Gold supported on a mesoporous CeO₂ matrix as an efficient catalyst in the selective aerobic oxidation of aldehydes in the liquid phase†

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Gold supported on CeO₂ catalyses the selective aerobic oxidation of aliphatic and aromatic aldehydes better than other reported catalysts such as Pt/C/Bi materials; the activity is due to the nanometric particle size of Au and CeO₂.

A wide range of aliphatic and aromatic aldehydes can be oxidised to carboxylic acids under mild reaction conditions using H_2O_2, peracids, NaOCl, or O_3 as oxidants.[1,2] Molecular oxygen in combination with Mn(II), Cu(II), Co(II) or Ni(II), in the form of salts or in organic complexes, are efficient homogeneous systems for the catalytic oxidation of aldehydes to acids at the laboratory[3] and industrial scales.[4]

With heterogeneous catalysts, high yields of carboxylic acids have already been reported in the liquid oxidation of aromatic aldehydes with O_2 (or air) at atmospheric pressure using an organic solvent and with Pd or Pt supported on carbon.[5,6] In this case, the presence of Bi as co-catalyst enhances the activity of Pt or Pd. However, leaching of the Bi occurs that, together with environmental issues, results in an irreversible deactivation of the catalyst.[6]

After the seminal work of Bond and Sermon,[7] Hutchings[8] and Haruta *et al.*,[9] gold has irrupted into the field of homogeneous and heterogeneous catalysis, showing interesting properties for liquid and gas phase oxidations,[10–12] WGS reaction,[13] decomposition of NO_x with hydrocarbons,[14] selective hydrogenations,[15] and also C–C bond formation with boronic acid.[16]

Here we present that Au supported on CeO₂ nanoparticles and meso-structured CeO₂ nanoparticles are highly active and selective catalysts for the oxidation of aliphatic and aromatic aldehydes to the corresponding carboxylic acids. Their activity and selectivity is higher than with soluble transition metal catalysts, and better than those reported using Pt/C/Bi catalysts for the industrially relevant oxidation of 4-iso-propylbenzaldehyde into 4-iso-propylbenzoic acid, which is an important intermediate for the production of nateglinide, a chemical used for the treatment of diabetes.

Synthesis of regular-sized CeO₂ was performed starting from $Ce(NO_3)_3$ by following a well known procedure (see supplementary information†). Nanocrystalline CeO₂ and meso-structured CeO₂ were prepared as in refs. 17 and 18. Deposition of the Au particles on CeO₂ supports was performed by a deposition–precipitation method[12] (see also supplementary information†).

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† Electronic supplementary information (ESI) available: Synthesis of regular-sized CeO₂, and deposition of Au on a CeO₂ matrix. See http://dx.doi.org/10.1039/b506685a

For comparison, Au/Fe₂O₃ [#02-03-WG-C] and Au/TiO₂ [#02-04-WG-C] samples from the World Gold Council as Au supported European standard catalysts were tested.

All catalysts were analysed by available spectroscopic techniques and by N_2 adsorption and chemical methods. The physical and textural properties of the solid catalysts used in this work are summarized in Table 1.

The homogeneous metal catalysts were: Co(II) chloride (Aldrich, 97%), Mn(II) acetate tetrahydrate (Panreac, *puriss.*), Ni(II) acetate tetrahydrate (Aldrich, 98%), Co(II)-acetylacetonate (Aldrich, 97%), Mn(II)-acetylacetonate (Aldrich, 97%), Ni(II)-acetylacetonate (Aldrich, 95%).

The catalytic reactions were carried out in a glass flask batch reactor equipped with a magnetic stirrer and a condenser, and immersed in a silicon oil bath with temperature control. In a typical experiment, 0.45 g (3.9 mmol) of *n*-heptanal, 3.5 g of acetonitrile as solvent, and 0.035 g of *n*-decane as an internal standard were mixed in the flask under stirring until the reaction temperature (25 or 50 °C) was reached. At this time, 0.05 g of the solid catalysts (0.01–0.015 g of homogeneous metallic catalysts) were added (time zero). Then, a continuous flow of air (1–2 ml min⁻¹ approx.) was bubbled into the reaction mixture at atmospheric pressure. Small aliquots were taken at selected reactions times. The liquids obtained were filtered off and analysed by GC, GC-MS and HPLC-MS.

Results from Fig. 1a show that the nanocrystalline CeO₂ has some activity for the oxidation of *n*-heptanal, but the selectivity to the acid is slightly lower than for the thermal oxidation (Fig. 1b). When gold was deposited on nanocrystalline CeO₂, the initial rate of the reaction increased by a factor of 3, with selectivity ⩾95%. When the gold catalyst was prepared on meso-structured CeO₂,

Table 1 Physical and textural properties of different Au supported catalysts

Catalyst	wt.% Au[b]	Surface area (BET)/m² g⁻¹	Metal particle size/nm[c]
CeO₂	—	170	—
CeO₂ nano	—	215	5
Meso CeO₂ nano	—	225	—
Au/CeO₂ precipitated	4.65	145	4.5
Au/CeO₂ nano	2.30	163	<4
Meso Au/CeO₂ nano	5.00	152	<4
Au/Fe₂O₃[a]	5.00	—	—
Au/TiO₂[a]	1.50	—	—

[a] World Gold Council standard catalyst. [b] Measured by X-ray fluorescence spectroscopy (XRF). [c] Calculated as the medium value from transmission electron microscopy data (TEM).

and the initial rate was normalized with respect to the Au content (See Table 1), it can be seen that catalytic activity is similar to that of nanocrystalline Au/CeO$_2$. Therefore, we do not see in this case any benefit of potential reactant confinement within the regular pores of the meso-structured catalyst. It has to be noticed (Fig. 1a) that the oxidation activity of gold deposited on conventionally precipitated CeO$_2$ gives lower activity than on nanocrystalline CeO$_2$, despite the fact that the size of the Au particle is very similar (≈ 4 and 4.5 nm, respectively). The differences in catalytic activity between these two Au/CeO$_2$ catalysts can be based on the different oxygen activated species formed on the nanocrystalline and amorphous CeO$_2$.[16,19]

From the point of view of selectivity, gold on both nanocrystalline and meso-structured nanocrystalline CeO$_2$ give the highest values ($\geqslant 95\%$ selectivity for $\approx 100\%$ conversion). It has to be taken into account that selectivity to heptanoic acid is generally very high, even in the absence of catalyst. The competing reactions observed are the formation of dimers, decarboxylation and oxidation of secondary carbon atoms. In the case of gold on nano and meso CeO$_2$ the rate of oxidation of aldehyde is enhanced, with respect to competing reactions, when compared with the non catalyzed reactions. Thus, the selectivity to dimers, decarboxylation and oxidation of secondary carbons decreases. The much lower selectivity to acid achieved with gold on precipitated CeO$_2$ is remarkable. This is mainly due to the formation of a large amount of dimers and trimers (selectivity 30%) on this catalyst.

We have compared the conversion and selectivity of the best Au/CeO$_2$ catalysts with those of gold deposited on Fe$_2$O$_3$ and TiO$_2$, as well as with soluble Co, Mn, and Ni catalysts, on the basis of the same amount of metals added (Figs. 2 and 3, respectively). Results from Fig. 2 and 3 indicate that Au on a nanocrystalline CeO$_2$ support is the most active and selective catalyst. The differences in catalytic activities were maintained when the reaction temperature was dropped to 25 °C. At these reaction conditions, the TON ratio calculated between the gold on ceria and Co(II) acetylacetonate homogeneous catalyst was around 6 (TON ratio = 240/41, from Table 2). Furthermore, after reacting, filtering and washing the Au/CeO$_2$ catalyst with a mixture of acetonitrile–acetone (50 : 50), the conversion and selectivity were maintained even after three consecutives re-uses of

Fig. 2 Comparative catalytic activity of Au metal supported on different inorganic matrices in the air oxidation reaction of *n*-heptanal at 50 °C during 3.5 h.

Fig. 3 Comparative catalytic activity (yield of carboxylic acid, mol.%) of Au/CeO$_2$ and different metallic homogeneous catalysts for air oxidation of *n*-heptanal at 50 °C during 3.5 h.
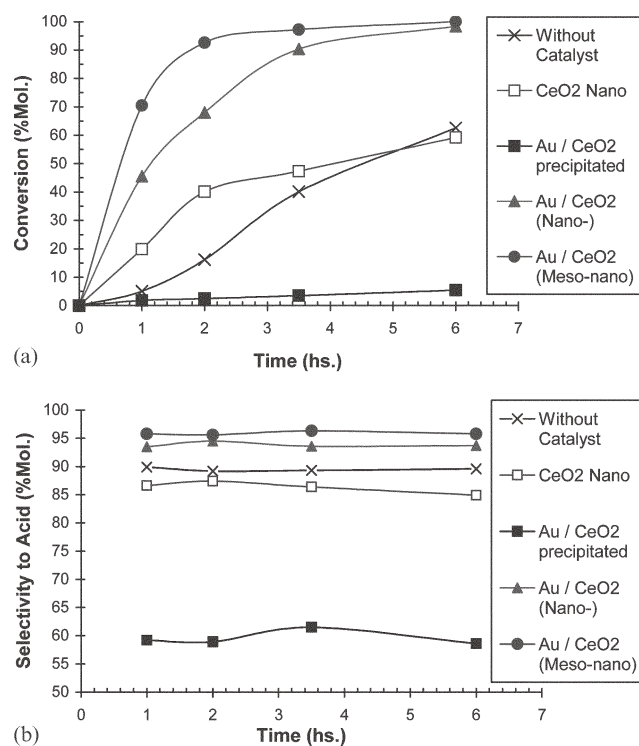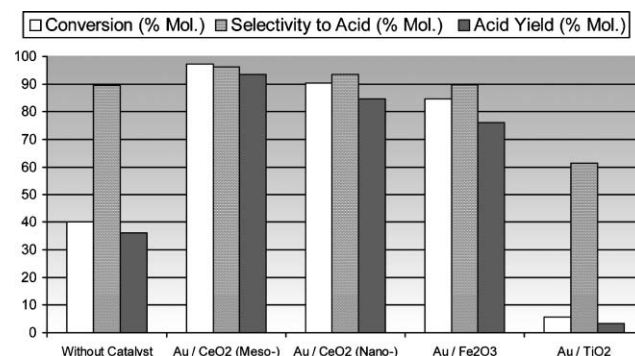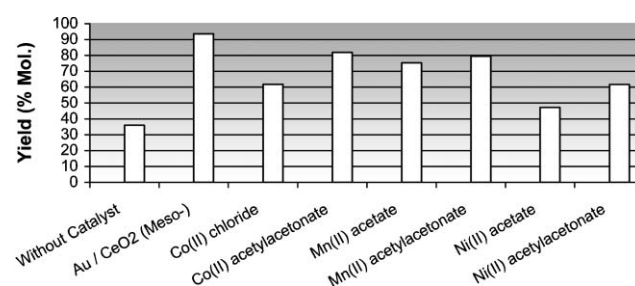

Fig. 1 (a) Conversion of *n*-heptanal in the catalytic air oxidation reaction over different heterogeneous metal catalysts at 50 °C during 6 h. (b) Selectivity to *n*-heptanoic acid in the catalytic air oxidation reaction of *n*-heptanal over different heterogeneous metal catalysts at 50 °C during 6 h.

Table 2 Comparison of catalytic activity between Au/CeO$_2$ (meso-nano) material and Co(II)-acetylacetonate catalysts in the *n*-heptanal air oxidation under different reaction conditions

Reaction conditions[a]	Without catalyst Yield (mol.%)	Au/CeO$_2$ (meso-nano) Yield (mol.%)	Au/CeO$_2$ (meso-nano) TON[b]	Co(II)–acac. Yield (mol.%)	Co(II)–acac. TON[b]
50 °C	37.0	93.6 (88.9)[e]	287 (273)[e]	81.8	54
25 °C	<12.0	78.1	240	61.9	41
With BHT[c]	1.8	1.9	6	46.2	30
With AIBN[d]	40.0	82.7	254	85.6	57

[a] Reaction conditions: 3.9 mmol of aldehyde, 3.5 g of acetonitrile, 0,05 g of catalyst, during 3.5 h. [b] Calculated as mols of carboxylic acid/mols of metal. [c] With 6 mg BHT. [d] With 8 mg of AIBN. [e] Values obtained after 3 consecutive re-uses of the catalyst.

the solid, whereas negligible leaching of the metal to the liquids was observed (Table 2). Particularly noteworthy is that the Au/CeO$_2$ catalyst shows excellent activity ($\approx$70% of conversion and >73% of selectivity to acid, time = 6 h) for aerobic oxidation of aldehydes in the absence of acetonitrile as solvent. Under these reaction conditions most gold supported materials failed to catalyse oxidation.

In the case of aerobic oxidation reactions mediated by transition metal homogeneous or heterogeneous catalysts, a radical or an ionic reaction mechanism has been proposed when working with organic or aqueous solvent, respectively.[10] In the case of Au/CeO$_2$ working in organic media, we have seen (Table 2) that the introduction of a radical inhibitor (2,6-di-*tert*-butyl-4-methylphenol, BHT) strongly diminishes the oxidation of *n*-heptanal. On the other hand, the presence of a radical initiator, such as α,α′-azo-iso-butyronitrile (AIBN) has no effect on conversion. Taking into account that the amount of radical inhibitor is not enough to totally inhibit the reaction on Au/CeO$_2$ catalyst, it appears reasonable to think that the oxidation of *n*-heptanal to *n*-heptanoic acid by air takes place through a radical mechanism. Nevertheless, these results are not conclusive and further research is needed to confirm the oxidation pathway.

Different types of both saturated and unsaturated aliphatic aldehydes of industrial interest can be converted to the corresponding mono-carboxylic acids over our Au/CeO$_2$ in the presence of air. The results given in Table 3 show the versatility of the gold catalyst, offering a high conversion level (>90%) for aliphatic aldehydes. In the case of an unsaturated aldehyde, such as cinammaldehyde, high selectivity to carboxylic acid (77.5%) at moderated conversion was achieved.

We have applied the Au/CeO$_2$ catalyst to carry out the oxidation of 4-iso-propylbenzaldehyde to cumic acid (4-iso-propylbenzoic acid), which is an intermediate for the manufacturing of nateglinide. The reaction was carried out at similar reaction conditions as reported in the patent literature[5] when using Pt/C as catalyst and Bi as co-catalyst. The results given in Table 3 show that Au/CeO$_2$ is able to perform the reaction with air, at 65 °C and atmospheric pressure, giving higher conversion and selectivity than the reported catalyst.

In conclusion, nanoparticulated Au on nanocrystalline or on meso-structured nanocrystalline CeO$_2$ supports represent an alternative to actual metal soluble or heterogeneous catalysts for the selective oxidation of aldehydes to carboxylic acids by air, under mild reaction conditions.

Table 3 Selective aerobic oxidation of different type of aldehydes over Au/CeO$_2$ (meso-nano) catalyst at 65 °C during 3.5 h[a]

Aldehyde	Conversion (mol.%)	Selectivity to Acid (mol.%)	Yield (mol.%)
Dihydro cyclocitral	92.0	70.0	64.4
Cinammaldehyde	40.7	77.5	31.5
4-Iso-propyl-benzaldehyde	91.0	94.7	86.2
4-Iso-propyl-benzaldehyde[b]	89.9	93.2	83.7
4-Iso-propyl-benzaldehyde[c]	—	—	74–76

[a] Reaction conditions: 3.9 mmol of aldehyde, 3.5 g of acetonitrile, 0.05 g of catalyst. [b] After the 2nd re-use of the catalyst. [c] Data from ref. 5 with Pt (Bi)/C catalyst (55–75 °C).

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