles have similar dimensions, being both spheroidal particles in shape.

The catalyst series was completed with a third catalyst consisting of palladium nanoparticles supported on hydroxyapatite (Pd/apatite). This catalyst has been recently reported by Kaneda and co-workers[18] as one of the most active for the aerobic oxidation of alcohols exhibiting turnover numbers of 250,000. This means that on average a palladium atom is able to form 250,000 molecules of ketone, or that Pd/apatite is active at molar ratios below 0.0004 mol %. Pd/apatite is analogous to Pd/CeO_2 except that the support has a composition of $CaHPO_4$ and is obtained synthetically by precipitating phosphate with calcium under controlled pH conditions.

2.2. Catalytic activity

It has been reported that Pd/apatite is an extremely active heterogeneous catalyst for the oxidation of 1-phenylethanol. In the first stage of our work we have performed preliminary studies in the solventless aerobic oxidation of this alcohol, being able to reproduce the activity reported by Kaneda et al.

Aerobic oxidation of 1-phenylethanol was performed at atmospheric pressure by bubbling oxygen through 1-phenylethanol in the absence of solvent using a Dean–Stark apparatus to remove the water formed in the process.

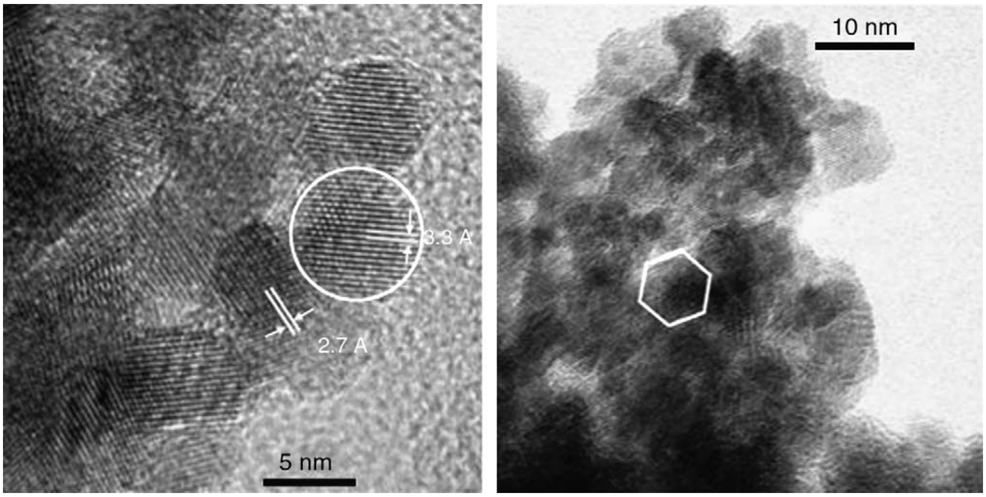

Figure 1. Left: High resolution TEM of the $Au\subset CeO_2$ sample, the white lines correspond to the (202) (3.3 Å) Ce_6O_{11} and the (200) CeO_2 (2.7 Å) lattice spacing. Right: A hexagonal faceted (111) Au crystal is circled.

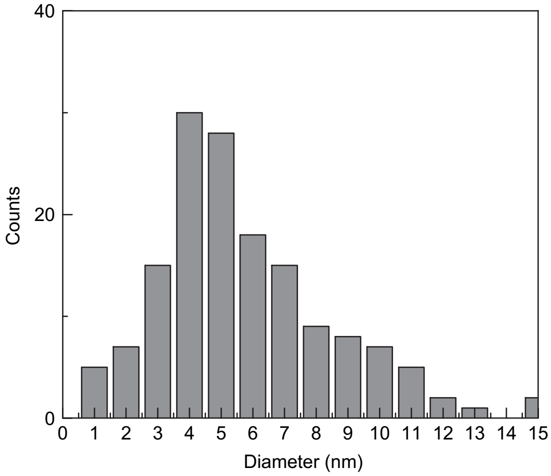

Figure 2. Au particle size distribution determined by statistical analysis of Au$\subset$CeO$_2$.

According to Eq. 1, as the oxidation progresses significant volumes of water are formed and they were separated from the reaction mixture with the Dean–Stark apparatus. This experimental procedure has the additional advantage of avoiding the use of any solvent, thus conforming the eighth principle of Green Chemistry. Two reaction temperatures (over the 100 °C necessary for the operation of the Dean–Stark apparatus) were studied. Complete conversions with high selectivity towards acetophenone were obtained when the reaction was conducted at 160 °C for Pd catalysts (see Table 1). For catalysts that exhibit almost quantitative conversion and selectivity, a way to rank their activity is to consider the turnover frequency (TOF) that is calculated by dividing the initial reaction rate to the number of catalytic sites. Initial reaction rates can be obtained from the slope of the time-conversion plot at zero time. Figure 5 shows the aerobic oxidation of 1-phenylethanol and 3-octanol as a function of time in the presence of the series of catalysts used. The estimated TOF values are also given in Table 1.

It can be seen in Figure 5 and Table 1 that both supported palladium catalysts are more active than Au/CeO$_2$ when the reaction is carried out at 160 °C. However, the reverse behavior is observed at 120 °C where Au/CeO$_2$ becomes the most active catalyst and the activity of palladium catalysts was significantly lower.

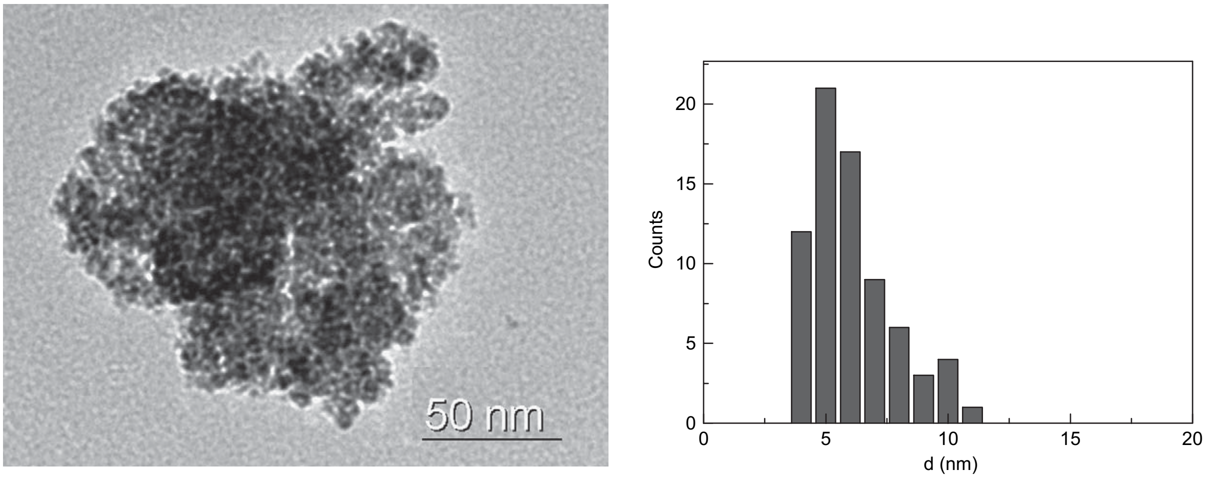

Figure 3. Left: High resolution TEM image of the Pd/CeO$_2$ catalyst. Darker spots correspond to palladium nanoparticles. Right: Pd particle size distribution determined by statistical analysis of the left image.

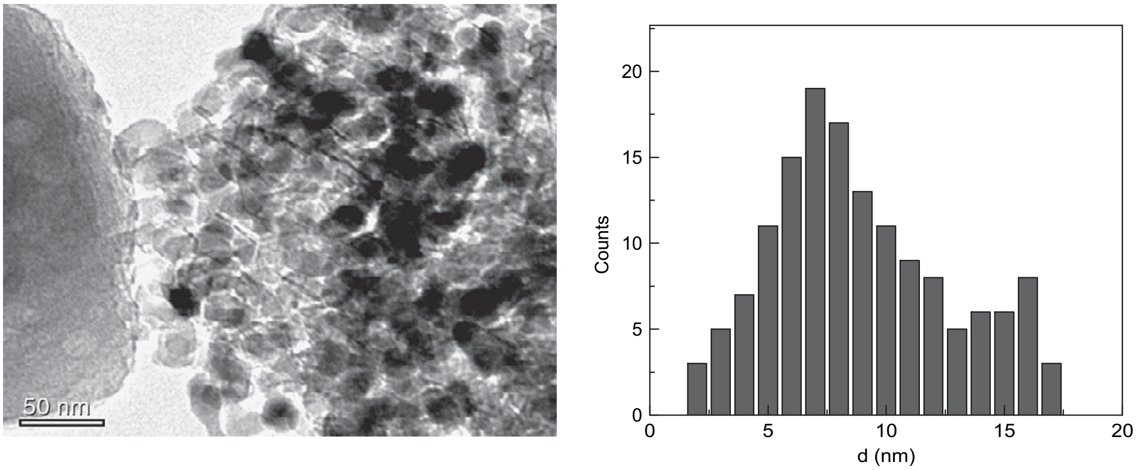

Figure 4. Left: High resolution TEM image of the Pd/apatite catalyst. Right: Pd particle size distribution determined by statistical analysis of Pd/apatite.

Table 1. Results of the solventless, atmospheric-pressure aerobic oxidation of two secondary alcohols using a Dean–Stark apparatus in the presence of heterogeneous gold or palladium catalyst

Substrate	T (°C)	Catalyst	Ketone yield (%)	TOF (h^{-1})
1-Phenylethanol	160	Au/CeO_2[a]	33	12,480
		Pd/CeO_2[a]	>95	32,558
		Pd/apatite[a]	>95	33,223
	120	Au/CeO_2	>95	1511
		Pd/CeO_2	91	645
		Pd/apatite	90	1127
3-Octanol	120	Au/CeO_2	>95	2337
		Pd/CeO_2	3	63
		Pd/apatite	45	379

Reaction conditions: 12.5 mmol of alcohol, 0.154 mol % (substrate to catalyst ratio), and PO_2 1 atm (35 mL min^{-1} flow).

[a] Substrate to catalyst ratio is 0.0004%.

Moreover, aliphatic secondary alcohols, such as 3-octanol, can also be equally well oxidized at 120 °C in almost quantitative yield by oxygen at atmospheric pressure in the absence of solvent using supported gold as heterogeneous catalyst. Working at temperatures of 120 °C or below, the activity of Au/CeO_2 was higher than that of analogous supported palladium catalysts, for which the yield of ketone for palladium catalysts was unsatisfactory under the substrate to catalyst ratio and conditions studied. The TOF values of Au/CeO_2 were correspondingly considerably much higher than those of the supported palladium catalysts.

In order to demonstrate the generality of ceria-supported gold as catalyst for the aerobic oxidation of alcohols and its higher performance compared to analogous palladium catalyst, we studied under the same experimental conditions, the oxidations of three other substrates, namely, a primary benzylic alcohol, a primary aliphatic alcohol, and an allylic alcohol. In all the cases the reaction product was the corresponding aldehyde or ketone, except in the case of 3-phenyl-1-propanol that gives the ester 3-phenylpropyl 3-phenyl-1-propanoate as the reaction product. The results of conversion, selectivity, and TOF values are tabulated in Table 2.

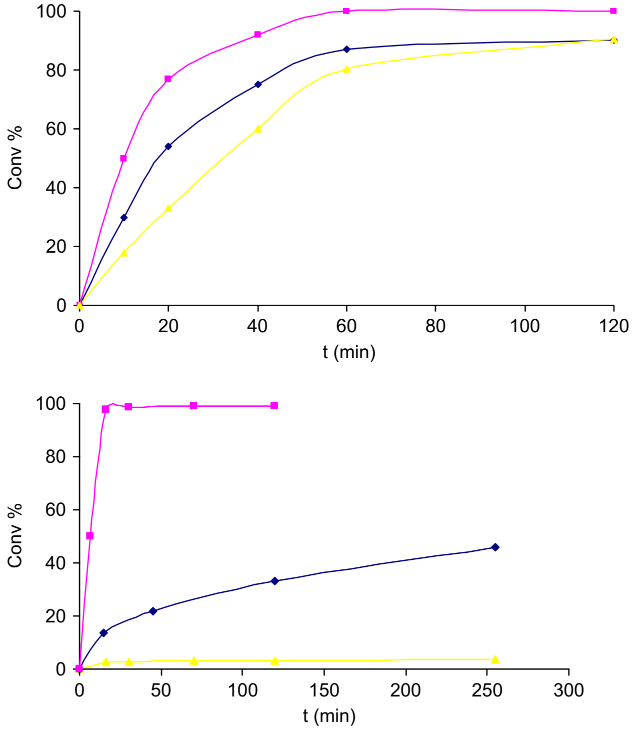

Figure 5. Comparison of the catalytic activity of Pd/CeO_2 ▲, Au/CeO_2 ■, and Pd/apatite ◆ for the aerobic alcohol oxidation at 120 °C (substrate to catalyst ratio 0.154 mol %). Top: 1-phenylethanol. Bottom: 3-octanol.

As it can be seen in Table 2, Au/CeO_2 exhibits high activity and selectivity for the alcohols studied, being considerably more active than the analogous supported palladium catalysts. There are also some distinctive features that deserve some comments. Thus, the presence of reduction products (see footnotes a and b in Table 2) was observed in minor quantities using supported palladium catalysts, but were absent using Au/CeO_2. Also allylic alcohol 1-octen-3-ol undergoes a chemoselective oxidation in the presence of Au/CeO_2 to the corresponding ketone without oxidizing or isomerizing the C═C double bond. In contrast to this, palladium catalysts promote a considerable degree of C═C double bond isomerization with the formation of 3-octanone as the final product.

Also benzylic alcohols can be oxidized selectively by oxygen to the corresponding benzaldehydes in the presence of Au/CeO_2 as catalyst. Again, the activity of Pd/CeO_2 was significantly lower and, moreover, exhibited less selectivity towards the corresponding benzaldehyde.

Aliphatic primary alcohols can also be oxidized by oxygen using Au/CeO_2 as catalyst. In this case, however, the product was the corresponding esters rather than aldehydes. The presence of minor quantities of the corresponding carboxylic acid was also observed. This indicates that under the experimental conditions used, the carboxylic acid must be the predominant oxidation product and as the reaction progresses it

Table 2. Results of the solventless, atmospheric-pressure aerobic oxidation of alcohols at 120 °C using a Dean–Stark apparatus in the presence of heterogeneous gold or palladium catalyst

Substrate	Time (h)	Catalyst	Conversion (%)	Selectivity (%)
1-Phenylethanol	2	Au/CeO_2	>99	>99
		Pd/CeO_2	91[a]	>99
		Pd/apatite	91[a]	93
3-Octanol	4.5	Au/CeO_2	99	>99
		Pd/CeO_2	3	>99
		Pd/apatite	45	>99
1-Octen-3-ol	3	Au/CeO_2	>99	93
		Pd/CeO_2	>99	58
		Pd/apatite	>99	23
3,4-Dimethoxybenzyl alcohol	5	Au/CeO_2	>99	83
		Pd/CeO_2	>99	47[b]
3-Phenyl-1-propanol[c,d]	7	Au/CeO_2	>99	88
		Pd/CeO_2	79	69

Reaction conditions: 12.5 mmol of alcohol, 0.154 mol % (substrate to catalyst ratio), PO_2 1 atm (35 mL min^{-1} flow), and T at 120 °C.

[a] Ethylbenzene was also formed as product.

[b] 3,4-Dimethoxytoluene was also formed as product.

[c] The reaction temperature was 160 °C.

[d] The reaction product was 3-phenylpropyl 3-phenyl-1-propanoate.

undergoes esterification with the alcohol to give the ester. As in the previous cases, also for primary aliphatic alcohols the activity of the palladium catalysts was considerably lower than that of gold.

The above reactions were carried out under solventless conditions. It is evident that this procedure is greener and convenient for the oxidation of alcohols in large volumes. However, it is obvious that this cannot be applied for the oxidation of high melting point, solid alcohols. Also, this procedure may be less suitable for the oxidation of small amounts of alcohol. It is frequent situation in Organic synthesis that the amount of alcohol available as intermediate in a synthetic route is not large enough to allow solventless processes.

For this reason, we have also tested the activity of the ceria-supported catalyst in other solvents. There is an increasing interest in developing organic reactions in water, that is considered the greenest solvent. Water in the presence of base at reflux temperature is also a suitable reaction medium to perform aerobic oxidation catalyzed by supported gold. The main peculiarity of water as solvent is, however, that primary alcohol such as 1-hexanol undergoes oxidation to the corresponding carboxylic acid (>95% yield) rather than to aldehyde, although the selectivity to carboxylic acid can also be very high. We notice that as it has been indicated in the footnotes of Table 2, also in solventless conditions 3-phenyl-1-propanol undergoes oxidation to ester rather than to aldehyde.

Water, even at high reaction temperatures, has the limitation of its low solubility for most alcohols. For this reason, we are currently studying aerobic alcohol oxidation in other solvents that while still being environmentally benign can be of more general use in Organic Chemistry. In this context we have performed some preliminary tests using imidazolium ionic liquid as medium. Although aerobic oxidation of alcohols can also be performed in 1-butyl-3-methylimidazolium hexafluorophosphate, the catalyst becomes strongly deactivated over the course of the reaction and the conversion suddenly stops before complete disappearance of the alcohols. For this reason, 3,4-dimethoxybenzyl alcohol gives only 45% of the corresponding benzaldehyde when the reaction is carried out in imidazolium ionic liquid.

One important issue when testing a heterogeneous catalyst is to determine its reusability. We have found that for the solventless alcohol oxidation, once the reaction has finished and the solid recovered, it can be reused by washing it with copious basic water (pH 10), drying in an oven for 2 h with only a marginal decrease in its catalytic activity. We have determined that carboxylic acids act as poisons of Au/CeO_2. Most probably they strongly coordinate to positive gold species reducing their ability to bind with alcohols forming the gold-alcoholate intermediate. Poisoning by carboxylic acid is the most probable cause of the catalyst deactivation under our solvent-less conditions.

Concerning the reaction mechanism of the aerobic oxidation, Figure 6 shows the most reasonable mechanism that accounts for the known facts. The process will start with oxygen physisorption at the oxygen defective sites on the ceria surface that initiates oxygen activation. Upon physisorption, the interaction between defective cerium(III) and oxygen can be understood as forming a metal peroxyl radical such as Ce^{iv}–O–$O^{\bullet}$. On the other hand the presence of positive gold atoms at the interface between gold and ceria has been demonstrated and will be ready to form a gold-alcoholate species. The combination of surface bound peroxyl radicals and metal alcoholate will end-up in the ketone and metal hydroperoxide. This cerium peroxide will decompose by the action of gold. Although it is clear that many details of the mechanism are still to be unveiled, the key point concerning the excellent activity of the Au/CeO_2 solid for the aerobic oxidation is the presence of surface oxygen vacants, a structural feature that arises from the nanometric size of ceria, and the presence of positive gold species in a cluster that contains many gold(0) atoms. The presence of positive gold species also arises from the high interfacial contact

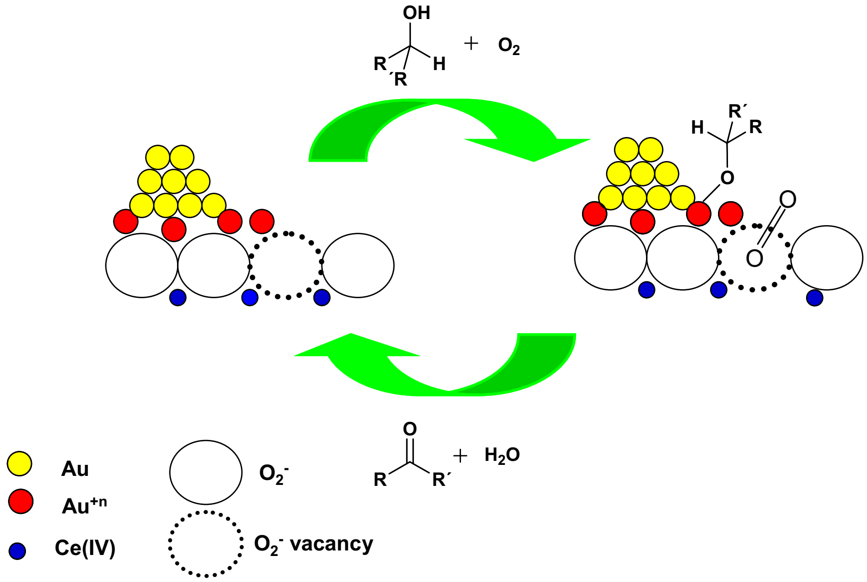

Figure 6. Reasonable mechanism for aerobic alcohol oxidation on $Au\subset CeO_2$ catalyst.

between gold and ceria that at the end is also the result of the nanometric size of the particles.

3. Conclusions

Contrary to the general belief in Organic synthesis, homogeneous and heterogeneous catalysis have been developing excellent systems to effect the aerobic oxidation of alcohols using molecular oxygen as oxidant. This process has been regarded by Organic chemists as being limited and specific for large-scale industrial oxidation processes. But, currently there are several noble metal catalysts that exhibit a general activity to oxidize any hydroxyl group to the corresponding carbonyl compound. Among this extremely active catalysts, we have shown in the present work that commercially available, air- and moisture-stable Au/CeO_2 shows a wide generality for the oxidation of primary and secondary, aliphatic and benzylic hydroxy groups, thus, making aerobic oxidation amenable to general Organic Chemistry. The current work in this area is focused in further expanding the solvents that can be used, determining compatibility with substrate functional groups and the reusability of the gold catalyst.

4. Experimental

4.1. General

$HAuCl_4$, $(NH_4)_2HPO_4$, $Mg(CH_3COO)_2\cdot 4H_2O$, NH_3 (25%), $Ca(NO_3)_2\cdot 4H_2O$, and $Ce(NO_3)_4$ were purchased from Sigma–Aldrich Chemical Co. $PdCl_2(PhCN)_2$ was purchased from ABCR GmbH Co. All reagents were used without further purification. All solvents and acids used were reagent grade, purchased from Sigma–Aldrich Chemical Co., and used as received. All the experiments were performed using mQ water.

4.2. Catalysts

4.2.1. Synthesis of nanoparticulated ceria. A colloidal dispersion of CeO_2 nanoparticles was prepared by thermolysis of an acidified $Ce(NO_3)_4$ solution followed by re-dispersion. The dispersion was purified and concentrated using an ultrafiltration cell equipped with a 3KD membrane. The purification was monitored by the residual acidity of the dispersion, determined by an acid titration of the supernatant after ultracentrifugation at 50,000 rpm for 6 h. The resulting cerium oxide has, owing to the small size of the nanoparticles, a very high surface area ($180\ m^2\ g^{-1}$) as determined by isothermal nitrogen adsorption.

4.2.2. Synthesis of hydroxyapatite. Hydroxyapatite was prepared using a method as described in the literature. A solution of $(NH_4)_2HPO_4$ (40.0 mmol) in deionized water (150 mL) was set at pH 11 with aqueous NH_3 solution. This solution was added dropwise over 30 min to a solution of $Ca(NO_3)\cdot 4H_2O$ (66.7 mmol) in deionized water (120 mL) adjusted to pH 11 with aqueous NH_3 solution. Vigorous stirring at room temperature was maintained during the addition process. The resulting milky solution was heated at 90 °C for 10 min. The precipitate was filtered, washed with deionized water, and dried at 110 °C giving a solid with the stoichiometry of $Ca_{10}(PO_4)_6(OH)_2$ corresponding to hydroxyapatite.

4.2.3. Preparation of Au/CeO_2 catalyst. Au was deposited on the nanoparticulated ceria by the following procedure: a solution of $HAuCl_4\cdot 3H_2O$ (296 mg) in 60 mL of deionized water was brought to pH 10 by addition of a solution of NaOH 0.2 M. Once the pH value was stable the solution was added to a gel containing of colloidal CeO_2 (4.01 g) in H_2O (50 mL). After adjusting the pH of the slurry to a value of 10 by addition of a solution of NaOH 0.2 M, the slurry was left under vigorous stirring for 18 h at room temperature. The Au/CeO_2 solid was then filtrated and exhaustively washed with distilled water until no traces of chlorides were detected by the $AgNO_3$ test. The catalyst was dried at vacuum at room temperature for 1 h. Then 3.5 g of the supported catalyst was added over 30 g of 1-phenylethanol at 160 °C and the mixture was allowed for reduction during 20 min. The catalyst was filtered, washed, with acetone and water, and dried under vacuum at room temperature. The total Au content of the final catalyst Au/CeO_2 was 1.54 wt % as determined by chemical analysis. This catalyst Au/CeO_2 is commercially available at www.upv.es/itq.

4.2.4. Preparation of Pd supported catalysts. Colloidal ceria or hydroxyapatite (4 g) was stirred at room temperature for 3 h in 400 mL of acetone solution of $PdCl_2(PhCN)_2$ (1.5×10^{-3} M). The obtained mixture was filtered, washed with acetone, and dried under vacuum at room temperature. Then 3.5 g of the supported catalyst was added over 30 g of 1-phenylethanol at 160 °C and the mixture was allowed for reduction during 20 min. The catalysts were filtered, washed, with acetone and water, and dried under vacuum at room temperature. The total Pd content of the final catalyst as determined by chemical analysis was 1.57 and 1.44% for Pd/CeO_2 and Pd/apatite, respectively.

4.2.5. Catalyst characterization. For crystal analysis and indexation, the samples were examined by bright- and dark-field electron microscopy in a Jeol 2200 HRTEM operated at an accelerating voltage of 200 kV. Dark field consists on observing the image produced by diffracted electrons corresponding to a determined lattice spacing leaving the rest dark.

Chemical analyses of gold and palladium metals in the catalysts were carried out after dissolving the solids by attack with a 2:1 mixture of HNO_3/HF on a Varian-10 Plus Atomic Absorption Spectrometer or directly of the solids using on a Philips MiniPal 25 fm Analytic X-ray apparatus and a calibration plot. Analysis of reaction products was carried out by GC on an HP−Agilent 5973 with a 6980N mass selective detector.

4.3. Typical procedure for the aerobic solventless oxidation of alcohols

All alcohols provided by Aldrich were used without further purification. The corresponding alcohol (12.5 mmol) was added over Au/CeO_2 catalyst (0.252 g), molecular oxygen was bubbled continuously through the suspension ($35\ mL\ m^{-1}$). The resulting mixture was then heated at 120 °C. After the reaction, acetone was added and the catalyst was separated by centrifugation. The products in the solution were analyzed by GC–MS and conversion and selectivity were determined by GC using undecane as external standard. Supported catalyst was washed with 1 M aqueous solution of NaOH, and dried in vacuum before reuse.

Acknowledgements

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