Supported Catalysts

A Collaborative Effect between Gold and a Support Induces the Selective Oxidation of Alcohols**

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The selective oxidation of alcohols is one of the most challenging reactions in green chemistry.[1–4] An ideal green oxidation process should involve a highly active and selective recyclable catalyst that is able to work at atmospheric pressure in the presence of oxygen and the absence of solvents and bases.[5] Stoichiometric oxidations using transition metal compounds or sulfoxides (Swern oxidation) are still commonly used, despite the formation of a large amount of undesirable products. Several homogeneous Pd-, Cu-, or Ru-based catalysts are able to perform the selective oxidation of alcohols, but they require the use of organic solvents or high oxygen pressure.[6–11]

From the point of view of heterogeneous catalysis, probably the best system has been reported recently by Kaneda et al.,[12] where a palladium-containing apatite is able to oxidize alcohols at atmospheric oxygen pressure even in the absence of solvents. Mizuno et al.[13,14] have described a ruthenium-containing solid catalyst that is able to selectively produce carbonyl compounds from alcohols in the presence of oxygen at atmospheric pressure. Other solid catalysts based on hydrotalcites,[15] apatites and mixed oxides,[16] or supported Pt and Pd[17,18] have also been studied.

Small-crystal-size gold supported on inorganic oxides or active carbon has recently attracted considerable attention since these catalysts are able to promote the selective oxidation of alcohols.[19–25] Taking into account that inorganic oxides contain some sites that are able to oxidize alcohols stoichiometrically, it appeared to us that a new concept of catalyst could be put forward if these stoichiometric sites can be converted into catalytic sites by introducing a solid co-catalyst that facilitates the reoxidation of the intermediate metal hydrides to water and the original inorganic oxide. To prove this concept we selected cerium oxide, which contains stoichiometric oxidation sites of alcohols, and cationic gold, which is a metal that transfers hydrides reversibly.

In particular, the combination[26] of small-crystal-size gold (2–5 nm) and nanocrystalline ceria ($\approx$5 nm) turned out to give a highly active, selective, and recyclable catalyst for the oxidation of alcohols into aldehydes and ketones with high turnover numbers (TON) and frequencies (TOF) using oxygen at atmospheric pressure as oxidant in the absence of solvent and base.

Pure, nanocrystalline cerium oxide contains sites that are able to perform the oxidation of alcohols in a stoichiometric manner. Indeed, when IR experiments were carried out in situ by adsorbing 2-propanol on nanocrystalline cerium oxide (see Supporting Information), two IR bands associated with cerium alkoxide appeared; the growth of a band attributable to cerium hydride, was also observed. The appearance of a carbonyl band indicates that acetone was formed at the same time as the cerium hydride. Upon subsequent introduction of O_2 into the IR cell at room temperature, the band due to cerium hydride remained unaltered and the formation of water was not observed. These experiments show that cerium oxide alone is able to perform one reaction cycle, but the reduced cerium is stable in the presence of physisorbed O_2 and the catalytic cycle is not closed.

When gold nanoparticles were deposited onto the nanocrystalline cerium oxide (see Supporting Information for the detailed preparation procedure), the XPS spectrum of the Au 4f7/2 core level shows three bands (see Supporting Information), which correspond to Au^{3+}, Au^{+}, and Au^{0}.[27] The presence of cationic gold was also confirmed by the IR band of adsorbed CO (see Supporting Information).[28] These results can be rationalized by assuming that the gold nanoparticles formed on the $Au\subset CeO_2$ catalyst (see HRTEM images in the Supporting Information) interact with the nanometric ceria surface, which stabilizes the positive oxidation states of gold[26,29,30] by creating Ce^{3+} and oxygen-deficient sites in the ceria.

When the anaerobic oxidation of 2-propanol on $Au\subset CeO_2$ was monitored in situ by IR spectroscopy (see Supporting Information) in the same way as with pure nanocrystalline CeO_2, the IR bands of the cerium alkoxide

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and hydride were again observed, and acetone was also formed. However, when O_2 was subsequently introduced the metal hydride disappeared and water was formed, contrary to what occurred with CeO_2. At this point the cerium oxide is therefore ready to perform another catalytic cycle.

After these spectroscopic studies, Au$\subset$$CeO_2$ was tested as a solid catalyst for the selective aerobic oxidation of a large variety of alcohols. The reactions were performed in a magnetically stirred, glass batch reactor in the absence of solvent and base at 80 °C, with O_2 at atmospheric pressure. In other cases the oxidations were also performed in basic water (see Supporting Information for experimental details). High conversions and selectivities were obtained with short reaction times (Table 1).

The benefit of using nanoparticles of CeO_2 as a support for the gold becomes obvious when comparing the activity (TOF) of Au$\subset$$CeO_2$ with the activities of Au supported on conventional CeO_2 (Au/CeO_2), Au/carbon (Au/C) (see Supporting Information for experimental details of the preparation), Au/TiO_2, and Au/Fe_2O_3 (these two last catalysts were supplied by the International Gold Council; Figure 1).[31] Note that Au$\subset$$CeO_2$ is active for the oxidation of alcohols in the absence of solvent and base, conditions under which most other supported gold catalysts are inefficient.[5] For instance, Au/C does not catalyze oxidation reactions in the absence of base and water.

Secondary alcohols can be oxidized with essentially complete conversion and high selectivities on Au$\subset$$CeO_2$ in the absence of solvent, and benzylic or allylic alcohols are selectively oxidized to the corresponding unsaturated aldehydes, although longer reaction times are required. Aliphatic primary alcohols are more reluctant to undergo oxidation in the absence of solvent. Notably, they give predominantly the corresponding ester with high selectivity, accompanied by lesser amounts of the aldehyde. We have found that esters are directly formed via the hemiacetal, which is detectable by ^1H NMR spectroscopy, as indicated in Scheme 1. Indeed, we have seen that the introduction of trimethyl orthoformate, which acts as a scavenger for aldehydes, into the reaction mixture gives the dimethyl acetal of the aldehyde with very high selectivity and completely inhibits the formation of the ester. Note that Au$\subset$$CeO_2$ is also very active for the oxidation of alcohols in basic aqueous solution. In this case pH plays an important role, with the TOF decreasing upon lowering the pH. In basic aqueous solution, the oxidation of primary alcohols gives the carboxylic acids rather than the esters.

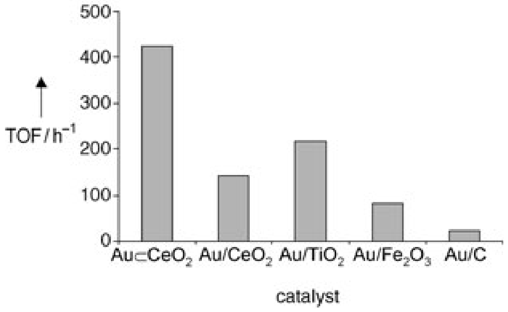
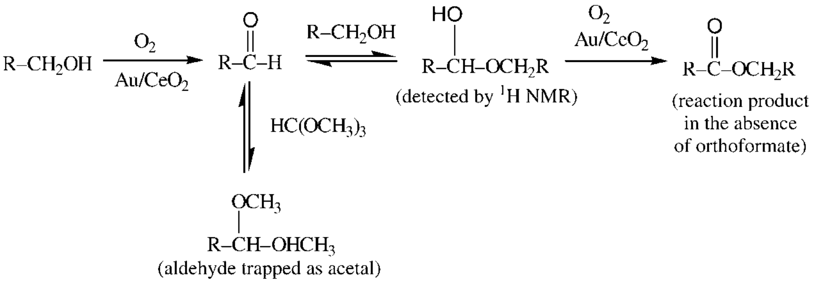


Figure 1. Turnover frequencies for the oxidation of 3-octanol, given as the ratio of moles of 3-octanone per mole of Au per hour, measured at $t = 10$ min (see Table 1 for reaction conditions).



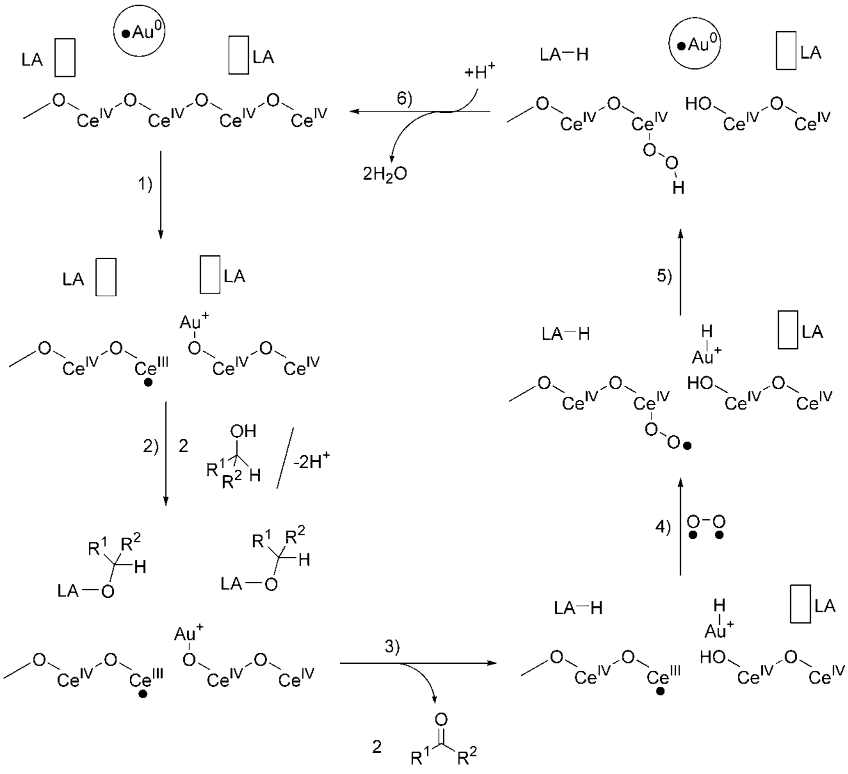
Scheme 1. Reaction route proposed for the formation of esters in the oxidation of primary alcohols.

Table 1: Aerobic alcohol oxidation catalyzed by Au$\subset$$CeO_2$.[a]

Entry	Substrate	t [h]	Conversion [%]	Product	Selectivity [%]
1[b]	3-octanol	3.5	97	3-octanone	>99
2[c]	3-octanol	2.5	89	3-octanone	96
3[b]	2-phenylethanol	2.5	92	acetophenone	97
4[b]	2,6-dimethylcyclohexanol	2.5	78	2,6-dimethylcyclohexanone	94
5[b]	1-octen-3-ol	3.5	80	1-octen-3-one	>99
6[b]	cinnamyl alcohol	7	66	cinnamaldehyde	73
7[b]	3,4-dimethoxybenzyl alcohol	7	73	3,4-dimethoxybenzaldehyde	83
8[b]	3-phenyl-1-propanol	6	70	3-phenylpropyl 3-phenylpropanoate	98
9[d]	vanillin alcohol	2	96	vanillin	98
10[d]	2-hydroxybenzyl alcohol	2	>99	2-hydroxybenzaldehyde	87
11[d]	3,4-dimethoxybenzyl alcohol	2	>99	3,4-dimethoxybenzylic acid	>99
12[d]	cinnamyl alcohol	3	>99	cinnamylic acid	98
13[e]	*n*-hexanol	10	>99	hexanoic acid	>99
14[d]	2-phenylethanol	5	>99	acetophenone	51

[a] Conversion and selectivity were determined by GC using nonane and nitrobenzene as external standards. [b] Substrate (4.85 mmol), Au$\subset$$CeO_2$ (0.5 mol%), 353 K, $p = 1$ atm O_2 (flow: 25 mL min^{-1}). [c] As [b], but TEMPO (2,2,6,6-tetramethylpiperidine oxide; 4 equiv with respect to Au) was added. [d] Substrate (0.4 mmol), Au$\subset$$CeO_2$ (0.66 mol%), H_2O (5 mL), Na_2CO_3 (0.3 g), 323 K, $p = 1$ atm O_2 (flow: 25 mL m^{-1}). [e] Substrate (1 mmol), Au$\subset$$CeO_2$ (0.25 mol%), H_2O (5 mL), Na_2CO_3 (0.71 g), 373 K, $p = 25$ atm (synthetic air).

On the basis of the Au⊂CeO_2 characterization and IR study, a reasonable mechanism for the catalytic reaction is depicted in Scheme 2. According to this mechanism, the interaction between gold and ceria will give rise to an important population of positively charged gold and Ce^{3+} species (detectable by XPS; step 1). The alcohol or the corresponding alkoxide will then react with the Lewis acid sites of Au⊂CeO_2 to give a metal alkoxide (step 2), which subsequently undergoes a rapid hydride transfer from C–H to Ce^{3+} and Au^+ to give the ketone and Ce–H (indicated as LA–H in Scheme 2) and Au–H (as observed by IR spectroscopy; step 3). Upon admission of oxygen into the system and coordination to the oxygen-deficient sites of ceria, formation of cerium-coordinated superoxide (Ce–OO$^•$) species occurs (step 4).[32] These superoxide species evolve into cerium hydroperoxide by hydrogen abstraction from Au–H (step 5), and are responsible for the formation, after reduction of Ce^{IV}, of the initial Au^+ species. The absence of gold would render this step impossible and lead to a depletion of Ce^{III}. This mechanism is compatible with the lack of influence of an excess of TEMPO in the reaction (see footnote [e] in Table 1), since TEMPO is not able to quench oxygen-centered radicals.



Scheme 2. Proposed mechanism for the oxidation of alcohols in the presence of Au⊂CeO_2 as the catalyst. LA = Lewis acid.

Kaneda et al. have reported recently that Pd supported on hydroxyapatite is the most active solid catalyst, with a turnover number of 236000 and a TOF of 9800 h^{-1}.[12] We have been able to reproduce these results. Under the reported conditions our catalyst gives a TOF of 12500 h^{-1} for the conversion of 1-phenylethanol into acetophenone at 160 °C, with greater than 99 % selectivity for the desired product. The catalyst is fully recyclable after filtering and washing (NaOH 0.5 M), with a TON of 250000 after three recycles. This shows that gold, which was previously believed to be of little catalytic interest, can become an interesting oxidation catalyst when combined with the right support.

In conclusion, we have shown that gold nanoparticles transform nanocrystalline cerium oxide from a stoichiometric oxidant into a catalytic material for the selective oxidation of primary and secondary alcohols to aldehydes and ketones in the presence of oxygen at atmospheric pressure, with high TOFs and selectivities observed. This catalyst makes the process interesting from both an economic and environmental point of view.

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