A highly active catalyst for CO oxidation at 298 K: mononuclear Au^{III} complexes anchored to La_2O_3 nanoparticles†

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Mononuclear La_2O_3-supported Au^{III} complexes synthesised from $Au^{III}(CH_3)_2(C_5H_7O_2)$ and characterised by X-ray absorption spectroscopy are highly active, stable CO oxidation catalysts at room temperature, demonstrating the importance of the support in stabilizing catalytically active gold species, which need not include zerovalent gold for high activity.

Gold highly dispersed on oxide supports is highly active as a catalyst for many reactions, including CO oxidation[1] (even in the presence of excess H_2[2]) and the water gas shift.[3] Gold on La_2O_3 supports is among the most active catalysts for the oxidative decomposition of dioxins,[4] and it is highly selective for styrene oxidation to styrene oxide.[5]

Contradictory hypotheses have been proposed to explain the catalytic activity of supported gold.[6] Roles have been attributed to both zerovalent and cationic gold, present either in mixtures[7,8] or as individual species[9] in the catalysts, and moisture affects the catalytic activity and stability.[10,11] Because typical supported gold catalysts are complicated in structure, containing gold nanoparticles of various sizes and shapes, it has not been possible to resolve the roles of the different gold species. We have reported[9] evidence that zeolite-supported mononuclear complexes catalyse CO oxidation at steady state at 298 K in the absence of gold nanoparticles. However, the activities of these complexes are much lower than those of the most active oxide-supported gold catalysts, which contain gold nanoparticles.[12,13] Thus, whether zerovalent gold is needed for a highly active CO oxidation catalyst remains an open question.

We now report the synthesis of mononuclear Au^{III} complexes bonded to nanoparticles of La_2O_3 and their characterization by X-ray absorption spectroscopy. These complexes have been found to be almost as active for CO oxidation catalysis at 298 K as the most active supported gold catalysts yet reported.[12,13] Furthermore, these catalysts did not deactivate even after 50 h of continuous operation in a flow reactor.

In the synthesis, $Au^{III}(CH_3)_2(C_5H_7O_2)$ was adsorbed on partially dehydroxylated La_2O_3 from a slurry in *n*-pentane. The La_2O_3, synthesized as reported elsewhere,[14] had a BET surface area of approximately 75 m^2g^{-1}; the average particle size was calculated to be 12 nm (assuming spherical particles). Extended X-ray absorption fine structure (EXAFS) spectra characterizing the initially prepared supported gold sample show the lack of any detectable Au–Au contributions (and thus the lack of detectable gold nanoclusters) and the presence of approximately two O atoms bonded to each gold atom, on average (at a Au–O distance of approximately 2.15 Å) (Table 1), consistent with the presence of mononuclear gold complexes bonded to approximately 2 O atoms of the La_2O_3. X-ray absorption near edge structure (XANES) spectra indicate the presence of Au^{III} (Fig. 1). Analogous supported Au^{III} complexes have been prepared on MgO,[15] γ-Al_2O_3,[16] and TiO_2.[17]

EXAFS spectra characterizing the sample as it was treated in a reactor/cell[18] in a flowing mixture of CO and excess O_2 (P_{CO} = 8 Torr, P_{O_2} = 40 Torr) show the lack of Au–Au contributions (Table 1), even after 90 min time on stream (TOS), and XANES spectra recorded simultaneously show essentially the same features as the initially prepared sample (Fig. 1), confirming the lack of aggregation of the gold and the presence of mononuclear Au^{III}, even in the functioning catalyst. Mass spectra of the effluent gases from the reactor/cell recorded in a separate experiment under the same conditions confirm the catalytic formation of CO_2, which after 90 min TOS had essentially reached steady-state conversion. Therefore, mononuclear Au^{III} was present during CO oxidation catalysis and is identified as the catalytically active species (the La_2O_3 support alone lacked measurable catalytic activity).

When the initially prepared sample (0.2 g) was exposed to an equimolar mixture of CO and O_2 at 298 K and 760 Torr (P_{CO} = 11.7 Torr in He; total flow rate = 100 mL (NTP) min^{-1}) in a plug–flow reactor, the initial CO conversion to CO_2 was approximately 3%, and it increased with TOS, reaching a steady-state value of approximately 10%. This conversion was maintained for 50 h of continuous operation, after which the experiment was terminated. The corresponding turnover frequency (TOF) under these conditions is approximately 1.0×10^{-2} s^{-1}, which approximately matches the activities observed for the most active supported gold CO oxidation catalysts that have been investigated under comparable conditions (Table 2).[12,13]

During catalysis, Au^{III} on other supports (a zeolite[9] and MgO[19]) underwent structural changes, either forming Au^{I} or nanoclusters of gold, respectively—always with a simultaneous decrease in the catalytic activity. Thus, the results presented here emphasize the importance of the support in stabilizing catalytically active Au^{III} species.

It was reported recently[13] that gold supported on other nanocrystalline rare-earth metal oxides, such as CeO_{2-x} and Y_2O_3, also gave highly active CO oxidation catalysts (the average particle size of each of these supports was 5 nm, as indicated by transmission electron microscopy). The CeO_{2-x}-supported catalyst

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Table 1 EXAFS parameters characterizing the La_2O_3-supported Au catalyst at 298 K[a]

Treatment gas/temperature/K	Absorber–backscatterer pair	N	R/Å	$10^3 \times \Delta\sigma^2/Å^2$	ΔE_0/eV
He/298	Au–Au	[b]	[b]	[b]	[b]
	Au–O	2.1	2.15	4.34	−1.34
	Au–C	0.4	1.84	4.41	2.94
	Au–O	2.4	3.78	8.4	0.22
$CO + O_2$ during CO oxidation catalysis/298	Au–Au	[b]	[b]	[b]	[b]
	Au–O	1.06	2.16	3.65	−4.21
	Au–O	1.14	3.81	8.54	−2.61
	Au–C	0.95	1.86	9.05	5.56
	Au–La	1.01	3.27	4.97	0.46

[a] Notation: N, coordination number; R, distance between absorber and backscatterer atoms; $\Delta\sigma^2$, Debye–Waller factor; ΔE_0, inner potential correction. Data were obtained with samples in a flow system after 90 min TOS. Expected errors: N, ± 10%, R, ± 0.02 Å; $\Delta\sigma^2$, ± 20%; ΔE_0, ± 20%. [b] Contribution undetectable.

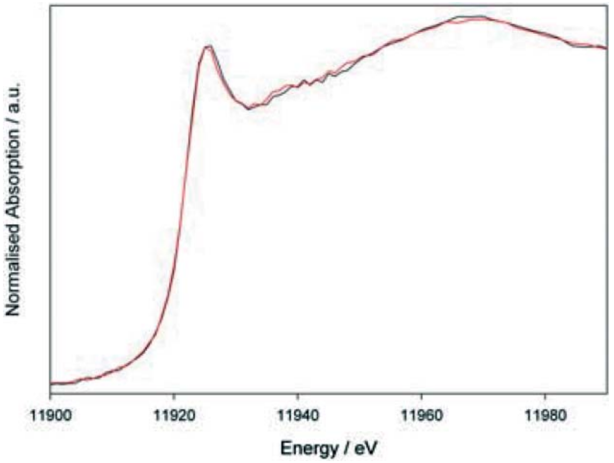

Fig. 1 XANES spectra characterising initially prepared La_2O_3-supported Au^{III} complexes in flowing He at 298 K (black) and in flowing $CO + O_2$ undergoing catalytic reaction to give CO_2 at 298 K (red).

incorporated gold nanoparticles with an average diameter of 3–4 nm, and XANES spectra characterizing this catalyst in the functioning state gave evidence of both cationic gold and zerovalent gold nanoparticles; thus, these results characterizing the CeO_{2-x}-supported catalyst are consistent with the possible role of cationic gold in highly active CO oxidation catalysts, but they do not exclude a role of the zerovalent gold.[20] Furthermore, EXAFS spectra characterising the functioning CeO_{2-x}-supported gold catalysts show the presence of O atoms in the vicinity of the gold (at an average Au–O distance of 3.5 Å), and Raman spectra gave evidence of reactive oxygen species on the CeO_{2-x} surface in the form of peroxides and superoxides. These results suggest the presence of redox-active sites where these intermediates are stabilized;[20] thus, the redox-reactive support was invoked as a participant in the catalytic oxidation of CO. Our results, showing Au–O contributions at approximately 3.8 Å, are consistent with the involvement of reactive oxygen intermediates in the catalysis and suggest that the La_2O_3 might activate the oxygen on the support near the gold. We could speculate that species such as peroxides and superoxides are common to highly active supported catalysts containing Au^{III} and that these species may help stabilize Au^{III}.

Although there are no data allowing a comparison of our catalyst formed from $Au(CH_3)_2(C_5H_7O_2)$ and high-area La_2O_3 with any prepared from the same precursor and high-area CeO_{2-x}, the relatively high activities reported for CeO_{2-x}-supported gold catalysts and the evidence that they contain Au^{III} in the working state suggest the worthiness of investigating samples made from $Au(CH_3)_2(C_5H_7O_2)$ and CeO_{2-x}.[20] We stress that both the CeO_{2-x}- and conventional CeO_2-supported catalysts, in contrast to ours, contained substantial amounts of zerovalent gold. It is still not known how the preparation method affects the distribution of cationic and zerovalent gold in these samples or whether redox activity is necessary for high catalytic activity or stabilization of cationic gold.

In conclusion, we report that mononuclear gold complexes supported on nanoparticles of La_2O_3 are among the most active supported gold catalysts. These results raise the question of whether zerovalent gold plays a role at all in highly active CO oxidation catalysts. Furthermore, because the functioning

Table 2 Comparison of activities of supported gold catalysts for CO oxidation

Catalyst	State of gold in catalyst	Average Au cluster diameter/nm	T/K	TOF/s^{-1}	TOS/h	Reference
Au/La_2O_3	Au^{III}	[a]	298	1×10^{-2}	50	This work
Au/zeolite NaY	Au^{I} (steady-state catalyst)	[a]	298	3×10^{-3}	1	9
Au/γ-Al_2O_3	Zero-valent and cationic gold	2.4	273	2×10^{-2}[d]	>0.5	7
Au/Fe_2O_3	Zero-valent gold and Au^{III}	<1 nm[b]	293	[c]	10	12
Au/CeO_{2-x}	Zero-valent and cationic gold	4	278	2×10^{-2}[d]	10	13
Au/La_2O_3	No quantitative data available					4

[a] No gold clusters detected in sample; gold inferred to be present as mononuclear complexes, as evidenced by the lack of detectable Au–Au contributions in the EXAFS spectra. [b] Inferred, as the authors[12] did not observe any gold nanoparticles by TEM. [c] TOF indeterminate because CO conversion was 100% under reported reaction conditions.[12] [d] TOF reported was calculated as rate per surface Au atom, estimated on the basis of the assumption that the gold was present as hemispherical particles in all the samples except those in which gold was exclusively present as mononuclear cationic species.

La_2O_3-supported catalyst has been found to contain cationic gold but no detectable zerovalent gold and to be among the most stable gold catalysts for CO oxidation, our results highlight the importance of nanoparticle supports stabilizing both cationic gold and the catalytically active species.

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