Genesis of a highly active cerium oxide-supported gold catalyst for CO oxidation†

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X-Ray absorption spectra show that a CeO_2-supported CO oxidation catalyst prepared from $Au^{III}(CH_3)_2(C_5H_7O_2)$ initially incorporated Au^{III} complexes that were catalytically active at 353 K; during operation in a flow reactor, the gold aggregated into clusters and the catalytic activity increased.

Gold on hydroxylated metal oxide supports is an active and selective catalyst for numerous reactions, the most thoroughly investigated being CO oxidation.[1–3] EXAFS spectra and TEM images demonstrate the presence of small gold clusters in the typical catalyst, and the catalytic activity apparently depends on the cluster size; most researchers identify the clusters as the catalytically active species.[4] However, site-isolated gold cations on oxide and zeolite supports have alternatively been identified as catalytic sites.[5,6] Some authors have (speculatively) suggested that gold at the cluster–support interface is involved in the catalysis.[7]

Although supported gold clusters have been considered to be zero-valent and bulk-like, spectroscopic characterizations (XANES,[8] Mössbauer,[9] and X-ray photoelectron[9]), temperature-programmed oxidation–reduction data,[10] and calculations based on theory at the density functional level indicate that gold in small supported clusters may be cationic under conditions of CO oxidation catalysis;[11–13] recent experimental results are also consistent with this interpretation, with the evidence being XANES[9] and X-ray photoelectron spectra.[14]

Thus, the catalytic roles of complexes and clusters and of cationic and zerovalent gold are unresolved.

High-area porous nanostructured CeO_2 was chosen as the support in this work because some of the most highly active catalysts for CO oxidation incorporate it,[15–17] at least in part because it reacts with O_2 to form highly reactive superoxide and peroxide species,[18] which are inferred to be reaction intermediates.[15] We now report data indicating the activity of CeO_2-supported gold complexes and the genesis from them of a more active catalyst as they are converted into clusters of only a few atoms each, on average.

The catalyst was prepared from $Au(CH_3)_2(acac)$ (acac = $C_5H_7O_2$) (Strem 99.9%), chosen for the opportunities it affords for synthesis of highly dispersed cationic gold species.[6,10,19–21] This precursor was adsorbed on partially dehydroxylated CeO_2 powder (Daiichi, 99.9%, 173 m^2 g^{-1}, average particle diameter 46 nm). After slurrying for 24 h in *n*-pentane, the solvent was removed by evacuation, leaving all the gold on the support. Sample handling was done with standard air-exclusion methods.

EXAFS/XANES characterization of catalysts was done in fluorescence mode because of the high absorbance of cerium at the Au L_{III} edge (11919 eV). An EXAFS cell that was a once-through flow reactor was used to scan samples under catalytic reaction conditions;[22] some measurements were also made with a conventional EXAFS cell (Table 1). Samples that had been onstream for longer periods were removed from the reactor, mounted on plates, sealed with Kapton® tape, and scanned at room temperature in the conventional cell. Each spectrum is the average of $\geqslant$4 scans. More experimental details are given in ESI.†

Analysis of the EXAFS data characterizing the as-prepared sample gave no evidence of Au–Au contributions—attempts to include them in the fitting process always led to values of the Au–Au coordination number indistinguishable from zero. Thus, the best fit of the EXAFS data characterizing this sample (Table 1) indicates mononuclear gold species.

The spectra include Au–O and Au–C contributions at distances of 2.09 and 2.05 Å, respectively. The XANES features essentially match those of Au compounds in which Au is present as Au^{III} (Fig. 1), as shown by a comparison with reference data (Fig. 1; also see ESI†).

The initially prepared sample showed no measurable catalytic activity for CO oxidation at room temperature and CO and O_2 partial pressures of 10.1 and 5.7 mbar, respectively, at a total pressure of 1 bar (the balance was He). However, as the temperature was raised with the catalyst in the flow reactor, conversion was observed at 323 K (and at higher temperatures). With the temperature held at 353 K, the activity was relatively low, and it increased during operation as the initially present mononuclear gold complexes were converted into clusters, which grew over time.

These data, combined with the physical characterization data, show that the catalyst in which the gold was present as mononuclear complexes in the absence of detectable gold clusters was active (consistent with the aforementioned reports[5,6] characterizing gold complexes on other supports), and the higher activity of the catalyst after formation of the clusters shows that the clusters were more active. Blank experiments were done with calcined CeO_2 lacking gold under the same reaction conditions, and no conversion was observed. This result confirms the inference that the gold was necessary for the catalysis.

Details follow:

When the temperature was raised to 353 K and held at that value, a period of nearly steady-state conversion was attained rapidly and maintained for about 2 h (inset, Fig. 2), corresponding

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† Electronic supplementary information (ESI) available: Figures showing EXAFS results and errors. Extensive experimental details are provided as well. See DOI: 10.1039/b705562e

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Table 1 EXAFS results characterizing CeO_2-supported gold catalysts[a]

Sample/conditions of scan	Shell	N	R/Å	$10^3 \times \Delta\sigma^2$/Å^2	ΔE_0/eV
As-prepared catalyst/298 K under He flow at 100 mL/min	Au–Au	[b]	[b]	[b]	[b]
	Au–O	2.0	2.09	5.6	−6.9
	Au–C	2.1	2.05	11.0	−12.3
After 2 h of CO oxidation catalysis at 353 K/353 K during catalysis	Au–Au	[b]	[b]	[b]	[b]
	Au–O	2.2	2.09	−0.1[c]	−6.8
	Au–C	2.0	2.13	7.3	−11.9
After 24 h of CO oxidation catalysis at 353 K/298 K in N_2 after catalysis	Au–Au	4.0	2.82	11.3	−5.8
	Au–O	0.7	2.08	1.6	2.2
After 48 h of CO oxidation catalysis at 353 K/298 K in N_2 after catalysis[d]	Au–Au	5.9	2.79	10.0	0.4

[a] Notation: N, coordination number; R, absorber–backscatterer distance; $\Delta\sigma^2$, Debye–Waller factor relative to reference; ΔE_0, inner potential correction. [b] Undetectable. Estimated EXAFS errors, N: ±20%; R: ±0.02 Å. [c] Sample was scanned at 353 K and errors are expected to be greater than those characterizing samples scanned at lower temperatures; the Debye–Waller factor, within error, includes both positive and negative values. [d] The quality of the EXAFS data characterizing this sample was not sufficient to provide a reliable characterization of the Au–O contribution.

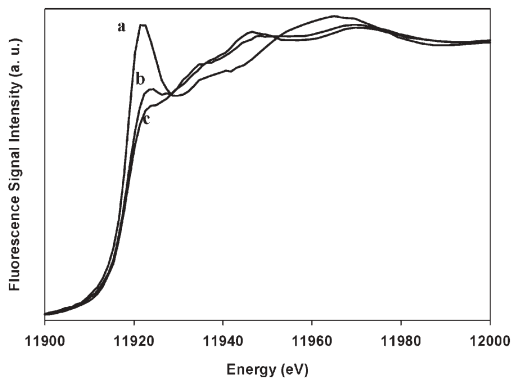

Fig. 1 XANES spectra of (a) gold supported on CeO_2, as prepared; gold on CeO_2 after (b) 24 h and (c) 48 h on stream during catalysis of CO oxidation at 353 K.

to a (differential) CO conversion of 1.3% after 1 h on stream and a turnover frequency of $(6.5 \pm 0.6) \times 10^{-3}$ molecules of CO (Au atom)$^{-1}$ s^{-1}.

After an additional period of operation at this temperature, the CO conversion increased sharply (Fig. 2) and then continued to increase slightly for as long as the experiment continued (50 h). When this—now activated—catalyst was cooled to room temperature with reactants flowing, it was found to have become active, characterized by a conversion of approximately 30%; the conversion increased to >40% after an additional 68 h on stream at room temperature, when the experiment was stopped (ESI†). These conversions are too high to be considered differential and determine only a lower limit of the turnover frequency, namely, $3.2 \pm 0.1 \times 10^{-2}$ molecules of CO (Au atom)$^{-1}$ s^{-1}.

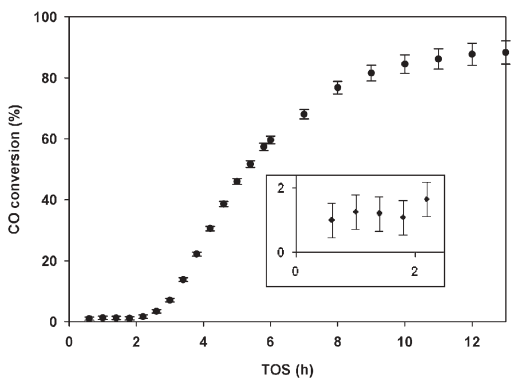

Fig. 2 Catalytic activity of gold supported on CeO_2 for CO oxidation at 353 K. Conversions were determined by gas chromatography; products were confirmed by mass spectrometry (ESI). Reaction conditions are stated in the text. The catalyst mass was 25 mg; it contained 1 wt% Au.

As the activity of the catalyst increased, the Au–Au contribution in the EXAFS spectra increased as well (Fig. 3).

IR spectra of the functioning catalyst during the initial 2 h of operation indicated removal of acac ligands from the gold; concomitantly, new bands appeared, suggesting the formation of formates on the support.[23] The removal of the acac ligands from the gold, which occurred similarly in a sample supported on γ-Al_2O_3,[24] may at least in part explain the onset of catalytic activity.

Subsequent IR measurements of samples that had been onstream longer than 2 h were made *ex situ*, as the feed to the reactor was stopped and catalyst samples were removed. The IR spectra (ESI†) show the further removal of acac ligands form the gold over a period of 24 h. The formates were also removed during the continuing operation of the catalyst.

A comparison of the activities of our catalyst at various stages of activation with those of other highly active gold catalysts used at

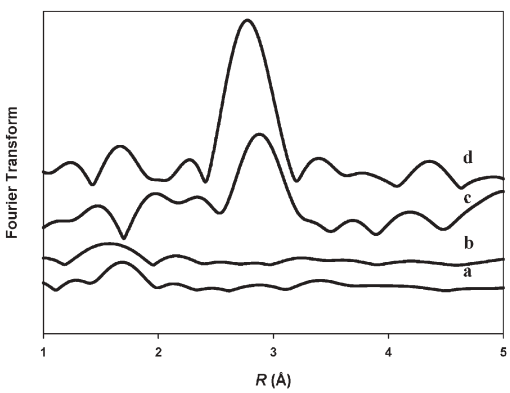

Fig. 3 Radial distribution functions determined by Fourier transformation of raw EXAFS data (k^3-weighting) recorded for gold supported on CeO_2 after various periods of CO oxidation catalysis in a flow reactor (a) at 298 K (prior to catalysis; as-prepared sample), (b) after 2 h of operation at 353 K (sample scanned at this temperature), (c) sample after 24 h of operation at 353 K (sample scanned at 298 K), and (d) sample after 48 h of operation at 353 K (sample scanned at 298 K). Spectra c and d are phase- and amplitude-corrected with the Au–Au reference. Spectra a and b are not corrected because of the lack of Au–Au contributions.

Table 2 Comparison of activities of supported gold catalysts for CO oxidation at 1 bar

Catalyst	TOS/h[b,c]	*T*/K	TOF/s^{-1}
Au/CeO_2[e] (initially)	2.5	353	6.5×10^{-3}
Au/CeO_2[e] (after activation, Fig. 2)	50	353	[a]
Au/CeO_2[e] (activated, Fig. 3)	68[d]	298	$>3.2 \times 10^{-2}$
Au/La_2O_3[5]	50	298	1.2×10^{-2}
Au/CeO_{2-x}[25]	10	278	2×10^{-2}
Au/zeolite NaY[6]	1	298	3×10^{-3}
Au/Al_2O_3[26]	>0.5	273	3×10^{-2}
Au/Fe_2O_3[27]	10	293	[a]
Au/Fe_2O_3[9]	10	293	[a]
Au/TiO_2[28]	NA	282	3.4×10^{-2}

[a] Cannot be calculated because conversions exceeded differential. [b] Turnover frequencies calculated by various authors are not consistent; see ESI. [c] Time corresponds to the time the catalyst was on stream under the conditions specified. [d] Time of operation in CO oxidation at 298 K after 50 h of operation in CO oxidation at 353 K. [e] This work.

nearly the same temperature (Table 2) places ours among the most active supported gold catalysts for CO oxidation.

XANES spectra of the catalyst after various times on stream indicate the disappearance of the mononuclear cationic species characterized by the intense white line shown in Fig. 1.

Catalyst samples that had been on stream for 24 and 48 h under the conditions described above, giving high conversions (Fig. 2), were removed from the reactor and characterized by EXAFS spectroscopy (Table 1). The data representing the sample after 24 h on stream (specifically, a non-zero Au–Au coordination number) demonstrate that gold clusters had formed; the coordination number of 4.0 $\pm$ 0.1 (the error represents the precision) indicates clusters approximated as Au_6, on average.[29] The Au–O coordination number of approximately 0.8 at a distance of 2.08 Å indicates bonding of gold to the support; this distance is as expected for bonds between cationic gold and oxygen of the support.[5]

An Au–Au coordination number of 5.9 $\pm$ 0.1 was found for the sample after 48 h on stream, indicating the presence of clusters of approximately 14 Au atoms each, on average; assuming that they may be approximated as having a cubic structure, the average cluster had a diameter of approximately 7 Å.[30] The smallness of the clusters suggests strong interactions between the gold and the support,[5] and the data in Table 1 provide evidence of these interactions (represented by the Au–O contributions). The intensities of the features that correspond to cationic gold in the XANES spectra of the catalysts are intermediate between those of the cationic gold complexes in the initially prepared catalyst and zerovalent gold (Fig. 1 and ESI†), consistent with nanoclusters that are too small to be considered metallic. (The XANES data are not sufficient to determine the gold oxidation state, because they depend both on the oxidation state and coordination of the gold.)

In agreement with our results, recent theoretical work of Sicolo *et al.*[20] showed that conversion of $Au(CH_3)_2(acac)$ on MgO can proceed *via* positively charged mononuclear gold complexes that can easily be nucleated to give gold clusters—and this work showed that the clusters on MgO are cationic.

The results presented here are consistent with the broad literature of gold catalysts showing that the support has a significant influence on the activity for CO oxidation;[31] specifically, the results indicating activity of supported mononuclear gold complexes demonstate a strong support effect.[5,6] Our results indicate that CeO_2 as a support does not give highly active mononuclear gold complexes, and the relative lack of activity of the initially prepared sample implies that we should not rule out the possibility that gold clusters present in undetectable amounts might have been the active species.

In summary, we synthesized mononuclear gold species on CeO_2 and activated them under catalytic CO oxidation conditions in a flow reactor. The gold was initially present as site-isolated cationic complexes and this sample was slightly active as a catalyst, but after a short period of operation, the catalyst underwent activation as gold clusters formed. Some of the clusters were as small as Au_6, on average, and inferred to be non-metallic.[20] The results demonstrate that, at least on the CeO_2 support, the clusters are more active than the complexes.

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