

Unique gold chemoselectivity for the aerobic oxidation of allylic alcohols†

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Gold nanoparticles supported on nanocrystalline ceria has been found to be more active and chemoselective than palladium and gold(core)–palladium(shell) nanoparticles for the aerobic oxidation of allylic alcohols.

Alcohol oxidation to aldehydes or ketones is one of the pivotal functional group transformations in organic chemistry.¹ Classically this oxidation is performed in high yields using stoichiometric amounts of transition metal oxidants or halooxoacids. Although these reagents are quite general in scope, they are no longer tolerable from a green chemistry point of view.² Development of environmentally-friendly catalytic oxidations that can be used for any alcohol, including multifunctional ones as allylic alcohols, would constitute a significant breakthrough in organic chemistry.^{3–5} The ideal oxidant should be molecular oxygen at atmospheric pressure and the reaction should be performed under solventless conditions or (for solid alcohols) in green organic solvents. In addition, the catalyst should be moisture-stable and reusable.

Gold nanoparticles supported on cerium oxide,⁶ other inorganic oxides,^{7–9} active carbon^{10–13} or even unsupported gold nanoparticles¹⁴ have recently attracted considerable attention since these catalysts are able to promote the selective oxidation of alcohols. Very recently we have presented the benefit of using nanoparticulated CeO₂ instead of the conventional ceria as a support for gold nanoparticles resulting in a highly active, selective and recyclable catalyst for the oxidation of alcohols into aldehydes and ketones using oxygen at atmospheric pressure as oxidant in the absence of solvent and base.¹⁵ High turnover frequencies for the oxidation of selected alcohols with oxygen under mild condition have been achieved using Pd supported on hydroxyapatite,¹⁶ and titania-supported gold(core)–palladium (shell) nanoparticles.¹⁷ An air and moisture stable oxidation catalyst has, in order to be useful for organic chemists, to give not only high conversion with some selected alcohols, but has to be chemoselective when the molecule contains other oxidizable functional groups. In this case, one important family of alcohols that has industrial relevance are allylic alcohols. In this common type of alcohol chemoselective oxidation of hydroxyl groups avoiding oxidation, isomerization or polymerization of the olefinic group is required.

We will show that for the relevant oxidation of allylic alcohols, gold presents unique selectivity when compared with Pd or Au–Pd catalysts. Au/CeO₂ was prepared by deposition–precipitation of

HAuCl₄ on colloidal ceria (5 nm),¹⁸ the resulting material was reduced by the solvent-free oxidation of 1-phenylethanol giving gold nanoparticles with a crystallite size of 2–5 nm. Pd–hydroxyapatite and Au–Pd/TiO₂ were prepared following ref. 16 and 17 respectively (see supplementary information†).

Air oxidation of allylic alcohols was carried out at 393 K, PO₂ = 10⁵ Pa and without solvent (unless specified). The metal substrate molar ratio was varied between 1–125 × 10^{−4}, depending on the alcohol. The results obtained with the different catalysts are given in Table 1. In this Table the percentage of isomerization represents products where double bond migration has occurred, while the selectivity column refers to the formation of the α,β -unsaturated carbonyl compound that is the desired product. The rest up to 100% corresponds to unidentified polymerized by-products. For comparison and in addition to Au/CeO₂, Pd–hydroxyapatite, Au–Pd/TiO₂ as well as two related solids have also been included as catalysts. One of the unprecedented catalysts consists of a CeO₂ support that contains simultaneously independent gold and palladium nanoparticles (Au–Pd/CeO₂), and the other consists of gold nanoparticles supported on TiO₂ (Au/TiO₂) (this catalyst was supplied by the International Gold Council).¹⁹

The most salient feature of Table 1 is the high yields and the unique chemoselectivity attained using supported gold nanoparticles as catalysts for the production of α,β -unsaturated ketones. Minimum yields over 90% are obtained for the solventless oxidation except in the case of 2-octen-1-ol, for which the presence of an organic solvent is necessary in order to obtain the desired α,β -unsaturated aldehyde with high yield (see entry 16 and footnote b). In this context, it is worth noticing that in addition to solvent-less conditions Au–CeO₂ is also very active and selective for the oxidation of primary allylic alcohols in organic solvents such as toluene.

Particularly, in the oxidation of cinnamyl alcohol to cinnamaldehyde, Au–CeO₂ combines excellent selectivity (see entry 20 in table 1) and the highest turnover frequency (538 h^{−1}) among those reported so far: Ru–Al₂O₃ (27 h^{−1}),^{20,21} Ru–Co (38 h^{−1}),^{21,22} Pd–hydroxyapatite (73 h^{−1}),^{16,21} Au–Pd–TiO₂ (97 h^{−1}),¹⁷ Pt–Bi–Al₂O₃ (144 h^{−1}).²¹

We checked the reusability of the Au–CeO₂ catalyst in the case of *trans*-carveol oxidation. The solid was recovered by filtration, washed with a 1 M aqueous solution of NaOH and dried in vacuum. This recovered Au–CeO₂ sample was used in a consecutive run without observing any decay in its catalytic activity.

Table 1 also reveals that the presence of palladium in the catalyst is highly detrimental for chemoselectivity. This low

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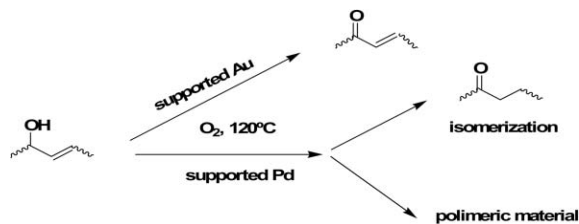
Table 1 Comparison of the catalytic performance of gold and palladium catalysts for the oxidation of allylic alcohols to the corresponding α,β -unsaturated carbonyl compounds

Entry	Substrate	Catalyst	Metal/S (10^{-4})	Conversion (%)	Selectivity (%)	Isomerization (%)
1 ^a	1-Octen-3-ol	Au–CeO ₂	1	>99	90	0
2 ^a		Pd–(OH)apatite	1	>99	49	49
3 ^a		Au–Pd–CeO ₂	1	>99	26	73
4 ^a		Au–Pd/TiO ₂	1	>99	40	54
5 ^a		Au–TiO ₂	10	>99	93	0
6 ^a	<i>trans</i> -Carveol	Au–CeO ₂	5	91	99	0
7 ^a		Pd–(OH)apatite	5	98	40	0
8 ^a		Au–Pd/TiO ₂	5	79	47	0
9 ^a	3-Octen-2-ol	Au–CeO ₂	2	96	91	0
10 ^a		Pd–(OH)apatite	2	98	19	45
11 ^a		Au–Pd–CeO ₂	2	99	38	32
12 ^a		Au–Pd/TiO ₂	2	99	35	5
12 ^a	2-Octen-1-ol	Au–CeO ₂	10	56	72	0
13 ^a		Pd–apatite	10	60	32	0
15 ^a		Au–Pd/TiO ₂	10	54	33	0
16 ^b		Au–CeO ₂	125	90	91	0
17 ^b		Pd–apatite	125	54	87	0
18 ^b		Au–Pd–CeO ₂	125	95	73	0
19 ^b		Au–Pd–TiO ₂	125	17	60	0
20 ^b	Cinnamyl alcohol	Au–CeO ₂	20	99	99	0
21 ^b		Pd–apatite	20	74	63	0
22 ^b		Au–Pd–CeO ₂	20	99	93	0
23 ^b		Au–Pd/TiO ₂	20	95	70	0

^a Substrates oxidized at 393 K, PO₂ = 10⁵ Pa and without solvent; catalysts mass varied in order to give the metal/substrate molar ratios indicated as Metal/S; Selectivity refers to the percentage of α,β -unsaturated carbonyl compound in the reaction mixture. Conversion and selectivity were determined by GC-MS using undecane as internal standard. ^b Analogous conditions as before but performing the oxidation in toluene (0.2 M) as solvent.

chemoselectivity of palladium containing catalysts is due to the fact that when palladium is present, other by-products arising from C–C double bond isomerization, C–C double bond hydrogenation, C–C double bond polymerization are also formed in significant amounts (Scheme 1). Table 1 lists the percentage of saturated ketone arising from the C=C double bond 1,2-migration (isomerization column) that is in some cases the major product of the palladium catalyzed reaction. These undesired by-products arising from reaction of the C=C double bond are absent, or present in a very minor proportion, when using Au–CeO₂ as catalyst. This high chemoselectivity is a property inherent to the gold nanoparticles since Au–TiO₂ although less active, also exhibits very high chemoselectivity at complete conversion (see entry 5 in Table 1).

The most likely reason for the high selectivity of gold catalysts as compared to palladium is the different stability and steady-state concentration of metal hydrides (Pd–H and Au–H) on the metal surface during the reaction. Pd–H species have been proposed to be formed during the aerobic alcohol oxidation in the step of hydride abstraction from the alkoxide, and there are spectroscopic evidence supporting the presence of this species in related

**Scheme 1** Main general differences in the product distribution for the atmospheric-pressure, aerobic oxidation of allylic alcohols under solventless conditions in the presence of gold and palladium catalysts.

oxidations under similar conditions.^{16,21} We have previously provided vibrational spectroscopy evidence in support of the intermediacy of Au–H in the aerobic oxidation of alcohol.¹⁵ Metal hydrides should normally be oxidized by oxygen and the steady state concentration during the catalytic cycle should remain low, since otherwise it is known that they can promote C=C reduction and isomerization.²³ Apparently, under our solventless conditions, oxidation of Pd–H species is not sufficiently fast and its concentration should be high enough to promote C–C double bond isomerization and reduction in a significant extent. This would be in contrast to the case of Au–CeO₂ for which the absence of side reactions points to an easier turnover oxidation of Au–H.

To provide some support to this proposal, we have studied the reactivity of 1-octen-3-ol under nitrogen atmosphere containing a small proportion (10% in N₂) of hydrogen in the presence of Au/CeO₂, Pd/hydroxyapatite and Au–Pd/TiO₂. Under these mild reducing conditions, it is expected that a stationary metal hydride concentration will form on the surface of the metal particles, and the purpose is to determine the reactivity of the alcohol with the metal hydrides. The results are summarized in Fig. 1. As can be seen, Pd/hydroxyapatite exhibits the highest TOF value for C=C double isomerization and C=C hydrogenation.‡ The relative contribution of these two processes is only a reflection of the reaction conditions and the low hydrogen concentration.

Importantly, Au–CeO₂ has the lowest TOF values for both undesired processes, *i.e.*, C=C isomerization and hydrogenation. Since both processes require the presence of metal hydrides, we interpret the results of Fig. 1 as an evidence of the lower tendency of gold nanoparticles to form reactive hydrides as compared to palladium catalysts. We suggest that lower tendency and/or reactivity of Au–H compared to Pd–H is beneficial for the selectivity of aerobic oxidations.

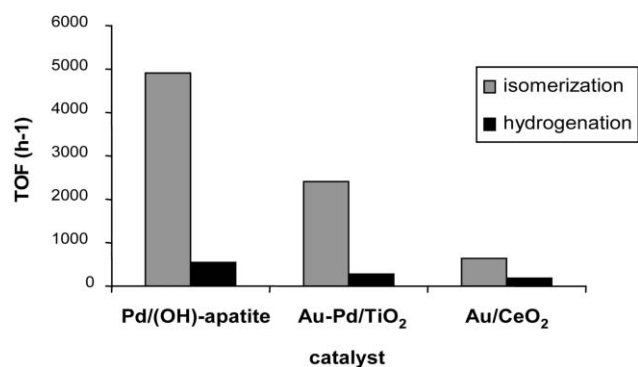


Fig. 1 Comparative catalytic activity between Au–CeO₂, Pd–hydroxyapatite and Au–Pd–TiO₂ for double bond isomerisation and hydrogenation of neat 1-octen-3-ol at 393 K using a H₂–N₂ (10 : 90) mixture.

In conclusion, Au/CeO₂ is a general and reusable catalyst for the oxidation of allylic alcohols without solvent and in organic media. Even more important, the chemoselectivity of Pd or Au–Pd for the solventless oxidation of this family of alcohols is very low when compared with gold catalysts and this selectivity can be correlated to the stability and concentration of metal hydrides, Au–H and Pd–H.

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Notes and references

‡ Turnover frequency related to mol double bond isomerization and hydrogenation compound formed and measured by GC using undecane as internal standard after first 0.5 h of reaction at 393 K.

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