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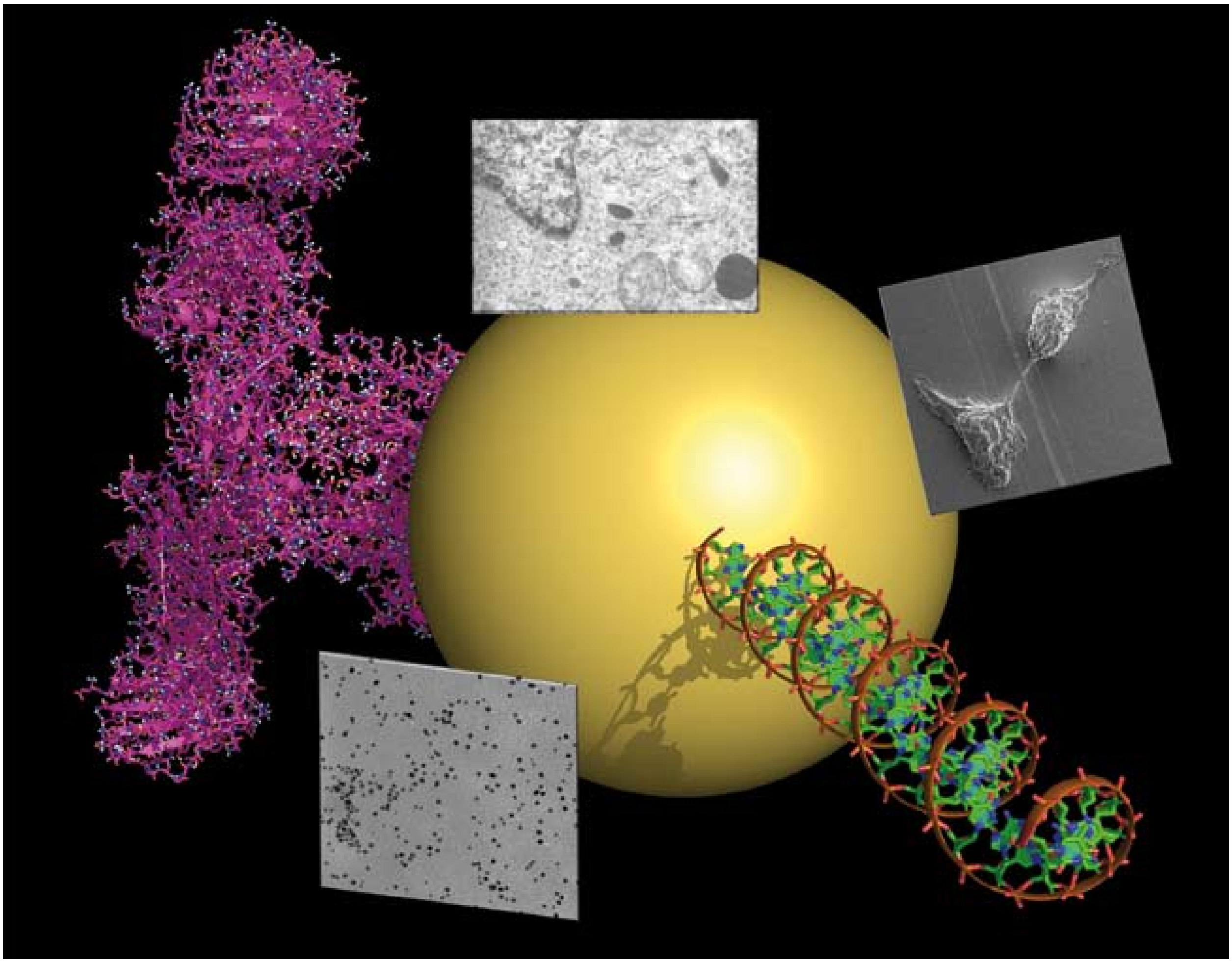

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Catalysis by gold dispersed on supports: the importance of cationic gold†

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There are many examples of catalysis in solution by cationic complexes of gold, and recent results, reviewed here in this *critical review*, demonstrate that cationic gold species on oxide and zeolite supports are also catalytically active, for reactions including ethylene hydrogenation and CO oxidation. The catalytically active gold species on supports are evidently not restricted to isolated mononuclear gold complexes, but include gold clusters, which for at least some reactions are more active than the mononuclear complexes and for some reactions less active. Fundamental questions remain about the nature of cationic gold in supported catalysts, such as the nature of the cationic gold clusters and the nature of gold atoms at metal–support interfaces (88 references).

Introduction: catalysis by gold

Gold is the most inert metal.[1] The inertness of bulk metallic gold preserves its lustre and colour; these properties, with its malleability, account for much of its timeless popularity in art, jewellery, and coins and for its use in dental medicine.[2] Metallic gold is also used for cancer treatment;[2] only metallic gold is believed to be biocompatible, with ''oxidic'' gold being toxic, consistent with the high reactivity of cationic gold.

Notwithstanding the inertness of the bulk metal, the chemistry of gold compounds is rich and varied, dating from early in the preceding century.[3] In most of its known complexes, gold is cationic, formally being either gold(I) or gold(III); common ligands in these complexes are chloride and phosphines, among many others.

Some gold complexes are highly reactive, with many reports[2–5] indicating their transformations under a wide range of conditions. For example, anhydrous gold(III) chloride reacts with benzene, toluene, or other aromatic compounds to give arylgold(III) complexes.[3] Gold(I) and gold(III) complexes undergo ligand exchange reactions,[4,5] some of which occur faster than those involving palladium or platinum.[2]

Because of gold's reactivity, it is not surprising that some gold complexes are catalytically active; mononuclear gold(I) and gold(III) complexes in solution are the typical catalyst precursors. Many reactions are also catalysed by gold that is highly dispersed on the surfaces of solid supports; identifications of the catalytically active species in these catalysts remain controversial, and we address this topic below, focusing on the evidence of catalysis by cationic gold on supports and leaving aside assessments of the catalytic properties of highly dispersed gold that might be approximated as zerovalent.

Homogeneous catalysis by gold complexes

Many complexes of gold with structures that are well established by spectroscopic methods are precursors of catalysts that function in solution (Table 1).[2,6–18] The catalytic reactions

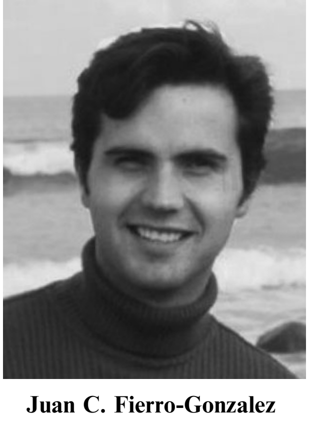

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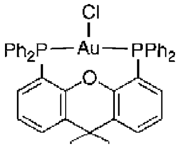
Table 1 Some reactions catalysed by gold(I) and gold(III) complexes in solution

Reaction	Gold precursor	Ref.
Ethylene hydrogenation	$HAuCl_4$	6
Enantioselective hydrogenation of imines	Gold(I)–Me-duphos[a]	7
Hydrochlorination of alkynes	$HAuCl_4$	8
Hydroamination of alkynes	$NaAuCl_4$	9
Hydrothiolation of allenes	AuCl	10
Hydroarylation of alkenes	$AuCl_3$	11
Asymmetric aldol reaction	Ferrocenylphosphine gold(I) complexes	12
Hydroarylation of alkynes	$AuCl_3$	13
Intramolecular addition of phenols and carboxylic acids to alkenes	Ph_3PAuCl	14
Carbonylation of olefins	Au^I(CO)	15
Dehydrogenative silylation of alcohols		16
Cycloisomerisation of α-aminoallenes to 3-pyrrolines	$AuCl_3$	17
Phenol synthesis	$AuCl_3$	18

[a] Me-duphos = 1,2-bis((2*R*,5*R*)-2,5-dimethylphospholano)benzene.

include hydrogenation of alkenes;[19] hydrochlorination of alkynes;[8] and hydroamination of alkynes,[9] allenes,[20] and alkenes,[21] among others.[6,7,10–18] Some catalytic cycles have been proposed, but evidence of the reactive species within the cycles is generally indirect and inferential, based on information such as the nature of the catalyst precursor and the products of the catalytic reaction rather than physical characterisation of the intermediates themselves.

For example, in a 1986 report, Ito *et al.*[12] showed that a chiral ferrocenylphosphine–gold(I) complex in solution catalysed the reactions of aldehydes with methyl isocyanate; the activity and selectivity of the gold complex were higher than those of comparable complexes of silver and of copper. The authors inferred that the strong affinity of gold(I) for phosphorus was responsible for the high activity, suggesting that the presence of gold(I) was crucial in the catalysis.

In 1991, Fukuda and Utimoto[22] reported that a gold(III) complex catalysed the hydration of alkynes to yield ketones. They had reported previously[9] that a gold(III) salt was active for the intramolecular addition of an amine to an alkyne under mild conditions, whereas a palladium(II) catalyst was less active. This result, showing that a gold catalyst was more active than a comparable palladium catalyst, is significant because of the rich and long history of homogeneous catalysis by palladium complexes.[23] Fukuda and Utimoto's results were ascribed to the effective activation of alkynes by gold(III), and they led to the broader use of gold(III) complexes as catalysts for reactions of alkynes, including hydroalkoxylation and hydration.[2] The inference of the participation of gold(III) in alkyne conversion was based on the observation that the catalyst precursor was gold(III) and, in some cases, the observation that gold(III) complexes could be recovered from the products after catalysis.

Recently, Shi and He[13] reported the use of $AuCl_3$ to functionalise arenes with electron-deficient alkynes or alkenes. The reaction was carried out at ambient temperature and with high yields. Although the report lacks details of the reaction mechanism, it provided a basis for investigation of other arene functionalisation reactions catalysed by gold complexes.[11,14,24–27] For example, in 2005, Yang and He[14] reported the addition of phenols and carboxylic acids to olefins catalysed by gold(I), illustrated by the conversion of 4-phenyl-1-butene in toluene solution to 4-phenyl-2-butene with a $Ph_3PAuOTf$ catalyst (Ph is phenyl; OTf is trifluoromethanesulfonyloxy). The authors proposed a mechanism by which the gold(I) binds and activates the olefin for nucleophilic addition by the phenols or carboxylic acids followed by a proton-transfer step that affords the final product and regenerates the gold(I) catalyst.

The authors[14] suggested that the activation of the alkene by gold(I) was similar to that occurring in the Wacker process, in which the palladium catalyst cycles between the oxidation states 0 and II. Recognizing that gold(III) is isoelectronic with palladium(II), and gold(I) with palladium(0), Corma and co-workers[27] suggested that gold and palladium would be active for some of the same reactions, undergoing comparable redox cycles; for example, they demonstrated the activity of gold for cross-coupling reactions.

It now seems evident that palladium complexes and gold complexes have comparable catalytic activities for a number of reactions.[2,9,28] For example, carbon–carbon coupling reactions, which are typically catalysed by palladium complexes, are also catalysed by gold complexes; examples are C–C and C–O coupling reactions.[11]

Supported metal complexes: analogies with homogeneous catalysis

The Wacker oxidation of ethylene to make acetaldehyde is a long-established industrial process, in which palladium(II) oxidizes ethylene, and copper(I) in the solution rapidly reoxidizes the palladium(0) formed as a result, thereby minimizing deposition of metallic palladium; O_2 is used to reoxidize the resultant copper(0), so that the reaction is catalytic in both palladium and copper.

Researchers[29] who were motivated to overcome the practical disadvantages of homogeneous catalysis (including corrosion and the expense of separation of products from the catalyst solution) prepared a V_2O_5-supported analogue of the palladium–copper catalyst, finding it to be highly active for ethylene oxidation; instead of copper, groups on the surface of the V_2O_5 support reoxidized the palladium(0) formed in the process, and these were in turn reoxidized by O_2. The surface chemistry is clearly analogous to that occurring in solution in the Wacker process.

Thus, one question that emerges from the foregoing examples is whether the chemistry of cationic gold complexes in solution can similarly be translated onto solid surfaces, and, beyond this, whether cationic gold on supports can be made to be both catalytically active and stable. The stability issue turns at least in part on the strong tendency of cationic gold to be reduced to the zerovalent state—the process of autoreduction can occur even at modest temperatures, either in a solution or on a support surface. We address this topic below.

Supported gold catalysts

Hutchings[30] was a pioneer in the application of supported gold as a catalyst, investigating the hydrochlorination of acetylene. His insights into the mechanism of this reaction indicated that the rate-determining step involved the addition of HCl to a metal–acetylene complex, and he inferred that metals capable of forming compounds with acetylene might catalyse the reaction. Furthermore, he predicted that cations with standard reduction potentials greater than those of mercury(II) and palladium(II) would give more active catalysts. Gold(III) has a high standard reduction potential, and Hutchings suggested that it might be a good catalyst for acetylene hydrochlorination. Indeed, he showed that supported gold (made from $HAuCl_4$ on activated carbon) was a better catalyst than supported mercury for acetylene hydrochlorination.[31] (In an earlier paper,[30] Hutchings cited patents pointing to gold(III) chloride supported on carbon as being more active than mercury catalysts.[32–35]) Because the reasoning for the selection of a gold catalyst was based on a possible reaction *via* a redox cycle involving the metal chloride and the zerovalent metal, the researchers suggested that it was essential that the metal be reoxidized to the metal chloride for continued catalytic activity.

These results, dating from the late 1980s, pointed to the involvement in catalysis of cationic gold on supports. The results are broadly consistent with later observations (mentioned above) indicating catalysis by cationic gold complexes in solution. Most of these later results emerged only recently; it has been estimated[2] that half of the publications on gold catalysis for organic synthesis as of 2006 had been published in the preceding two years.

In contrast, a surge in the literature of catalysis by supported gold started in the 1990s,[36–40] although there were reports that appeared much earlier, exemplified by Parravano's work.[41] Much of the heightened interest in supported gold catalysts was prompted by the discovery by the group of Haruta[42] that supported gold is an active CO oxidation catalyst at remarkably low temperatures (even −70 °C in some cases, such as for gold supported on iron oxide). Haruta's results are significant because they were unexpected and because the CO oxidation—a test reaction involving small and structurally simple molecules—seemed to many scientists to offer the prospect of being a prototype that would facilitate elucidation of the nature of the catalytically active gold species. The work of Haruta on the oxidation of CO catalyzed by supported gold was preceded by that of the group of Ozin,[43,44] who in the late 1970s reported the oxidation of CO to CO_2 in the presence of gold atoms in rare gas matrices at temperatures lower than 40 K.

Since the discoveries of Hutchings and Haruta, many more reactions have been found to be catalysed by highly dispersed supported gold, including the epoxidation of propylene,[45] synthesis of hydrogen peroxide[46] and of vinyl chloride,[47] selective oxidation of alcohols,[48] carbon–carbon bond coupling,[27] and selective reduction of nitro groups on aromatic rings in the presence of C=C bonds,[49] among others.[50,51]

As shown by Haruta's work,[36,42,52] the nature of supported gold catalysts for CO oxidation depends on the method of preparation as well as difficult-to-control details such as the amount of trace water in the reactant mixture. Typically, supported gold catalysts are prepared from gold salts containing anions such as chloride, leading to complicated structures, consisting of gold particles of various sizes (commonly, 2–10 nm) and shapes, dispersed on solids that are generally amorphous (powders of metal oxides); furthermore, the anions such as chloride are usually retained in the catalysts and influence their reactivities. The structural complexity of the supported gold species (which are typically extremely small and non-uniform) has hindered progress in understanding the catalyst structures and reaction mechanisms.

Various and contradictory hypotheses have been proposed to explain the catalytic activity of supported gold for CO oxidation. They variously attribute significant roles to the following:

(a) the size of the supported gold species;[53,54]

(b) the interface between gold particles and the support;[55] and

(c) the oxidation state(s) of gold in the catalysts,[56,57] among others.

The literature of this subject has grown too much to allow a full review here; summaries are available elsewhere.[58–61] Instead, we focus on the role of cationic gold in these catalysts.

Working from the hypothesis that cationic gold complexes on surfaces might be the active species for many reactions, several researchers have attempted to synthesise supported cationic gold species, testing them for catalytic reactions that were thought to be simple enough to be prototypical.[60] Much of the work that has provided insight into the nature of the catalytic species has involved spectroscopic characterization of the catalysts, sometimes in the working state.

Ethylene hydrogenation as a catalytic test reaction

Ethylene hydrogenation is a catalytic test reaction used commonly with supported metal complexes and supported metal particles; this reaction offers the benefits of small reactant molecules and a conversion that takes place rapidly at relatively low temperatures (*e.g.*, room temperature), facilitating the use of spectroscopic methods for investigation of the catalysts.

Guzman and Gates[62,63] used this reaction with supported gold catalysts prepared from the complex $Au(CH_3)_2(C_5H_7O_2)$, which reacted with the partially hydroxylated, high-area porous support MgO to form supported gold(III) complexes. The precursor was chosen because it contains gold(III) bonded covalently with methyl ligands that can be removed under mild conditions (in contrast to chloride, for example). The samples were characterised by X-ray absorption spectroscopy, with extended X-ray absorption fine structure (EXAFS) spectroscopy providing evidence of mononuclear gold species bonded to the surface of MgO (as evidenced by the lack of Au–Au contributions) and X-ray absorption near edge structure (XANES) spectroscopy indicating gold(III). Infrared spectra showed that the methyl ligands initially present on the gold were replaced by ligands formed from the reactants ethylene and H_2, suggested to include ethyl.[62]

The MgO-supported mononuclear gold(III) complexes were found to be active for ethylene hydrogenation catalysis at 353 K and atmospheric pressure. Because there was no evidence of reduction of the gold during catalysis (as would have been evident by EXAFS spectroscopy),[63] the authors suggested that these cationic gold species were involved in the catalysis.

When the catalyst was treated under conditions that led to reduction and aggregation of the gold (treatment in helium at various temperatures), as shown by EXAFS spectra, the catalytic activity declined (Fig. 1), confirming the inference that the catalytically active species were cationic gold (gold(III)) and that the zerovalent gold was not active for the ethylene hydrogenation under the conditions of the experiments.

These results are bolstered by work of the group of Corma,[64] who showed that gold(III)–Schiff base complexes in solution catalyse the hydrogenation of olefins. Because Pd(II) complexes are active for the hydrogenation of olefins and gold(III) is isoelectronic with Pd(II), the authors reasoned that gold(III) complexes would also be catalytically active for this reaction. Furthermore, they proposed that by selecting an appropriate support it would be possible to stabilize gold(III) on surfaces; such supported species were found to be active for the hydrogenation of olefins, in agreement with the results of Guzman and Gates.[62,63]

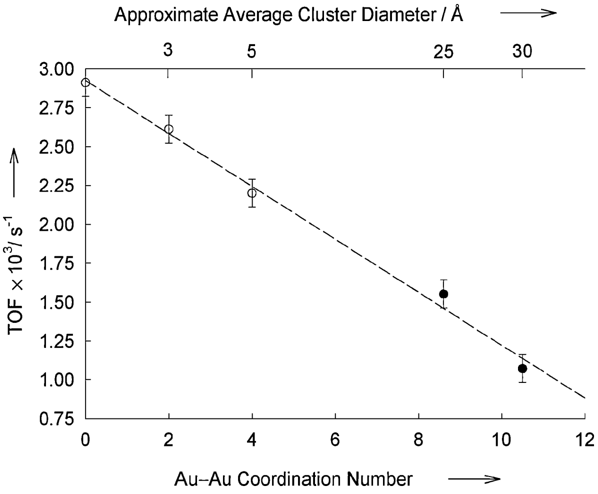


Fig. 1 Activities of MgO-supported catalysts (represented as turnover frequencies, TOF) containing cationic gold and gold clusters prepared from $Au(CH_3)_2(C_5H_7O_2)$. Note the nonlinearity of the scale at the top. XANES data were collected for the catalysts denoted by open symbols. From ref. 62. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

CO oxidation as a catalytic test reaction

CO oxidation is a catalytic reaction that has been investigated far more than any other with supported gold catalysts. Reasons for its popularity include the following:

(a) catalytic CO oxidation offers potential practical applications, specifically for the removal of traces of CO in H_2 streams for the purification of feeds to hydrogen fuel cells for automobiles (the fuel cell catalysts are poisoned by small amounts of CO);

(b) CO as a reactant offers the advantages of a good probe of catalyst surface structures, as adsorbed CO is easily characterised by a number of spectroscopic methods, prominently including infrared spectroscopy;[65,66] and

(c) because CO oxidation catalysis occurs at low temperatures, it can be investigated while it is occurring by methods such as infrared and X-ray absorption spectroscopies.

Notwithstanding all these prospective advantages, the CO oxidation reaction catalysed by supported gold has not turned out to be the simple, informative test reaction that was hoped for initially; it remains only partially understood.

Our attention is directed to the evidence for cationic gold in catalysts for CO oxidation. Work by Guzman and Gates,[56] for example, was related to that described above for ethylene hydrogenation; the support (MgO) and the catalyst precursor ($Au(CH_3)_2(acac)$) were the same.

Guzman found that the gold in his catalyst, used at 373 K and atmospheric pressure with a range of $CO : O_2$ ratios in the feed to a flow reactor, underwent reduction and aggregation to form gold nanoparticles.[56,67] Similar results were observed when the support was high-area TiO_2.[68]

EXAFS spectra characterizing the functioning catalysts showed that aggregation of the gold occurred in the presence of the reactant mixture. XANES spectra recorded simultaneously showed features that corresponded to the presence of gold(0). These results indicate the substantial challenge of preparing supported gold catalysts that contain gold only as cationic species that are stable enough to avoid the formation of zerovalent gold nanoparticles during catalysis.

Guzman's data showed that the working MgO-supported catalyst contained a mixture of cationic and zerovalent gold;[56,67,69] the amounts were quantified by temperature-programmed reduction and oxidation. The activity increased with an increasing fraction of gold that was cationic as the $O_2 : CO$ ratio increased (Fig. 2). These results led to the conclusion that the catalytic sites involved cationic gold, but they did not rule out the possible involvement of zerovalent gold (in the form of clusters, which were present, as shown by EXAFS spectroscopy).

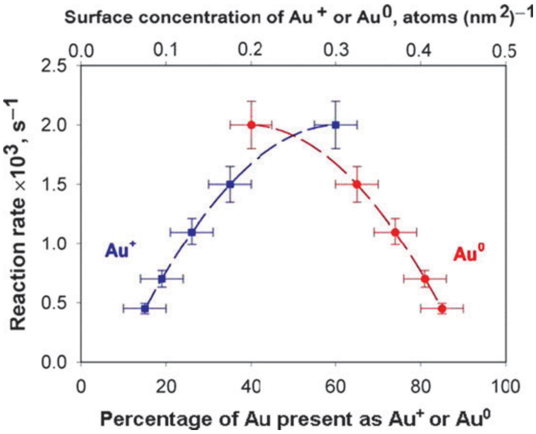


Fig. 2 Correlation of the catalytic activity with the percentage and surface concentration of cationic and zerovalent gold (the concentrations of gold were calculated on the basis of the approximate surface area of MgO). Reprinted with permission from 56. Copyright 2004 American Chemical Society.

Qualitatively similar results for CO oxidation catalysed by a more active catalyst, gold supported on iron oxide, were also reported, with a combination of physical characterisation data (EXAFS spectroscopy, XANES, Mössbauer spectroscopy, and X-ray photoelectron spectroscopy) showing that an increasing fraction of gold in a cationic form gave more active catalysts (Fig. 3).[70]

Thus, these data clearly indicate a role for cationic gold in CO oxidation catalysis, but the question remained about whether cationic gold alone on the support surface was catalytically active for this reaction. Consequently, we prepared zeolite-supported mononuclear gold(III) complexes by adsorbing the same precursor, $Au(CH_3)_2(C_5H_7O_2)$; the support was zeolite NaY.[57] The catalyst was active for CO oxidation catalysis at room temperature, but XANES spectra characterising the working catalyst in a flow reactor showed that during operation the gold(III) that was present initially was reduced to complexes suggested to be mononuclear gold(I). There was no evidence of the presence of gold(0) or of any aggregation of the gold in any form of the catalyst, as evidenced by the following: (a) XANES spectra showing no features characteristic of gold(0) and (b) EXAFS spectra showing the lack of detectable Au–Au contributions (which would be indicative of gold clusters). The lack of reduction to gold(0) and of aggregation of the gold was bolstered by IR spectra recorded during catalysis that gave no evidence of ν_{CO} bands attributed to CO bonded to gold(0) (Fig. 4).[57]

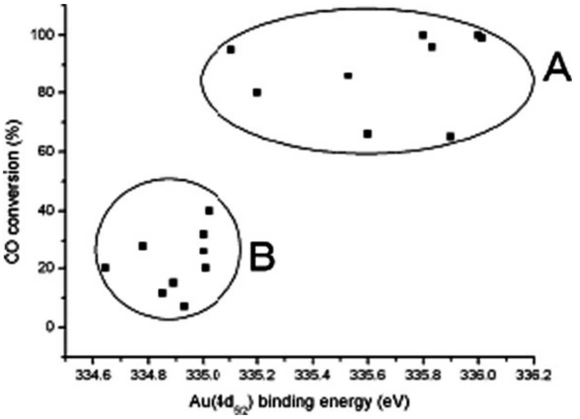


Fig. 3 Correlation between activity for CO conversion and Au(4d$_{5/2}$) binding energy. The data for a series of catalysts (5 wt% Au supported on Fe_2O_3) are shown; the cluster of points labelled A corresponds to catalysts dried at 393 K, and the cluster B to those calcined at 673 K. Reprinted from ref. 70. Copyright 2006 with permission from Elsevier.

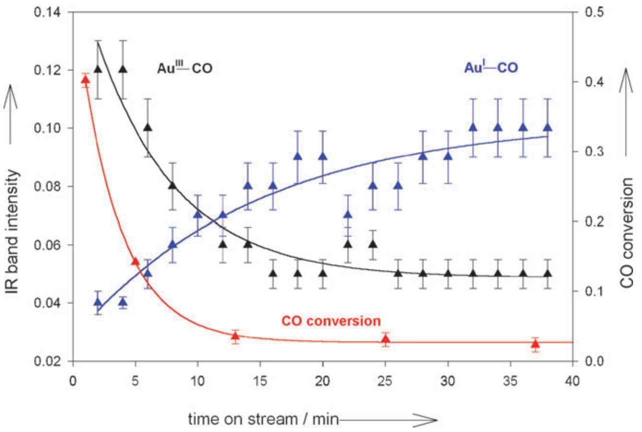


Fig. 4 Dependence of the CO conversion and the intensities of the 2169 cm^{-1} and the 2133 cm^{-1} bands in the IR spectrum of a zeolite-supported catalyst during catalytic oxidation of CO at 298 K and 760 torr. Reprinted with permission from 57. Copyright 2004 American Chemical Society.

This was the first example that seemed to show that a supported catalyst containing cationic gold without detectable zerovalent gold was active for CO oxidation catalysis. However, the activities of the zeolite-supported mononuclear gold(III) and gold(I) complexes were significantly lower than those of metal oxide-supported gold catalysts that contained gold nanoparticles (and by inference gold(0)). This result was taken as evidence of a role for the support.

Because there are reports[71,72] showing that catalysts prepared with rare-earth metal oxides as supports for gold are among the most active for CO oxidation, we[73] prepared mononuclear gold(III) complexes bonded to the surface of high-area nanocrystalline La_2O_3. The supported complexes were found to be highly active for CO oxidation catalysis at room temperature, and XANES spectra gave no evidence of reduction of the gold. Again, EXAFS spectra were consistent with the presence of mononuclear gold complexes, as evidenced by the lack of a detectable Au–Au contribution. Thus, the results suggest that the presence of gold nanoparticles on La_2O_3 was not necessary for a catalyst to have a high activity for CO oxidation (but this comparison pertains to the relatively high temperatures used for most CO oxidation catalysts; recall that Haruta reported supported gold catalysts that are active at much lower temperatures[42]).

Recent results[74] obtained with similar samples prepared on nanocrystalline CeO_2 show that, although mononuclear gold(III) species bonded to the support are evidently active themselves for CO oxidation, these complexes in the presence of flowing reactants are reduced and form small gold clusters that are even more active than the mononuclear gold complexes present initially. XANES spectra characterising catalysts containing the small clusters include features suggestive of the presence of both cationic and zerovalent gold—the spectra are not sufficient to distinguish between them, as the spectra depend not just on the oxidation state of gold, but also on the surroundings and degree of aggregation of the gold.

Thus, a question that arises is whether the samples contained (a) mixtures of cationic (mononuclear) gold complexes and zerovalent gold nanoclusters, or (b) only small nanoclusters in which some gold atoms were cationic. The cationic gold could be concentrated at the metal–support interface, as indicated by theoretical investigations of small clusters of metals on oxide and zeolite supports.[75]

There have been some attempts[76,77] to use high-energy resolution and time-resolved X-ray absorption spectroscopy under catalytic conditions to follow changes in the oxidation state(s) of gold during CO oxidation catalysis and to elucidate the identities of the various gold species that might be present in functioning catalysts. However, most samples are structurally complex—powerful as the time-resolved spectroscopic techniques are, when the samples are complicated structurally (containing mixtures of cationic and zerovalent gold, for example), the data do not provide a complete identification of the catalytically active species, because the techniques provide average information.

In general, the data are more incisive when the samples contain gold in a unique oxidation state. Thus, we believe that the better opportunities to elucidate the identities of the active species for CO oxidation catalysis will emerge from a combination of powerful characterisation techniques (such as time-resolved XANES) and structurally simple gold catalysts.

Theory has also been used to address the issue of the oxidation state(s) of gold. Early investigations were focused on explaining how gold clusters can be stabilized on supports.[78,79] In most cases, it was proposed that clusters could be stabilized by the presence of defect sites on the supports, such as F-centres on MgO,[78] which were proposed to enhance a charge-transfer from the support to the gold clusters, leading to the formation of negatively charged clusters.[79,80] Because there was some experimental evidence suggesting that cationic gold could be present during CO oxidation catalysis, some researchers[65,66,81–83] investigated whether the adsorption of CO was favoured on cationic, zerovalent, or anionic gold. In most cases it was agreed that CO can be readily adsorbed on gold in any of these oxidation states.

Thus, by inference, we suggest that there is a strong possibility that there are multiple reaction channels for catalysis of CO oxidation by supported gold, involving gold in various oxidation states. If this suggestion is correct, CO oxidation is clearly not the most satisfactory test reaction for catalysis by gold; preferred would be reactions that proceed at markedly different rates or with markedly different selectivities in the presence of gold in various structures and oxidation states.

Recently, the group of Pacchioni[84] used density functional theory to investigate the reactions of $Au(CH_3)_2(C_5H_7O_2)$ on the surface of MgO. They found that some of the reactions on the surface lead to the formation of neutral or positively charged mononuclear gold species, which can easily diffuse on the MgO surface and lead to the formation of "partially oxidized gold clusters." The calculations suggested that all the gold atoms present within small clusters (Au_2, Au_3, and Au_4) might be cationic (Fig. 5).

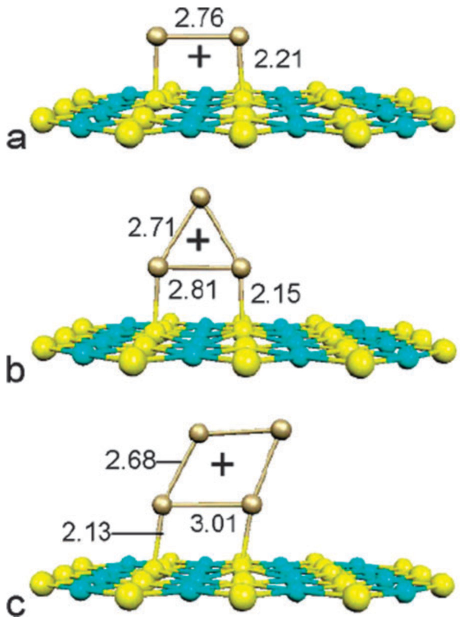


Fig. 5 Supported cluster cations on the MgO(100) surface. Distances are in Å. Reprinted with permission from 84. Copyright 2007 American Chemical Society.

Recently, Wang and Hammer[85] reported calculations at the density functional level representing the adhesion and catalytic activity of Au_7 clusters on $TiO_2(110)$. Their calculations indicate strong adhesion of the gold clusters to oxidized $TiO_2(110)$ surfaces. The authors predicted that the adsorbed clusters are cationic, as Au–O bonds form between gold atoms in the clusters and oxygen atoms of the support. This prediction agrees well with reported EXAFS results,[56,68,76,86] which consistently give evidence of such bonds, and with the aforementioned examples indicating the presence of cationic gold.

Theoretical work with supported rhodium catalysts shows that the Rh atoms in Rh_6 clusters at the interface with a zeolite support bear significant positive charges, whereas the Rh atoms that are not at the interface are nearly uncharged.[75] The metal ions at the interface bond the clusters to the support. (The bonding of metal clusters to supports by cations can apparently be accentuated when the clusters contain oxophilic metals; thus, highly dispersed Pt–W clusters on γ-Al_2O_3 are stable at quite high temperatures as the oxophilic tungsten helps to maintain the high dispersion of the platinum.[87])

A question that arises from the aforementioned reports[84,85] is whether cationic gold clusters might be stable during catalysis. Laursen and Linic[88] carried out DFT and *ab initio* thermodynamic calculations that indicated differences in the electronic structure of gold on various metal oxide supports. Their calculations suggest that the oxidation state(s) of supported gold are affected by the presence of reactants, with the gold predicted to be cationic when the oxygen chemical potential represents practical reaction conditions of CO oxidation.[88] These results suggest that the stability of supported gold in a given oxidation state depends on the reaction conditions and on the nature of the support, consistent with the various observations pointing to the involvement of gold(0), gold(I), and gold(III) (or mixtures of them) in CO oxidation catalysis.

Summary and research opportunities

There is clear evidence that cationic gold is catalytically active for numerous reactions, not only including those occurring in solutions but also those occurring on solid supports. But it would be inappropriate to ascribe all the catalytic properties of gold to cationic species, as there is also evidence linking catalytic activity to small gold clusters.

It is clear that the available data do not provide a consistent pattern regarding the relative importance of cationic gold and gold clusters in supported catalysts for CO oxidation. More work is needed; there is a good opportunity for research taking advantage of complementary experimental methods to investigate the oxidation state(s) of gold in catalysts in the working state. Spectroscopic techniques such as EXAFS, infrared, XANES, XPS, and Mössbauer spectroscopy are valuable but limited because they provide only average structural information. Thus, when mixtures of gold(I) and gold(III) are present in a catalyst, spectroscopic results cannot easily resolve whether they are present in the same species or in different ones. Again, the structural complexity of typical supported gold catalysts complicates the interpretation of experiments and motivates research with structurally well-defined supported catalysts.

The following fundamental questions remain and are pertinent to the issues raised here:

- Are there good molecular analogues of the supported gold clusters present in the catalysts that have been investigated so far?
- If so, what are their reactivities, are they catalytically active, and can they be prepared and stabilized on supports?
- Do gold atoms at the metal–support interface in supported gold clusters play a pivotal role in catalysis by supported gold?
- Are these interface atoms cationic?

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