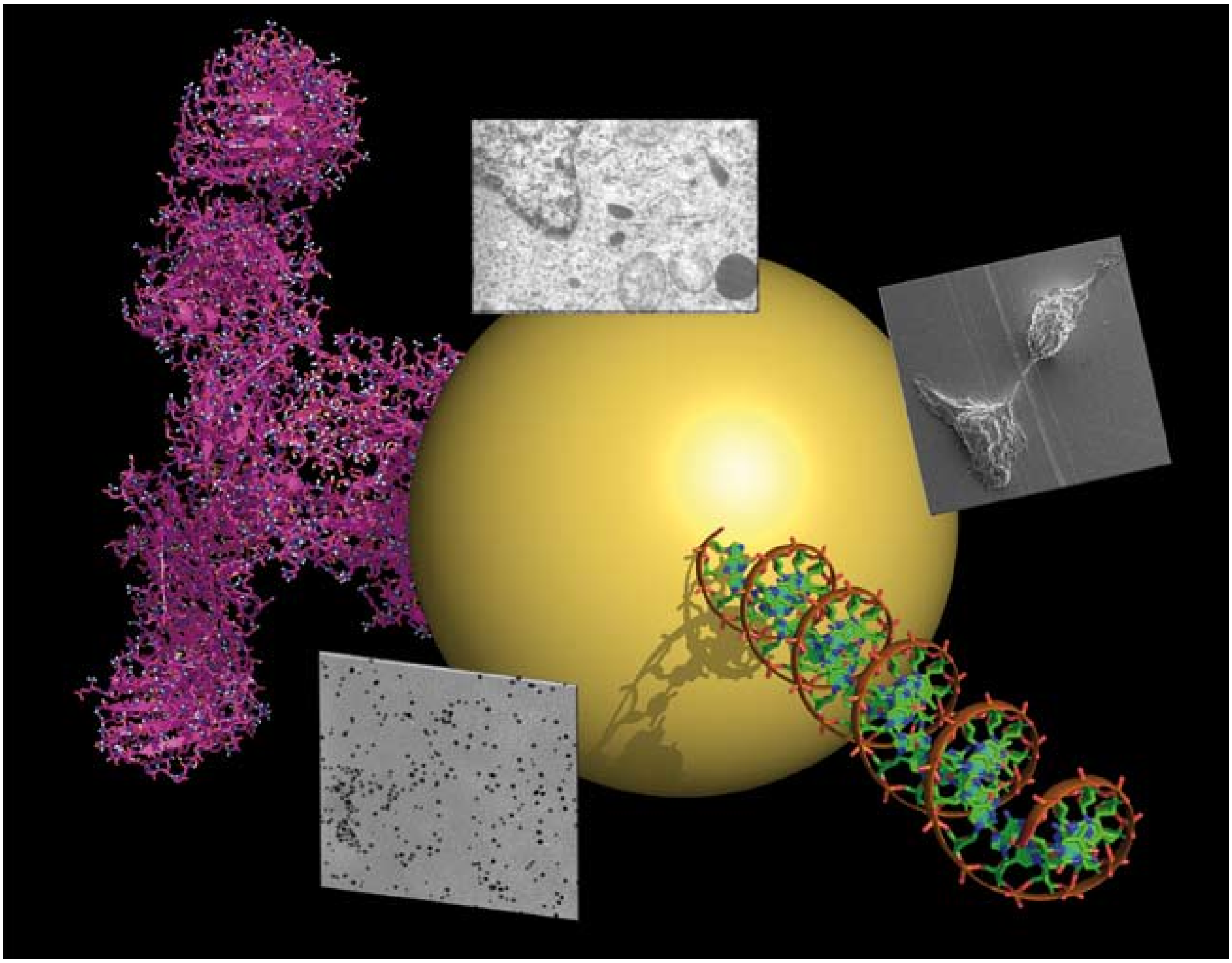
# Chem Soc Rev

## 2008 Gold: Chemistry, Materials and Catalysis Issue



# Supported gold nanoparticles as catalysts for organic reactions†

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This *critical review* is intended to attract the interest of organic chemists and researchers on green and sustainable chemistry on the catalytic activity of supported gold nanoparticles in organic transformations. In the general part of this critical review, emphasis is given to the different procedures to form supported gold nanoparticles and to the importance of the support cooperating in the catalysis. Also the convergence of homogeneous and heterogeneous catalysis in the study of gold nanoparticles has been discussed. The core part of this review is constituted by sections in which the reactions catalyzed by supported gold nanoparticles are described. Special emphasis is made on the unique ability of gold catalysts to promote additions to multiple C–C bonds, benzannulations and alcohol oxidation by oxygen (282 references).

## I. Introduction and scope

Catalysis using gold nanoparticles is a topic of much current interest. There are several general reasons that explain this interest. One of them is the fact that the catalytic activity of gold is directly related to the particle size in the nanometre length scale. Thus, gold catalysis is a paradigmatic example of those properties that are only observed in nanoparticles and can disappear completely as the particle size grows into the micrometric scale. Considering the current impetus of nanoscience, it is understandable that all the aspects related to the preparation of small nanoparticles of narrow size distribution, their stabilization and their unique properties compared to larger particle size are appealing to a large community of researchers from material science, computational chemistry and catalysis.

A second factor that explains the interest in catalysis by gold nanoparticles is the fact that it was believed for a long time that Au was devoid of any catalytic activity. Thus, understanding the reasons of this catalytic activity, expanding the scope to other reactions, optimizing and finding the reaction mechanisms for gold catalyzed reactions is a new field in heterogeneous catalysis.

Finally, there is a third factor that justifies the importance of the research in gold nanoparticles comes from the fact that since very small colloidal or supported gold particles have to be prepared, one can imagine that catalysis by gold nanoparticles represent a bridge between homogeneous and heterogeneous catalysis.[1] These two disciplines have developed fairly independently up to now, but nanoparticles can provide a point of convergence for both fields.

The interest in gold nanoparticles as catalysts can be quantitatively ascertained by the exponential growth in the number of publication in this subject. In particular, two books and several comprehensive and solid reviews have appeared recently on this topic.[2–6] In the book by Bond, Louis and Thompson there are five introductory chapters covering exhaustively all aspects related to physical properties and characterization of gold nanoparticles as well as preparation of supported gold catalysts. The reader is referred to this reference book for a comprehensive coverage of these important aspects in gold catalysis. Another key precedent is the review from Hashmi and Hutchings on gold catalysis covering both

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homogeneous catalysis using gold salts and heterogeneous catalysis using supported gold nanoparticles.[2] This review was organized based on the reaction type, and the aspects concerning historical perspective, catalyst preparation, influence of the support and reaction mechanism are clearly presented and addressed. Even more recently, Hashmi has published a comprehensive review on gold-catalyzed organic reactions covering both homogenous and heterogeneous catalysis that has been organized based on the chemical reaction.[3]

Considering that these books and reviews have recently appeared and in order to avoid unnecessary repetition minimizing overlapping, our review is mostly focused on catalysis of organic reactions by supported gold nanoparticles. The main emphasis will be on the design of the catalyst, *i.e.*, metal plus supports and the factors that have to be considered to understand their catalytic activity. Taking into account the rapid growth of this field, our report emphasizes open fields in which research is currently being actively pursued.

## II. Preparation and characterization of supported gold nanoparticles

The primary role of the support is to avoid coalescence and agglomeration of the gold nanoparticles. This is an important issue since as will be commented in detail later, the catalytic activity of gold nanoparticles diminishes considerably as the particle size grows beyond 10 nm. Characteristics of the support such as surface area, presence of surface hydroxyl groups, density of defects and crystal phase influence the adsorption ability of the support. In addition supports can go further than simple carriers and can play a direct or indirect role in gold catalyzed reactions as will be discussed later.

### Preparation of supported gold nanoparticles from direct adsorption of gold complexes: adsorption and deposition–precipitation procedures

The two most general preparation procedures used for the preparation of gold nanoparticles supported on metal oxides are known as *adsorption* and *deposition–precipitation*. The accepted mechanisms for the formation of the supported gold nanoparticles in both procedures have common steps starting from adsorption of the gold complexes on the solid surface, the main difference being that at the pH used for deposition–precipitation the gold species are neutral and not anionic as occurs in adsorption. Below we will comment separately on the features of both procedures.

**i. Adsorption.** For depositions carried out in aqueous media, the pH value plays a key role controlling the actual distribution of gold(III) species and the net charge of the solid support surface.

Concerning the actual gold species distribution upon dissolving $AuCl_4^-$ salts, there is a consecutive exchange of $Cl^-$ by $OH^-$ as the pH value increases forming hydroxychloro gold(III) complexes $[Au(OH)_xCl_{4-x}]^-$. The extent of hydrolysis also depends on the gold and chloride concentration due to variations in the ionic strength. Moreover, formation of $Au(OH)_3$ at pH higher than 9 that can cause gold precipitation is predicted by equilibrium calculations based on thermodynamic calculations. However, the formation of $Au(OH)_3$ has never been experimentally proved and it has even been reported that a $10^{-2}$ M solution of $AuCl_4^-$ in 1 M NaCl at pH 9.2 does not form $Au(OH)_3$.[7] The kinetics of the $Cl^-$ by $OH^-$ ligand exchange on gold(III) complexes seems to be slow and this fact explains the influence of aging time and temperature on the speciation. Detailed speciation of $HAuCl_4$ in aqueous solution can be found in the literature.[8–12]

A well established method that allows a certain control in the average particle size of the gold nanoparticles is the variation of the pH of the gold salt–solid support suspension during the first stage of the adsorption on the solid surface. pH value of the adsorption is a crucial parameter in the preparation procedure of gold nanoparticles supported on metal oxides. As a general rule, the particle size decreases in the range 5–25 nm when the pH increases from 4 to 9.[13–15]

With respect to the net charge, the surface of some supports can become positively charged when the solids are suspended in aqueous solutions at pH values below their isoelectric point. The presence of sufficiently high proton or hydroxide concentration in the aqueous medium can protonate or deprotonate the solid surface. At the pH of the isoelectric point or point of zero charge, the surface of the particles is neutral. However below or above this pH value the surface becomes positively or negatively charged, respectively. The isoelectric point of metal oxides has been determined and it serves to classify the supports as acidic or basic depending if the surface of the support is able to release a proton or to react with them.[16]

As one example, we have taken $TiO_2$, which is one of the supports widely used in heterogeneous catalysis by gold nanoparticles.[17,18] Below pH 6, the surface of titania is positively charged and can strongly adsorb through coulombic interaction anions such as $AuCl_4^-$ or $AuCl_3(OH)^-$. Based on this adsorption, one possibility to form gold nanoparticles on a solid surface starts as the first step with spontaneous Au anion adsorption at acid pH values. It has been reported that up to 60% of a $HAuCl_4$ solution can be adsorbed on titania at pH 3. At this pH value the predominant gold species is $AuCl_3(OH)^-$.[8,9] Zanella *et al.* have suggested that the mechanism of adsorption of gold hydroxychlorides is not purely a coulombic interaction but also involves the formation of covalent bonds with the solid surface by reaction with surface hydroxyl groups (Scheme 1).[19] Gavriilidis also proposed a similar mechanism involving the formation of covalent bonds between gold hydroxyl chlorides species in solution and the hydroxyl groups on the surface of alumina.[20] One likely possibility is that the initial interaction between the gold species and the support surface hydroxyl is more favourable for species having Au–OH groups than for Au–Cl, the presence of $Au(OH)_xCl_{4-x}^-$ species appearing above pH 3 being a prerequisite for deposition. An analogous mechanism has been proposed for the adsorption of anionic gold species on alumina.[10,21]

After attachment on the surface, formation of gold nanoparticles is believed to occur in two steps involving nucleation and growth. Nucleation is not by coalescence of single gold atoms but rather it involves complicated and ill-defined species containing gold atoms and ions of a size below 2 nm. Aurophilicity of gold, *i.e.*, the tendency to form Au–Au bonds will play a role in this stage.[22] Once the gold atoms are being organized in small nuclei, growth will occur to form the nanoparticle of the observed final size. Concentration, gold loading on the surface and the presence of chloride are the main parameters affecting to the growth. Although on solid surfaces growth is less studied, it has been found that in solution doubling the concentration of $AuCl_4^-$ in the range of $10^{-4}$ M produces fast nucleation leading to smaller nanoparticles and on ceria the particle size depends on the percentage of gold on the support.[23,24] Concerning the influence of chloride on particle size, it is known that the presence of $Cl^-$ favors nanoparticle aggregation during thermal treatment by promoting mobilization of gold atoms.[21,25–28] For this reason and also because chloride is a poison of gold catalytic activity, it is very important to ensure complete chloride removal during catalyst preparation. Exhaustive washing and stream treatments of hydrogen reduction are better chloride removal procedures than thermal treatments. It has been reported that temperatures below 600 °C do not efficiently remove chloride present on gold catalysts.[6]

**ii. Deposition–precipitation.** The most widely used procedure to obtain supported gold nanoparticles on metal oxides is known as deposition–precipitation. Deposition–precipitation is an alternative to the adsorption of Au anions in which ideally $AuCl_4^-$ is hydrolyzed by raising the pH of the solution to form insoluble $Au(OH)_3$ which becomes adsorbed onto the solid support as it precipitates.[29,30] In a simplistic approach, the higher gold loading on the support obtained by the deposition–precipitation method as compared to adsorption of Au anions has been ascribed to the precipitation of $Au(OH)_3$ from the solution to the solid, the lower solubility being responsible of the higher efficiency of the phase transfer. This procedure to support gold nanoparticles was first used by Haruta's group and has since then become the most widely used method.[31] Haruta has proposed that precipitation of $Au(OH)_3$ takes place exclusively on defects that act as nucleating sites.[19,32–34]

Also for this methodology the nature of the solid surfaces plays an important role and, more specifically, it works well for supports having a zero potential charge (ZPC) greater than five. Thus, deposition–precipitation is suitable for solids such as magnesia, titania, alumina, zirconia and ceria, but does not work well for silica (ZPC ~ 2) silica-alumina (ZPC ~1) or tungsten oxide (ZPC ~ 1).[25]

According to the deposition–precipitation mechanisms the ideal solid should have a high density of hydroxyl groups and large surface area to achieve stabilized gold nanoparticles of small size and narrow dispersion. However, experimentally it has been found for the case of P25 titania (80% anatase, 20% rutile) that the small gold nanoparticles are essentially located on the less functionalized rutile crystallites.[25,30] Furthermore, it has been shown that deposition–precipitation is actually less efficient with higher surface area titanias.[35] Considering these contradictions that may arise from difference in the reactivity of the hydroxyl groups, it is clear now that the actual steps occurring in the formation of supported gold nanoparticles are considerably more complex than the simple idea of deposition–precipitation proposed initially by Geus and Haruta.[29] Theoretical calculations will be very useful to rationalize and understand the initial steps of the deposition–precipitation method and the intrinsic tendency of each individual species $Au(OH)_xCl_{4-x}^-$ to become attached to the solid surface.

One issue in the deposition–precipitation procedure is whether or not chloride is present on the solid surface. Time-of-flight secondary-ion mass spectrometry analysis of the dry surface of P25 titania after deposition precipitation of gold nanoparticles has shown the presence of $AuCl^-$, $AuCl_2^-$, $Au_2Cl_2^-$, $Au_2Cl_3^-$ and $AuCl(OH)^-$ among other species.[36] Although the actual ion distribution present on the surface can be disguised by the preferential desorption of weakly bound gold species or by their inherent tendency to migrate to the gas phase, these mass spectrometry analyses clearly prove the presence of chloride-containing species adsorbed on the surface of the support immediately after the precipitation method.

After adsorption on the solid surface, gold nanoparticle formation will occur by nucleation and growth as indicated in the previous subsection, the final particle size being the result of the operation of different parameters including gold loading, nature of the solid surface, presence of chloride, thermal treatments, *etc.* Comparing adsorption with deposition–precipitation, the fact that the amount of chloride is reduced when the procedure is carried out at higher pH values (by replacing $Cl^-$ by $OH^-$ as Au ligand) can explain the lower mobility of gold (and smaller average nanoparticle size) in deposition–precipitation with respect to what has been commented in the adsorption procedure.[21,26–28]

As commented earlier, one of the most important roles of the solid support is to avoid particle growth and to stabilize nanoparticles against agglomeration. In the complete deposition–precipitation protocol the last step is the reduction of the gold ions to form the metal clusters. This chemical reduction can be accomplished conveniently by thermal treatment of the solid in a thin bed under a hydrogen or even oxygen flow.

By using XPS, it has been established that thermal treatment produces the migration of ions and nanoparticles over the support surface, leading to an increase in the average particle size.[20,32,37–42] It has been shown experimentally that while the initial metal dispersion obtained using the anionic adsorption is higher than using the deposition–precipitation method, the main difference between these two methodologies is the large mobility of the gold species formed in the anionic adsorption with respect to the deposition–precipitation method, during the thermal treatment that eventually leads to significantly larger (and therefore less active) nanoparticles with the anionic adsorption process.[43]

Characterization of the supported gold nanoparticles requires the combination of different experimental techniques, each of them providing specific information that complements the data obtained from others. TEM allows determining the shape and particle size distribution of the gold nanoparticles and their location. XPS and FT-IR serve to establish the Au oxidation states and the strength of interaction with probe molecules.

Concerning the interaction of gold nanoparticles with the support, it has been proposed that this interaction can lead to the stabilization of positive and negative gold atoms at the interphase between gold and the support.[44–47] Evidence for the presence of gold atoms having positive or negative charge density can be obtained by various techniques. XP spectroscopy of the Au $4f_{7/2}$ level gives an experimental band that can be fitted as corresponding to the contribution of three components due to Au(0), Au(I) and Au(III) (Fig. 1). Normally the population of Au(I) is significantly smaller than that of Au(III).

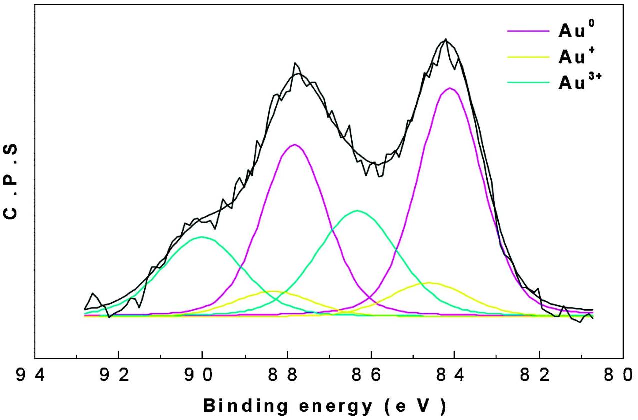


**Fig. 1** XP spectra of the Au $4f_{7/2}$ level recorded for gold nanoparticles supported on nanoparticulate ceria (reprinted from ref. 47).

There are numerous reports showing that the preparation procedure determines the nature of the gold dispersion on the support. TEM imaging is the most important experimental technique to establish the particle size distribution and gold dispersion on the surface. However, it is very common that the poor contrast between the support and the gold nanoparticles makes accurate measurements of particle size distribution difficult. In addition there is a natural bias in this technique towards larger particles that are more easily detectable than the smaller ones. Also in many cases, the detection limit of TEM is a few nanometers and it could be that catalytically more active smaller particles are barely detected or not detected at all. Also XP spectroscopy, determining the atomic ratio of Au $4f_{7/2}$ on the surface and comparing this value with the elemental analysis can be used to address gold dispersion on the external surface with respect to the bulk in the whole support particle.[48] XPS can also serve to detect and quantify the presence of other elements and particularly the presence of Cl that is considered a potent poison for many gold catalyzed reactions. Thus, Gaigneaux and co-workers by measuring XPS on samples after adsorbing $AuCl_4^-$ following either the anionic adsorption or the deposition–precipitation protocol, have detected a small signal corresponding to Cl 2p that could not be accurately quantified due to its weakness.[36] This result implies that most of the chloride ions are replaced by surface hydroxyl groups in the adsorption by interaction with the surface hydroxyl groups, but also cast doubts about what could be the catalytic activity of the supported gold catalyst in the total absence of chloride.

IR spectroscopy using CO as a probe and monitoring the C═O stretching vibration appearing in the region about 2100 $cm^{-1}$ has also been employed to assess the presence of Au(III), Au(I) and Au(0) (Fig. 2).[39,49–53] This technique is based on the different Lewis acid strength of the gold atoms depending on their oxidation state.

It has to be, however, noticed that both experimental XPS and FT-IR using CO as probe techniques may disguise the oxidation state of the gold on the support they are characterising. Thus, CO is a strong reducing agent that can decrease the population of Au(I) and Au(III) while recording the IR. This can certainly be diminished by performing the adsorption at low temperatures. Also the high vacuum required for XPS and the energy of the soft X rays can lead to the reduction of a significant fraction of Au(I) and Au(III) ions. In any case, it is believed that the percentages of positive gold atoms estimated by XPS or CO titration are lower limit values of the real positive gold atoms that can be present before analysis.

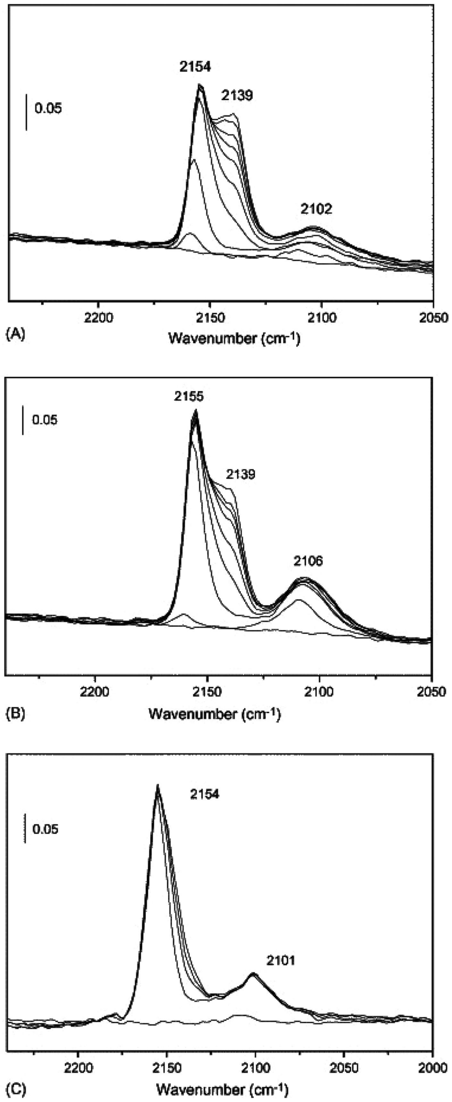
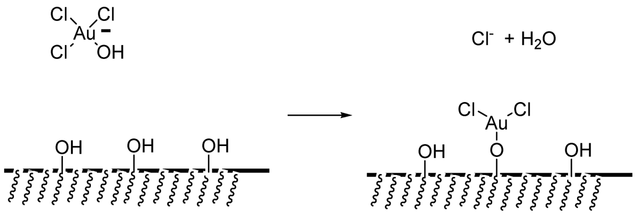


**Fig. 2** CO stretching bands recorded at liquid-$N_2$ temperature upon admitting CO on three different Au/$CeO_2$ catalysts: (A) as prepared, (B) reduced at 100 °C in $H_2$, and (C) reduced at 200 °C. The samples have been exposed "*in situ*" for the CO oxidation reaction at 100 °C for 2 h prior to CO adsorption experiments. This figure illustrates the potential of CO as a probe to characterize gold nanoparticles interacting with the solid support (taken from ref. 53).

## Supporting gold by adsorption of preformed nanoparticles

The presence of small gold nanoparticles is a pre-requisite for high catalytic activity of supported gold. The deposition–precipitation method is very useful when the support is a metal oxide, but this method produces unsuitable large aggregates with carbon supports. The very different structure of the active carbon surface compared to metal oxides is responsible for this contrasting behaviour. It is widely accepted that the hydrophobic nature of carbons and the low density of surface hydroxyl groups may be the reasons for this distinctive behaviour.



**Scheme 1** Initial step in the adsorption mechanism in which certain gold species in solution becomes attached covalently to the solid surface.

Noble metals supported on high-surface area active carbons are among the most widely used metallic catalysts and are widely used to promote hydrogenations and oxidations among other general reaction types, and consequently carbon has also been used to support gold nanoparticles. To deposit gold nanoparticles on active carbon, one suitable procedure is to prepare solutions of colloidal gold nanoparticles by reduction with citric acid or by a two-phase procedure and then adsorb the preformed colloidal gold onto active carbon.[54] An analogous procedure can be used to adsorb gold nanoparticles on polymers.

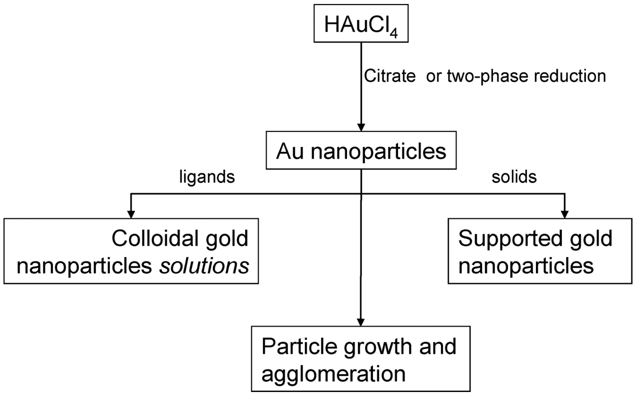
Gold is a unique element in its ability to form reliably persistent colloidal dispersions which show great stability. For this reason gold in its colloidal state has been among the preferred metals for material scientists to determine the specific properties of this state of matter. Turkevich *et al.* showed in the 1950s that colloidal gold can be formed by reduction of $AuCl_4^-$ with sodium citrate giving small nanoparticles (typically of 20 nm) of narrow size distribution.[55,56]

Freshly prepared colloidal gold nanoparticles rapidly undergo agglomeration and precipitation in a few minutes if they are not adequately stabilized by ligands or by supporting them on a solid surface (Scheme 2). Mercaptans, phosphines, phosphine oxides, quaternary ammonium salts and even polymers and dendrimers can be used as ligands of gold nanoparticles.[57–59] Apparently citrate has a dual role as reducing agent and as a ligand stabilizing colloidal gold and for this reason the Turkevich recipe of colloidal gold preparation gives persistent nanoparticles.

A variation to form colloidal gold suspensions is carried out in two liquid phases.[60] The reduction of $AuCl_4^-$ to form the nanoparticles takes place in water. But once formed the gold nanoparticles are sequestered to an immiscible organic phase, typically toluene. The driving force for this migration is that, in contrast to citrate, the ligands used in this procedure to bind the nanoparticles are highly soluble in the organic phase. This phase migration reduces the particle growth and tends to give smaller particle size (2–10 nm) than in a single phase.

Gold nanoparticles can also be formed by chemical vapor deposition and sonochemical or photochemical irradiation. In the last case, a recent finding has been to use light in combination with a curing agent that forms efficiently carbon-centred radicals in water to reduce $AuCl_4^-$ forming naked gold nanoparticles.[61]

Besides the use of ligands to avoid particle growth, supporting of the nanoparticles onto solid supports can be a viable alternative to stabilize small nanoparticles. Another alternative to inhibit particle growth involves embedding gold nanoparticles inside a polymeric or inorganic matrix rather than depositing on the external surface.[62]



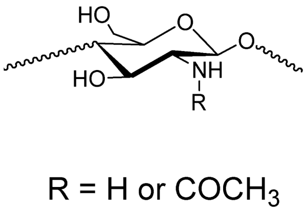
**Scheme 2** Strategies to stabilize gold nanoparticles against agglomeration.

The most used gold material for preparing colloidal supported gold catalysts is tetrachloroauric acid ($HAuCl_4$) obtained from the attack of a mixture of nitric and hydrochloric acids (*aqua regia*) on gold metal. Thus, starting from aqueous solutions of $HAuCl_4$, reliable procedures for the preparation of gold nanoparticles within a fairly homogeneous size distribution are based on the reduction in water with citrate or other $\alpha$-hydroxyacids or by reduction in the presence of toluene with a phase-transfer ligand (two-phase procedure).[55,56,63–67] The latter has the advantage of producing smaller gold nanoparticles. Excellent reviews by Daniel and Astruc and Bond, Louis and Thompson address in deeper coverage aspects related to the preparation and stabilization of gold nanoparticles.[6,63]

Polymers, particularly those having oxygen or nitrogen atoms, can act as polydentate ligands stabilizing colloidal gold. Polymers can be present during the formation of gold nanoparticles by reduction of $AuCl_4^-$ or added after nanoparticle formation. In some cases, the formation of gold nanoparticles on polymers relies first on an interaction between a gold salt ($HAuCl_4$ or $NaAuCl_4$) and the polymers followed by reduction of the adsorbed species.[68] The incorporation in the polymer of preformed particles may be advisable because the particle size can be controlled independently in the absence of the polymer. Poly(vinyl alcohol), poly(vinylpyrrolidone), poly(diallyldimethylammonium chloride) and even polystyrene have been used to stabilize colloidal gold.[68–71] In the last case, it has been reported that the $\pi$-interaction of aromatic rings with gold nanoparticles is the force that leads to nanoparticle stabilization.

A particular type of polymer in which gold nanoparticles have also been incorporated are dendrimers such as PAMAM and PPI.[60,72–75] The special morphology of dendrimers and the presence of functional groups in internal positions can serve to entrap and immobilize the nanoparticles.[60,72–75] Dendrimer stabilized nanoparticles can later be adsorbed on the surface of metal oxides such as titania and silica and this can be an alternative procedure to deposition–precipitation.[76,77] The interactions of colloidal gold with the surfaces of titania has been studied.[78]

Chitosan is an abundant natural biopolymer obtained from shrimp, prawns and other crustaceous shells that contains glucosamine units linked at 1,4-positions (Scheme 3). Chitosan



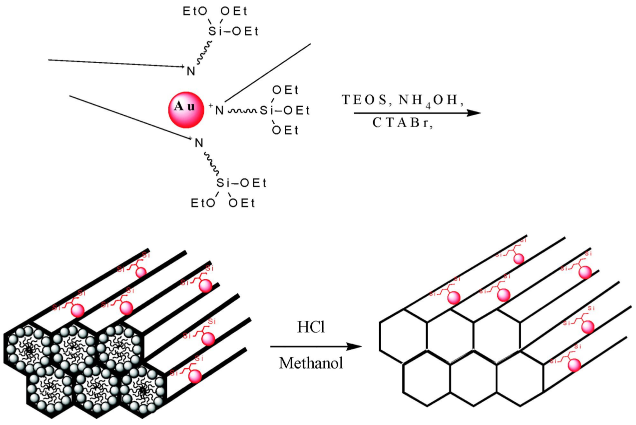
**Scheme 3** Glucosamine building unit of the natural chitosan polymer.

contains nitrogen and oxygen groups which can interact with gold salts and gold nanoparticles. The interaction between Au and the nitrogen and oxygen functionalities present in the biopolymer contributes positively to the activity and stability of the gold nanoparticles with respect to other supports. However the use of this biopolymer suffers from the problem of a low surface area and insufficient mechanical strength against abrasion.

To overcome these limitations, chitosan was dispersed on silica and the resulting composite was used as support of the gold nanoparticles.[79] Formation of the gold nanoparticles was achieved by impregnation with $NaAuCl_4$ followed by spontaneous thermally promoted reduction. The interaction of $AuCl_4^-$ with the amino and hydroxyl groups of chitosan was determined by $^{13}C$ NMR and Raman spectroscopy. The size of the gold nanoparticles was established by TEM with an average crystallite size between 2 and 6 nm, the particle size distribution decreasing with the percentage of chitosan dispersed on the silica. This effect has been explained by the positive influence that the presence of chitosan functional groups plays in stabilizing the gold nanoparticles.

## Gold nanoparticles embedded inside metal oxide matrices

In most of the heterogeneous gold catalysts, gold nanoparticles are supported on the external surface of the solid. Since the use of micro-/meso-porous silicas and metal oxides has become a general strategy to increase the total surface area and have some control on the selectivity of the process, there is an obvious interest in using these porous solids as hosts in which gold nanoparticles are incorporated.



**Scheme 4** Pictorial illustration of gold nanoparticles surrounded by a task specific ligand having three different functions: (i) silica source, (ii) interaction with the surfactant, and (iii) interaction with gold nanoparticles (taken from ref. 95).

Although some reports deal with gold colloids dispersed within a silicate matrix, encapsulation of gold nanoparticles within the void space of structured mesoporous silica has gained great attention due to the properties of MCM-41 and related materials, including highly ordered mesopores, controlled pore-size, specific surface areas of about 1000 $m^2\ g^{-1}$ and pore volumes of about 1 ml $g^{-1}$.[80,81] These materials have been the preferred hosts to incorporate in their internal voids guests that can exhibit catalytic properties. Considering the relevance of the support on the catalysis by gold nanoparticles, there is an obvious interest in the use of structured mesoporous silicas as supports. Methods such as aerosol-assisted self-assembly, the sonochemical reduction of $HAuCl_4$ or the use of task-specific ligands allow the confinement of gold particles (1–5 nm diameter) within the mesoporous channels of MCM-41, MCM-48, SBA-15, or at the surface of silica spheres.[82–91] However, the affinity of gold nanoparticles formed by hydrogen reduction of tetrachloroauric acid for pure silica surfaces is low and these nanoparticles can be easily removed by solvent extraction. A methodology consisting of pore functionalization with mercaptopropyl,[92] propylamine[93] or polydentate amine[94] ligands has been designed to strongly retain the gold nanoparticles inside the MCM-41 mesopores. The process of the reduction of $HAuCl_4$ into gold nanoparticles by the silanol groups inside the mesopores of MCM-41 silica has been studied by $^{13}C$ NMR.[94] Gold nanoparticles inside propylamine-functionalized mesoporous MCM-41 silica show catalytic activity and selectivity in the hydrogenation of styrene to ethylbenzene.[93]

In a similar concept to develop periodic mesoporous materials, instead of using commercial quaternary ammonium salts, task specific ligands have been used and synthesized to interact with the gold nanoparticles.[95] Thus, a ligand containing a cetylammonium moiety to act as structure directing agent and to interact with gold nanoparticles contains a trialkoxysilyl group that can co-condense with TEOS to form a mesoporous silica. Scheme 4 illustrates the triple functions of the quaternary ammonium, as surfactant, as ligand of gold nanoparticles, and as silica source. The resulting solid contains well dispersed gold nanoparticles embedded inside the mesopores of structured silica (Fig. 3).[95] This mesoporous solid

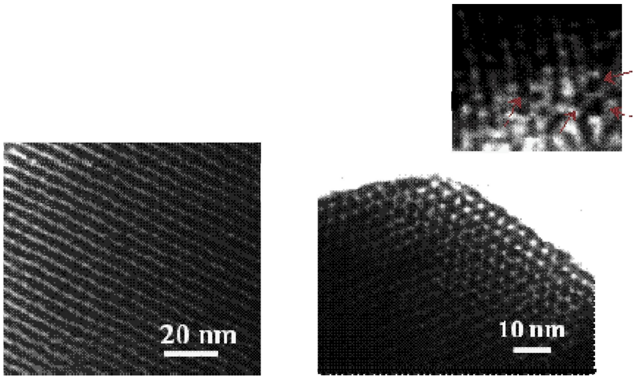
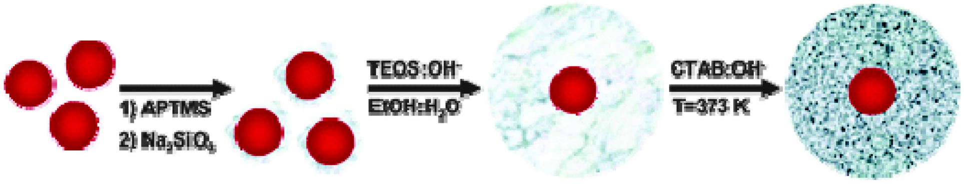


**Fig. 3** TEM images showing a side and top view of the channels of a mesoporous silica prepared using the concept of task specific ligands. The top most right images show the location of gold nanoparticles (taken from ref. 95).



**Scheme 5** Preparation of gold nanoparticles embedded within monodisperse mesoporous silica: APTMS: aminopropyltrimethoxysilane; TEOS: tetraethylorthosilicate (taken from ref. 98).

shows promising activity in the solventless aerobic oxidation of alcohols.

A variant of the encapsulation of gold nanoparticles consists in covering gold nanoparticles by a protecting shell that prevents the growth of the nanoparticles. Stabilization of gold nanoparticles against coagulation can be done conveniently by preparing core–shell particles in which the core is gold. This approach can be realized using as coating an organic polymer, as for example of PVP or PEG.[96] Nevertheless, the encapsulation of gold within silica is particularly advantageous as a method for both stabilizing nanoparticles and tailoring structural and textural parameters of the outer silica shell, while introducing numerous possibilities for particle functionalization.[97]

Preparation of encapsulated gold nanoparticles (15–30 nm) inside monodisperse mesoporous silica spheres ranging from 100 to 350 nm diameter forming a core–shell gold (core)–mesoporous silica (shell) has been reported.[98] Besides the Stöber method to prepare monodisperse silica spheres, the key step is the pseudomorphical transformation of preformed gold–amorphous silica nanospheres in an alkaline solution containing cetyltrimethylammonium bromide (CTAB) as agent of the silica structural changes.[98] During the hydrothermal treatment, the incorporation of CTAB into the amorphous silica matrix leads to a reorganization of the silica shell rendering a mesostructured material that after calcination gives a surface area of 1020 $m^2$ $g^{-1}$. No modification of the particle shape and size takes place during the reorganization of the silica shell, obtaining monodispersed spherical particles of mesoporous silica having central gold nanoparticles. Scheme 5 illustrates the process developed to obtain the core–shell gold (core)–mesoporous silica (shell) particles.

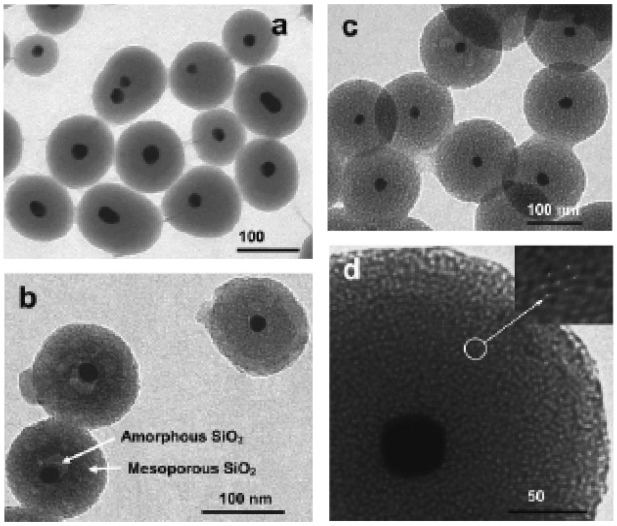
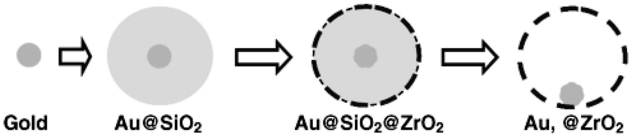


**Fig. 4** (a) Core–shell gold nanoparticles (core)–non-porous silica (shell) prepared by Stober's method; (b, c) Core–shell gold nanoparticles (core)–mesoporous silica (shell) synthesized by pseudomorphic transformation of preformed gold nanoparticles (core)–non porous silica (shell) at an intermediate state of the morphological transformation (b) and after complete change (c); and (d) detail of wormhole-like channels of core–shell gold nanoparticles (core)–mesoporous silica (shell) microstructure; the inset shows the local arrangement in hexagonal symmetry (reproduced from ref. 98).

The silica shell after the hydrothermal treatment exhibits a quite complex pore structure, where the mesochannels do not align over the entire nanoparticle but form wormhole-like pores that are randomly distributed in all directions, starting at the inner part of the sphere and going out to the external surface (Fig. 4). Nevertheless, the hexagonal symmetry is easily recognizable in the mesoporous wall at small domains.

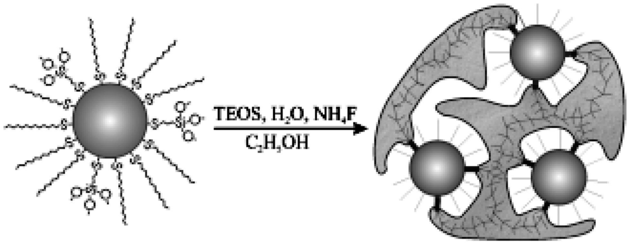
Working under appropriate conditions it is possible to obtain samples with narrow particle size distribution of 110–150 nm. These gold–mesoporous silica samples present typical type IV adsorption isotherms characteristic of MCM-41 silicas with an average pore diameter is 3.5 nm.

A more elaborate procedure reported by Schutz and coworkers can serve to prepare gold nanoparticles embedded within monodisperse spheres having a double shell of silica (internal) and zirconia (external).[99] Scheme 6 illustrates the preparation of these double shell spheres containing gold nanoparticles. After preparation, the silica can be dissolved with base, leaving the inner gold nanoparticles "floating" inside the zirconia shell.



**Scheme 6** Steps leading to the preparation of gold nanoparticles embedded inside spheres with double or single shells (taken from ref. 99, Arnal *et al. Angew. Chem., Int. Ed.*, 2006, **45**, 8224–8227, Copyright Wiley–VCH Verlag GmbH & Co, KGaA. Reproduced with permission).

A new concept on supported gold nanoparticles has been recently reported.[62] Using inverse water-in-oil emulsions, gold nanoparticles are formed in the submicroscopic water droplets using hydrazine as reducing agent in the presence of a mixture of 1-dodecanethiol and 3-mercaptopropyltrimethoxysilane in a molar ratio 13 : 1. In this way, the small gold nanoparticles become stabilized by the two ligands when formed. Latter in a second stage the 3-mercaptopropyltrimethoxysilane was co-condensed with tetraethyl orthosilicate promoted by $NH_4F$ to form a highly porous silica material that encloses the gold nanoparticles.[62] In the process of silica gelification, 1-dodecanethiol acts as a spacer preventing occlusion of gold nanoparticles by the silica. Scheme 7 summarizes the concept of this novel material in which at some point of the procedure there is a metal–organic–inorganic gold nanoparticle–dodecanethiol–silica solid.



**Scheme 7** Preparation of gold nanoparticles occluded in a porous amorphous silica matrix. Aggregation of the nanoparticles is avoided by 1-dodecanethiol ligands, while mercaptopropylsilane produces immobilization of the nanoparticles in the matrix (based on ref. 62).

The surface area of this material after calcination at 450 °C was 540 $m^2\ g^{-1}$.[62] The $N_2$ adsorption isotherm is typical of a mesoporous material with a relatively narrow distribution of pore sizes, centered at 7 nm.[62] Importantly, since the gold nanoparticles are isolated and surrounded by silica domains, thermal sintering is significantly hindered. Thus, it was determined that under identical conditions gold nanoparticle agglomeration occurs to a larger extent when gold is deposited on functionalized MCM-41 and SBA-15 (average particle size of 5–10 nm) than for the metal–organic–inorganic material (average particle size of *ca.* 3 nm).[62]

This small particle size and site isolation is apparently responsible for the high CO oxidation activity at 30 °C of these gold nanoparticles embedded on porous silica (0.48 $\mathrm{mol_{CO}\ g_{Au}^{-1}\ h^{-1}}$) that is at least one order of magnitude larger than that obtained with comparable catalysts based on gold on MCM-41 or SBA-15 mesoporous materials and is also higher than the specific rate (0.17 $\mathrm{mol_{CO}\ g_{Au}^{-1}\ h^{-1}}$) obtained by Okumura *et al.* with $Au/SiO_2$ prepared by CVD.[100,101] The special features of the gold nanoparticle supported on porous silica makes this material as active as the $Au/TiO_2$ catalyst and much more active than $Au/Fe_2O_3$ for low-temperature CO oxidation. This contrasts with the low activity of gold nanoparticles supported on the external surface of amorphous non-porous $SiO_2$ and emphasises the role that surface structuring plays on the activity of gold nanoparticles.

### Role of support on the catalytic activity

In addition to the primary role of reducing the mobility of the metal nanoparticles to diminish their tendency to agglomerate, a second role of the support that has been addressed in some cases is the possibility that the support acts actively in the reaction mechanism by redox cycling of the support metal ions.[37] Supports such as $MnO_2$ and $CeO_2$ and others that have a metal with two stable redox states, such as $Fe_2O_3$, could be representative examples. In this case the cooperation of the support with gold catalysis would arise from stabilization of positive gold species and by intervening in the reaction mechanism. Cooperation between gold nanoparticles and the support in the catalytic cycle has been claimed frequently to rationalize the variations of catalytic activity of gold nanoparticles on different supports. For instance, for CO oxidation it is considered that amorphous, unstructured silica is an inadequate support since gold supported on silica is a very inefficient catalyst compared to other metal oxides.

Concerning the role of the support on the mechanism of gold catalyzed reactions, one aspect that deserves a detailed study is the possibility to add promoters to the support to boost the ability to participate in the catalytic cycle. In this context, it has been recently reported that the addition of iron between 1 and 3.5 wt% to high-area $TiO_2$ (Degussa P25, a 80 : 20 mixture of anatase and rutile) increases the catalytic activity of $Au/TiO_2$ towards the low-temperature CO oxidation.[102] Thus, the activity of gold catalyst supported on iron-promoted $TiO_2$ for CO oxidation is approximately twice that of the most active comparable catalysts described in the literature.[102] This effect has been ascribed to an increase in the number of oxygen defect sites on titania that can react with $O_2$ to form peroxide and superoxide species. It has been frequently proposed that in the presence of gold nanoclusters on the $TiO_2$ surface, the superoxide species becomes highly reactive. Images of $Au/(Fe)TiO_2$ obtained by scanning transmission electron microscopy combined with spectra of the catalyst measured during reaction (Raman, extended X-ray absorption fine structure, and X-ray absorption near-edge structure) indicate strong interactions of gold with the support and the presence of iron near the interfaces between the gold clusters and the $TiO_2$ support.[102]

## III. Bridging homogeneous and heterogeneous gold catalysis

In a seminal work responsible for a large part of the surge for gold catalysis, Haruta showed that small size gold nanoparticles are exceedingly good catalysts to promote low-temperature CO oxidation.[103] In contrast to the activity of small nanoparticles, gold nanoparticles of diameter above 20 nm are devoid of significant catalytic activity. Moreover, it has been established that there is an exponential inverse relationship between the particle size and the catalytic activity for CO oxidation.[31] In view of this, there has been a continued interest in reducing the particle size, the limit being a cluster of a discrete number of atoms corresponding to the closed shell packing of gold atoms such as 13, 54, *etc.* according to eqn (1), where *n* is the number of full shells in the nanoparticle.[63]

$$\text{Total number of gold atoms in a closed-shell particle} = \sum(10n^2 + 2) \qquad (1)$$

On the other hand, molecular complexes having a single gold atom are also active for a considerable number of organic reactions, many of them based on the unique ability of gold to act as a carbonophile Lewis acid.[2,3] Considering the instability of some of these complexes and the appearance of gold nanoparticles under the experimental conditions employed in some of the organic reactions, it is of interest to assess if the complexes are the catalytic species or if they are the precatalysts forming gold nanoparticles or other gold species as the reaction starts.

This issue of the possible contribution to the activity of gold complexes by evolved nanoparticles, not sufficiently addressed in homogeneous gold catalysis, has emerged from the recent studies in palladium catalysis.[104,105] It has been shown that in many reactions initially believed as catalyzed by palladium complexes, the complex decomposes in the very early stages of the reaction and, thus, they really act as a precursor of the catalytically active species present during most part of the reaction.[106,107] These species have been shown to be small palladium nanoparticles present in colloidal *solution*[105] and, as in the case of supported gold nanoparticles established by Haruta, the catalytic activity of these palladium nanoparticles depends on the particle size.

Thus, the current scenario is that two traditionally separate and independent disciplines: heterogeneous and homogeneous catalysis have converged to study the catalytic activity of metal nanoparticles. This concept and the use of metal nanoparticles (including gold) as catalytically relevant species has been recently reviewed by Astruc *et al.*[60]

After having presented some general aspects of gold catalysis, the following sections of this review are focused on describing some of the recent uses of supported gold nanoparticles as catalysts in organic reactions.

## IV. Addition to multiple C–C bonds

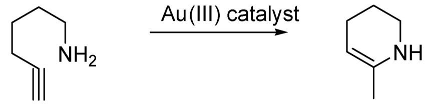
### Addition of nucleophiles to alkynes

Gold exhibits a strong tendency to act as a Lewis acid for C–C multiple bonds acting as bases. Particularly, the ability of gold to coordinate with C≡C triple bonds is remarkable and has no parallel with other transition metals. The term *alkynophile* has been coined to reflect this preference of gold to coordinate with C≡C triple bonds in the presence of other functional groups including C=C double bonds.

Upon coordination and formation of the corresponding adduct, the alkyne becomes activated and more reactive towards nucleophiles. Typically, the attack of the nucleophile is *anti* with respect to Au. The last step in the mechanism is the proteolytic cleavage of the Au–C bond. Scheme 8 summarizes a general reaction mechanism.

Gold-catalyzed activation of C≡C triple bonds has been generally performed using homogeneous Au(I) complexes and this topic has been extensively covered by recent reviews.[2,3]

Over the past five years, gold(I) complexes have been applied as catalysts for the hydroamination of alkynes, allenes and 1,3-dienes.[108–118] Intramolecular cyclization of 5-alkynylamines to form tetrahydropyridine derivatives is a process kinetically and thermodynamically favored by entropic reasons that has been reported to be catalyzed by Au(III)[119,120] (Scheme 9).

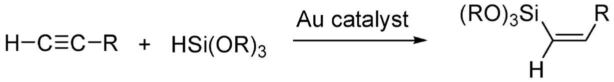


**Scheme 9** Cyclization of 5-alkynylamines to tetrahydropyridines.

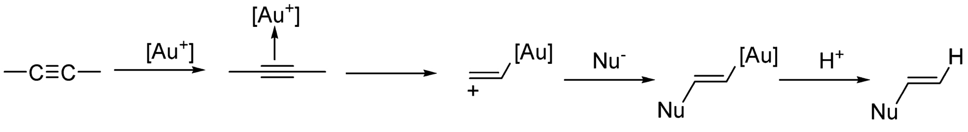
Compared to intramolecular cyclizations to give five-, six- or seven-membered heterocycles, the intermolecular hydroamination process is considerably more difficult to achieve and, therefore, it remains far less developed. In this respect, it has been recently reported that Au(I) catalyzes the intermolecular hydroamination of alkynes in the presence of acidic promoters and preferably in absence of air.[121] The role of the acidic promoter is explained through protonolysis of the precatalyst $(PPh_3)AuCH_3$ to give $Au(PPh_3)^+$, which is the active species involved in the mechanism. It remains to be seen whether if starting directly from $Au(PPh)_3{}^+$ makes unnecessary the addition of any acidic promoter. The absence of oxygen is, on the other hand, always advisable when working with easily oxidizable amines.

The heterogeneous version of both the intermolecular and intramolecular hydroamination of alkynes has been accomplished with different cationic metals (*e.g.*, $Ag^+$, $Cu^{2+}$, $Zn^{2+}$, $Pd^{2+}$) supported on acidic materials such as montmorillonite clay K-10, phosphotungstic acid and zeolite HBEA.[122,123] In the latter case, it has been proposed that the high activity of the ion-exchanged BEA zeolite could be a result of either structural properties or the particular environment of metal cations in the pore system. In this regard, it is worth noting the paucity of studies using zeolites containing Au(III) as heterogeneous catalysts, and from the results obtained for other metal cations, it would be of interest to know the behaviour of Au(III)-exchanged zeolites. One of the main reasons of the lack of abundant literature on the activity of Au-containing zeolites as catalysts is the difficulty to prepare well-characterized samples.[6] Whatever the reason, it is obvious that more effort is still needed to fully implement the use of solid acids, and zeolites in particular, in combination with metal sites to develop bifunctional metal/acid heterogeneous catalysts.

Hydrosilylation of C–C multiple bonds is an important reaction forming C–Si bonds that is typically catalyzed by platinum catalysts. Very recently excellent activities and regioselectivities for hydrosilylation of terminal alkynes has been obtained with homogeneous and heterogeneous Au catalysts (Scheme 10).[124,125]



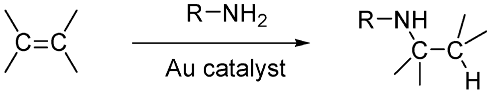
**Scheme 10** Hydrosilylation of C≡C triple bonds.



**Scheme 8** General reaction mechanism for the gold catalyzed nucleophilic addition to C≡C triple bonds.

## Additions to olefins

Addition of amines to multiple C–C bonds is a simple and general procedure for the formation of C–N bonds, giving access to the selective formation of amines and other nitrogenated compounds. However, since unsaturated C–C bonds and, particularly C=C double bonds, prefer to react with electrophiles, amines are generally unsuitable reagents for C=C addition (Scheme 11). For this reason, development of catalytic hydroamination of olefins will be a highly valuable tool in organic synthesis providing a simple and straightforward route to numerous organic nitrogen molecules. At present, no general hydroamination procedure is known, due to the high activation barrier for this reaction, especially when applied to alkenes. In contrast to alkenes, alkynes are more prone to undergo nucleophilic additions, hydroamination of alkynes being also thermodynamically more favorable than for alkenes.



**Scheme 11** Hydroamination of olefins.

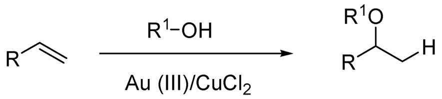
It has been recently reported that gold nanoparticles supported on a natural polysaccharide biopolymer (chitosan) is especially active to promote hydroamination of alkynes.[79] The performance of gold nanoparticles deposited on chitosan/silica was compared to that of gold nanoparticles supported on typical metal oxides including titania, iron oxide and ceria.[79] It was found that gold on chitosan/silica outperforms the activity of gold supported on metal oxides as a hydroamination catalyst (Table 1). In addition, particle size growth and agglomeration after the reaction was found for all the gold catalysts. This undesirable effect was less pronounced when gold was supported on the chitosan/silica composite.[79]

The activity of gold supported on chitosan–silica support was found to be general for a series of anilines substituted with both electron withdrawing (trifluoromethyl) or donor (methoxy) groups as well as for other 1-alkynes (phenylacetylene).

The efficient use of energy and minimization of energy consumption in chemical processes is an important principle of Green Chemistry. Compared to conventional heating using fluids, microwaves are considerably faster and represent a more rational way to use energy.[126–129] In some cases it has been reported that even the reactivity can vary with respect to conventional routes, microwave irradiation favoring the reactivity of molecules with high dipole moment. In this regard, also heating in gold catalysis can be performed using microwaves as for instance in the phosphine gold(I) catalyzed isomerization of terminal alkenes and hydroamination of unactivated alkenes.[130]

**Table 1** Conversion and yield for the reaction of aniline with 1-octyne in toluene catalyzed by gold catalysts on different supports (data taken from ref. 79)

| Entry | Catalyst | Conv. (%) | Yield (%) | Imine : ketone |
|---|---|---|---|---|
| 1 | Au–$CeO_2$ | 96 | 89 | 40:60 |
| 2 | Au–$Fe_2O_3$ | 68 | 63 | 93:3 |
| 3 | Au–$TiO_2$ | 92 | 57 | 64:36 |
| 4 | Au–$SiO_2$ | 68 | 64 | 88:12 |
| 5 | Au–Ch–$SiO_2$ (2 h) | 100 | 99 | 55:45 |



**Scheme 12** Addition of alcohols to alkenes catalyzed by $AuCl_3$ stabilized by $CuCl_2$.

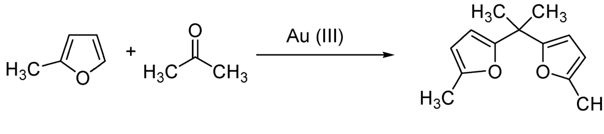
Alkenes can be activated by Au(III) catalysts and the effective addition of alcohols to alkenes can be carried out under mild conditions with Au(III) (Scheme 12). It has been observed that catalytic amounts of $CuCl_2$ are necessary in order stabilize the cationic Au(III).[131] Apparently, in the absence of $CuCl_2$ Au(III) is not stable and during the course of the reaction evolves towards the formation of catalytically less active gold nanoparticles. This process of reduction and agglomeration of Au(III) leads to deactivation. However, if Cu(II) is present in the system reoxidation of Au(I) is favored, the service life of the Au(III) is prolonged and the efficiency of the catalyst considerably increased. The key point is that Cu(I) can be reoxidized by ambient oxygen, while Au(I) is not. Overall, this report emphasized one aspect that has been largely ignored in gold catalysis, namely, the formation of metal gold nanoparticles during the course of the reaction while the initial presumed catalyst is a gold salt and the relative catalytic performance of unsupported and unstabilized gold nanoparticles with respect to the activity of the initial gold salts.

Related to the formation of ethers from alcohols, it has been reported that gold and other transition metal salts can serve as catalysts for the transesterification of inorganic esters with organic acids.[132] For instance stearyl stearate can be prepared in 95% yield by reacting stearyl borates with stearic acid in xylene as solvent. This transesterification process is particularly interesting for the formation of esters of polyols such as glycerine and saccharides.[132]

## Alkylation of activated heterocycles by carbonylic compounds

Gold(III) chloride has been a convenient catalyst for the low-temperature condensation of furans with carbonylic compounds (Scheme 13).[133] Furans are among the most reactive heterocycles and it can react with carbonyl compounds under mild conditions. Due to environmental problems, gold(III) was preferred to other highly poisonous metals such as mercury(II) and thallium(III). Also gold(III) competes favourably with Brønsted acids to promote this reaction.

Isolated C=C double bonds do not react under these conditions. However, in the case of α,β-unsaturated carbonylic compounds, the conjugated C=C double bond readily reacts,



**Scheme 13** Condensation of carbonylic compounds catalyzed by gold salts.

even before the carbonyl group.[133] For α,β-enals the final product corresponds to the triple addition of furan.[133] Considering that these reactions have been studied in zeolites and other solid acids,[134] it will be of interest to determine if they can also be catalyzed by supported gold nanoparticles acting as Lewis acids.

## V. Cyclization reactions

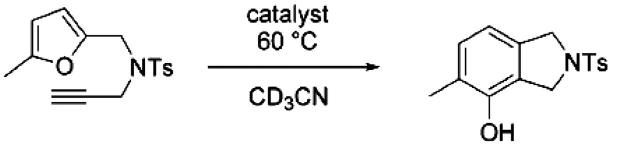
In their review on gold catalysis in organic synthesis, Arcadi and Di Giuseppe combine gold nanoparticles and gold(III) catalysis, emphasising the regio-/chemoselective nucleophilic additions to C≡C triple bonds. The leading ideas of this review is that gold complexes are exceptionally carbophilic Lewis acids to promote reactions of C≡C triple bonds and that the dual (Lewis acid and oxidation catalyst) activity of gold(III) catalysts makes them especially suitable to promote the synthesis of a variety of heterocycles through mechanisms involving both types of elementary reactions.[4] The entire process can be denoted as *domino* or *tandem* reactions.[4]

## VI. Rearrangements

### Ring expansions

Hashmi and coworkers have reported that gold salts are able to promote the conversion of 2-substituted furans having terminal C≡C triple bonds into phenol derivatives (Scheme 14).[135–138] This remarkable rearrangement can afford access to elaborated and substituted phenols from furans. It was observed that while this rearrangement is catalyzed smoothly in the homogeneous phase using Au(III) chlorides, initial attempts to perform this reaction using supported gold nanoparticles met with failure. Thus, gold on carbon, gold on $Fe_2O_3$, gold on $SiO_2$, gold on $TiO_2$ and stabilised colloidal gold nanoparticles were inactive to promote this reaction.

In contrast to those gold-containing solids, Corma and coworkers have showed that gold nanoparticles supported on nanocrystalline $CeO_2$ were able to catalyse the rearrangement of ω-alkynylfurans to phenols.[139] These results show the important role that the support can play cooperating in the activity of supported gold. In this particular reaction, the rearrangement apparently requires the presence of Au(III) ions on the gold clusters that should act as carbonophilic Lewis acid sites. By XPS and CO titration it has been determined that nanoparticulate ceria as support favors the presence of a larger population of positive gold species. The main reason for this feature of nanoparticulate ceria is the fact that ceria nanoparticles have a large deviation from the $CeO_2$ stoichiometry with a large number of lattice oxygen vacancies and a considerable 'confusion' between the IV and III cerium oxidation states. These well established facts are responsible, for instance, for a change in the behaviour of ceria from insulator in the case of large particle size to semiconductor for nanoparticles.[140] These properties specifically derived from the nanoparticulate size of the ceria are supposed to be responsible for the stabilization of positive gold at the gold/ceria interphase.

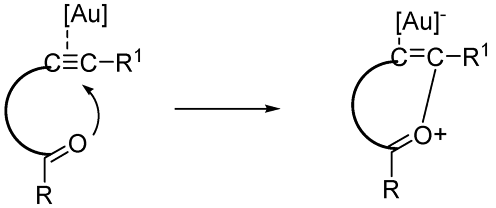


**Scheme 14** Rearrangement of ω-alkynyl substituted furans into phenols.

For the alkynyl furan to phenol rearrangement, it was observed that gold can leach from the support, unless properly calcined. Indeed, with the adequate catalyst pre-treatment, a sample of gold nanoparticles supported on nanoparticulate ceria was prepared that exhibits turnover numbers of up to 391.[139] Overall, the case of the relative activity of various supported gold nanoparticles for the alkynyl furan to phenol rearrangement illustrates the issue that, in principle, most of the reactions carried out using gold salts in homogeneous phase could also be performed with supported gold nanoparticles, provided that the support is properly adapted to the operating mechanism and the supported gold contains similar sites as those active in homogeneous catalysis.

### Benzannulation

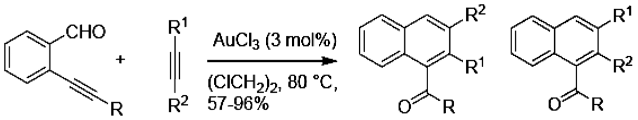
Au(III) and Au(I) salts and complexes are able to promote complex benzannulations of compounds containing enynal, enynones and alkynoates substructures with C–C multiple bonds, particularly alkynes.[141–148] In this cascade reaction including cycloaddition and rearrangement, several C–C bonds are simultaneously formed and skeletal rearrangement occurs in a single pot. The key feature of these reactions is the unique ability of gold(I) and gold(III) in promoting nucleophilic additions to alkynes of uncommon low-nucleophilic functional groups such as the negative carbonyl oxygen (Scheme 15).



**Scheme 15** Key step in the benzannulation reaction in which π coordination of C≡C triple bond with gold promotes the nucleophilic attack of carbonyl oxygen.

This chemistry is extremely interesting to access to complex molecules such as (+)-ochromycinone[145,149] and (+)-[145,149] B2, *rac*-heliophenanthrone,[150] whose alternative synthesis would otherwise require several steps. Thus, gold catalysis results in a remarkable atom economy and a reduction of the total amount of wastes, thus, complying with the principles of *green chemistry*.

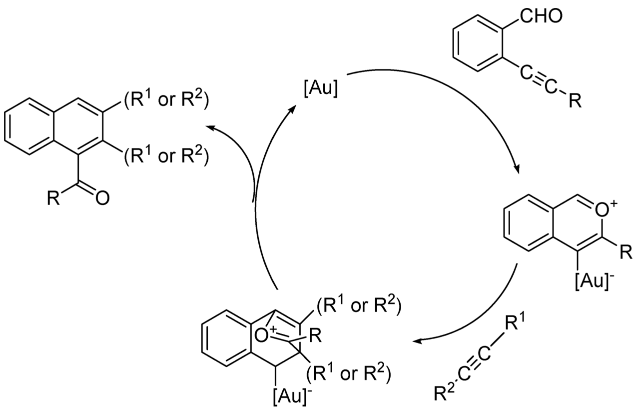
Yamamoto and co-workers reported the $AuCl_3$-catalyzed formal [4 + 2] benzannulation between *o*-alkynylbenzaldehydes and alkynes (Scheme 16).[147,148] Various naphthyl ketones were obtained in good to high yields. It was found that the reaction exhibits a remarkable regioselectivity and that only one of the two possible regioisomers is obtained



**Scheme 16** Synthesis of 1-naphthyl ketones through benzannulation of aromatic ynals promoted by $AuCl_3$.

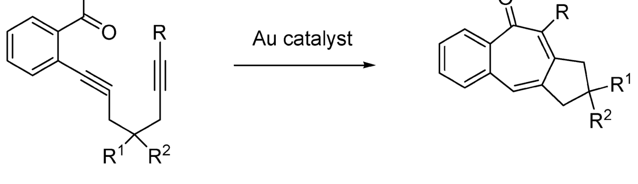
predominantly. Examples of an intramolecular version of this benzannulation in which the C≡C triple bond is covalently attached to the alkynylbenzaldehyde core has also been reported.[151]

A plausible mechanism for the $AuCl_3$-catalyzed formal [4 + 2] benzannulation is shown (Scheme 17). The coordination of the triple bond of the *o*-alkynylbenzaldehyde to $AuCl_3$ enhances the electrophilicity of the alkyne making possible the intramolecular nucleophilic attack of the carbonyl oxygen to the electron-deficient alkyne. The key intermediate is a pyrylium aurate. The Diels–Alder type [4 + 2] cycloaddition of this pyrylium and an alkyne followed by subsequent bond rearrangements to re-form the carbonyl group will lead to the final naphthalene derivative and regenerate $AuCl_3$. This field has recently been reviewed by Patil and Yamamoto giving an overview of the potential application of this reaction type for the synthesis of some natural six- and five-membered carbocycles.[143]



**Scheme 17** Proposed mechanism for the benzannulation reaction promoted by gold catalysts.

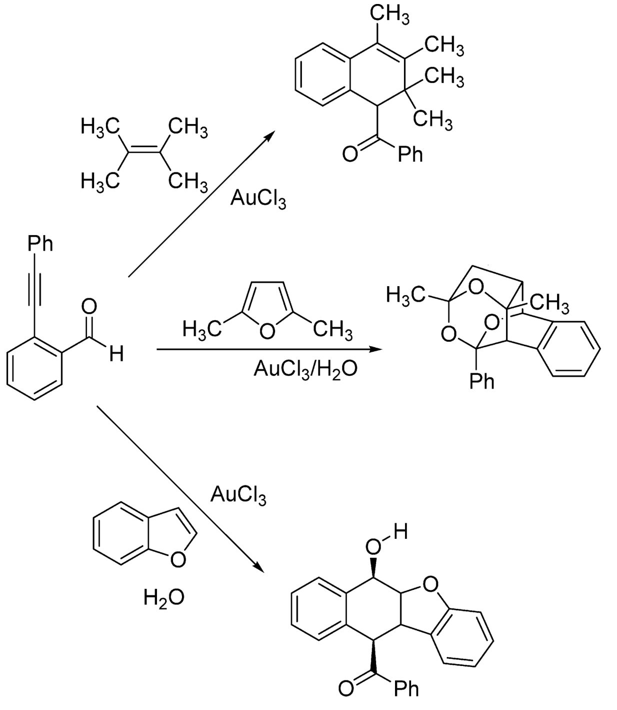
In addition of six-membered carbocycles the intramolecular version of benzannulation reactions involving single steps of C–C bond formation and skeletal rearrangement in oxo alkynals can also serve to form penta- and hepta-cycles (Scheme 18). Two of the main features of the gold(I)-catalyzed pentacycle formation are the very mild reaction conditions and the possibility to introduce enantioselectivity in the reaction, cyclization of enantiomerically enriched propargyl alcohols giving enantio-enriched products.



**Scheme 18** Intramolecular benzannulation leading to the formation of a tricyclic product with five and seven member rings.

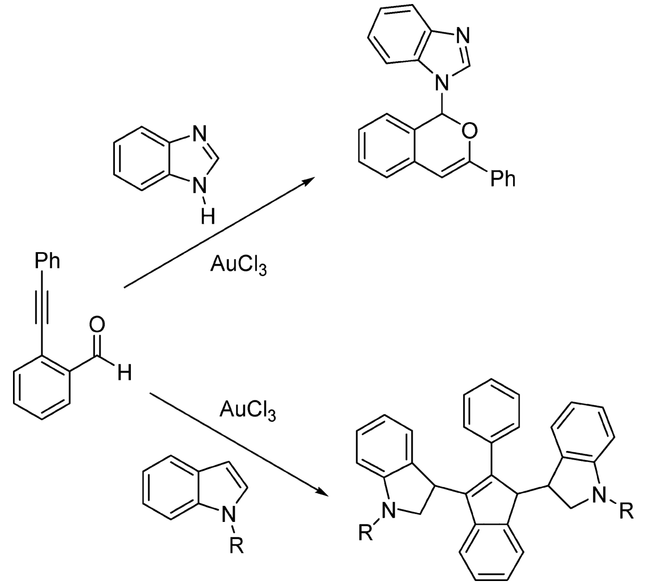
It has to be remarked that although reasonable reaction mechanisms have been proposed to rationalize the product formation, given the considerable number of consecutive steps there is a large extent of speculation at this stage and it would be highly desirable to get firm evidence for some of the gold intermediates proposed. Also the influence of the gold oxidation state and the implications on the catalysis and product distribution is unclear and requires a deeper study.

Dyker *et al.* have studied a variation of this benzannulation reaction in which *o*-ethynylbenzaldehydes react with electron-rich C═C double bonds rather than with alkynes.[152] The starting assumption for the discovery of this reaction is that aromatization that is the final step in the benzannulation is not necessary in order the [4 + 2] Diels–Alder reaction to occur. Tetramethylethylene, 2,5-dimethylfuran and benzofuran are substrates that react with *o*-(phenylethynyl)benzaldehyde as indicated in Scheme 19.[152] The fact that water is needed in some reaction points to the cooperation of a Brønsted catalysis. However, typical Brønsted acids such as HCl, *p*-toluenesulfonic or trifluoroacetic acid fail to catalyze the reaction.



**Scheme 19** Benzannulations of *o*-ethynylbenzaldehyde with C═C double bonds promoted by $AuCl_3$ in the presence of water (from ref. 152).

Benzimidazole and indole also react with *o*-phenylethynylbenzaldehyde in the presence of gold(III) to give products in which one (benzimidazole) or two (indole) molecules have been incorporated to the *o*-substituted benzaldehyde (Scheme 20).[152]



**Scheme 20** Trapping of the isobenzopyrylium cation intermediate formed in the presence of AuCl$_3$ with benzimidazole and indole.

As commented earlier, it is very likely that during the course of the reaction, gold nanoparticles are formed. The role of these gold nanoparticles and specifically their catalytic activity in relation with the starting gold salts and complexes remains unknown and is worth to be investigated. In fact, considering that the active sites in the reactions catalyzed by soluble gold salts and complexes are stabilized positive gold atoms and that supported gold nanoparticles can also have a population of positive gold(I) and gold(III) ions, it was of interest to establish whether or not benzoannulations can also be catalyzed by heterogeneous gold catalysts.

In this context, it has been recently reported that the cycloaddition of *o*-(phenylethynyl)benzaldehyde with phenylacetylene to form 1-benzoyl-2-phenylnaphthalene can also be efficiently promoted by supported gold nanoparticles.[153] CeO$_2$, TiO$_2$, Fe$_2$O$_3$ and C were used successfully as supports of the gold nanoparticles for this benzannulation reaction.[153] Concerning the differences between homogeneous and heterogeneous catalysis, it is worth commenting that although the use of supported gold catalysts also gives rise with high selectivity (above 82%, reaching in some cases 95%) to the same regioisomer formed using AuCl$_3$, the presence of other benzannulation regioisomers were also detected.[153] Attempts to isolate these minor regioisomers by chromatography were, however, unsuccessful due to their low yields.[153]

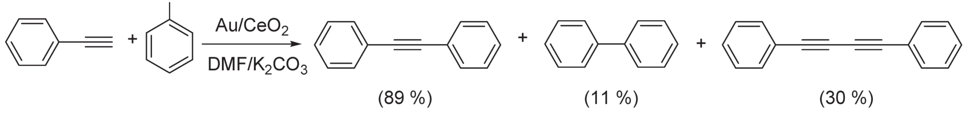
The advantage of using supported gold as catalyst to carry out the benzannulation is illustrated by the fact that the solid can be recovered and reused with only a small decrease in activity. In this way the overall productivity, measured as turnover number (mol of product formed per mol of Au) of 33 reported for AuCl$_3$ in homogeneous catalysis[148] can be raised to 125 using Au/CeO$_2$.[153] No leaching of the gold nanoparticles from the support to the solution under the reactions conditions was observed.[153] A study of the influence of the particle size on the catalytic activity of Au/TiO$_2$ shows a clear dependence on the particle size: the larger the particle size, the smaller the catalytic activity of supported gold. Gold nanoparticles above 8 nm were found to be inactive to promote benzannulation.[153]

## VII. C–C coupling reactions

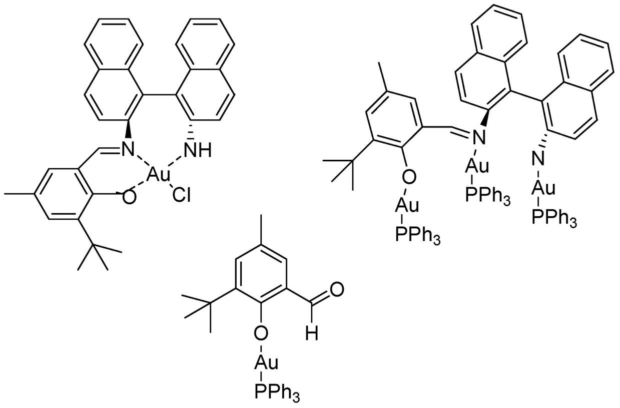
Gold complexes as homogeneous catalysts have been found to play the same role as those of Pd for the Suzuki–Miyaura coupling.[154] Considering that Au(I) has the same d$^{10}$ electronic configuration as Cu(I) and that it is known that Au(I) readily interacts with C$\equiv$C triple bonds, Corma and co-workers anticipated that gold nanoparticles should also catalyze the copper-free Sonogashira cross-coupling reaction provided that they containing a population of Au(I) atoms.[155] This is the case of Au/CeO$_2$ a solid in which XPS and CO titration have established the simultaneous presence of a population of gold(I) and gold(III) together with gold(0).[156] Thus, it could be anticipated that Au/CeO$_2$ should catalyze the Sonogashira cross-coupling of aryl halides and terminal alkynes. In fact it was found that Au/CeO$_2$ is able to catalyze the coupling of iodobenzene and phenylacetylene (2 equivalents) in DMF at 150 °C using carbonate as base giving 89% of 1,2-diphenylacetylene, together with a 11% of biphenyl arising from iodobenzene homocoupling (Scheme 21).[155] Interestingly, gold leaching was not observed and after washing with acetonitrile, the Au/CeO$_2$ catalyst could be reused, maintaining its activity and selectivity.

By determining the activity of colloidal gold with 5 nm particle size for the same process and observing a significantly reduced conversion of 6% with 46% selectivity towards Sonogashira coupling, it was concluded that the activity for the copper-free Sonogashira cross-coupling of Au(0) atoms predominantly present in unsupported reduced colloidal gold nanoparticles is much lower than those of oxidized Au(III) and Au(I) species.[155] This conclusion was also supported by preparing well-characterized Au(I) and Au(III) complexes of Schiff bases (Scheme 22) and using them as models for the individual activity and selectivity of Au(I) and Au(III) atoms present in the nanoparticles.[155] It has to be noted, however, that agglomeration of colloidal gold is an adverse phenomenon disfavouring the activity of unsupported nanoparticles.

In the case of Au(I) complexes moderate to excellent yields with very high selectivity (99%) for the Sonogashira reaction were obtained. Much lower selectivity was observed for Au(III) complexes that promote preferentially the homocoupling of

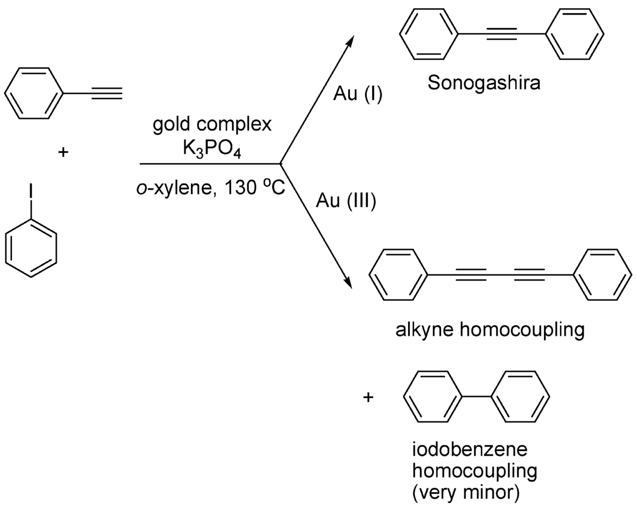


**Scheme 21** Sonogashira cross-coupling promoted by ceria supported gold nanoparticles.



Scheme 22 Structure of Au(III) and Au(I) complexes used to test the specific activity for the Sonogashira coupling.

alkyne giving a 10% of 1,4-diphenylbutadiyne.[155] The results obtained are illustrated in Scheme 23. Thus, it was concluded that the Au(I) atoms present in gold nanoparticles are the most suitable sites to promote Sonogashira, while Au(III) do not catalyze cross-coupling, but undesired alkyne homocoupling although at a much lower rate than Au(I) catalyzes the Sonogashira cross-coupling. This conclusion can serve to the rational design of a more active and selective generation of supported gold catalyst in which sites alike to Au(I) complexes should be created while higher oxidation states should be avoided.



Scheme 23 Specific reactivity of Au(I) and Au(III) complexes for the Sonogahisra coupling.

For comparison, Pd(II) and Pd(0) complexes were tested under similar conditions giving similar results to that of the gold analogs, with also a very high selectivity towards the Sonogashira product.

## VIII. Oxidation reactions

There is an important move in chemistry towards the development of novel environmentally-friendly and sustainable processes.[157,158] Oxidation using transition metals or halooxo acids is regarded as the paradigmatic example of unsatisfactory processes that need immediate replacement.[159,160] Oxygen should be the oxidizing reagent of preference in as many reactions as possible. In the development of oxidations by oxygen, gold nanoparticles are the key catalysts and it can be anticipated that in the near future oxygen oxidations will be associated to the use of gold catalysts.[161] The current situation presents a scenario in which aerobic alcohol oxidation is considerably more advanced than oxidation of hydrocarbons that awaits for breakthroughs to achieve a similar level of catalyst efficiency as alcohols.

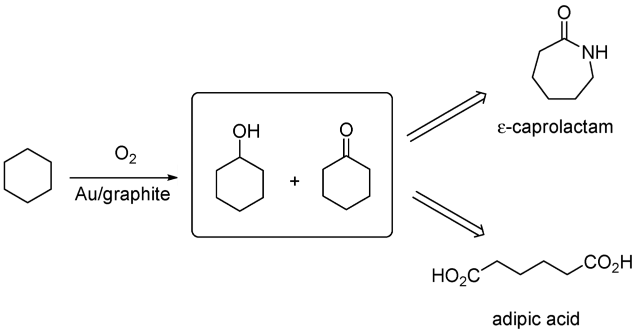
### Oxidation of alkanes

Due to the lack of coordination of hydrocarbons with Lewis acid sites, gold catalysts are inefficient to promote hydrocarbon oxidation by oxygen. Thus, the mechanism generally accepted for carbon monoxide or alcohol oxidation starts with the formation of an adduct that cannot occur in the case of hydrocarbons.[6,162] Nevertheless, there are some recent developments that can serve to foresee that also gold catalysts can also be useful for oxidation of hydrocarbons by oxygen. The strategies are based on the use of radical initiators to trigger a controlled radical mediated oxygenation or use hydrogen to produce gold promoted hydrogen peroxide formation. Thus, considering the importance of alkane oxidation, much effort will be devoted in this field trying to optimize gold catalysts, promoters and conditions. Obviously when working with mixtures of hydrocarbons and oxygen, special precautions have to be taken to minimize explosion risks.

Oxidation of cyclohexane and cyclododecane by oxygen to a mixture of cycloalkanol and cycloalkanone is a reaction of large industrial importance that is currently carried out with cobalt naphthanoate in acetic acid.[163] Operating at temperatures about 150 °C, selectivities in the range 70–90% at 5% conversion are typically achieved. Cycloalkanones are the precursors of the corresponding ω-lactams and for adipic acid, the monomers of Nylons.[163] Gold on graphite has been found to promote the oxygenation of cyclohexane with selectivity over 90% at conversions about 1% (Scheme 24).[164] This performance being comparable to that of analogous catalysts based on platinum and palladium. Other catalysts that have been tested are Au/ZSM-5 and gold supported on mesoporous MCM-41.[165–167]

### Oxidation of olefins

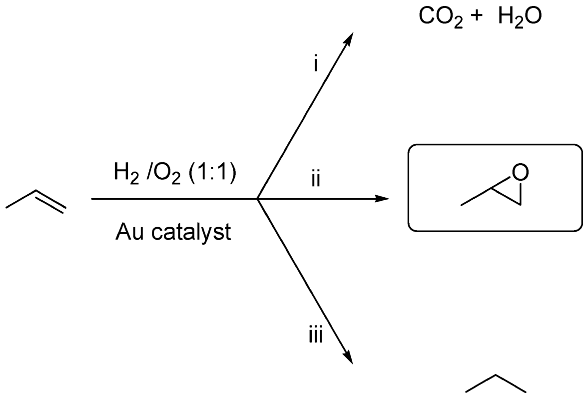
Ethene and propene are primary products for the chemical industry from which derive a large number of bulk chemicals.[163]



Scheme 24 Oxidation of cyclohexane to a mixture of equal proportions of cyclohexanol and cyclohexanone.

Epoxidation to their corresponding oxiranes is a process of huge industrial importance. In the case of ethylene, epoxidation can be selectively accomplished by oxygen using silver nanoparticles.[163] Much less satisfactory is the case of propylene epoxidation, since currently there is no suitable catalyst to carry out this oxidation by oxygen and the industrial process to obtain this propylene oxide is based on the use of organic hydroperoxides.[163] The silver catalyst used for the synthesis of ethylene oxide fails to promote the formation of propylene oxide due to the reactivity at the allylic methyl group.

A key observation in this area was the fact that in the presence of hydrogen supported gold nanoparticles are highly selective (99%) for propylene oxide at conversions around 1%.[168] Industrial application would be possible starting from 90% selectivity towards propylene oxide at propylene conversions of 10%. Thus, it seems that a gold based epoxidation catalyst could be feasible. The main limitations are maintenance of a high selectivity at conversions above 1% and avoidance of catalyst deactivation. The main reactions competing with epoxidation are C═C hydrogenation and full oxidation (Scheme 25).

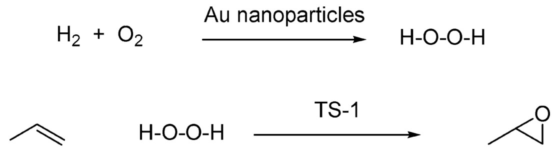


**Scheme 25** Reactions competing with propylene epoxidation.

All the gold catalysts that exhibit activity for propylene epoxidation contain titania as support, the most active up to now being Au/TS-1.[169,170] TS-1 is a silicalite containing isolated titanium atoms replacing isomorphically framework silicon atoms. TS-1 is a well known (ep)oxidation catalyst using hydrogen peroxide as reagent.[171] Using Au/TS-1 selectivities about 80% to propylene oxide have been obtained at conversions around 5% working at temperatures between 150–200 °C.[169,170]

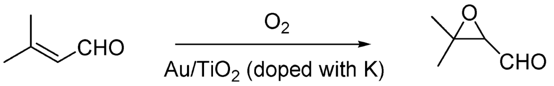
Concerning silica-supported gold catalysts several parameters including gold particle size, gold loading, titanium coordination sphere, site isolation, hydrophobicity and pore size affect the catalytic activity.[168–170,172–174] The presence of additives, particularly amines, also affect the selectivity of the epoxide.

The most likely epoxidation mechanism for Au/TS-1 is based on the fact that gold nanoparticles are able to promote the formation of hydrogen peroxide from hydrogen and oxygen and that TS-1 is an efficient epoxidation catalyst in combination with hydrogen peroxide.[171,175–179] Scheme 26 summarizes the coupling of *in situ* hydrogen peroxide formation and epoxidation of propylene. There is no doubt that a considerable amount of work will be aimed in the near future to optimization of gold catalysts for propylene epoxidation.



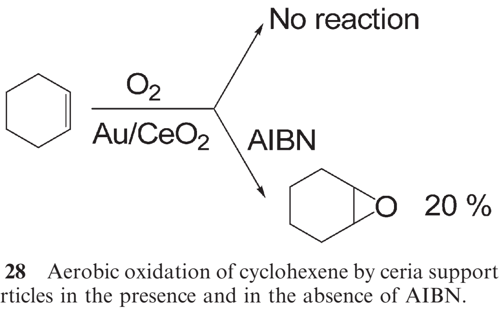
**Scheme 26** Probable mechanism for propylene epoxidation on Au/TS-1.

In a related precedent about the aerobic oxidation of alkenes, it has been reported that gold nanoparticles on titania doped with potassium is active for the aerobic epoxidation of methacrolein at 230 °C to give 2-methyl-2,3-epoxypropanal with a space time yield of 20.6 g $h^{-1}$ at 8.1% conversion (Scheme 27).[180]



**Scheme 27** Aerobic oxidation of methacrolein by a gold catalyst.

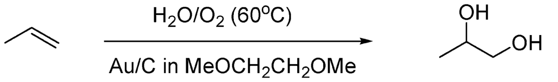
Other alkenes have also been subjected to oxidation in the presence of gold catalysts including cyclohexene, cyclooctene, styrene and stilbene.[181–184] The reaction has been tested in the gas or liquid phase using gold nanoparticles supported on active carbon, graphite, ceria or titania. It was found that gold catalysts are inactive, while addition in the feed of *tert*-butylhydroperoxide or a typical radical initiator promotes the catalytic activity of gold.[181,182] For instance, the presence of minor quantities of AIBN as radical initiator (1%) can serve to promote cyclohexene oxidation catalyzed by supported gold nanoparticles (Scheme 28).[182] The product distribution included the corresponding cyclohexene epoxide (20%), together with 2-cyclohexenol (15%) and some other minor products. In the absence of these radical initiators no oxidation takes place under analogous conditions. Although the actual way in which organic hydroperoxides promotes the reaction is not understood, the fact that gold halides can trap radicals forming organometallic intermediates could play a role in the process.[185] Thus, it has been found that $AuCl_3$ traps the radicals derived from AIBN.[182] Activity could arise from the association of the radicals to the gold surface rather than acting as unselective free radical reactions. These organogold species on the surface of solid gold catalysts can act as *dormant* radicals as it has been found in related living polymerization using CuCl.[186–190] The interaction of radical with gold halides



**Scheme 28** Aerobic oxidation of cyclohexene by ceria supported gold nanoparticles in the presence and in the absence of AIBN.

and gold nanoparticles will be discussed in more detail in section X. In general, the process is, however, unselective and together with some epoxide other products arising from oxidation at the allylic position occur when available.

Hydroxylation of olefins is another oxidation reaction that is useful in the preparation of bulk chemicals from primary alkenes and also in general organic synthesis. Actually connected with propylene epoxidation, one of the main products derived from propylene epoxide is the corresponding propylene glycol. A catalyst consisting of gold supported on granular active carbon has been used for the preparation of diols from simple olefins by a tandem process of electrophilic addition and oxidation.[191] The catalyst is prepared by $HAuCl_4$ impregnation of active carbon followed by drying and calcination under hydrogen.[191] In this process propene is reacted at 60 °C with $H_2O$ and $O_2$ in the presence of the catalysts in acidic ethylene glycol dimethyl ether to give 29% of propylene glycol at 62% conversion (Scheme 29).[191]



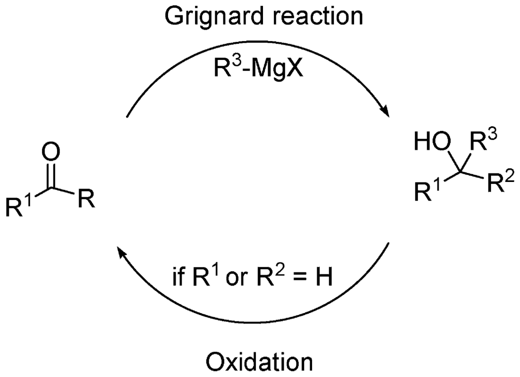
**Scheme 29** Preparation of propanediol from propene catalyzed by carbon supported gold nanoparticles.

## Oxidation of alcohols

Alcohol oxidation to carbonylic or carboxylic compounds is one of the key transformations in organic chemistry.[192] Besides the large availability of alcohols and the interest in forming specific desired carbonylic compounds, the importance of alcohol oxidation derives largely from the central role played by this functional group transformation in organic synthesis. One simple strategy in organic synthesis for preparing organic molecules is based on classical C–C bond forming reactions using Grignard and related organometallic nucleophilic reagents. In this route, when forming a new C–C bond, a starting carbonyl compound gives rise to alcohols with a different skeleton. To close the loop allowing the iterative use of Grignard reagents to construct the desired target molecule, there is a need to perform subsequently the oxidation of the alcohol into the carbonylic compound (Scheme 30).

In spite of the importance of the alcohol oxidation, the classical alcohol oxidation methods described in textbooks are far from being environmentally benign and significant amounts of undesirable by-products are formed.[192] None of the conventional, general alcohol oxidation methods comply the principles of *green chemistry* mainly because they use noxious chemicals, generate undesirable by-products and make use of stoichiometric reactions instead of catalytic transformation.[159,160,193,194] Typical oxidizing reagents are transition metal oxo compounds, halogenated compounds or sulfur oxides.[159,160,193,194]

From the environmental point of view, reactions based on the use of oxygen as oxidizing reagent forming water as by-product will be the definite preferable process.[193] Moreover, since a mixture of flammable alcohols with oxygen at high pressure and temperature may be explosive, the ideal process should be performed with air at atmospheric pressure and moderate temperatures. In addition the aerobic oxidation process should be of general use regardless of the aliphatic, aromatic, primary or secondary structure of the alcohol. Recent developments in gold nanoparticles are close to reach a general catalyst that can carry out the aerobic alcohol oxidation at atmospheric pressure either in solventless conditions or in water or organic solvents. Thus, supported gold nanoparticles have been found to be extremely active catalysts to effect the aerobic oxidation of benzylic, allylic and aliphatic primary and secondary alcohols. It is worth noting that the aerobic oxidation in organic solvents can proceed in the absence of bases.

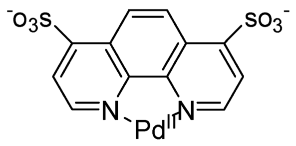


**Scheme 30** Iterative loop used on organic synthesis based on Grignard-type C–C bond forming reactions to obtain compounds with the desired skeleton.

Since Haruta showed that gold nanoparticles are highly active for the low-temperature CO oxidation,[31,103] there was a logical move to widen the scope of gold nanoparticles in oxidation reactions, alcohols being an obvious target. Parallel to the development in gold catalysis, there have been simultaneously important advances in alcohol oxidation using other noble metal, particularly Pt and Pd, either using complexes as homogeneous catalysts or as supported heterogeneous catalysts. The use of noble metals as catalysts for alcohol oxidation has been reviewed recently by Mallat and Baiker.[162] To understand the prevalent position of gold catalysis for alcohol oxidation, it is convenient to comment briefly the most active oxidation catalysts reported for metals other than gold.

In this regard, Sheldon and co-workers reported the use of a palladium bathophenanthroline sulfonate as a soluble, but recoverable catalyst to effect alcohol oxidation in aqueous medium (Scheme 31).[195] The effective catalyst has, however, as drawbacks the low solubility of many alcohols in water and the need for oxygen pressure.

More related to the subject of our review, Mizuno and co-workers reported that ruthenium oxide supported on γ-$Al_2O_3$ was active to promote aerobic alcohol oxidation.[196,197] The



**Scheme 31** A water-soluble palladium complex that can be used as recoverable catalyst for alcohol oxidation by oxygen in aqueous suspensions.

system is active at atmospheric pressure but is sensitive to moisture. The benchmark in heterogeneous catalysts for the aerobic oxidation of alcohols has been the one reported by Kaneda and coworkers based on palladium nanoparticles supported on hydroxyapatite (Pd/HAP).[198] For the oxidation of 1-phenylethanol at atmospheric $O_2$ pressure turnover numbers (TON) as high as 236 000 mol alcohol (mol of Pd)$^{-1}$ with an excellent turnover frequency (TOF) of 9800 h$^{-1}$ were obtained.

A systematic comparison of the activity of gold nanoparticles with respect to that of palladium supported on hydroxyapatite has shown that although palladium nanoparticles exhibits higher turnover frequency than gold at 160 °C, some supported gold catalysts such as $Au/CeO_2$ become more active than palladium at 120 °C.[199] This reflects the higher activation barrier for alcohol oxidation using palladium catalysts as compared to those of gold. Besides that, for several alcohols, both TON and TOF were higher with $Au/CeO_2$ than with Pd/HAP.

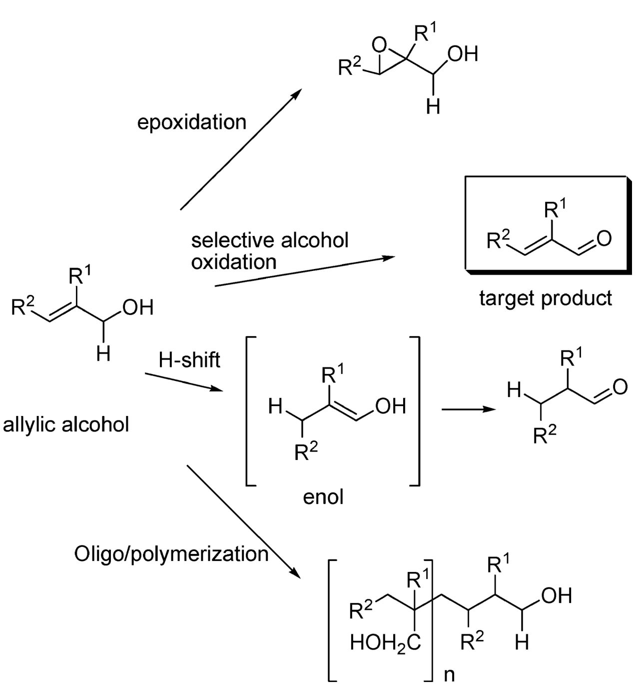
Hutchings and coworkers have reported the preparation of core–shell Au (core)–palladium (shell) exhibiting an extraordinary activity for the aerobic oxidation of benzyl alcohol and primary alcohols to aldehydes, reaching turnover frequencies up to 270 000 turnovers h$^{-1}$.[200] The presence of a gold core improves the overall selectivity of the palladium nanocrystals for the process. However, for many other alcohols TOFs are lower for the Pd–Au catalyst than for $Au/CeO_2$.

In general, it can be said that, even though under certain conditions supported gold nanoparticles are less active than palladium, gold is a more general catalyst since it promotes the selective oxidation of the OH functional group for a wider range of alcohols, including those on which palladium is highly active, and always exhibits higher selectivity.[199] Thus, supported gold nanoparticles appear as the first choice in organic synthesis to effect oxidation of multifunctional alcohols.

The difference in selectivity between palladium and gold is clearly exemplified in the oxidation of allylic alcohols.[201,202] In this case the presence of a C=C double bond in the structure makes possible the occurrence of several possible processes including oligo/polymerization of the C=C double bond, C=C double bond isomerization, C=C double bond oxidation, *etc.* (Scheme 32). It was found that gold nanoparticles cleanly promote the selective hydroxyl oxidation to the corresponding conjugated carbonylic compound without affecting to the C=C double bond. This is in contrast to the behaviour of palladium supported on hydroxyapatite or even core–shell Au–Pd nanoparticles.[202] Table 2 illustrates the different catalytic behaviour among this series of catalysts.

One important issue when testing a heterogeneous catalyst is to determine its reusability. We have found that for the solventless alcohol oxidation, once the reaction has finished and the solid is recovered, it can be reused with only a marginal decrease in its catalytic activity by washing it with copious basic water (pH 10) and drying in an oven for 2 h. The rationale behind basic washings is that carboxylic acids act as poisons of supported gold nanoparticles including $Au/CeO_2$.[203]

In addition to solventless or the use of aqueous media, the practicality of the gold catalyzed aerobic oxidation of alcohol depends to a large extent on the possibility to effect this reaction in organic solvents. In many cases, complex alcohols are solids of high melting point and totally water insoluble. In addition, the amount of alcohol may be limited and there is not possibility to perform the oxidation in the absence of solvents. For these reasons, the use of organic solvents to carry out the oxidation is a very common situation, particularly in organic synthesis. Other alternatives, such as the use of water as solvent and addition of a surfactant to increase alcohol solubility, have also been reported.[162]

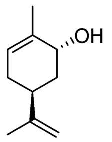


**Scheme 32** Possible processes competing with selective hydroxyl oxidation in allylic alcohols.

The aerobic oxidation using gold supported on nanoparticulate ceria ($Au/CeO_2$) has been tested within a series of organic solvents including ethanol, ethyl acetate, α,α,α-trifluorotoluene and toluene.[24] Most of the solvents tested were inappropriate and alcohol oxidation stops at low conversions. Toluene and α,α,α-trifluoromethylbenzene were found to be very convenient solvents and alcohols were totally converted in the absence of base. The need of strong basic conditions is a common feature in aqueous media with most supported gold catalysts and in the case of primary alcohols these conditions lead to the formation of carboxylates rather than aldehydes.[162] The use of non-aqueous organic solvents in the absence of base leads, however, to the preferential formation of aldehydes. As a matter of fact, aerobic oxidation of aromatic aldehydes to carboxylic acids can also be carried out by $Au/CeO_2$, that exhibits superior activity than other reported catalysts such as Pt/C/Bi materials.[204] Prati and Rossi have also reported the use of active carbon supported gold to carry out aldehydes oxidation in water with higher activity than analogous platinum catalysts.[205]

Following the lead on low-temperature CO oxidation, a systematic study of the influence of particle size and the nature of the support on aerobic alcohol oxidation has been reported for the oxidation of cinnamyl alcohol.[24] Using P-25 titania as

**Table 2** Comparison of the catalytic performance of gold and palladium catalysts for the oxidation of allylic alcohols to the corresponding α,β-unsaturated carbonyl compounds. Pd/(OH)-apatite: palladium nanoparticles supported on hydroxyapatite, Au–Pd/$CeO_2$ and Au–Pd/$TiO_2$ core (gold)–shell (palladium) nanoparticles supported on ceria or titania. Sel. and Isom. refer to the selectivity to α,β-unsaturated ketone and saturated ketone, respectively

| Substrate (S) | Catalyst (M) | $10^4$(M/S) | Conv. (%) | Sel. (%) | Isom. (%) |
|---|---|---|---|---|---|
| 1-Octen-3-ol | Au/$CeO_2$ | 1 | >99 | 90 | 0 |
| | Pd/(OH)-apatite | 1 | >99 | 49 | 49 |
| | Au–Pd/$CeO_2$ | 1 | >99 | 26 | 73 |
| | Au–Pd/$TiO_2$ | 1 | >99 | 40 | 54 |
| | Au/$TiO_2$ | 10 | >99 | 93 | 0 |
| *trans*-Carveol<br> | Au/$CeO_2$ | 5 | 91 | 99 | 0 |
| | Pd/(OH)-apatite | 5 | 98 | 40 | 0 |
| | Au–Pd/$TiO_2$ | 5 | 79 | 47 | 0 |
| 3-Octen-2-ol | Au/$CeO_2$ | 2 | 96 | 91 | 0 |
| | Pd/(OH)-apatite | 2 | 98 | 19 | 45 |
| | Au–Pd/$CeO_2$ | 2 | 99 | 38 | 32 |
| | Au–Pd/$TiO_2$ | 2 | 99 | 35 | 5 |
| 2-Octen-1-ol | Au/$CeO_2$ | 125 | 90 | 91 | 0 |
| | Pd/(OH)-apatite | 125 | 54 | 87 | 0 |
| | Au–Pd/$CeO_2$ | 125 | 95 | 73 | 0 |
| | Au–Pd/$TiO_2$ | 125 | 17 | 60 | 0 |
| Cinnamyl alcohol | Au/$CeO_2$ | 20 | 99 | 99 | 0 |
| | Pd/(OH)-apatite | 20 | 74 | 63 | 0 |
| | Au–Pd/$CeO_2$ | 20 | 99 | 93 | 0 |
| | Au–Pd/$TiO_2$ | 20 | 95 | 70 | 0 |

support (average particle size of $TiO_2$ 35 nm), a linear relationship between the number of gold atoms at the external surface of the gold crystallites and their catalytic activity has been established for a consistent series of Au/$TiO_2$ catalysts having constant gold loading and a nanoparticle size in the range 5–25 nm (Fig. 5). This finding establishes that the aerobic alcohol oxidation on gold is a structure insensitive reaction in where, the only parameter controlling the catalytic activity is the total number of external gold atoms. Similar conclusions were reached using *naked* gold nanoparticles in basic aqueous media for the oxidation of glucose.[206]

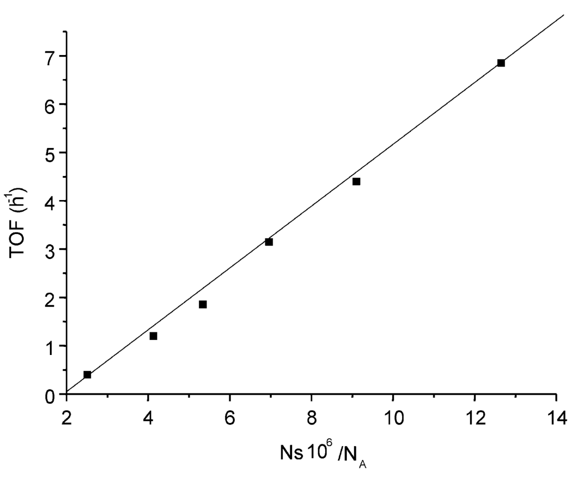
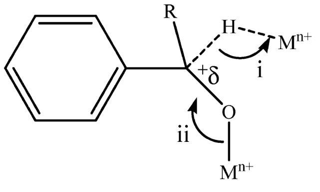


**Fig. 5** TOF values for the aerobic oxidation of cinnamyl alcohol *vs.* the number of external gold atoms ($N_S$) present in Au/$TiO_2$ catalysts with different particle size (taken from ref. 24).

Concerning the influence of the support on the catalytic activity for the aerobic oxidation, it was also found that nanoparticulate $CeO_2$ renders the most active catalyst compared to titania P25 or activated carbon. It has been proposed that the reasons for this better performance of ceria nanoparticles as support derive from the lack of stoichiometry of the support and the presence of oxygen lattice defects that can be the sites where molecular dioxygen can absorb on the support. It was observed, on the other hand that the preparation procedure including reduction by 1-phenylethanol at low (70 °C) or high temperature (160 °C), reduction by a hydrogen flow at 300 °C or reduction by thermal treatment under air flow at temperatures between 100 and 400 °C does not influence at all the catalytic activity of the resulting Au/np$CeO_2$ catalyst for the aerobic oxidation of alcohol.[24] Gold loading on the support is, however, a parameter that controls the activity of the catalyst, those materials having lower loading being more active. This fact has been interpreted as derived from the cooperative effect on the catalyst of the support surface on the reaction. Thus, if the support surface is largely covered by gold nanoparticles the catalyst activity decreases and eventually it can become inactive.[24]

This view has been recently challenged by the claim that gold nanoparticles embedded in a polystyrene matrix is more active than Au/$CeO_2$.[71] The polymeric backbone is a copolymer of three styrene derivatives. After incorporation of the gold nanoparticles, the polymer is crosslinked in a way that gold nanoparticles are permanently retained in the entangled polymer.[71] This polymer containing gold is remarkable because it can carry out alcohol oxidation at room temperature and atmospheric pressure and can be recycled indefinitely.[71] However, comparison of the catalytic activity of Au/$CeO_2$ and Au in crosslinked styrene has not been made under exactly the same conditions and it would be of interest to establish the actual activity rank and generality between Au/$CeO_2$ and Au/polystyrene. Whatever is the most active catalyst, what is clear at the present stage of development in the field is that the influence of the nature of the support and its role in the reaction mechanism is one of the less understood aspects. Clarification of the multiple roles of the gold support could eventually lead to more active and selective catalysts.

With respect to aerobic alcohol oxidation mechanism there is some evidence based on deuterium labelling and the influence of the electron donating or withdrawing ability of substituents on benzyl alcohols, which indicates that the rate limiting step is the hydride transfer from the carbon bonded to the OH group to the metal.[24] This hydride transfer is concerted but asynchronous with the formation of the C=O double bond. The proposed transition state is indicated in Scheme 33.[24] Thus, water formation occurs in subsequent and independent steps unrelated to the carbonyl formation. Evidence for this has been obtained by IR spectroscopy in which, in the absence of oxygen, appearance of a carbonyl group and a metal–hydride bond is observed.[47] Subsequently, upon oxygen admission into the cell, the metal–hydride disappears and water is formed.[47] Actually the details of how the metal hydride is transformed into water and a free metal atom is a key point that deserves a detailed study by its own since this process can also be useful in apparently unrelated processes such as the synthesis of peroxides or water splitting for energy production.

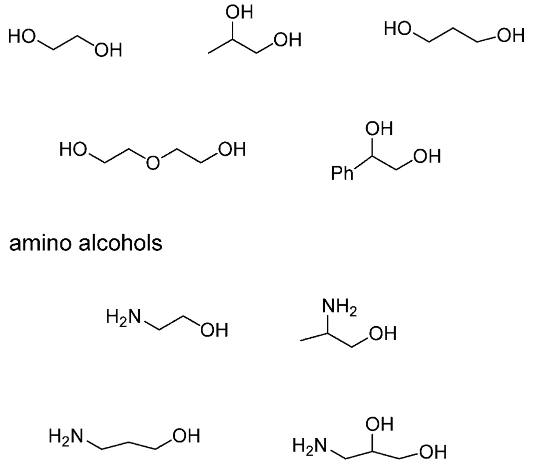


**Scheme 33** Transition state and bond changes proposed for the aerobic oxidation of benzylic alcohols: i) hydride transfer; ii) C=O double bond formation; i progresses earlier than ii.

In summary, it appears that Au/np$CeO_2$ is a quite general and reusable catalyst for the oxidation of primary and secondary, aliphatic and benzylic alcohols in organic solvents to the corresponding carbonyl compounds with high selectivity even in the presence of other functional groups working at atmospheric pressure of air. The most important present limitation appears to be the low yield (currently 45%) for the oxidation of primary alcohols to aldehydes in organic solvents. It has to be reminded that in aqueous solvents, high yields to the formation of carboxylic acids from primary alcohols can be obtained in the presence of a base. Obviously, higher activity and, therefore, lower molar ratio of gold in the catalyst is a continuous task that will attract future work.

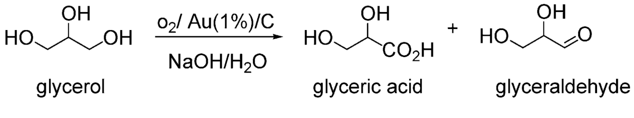
**Oxidation of diols and polyfunctional alcohols**

Most of the early work on the aerobic oxidation of diols and polyols was performed by the groups of Hutchings, Rossi and Luca.[68,206–224] Selective oxidation of these polyols is relevant in the context of sustainable chemistry based on the use of renewable feedstocks and particularly those derived from carbohydrates and fats.[225] As an example, the implementation of biodiesel will lead to an overproduction of glycerine that will make attractive to develop new processes based on this triol.[68,207–212] Also the selective oxidation of glucose can be a process of large industrial relevance in the near future. The structure of diols and amino alcohols that can be selectively oxidized in aqueous medium using supported gold nanoparticles as catalyst is shown in Scheme 34.



**Scheme 34** Structure of polyfunctional alcohols that can be selectively oxidized by oxygen using supported gold catalysts.

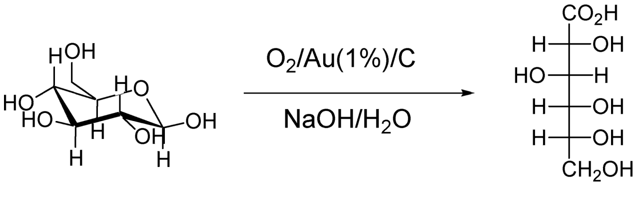
The common feature of these selective oxidations is that they are conducted in water, due to the high solubility of the substrates, under strong basic conditions, frequently using equimolar quantities of NaOH. In this way, polyhydroxylic alcohols are often selectively transformed into monocarboxylates by oxidation of the primary alcohol. Under these conditions, gold nanoparticles adsorbed on activated carbons appear to be a simple and general catalyst. As mentioned earlier, gold catalysts supported on carbon are notably inactive in the absence of bases. Thus, Hutchings and co-workers found that glycerol is transformed to glyceric acid with complete selectivity at high conversions using gold supported on active carbon or graphite (Scheme 35).[211,212] Analogous catalysts based on platinum were found much less selective since under the same conditions a significant amount of glyceraldehyde was obtained in addition of glyceric acid.[211,214] Importantly, the need of a high NaOH/glycerol ratio was



**Scheme 35** Aerobic oxidation of glycerol in basic aqueous medium. Using supported gold as catalyst, the only product obtained is glyceric acid.

established. It is clear that it will be desirable to understand the role of the base in this process, since the large excess of base represents a limitation of this process.

Likewise, D-glucose is oxidized to D-gluconic acid with total selectivity at about 100 °C in aqueous solution in the presence of gold on carbon catalyst (Scheme 36). Oxygen pressure (up to about 3 atm) is needed to carry out this oxidation.[215] No isomerization of glucose to fructose was observed during the reaction. Comparison of the performance of gold on carbon with respect to commercial palladium and platinum-derived catalysts shows that gold exhibits higher activity and the reaction even occurs at pH values as low as 2.5 units. Moreover, upon recycling, gold is more stable toward deactivation, although this also depends on the operative pH.[215]



**Scheme 36** Selective oxidation of D-glucose to D-gluconic acid by oxygen catalysed by carbon supported gold.

β-Amino alcohols also react with oxygen in basic aqueous media to form β-amino acids.[226] This chemoselectivity is also remarkable since primary amines can be easily oxidized, generally in an unselective way, to a variety of azo, azoxy, nitroso and nitro compounds.[192] Actually, selective oxidation of amines will constitute a logical evolution of supported gold catalysts that deserves a detailed study by its own.

Considering the expected growth of polyols as feedstocks in large scale industrial processes, the greenness of using water as solvent, the unique activity of supported gold catalysts and the remarkable selectivity of the process, it can be easily anticipated that the importance of this type of aerobic oxidations will experience a considerable increase in the next years.

### Heteroatom oxidation

Apart from C–H oxidation, Si–H oxidation is also of considerable interest. Gold nanoparticles can also promote the oxidation of trialkylsilanes to silanols that eventually condense forming siloxanes. (Scheme 37). Nanometric entities having discrete, observable structures such as elongated wires, tubes and coils having lengths about 100 nm and diameters from 2 to 200 nm can be prepared by silane oxidation in a two-solvent system comprising water and a polar organic solvent in the presence of gold.[227]

**Scheme 37** Silane oxidation catalyzed by gold nanoparticles.

### Low-temperature CO oxidation

The surge of gold as catalysts derived from the seminal work of Haruta who showed that gold nanoparticles are extremely active catalysts for the low-temperature oxidation of CO.[30,31,70,103,161] Haruta showed that the catalytic activity was directly related to the particle size, decreasing as the particle size increases.[31,37,42] Since these pioneering works, the low-temperature CO oxidation has remained as the favourite reaction to test the activity of various catalysts and the influence of supports and preparation procedure. Almost virtually all the supported gold catalysts that have been prepared have been tested for this reaction. Haruta established that gold nanoparticles exhibit high activity when supported on some metal oxides such as $TiO_2$, α-$Fe_2O_3$ and $Co_3O_4$.[31] A recent report by Friend focused exclusively on the low-temperature CO oxidation by heterogeneous gold catalysts covers extensively the new developments in this area and the reader is referred to this review for an in-depth coverage in this field.[228]

It has been shown how the catalytic activity of supported gold nanoparticles is strongly influenced by gold particle size, synthesis method, pre-treatment conditions and the nature of the support.[14,15,228–230]

Considering that the catalytic activity of gold derives from the nanometric dimensions and the structure of the nanoparticles, it is not surprising that the preparation procedure plays a significant role in its catalytic activity. For the low-temperature CO oxidation, preparation of the gold nanoparticles on alumina by deposition/precipitation ($AuCl_3$ as precursor) or by chemical vapor deposition (using an organogold complex as precursor) has been compared.[231] Chemical vapour deposition gives reproducible samples with high metal dispersion and average particle size lower than 5 nm. Due to the higher dispersion and smaller particle size, the activity of samples prepared by chemical vapour deposition is higher than those prepared by the more conventional deposition–precipitation procedure where samples contain large crystallites ($d_{Au} > 7$ nm).[231] These large crystals are believed to originate from the occlusion of gold complex solutions into the alumina mesopores. An improvement of the deposition–precipitation method to avoid the formation of these large crystallites consisting on the prealkalination of the alumina surface has been proposed. In addition a mild hydrogenation pre-treatment is effective in eliminating the induction period characteristic of the freshly prepared catalysts. Apparently reduction acts to remove poisonous chloride from the gold crystallites.[231]

Concerning the influence of the supports, metal oxides have been differentiated between those able to provide oxygen (reducible) and those not able to do so because of their inability to adsorb oxygen.[14,15,229,230] In the case of reducible oxides supports, oxygen is thought to adsorb on the support and successively interact with the CO adsorbed on the gold particles, for this reason the activity is extremely dependent on the type of structure of the metal–support interface. Thus, it has been presented that gold clusters supported on nanocrystalline and mesostructured nanocrystalline $CeO_2$ or $Y_2O_3$ is much more active for oxidations than gold clusters on conventional $CeO_2$ or $Y_2O_3$ supports.[44,156,204,232] More specifically, gold supported on nanocrystalline $CeO_2$ exhibits high activity for CO oxidation and the support supplies reactive oxygen (in the form of superoxide and peroxide species) to the active gold sites.[233]

The interface between metallic gold nanoparticles and the support appears to be critical for high CO oxidation activity.[14,15,230] Time-resolved XANES spectra have shown the presence of cationic gold clusters in the $Au/CeO_2$ catalyst, which were stable during CO oxidation.[156] The presence of $Au^+$ and $Au^{3+}$ species has also been evidenced by XPS analysis.[44] Several authors suggested the crucial role of oxidized gold species, or even the cooperative role of metallic and oxidized gold species for the low-temperature CO oxidation, while others propose only metallic gold as the active species.[228]

CO has in IR spectrum a very characteristic stretching vibration band in a region that is not overlapped or obscured by other bands, For this reason, FT-IR spectroscopy has also been one of the favourite techniques to characterize the active species in supported gold nanoparticles for low-temperature CO oxidation.[39,49–53,234–236] Due to the rapid reduction at room temperature of ionic gold in contact with CO, even in the presence of oxygen, the characterization of the catalyst has to be carried out by freezing the reaction in liquid $N_2$ before analyzing the nature of gold species using CO as a probe.[53] Otherwise, the results will be disguised and CO will not report on the real catalytic species.

The nature of the gold catalyst and the pre-treatment strongly influences the number and wavenumber of the CO stretching bands appearing in the FT-IR spectra. Recording the FT-IR spectra in the presence of CO at liquid $N_2$ temperature, the low frequency band at 2102 $\text{cm}^1$ was assigned to CO adsorbed on metallic gold species. In addition, the $Au/CeO_2$ catalyst exhibits in the high frequency region of the IR spectra of CO adsorption two strong bands at 2154 and 2139 $\text{cm}^{-1}$. The 2154 $\text{cm}^{-1}$ IR band has been tentatively assigned to $Au^+$ cations and the 2139 $\text{cm}^{-1}$ band to an oxidized $Au^{n+}$ ($n > 1$, probably $n = 3$) species in the perimeter interface with the support.[53]

What is important is that a linear relationship between the catalytic activity of the gold catalyst measured at 0 °C by the CO conversion and the population of positive gold atoms (Au(I) + Au(III)/Au(0)) on the catalyst based on the use of CO as FT-IR probe was established (Fig. 6).[53]

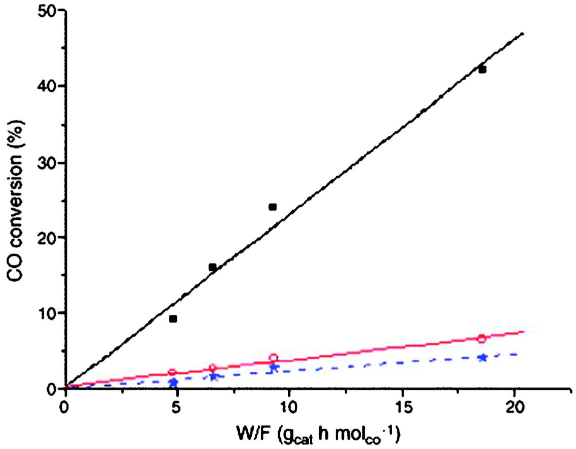


**Fig. 6** Linear relationship between the CO conversion and variation of the CO oxidation activity of the $Au/CeO_2$ catalysts: as-prepared (squares), reduced in $H_2$ at 373 K (circles), and at 573 K (stars) with contact time ($W/F = g_{cat}\ h\ mol_{CO}^{-1}$). *Reaction conditions*: 273 K; gas flow rate 50 ml $\text{min}^{-1}$; composition 2% CO–1% $O_2$–He (taken from ref. 53).

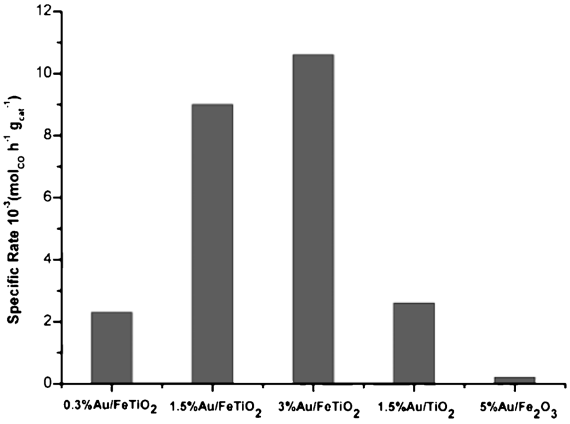


**Fig. 7** Catalytic activity for the low-temperature CO oxidation on a series of gold catalysts showing the promoting effect of iron doping on the titania support (taken from ref. 102).

One interesting issue is that the presence of promoters, *i.e.*, components in very small percentage, can increase the catalytic activity. Particularly in metal oxide catalysis the promoters can boost significantly their catalytic activity.[237,238] In this context, it has been reported that iron between 1 and 3.5 wt% enhances the catalytic activity of standard $Au/TiO_2$ (Fig. 7).[102] Actually $Au/FeTiO_2$ is apparently the most active catalyst for the low-temperature CO oxidation ever reported.[102]

It has been found that the effect of iron is to create increasing oxygen vacancies on titania, thus rendering the support more prone to physisorb oxygen. Spectroscopic studies have shown that in the presence of $O_2$ superoxide species are formed on $TiO_2$ P25, but their density is greater when the $TiO_2$ is modified with iron. Raman spectra of the sample in an $O_2$ atmosphere also show that the formation of activated oxygen species is favored on $Au/Fe–TiO_2$ relative to either $Au/TiO_2$ or $Au/Fe_2O_3$ (Fig. 8).

The reactivity of the species on the surfaces of the gold catalysts for the CO oxidation at −20 °C under atmospheric pressure was investigated *in situ* by bringing the catalysts into

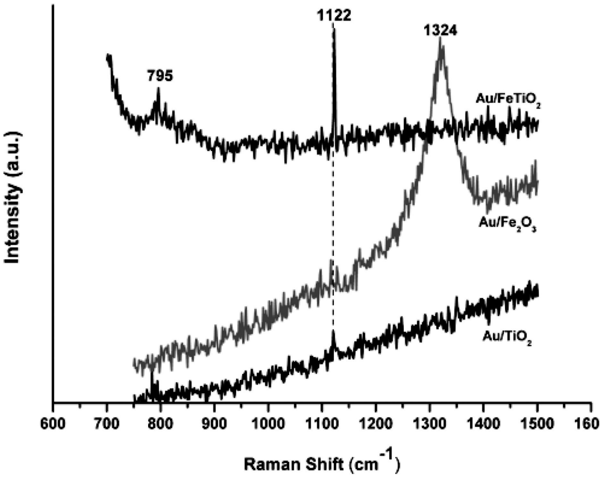


**Fig. 8** Thermally activated gold supported catalysts upon admission of $O_2$ showing the favored formation of superoxide species on the iron promoted $TiO_2$ support ($Au/FeTiO_2$) (taken from ref. 102).

contact with flowing $O_2$ to generate the superoxide intermediates prior to the introduction of a flowing CO + $O_2$ mixture. The initial spectra upon adsorption of $O_2$ onto Au/(Fe)$TiO_2$ catalyst showed a Raman band at 1122 $cm^{-1}$, assigned to $\eta^1$-superoxide species, and another band at 795 $cm^{-1}$, assigned to peroxide adsorbed species at one-electron defect sites. After contacting the sample with CO + $O_2$, the bands at 1122 and 795 $cm^{-1}$ disappeared indicating that these two species react with CO.[102] Related studies have also shown that the presence of alkali and alkaline-earth metals as well as sulfate ions promote the catalytic activity of supported gold catalysts for the low-temperature CO oxidation.[239–243] On the other hand, we have already commented that the presence of chloride in low concentration can be highly detrimental for the catalytic activity of gold, although in this regard, it has been reported that chloride could exhibit almost no detrimental effect if the iron oxide supported gold is not calcined.[244]

## IX. Selective hydrogenations

### Hydrogenation of α,β-unsaturated carbonylic compounds

Following the lead of platinum, palladium and other noble metals, hydrogenation of alkenes was among the first reaction type that was promoted by gold nanoparticles.[15,245,246] Hydrogenation of simple alkenes by gold was studied.[15,245] Also hydrogenation of α,β-unsaturated aldehydes into unsaturated alcohols has been reported.[247] In some cases, gold was used in combination with palladium to increase the reaction selectivity.[246] Concerning the industrial application of gold nanoparticles in large scale hydrogenations it has been reported that Au/Pd at a weight ratio among 0.1 and 1 can serve as catalysts for the fixed-bed reactor hydrogenation of dienes and acetylene impurities in effluents from catalytic cracking.[248]

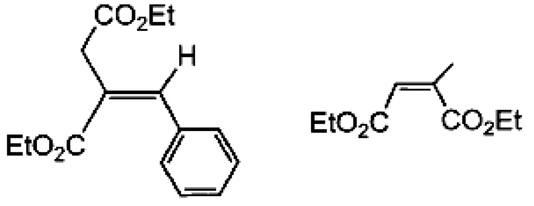
As mentioned in the introduction, one natural evolution in catalysis is to transform successful homogeneous complexes into heterogeneous catalysts.[1,249] One strategy that has not been sufficiently explored on gold catalysis is the covalent anchoring of gold complexes on large surface area supports. This contrasts with other transition metal complexes in where the transformation from homogeneous towards heterogeneous, recoverable and reusable catalyst can be easily undertaken by anchoring an appropriately functionalized complex on an organic polymer or a high-surface area support.[250] Among the inorganic supports, mesoporous silicas are the preferred hosts for this type of methodology due to their large total surface area and large pore size.[251] This methodology has already produced enantioselective hydrogenation catalysts[252] and it can be anticipated that this type of heterogenized catalysts will be developed considerably in the near future, provided that the stability of highly active gold complexes under the reaction conditions is demonstrated.

One of the common ligands that strongly bind to transition metals and also particularly to gold ions are nitrogen heterocyclic carbenes.[253] Nitrogen heterocyclic carbenes have been described as alternatives to tertiary phosphines in terms of bonding and reactivity, but metal carbene complexes are often more stable than similar metal–phosphine complexes. Au(I)–carbene complexes have been known since more than a quarter of a century,[254] but chemical reactions have been less studied than those of Au(I)–phosphine complexes. Although gold–carbene complexes are generally employed as *in situ* generated catalysts starting from the precursors, in some cases isolation and characterization of the gold(I) carbene complex has been reported.[255]

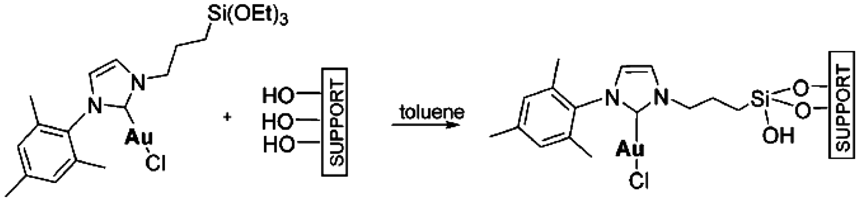
In this context, Au(I)–nitrogen heterocyclic carbenes have been anchored on MCM-41 and the resulting solid catalyst used as reusable catalysts for the selective C=C double bond hydrogenation of unsaturated esters. Scheme 38 illustrates the strategy and chemical structure of the complexes that have been reported.[252]

The most salient feature of the strategy used is that the actual complexes can be purified by recrystallization and fully characterized just before the last step consisting in the covalent anchoring to the support. Thus, this procedure leaves less space for uncertainty on the nature of the complexes and the purity of the supported catalyst can be better supported, particularly if the reaction used to anchor the complex to the support requires mild conditions to occur. This is the case of the procedure used to anchor the Au(I)–nitrogen heterocyclic carbene, whose structure prior to the anchoring was conclusively established by single-crystal XRD.[250]

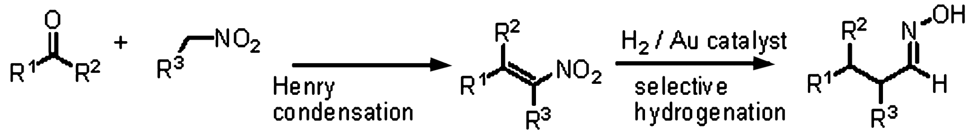
The heterogenized Au(I)–nitrogen heterocyclic carbene was used for the hydrogenation of α,β-unsaturated ethyl esters (Scheme 39). It was found that the activity as hydrogenation catalyst of the anchored complex was higher than that of the analogous complex in solution.[250] These results nicely exemplifies that the support can not only act as scaffold to immobilize and disperse the metal complexes, but, if properly designed, it can contribute in a collaborative way to the final



**Scheme 39** Structure of conjugated unsaturated esters that have been selectively hydrogenated to the corresponding saturated esters.



**Scheme 38** Structure of a Au(I) nitrogen carbene complex that has been anchored to mesoporous silica (taken from ref. 252).



**Scheme 40** Henri reaction and possible novel route to oximes.

activity and selectivity observed by stabilizing the complex. The origin of this increased activity can be preadsorption of the reactants, concentrating them near the active complex and/or preferential desorption of the products or even controlling the reaction mechanism.[1,256]

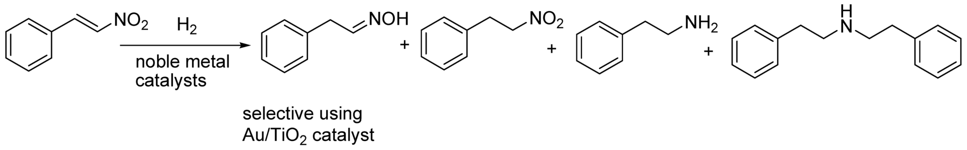
## Hydrogenation of nitro groups

The selective reduction of nitro groups in the presence of other reducible functions is a difficult process that often requires stoichiometric amounts of reducing agents or, if hydrogen is used, the addition of soluble metals.[192] It has been recently shown that gold nanoparticles supported on $TiO_2$ or $Fe_2O_3$ catalyzed the chemoselective hydrogenation of functionalized nitroarenes with $H_2$ under mild reaction conditions.[257] In this case, the support plays a determinant role avoiding the undesired hydroxylamines to accumulate during the reaction.[258] A detailed reaction mechanism of the chemoselective reduction of substituted nitroaromatics has shown that differences of reactant adsorption on different gold sites are responsible for the observed selectivity. In this case, the support also plays an important role.

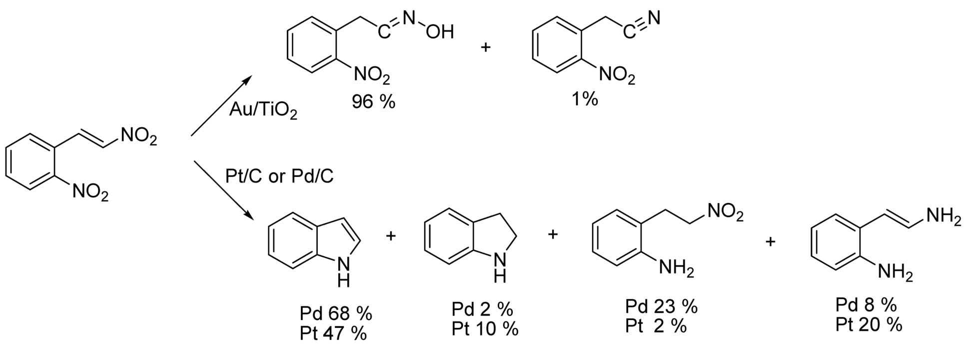
The chemoselective hydrogenation of nitro groups catalyzed by supported gold also provides a new route for the synthesis of the industrially relevant cyclohexanone oxime from 1-nitro-1-cyclohexene.[257] Oximes are valuable organic compounds that can be used in the synthesis of polymers, as fragrances, fungicides and drugs. Besides the general way to oximes consisting in the condensation of hydroxylamine with carbonylic compounds, the transformation of α,β-unsaturated nitro compounds into oximes could constitute also an important access route to these molecules. α,β-Unsaturated nitro compounds are easily synthesised through the Henri condensation of carbonylic compounds with nitromethane (Scheme 40).

The transformation of unsaturated nitro compounds into oximes is, however, not trivial and has been reported using only stoichiometric amounts of organic hydrogen donors such as ammonium formate and decaborane.[259,260] These processes are industrially inadvisable due to the stoichiometric formation of by-products giving a high E factor. In this context Au/$TiO_2$ is a suitable catalyst to carry out the chemoselective transformation of α,β-unsaturated nitro compounds into oximes by hydrogen.[261] This catalytic behavior of gold contrasts with that of Pt and Pd which, although are even more active for hydrogenation, exhibit a notable lack of chemoselectivity.[261] For example, hydrogenation of *trans*-nitrostyrene using Pd/C as catalyst gives 28% of 2-nitro-1-phenylethane showing the simultaneous hydrogenation of the C=C double bond. Other by-products such as the saturated 2-phenylethanamine arising from the complete hydrogenation of the system and *N*,*N*-bis(2-phenylethyl)amine were also observed using Pt/C as catalyst (Scheme 41).

The chemoselectivity of the process is still high regardless of the presence in the nitrostyrene aromatic ring of electron withdrawing or electron donors. One representative example



**Scheme 41** Products observed in the unselective hydrogenation of nitrostyrene. When using Au/$TiO_2$ as catalyst, only the oxime of 1-phenylethanal was formed in high yields.



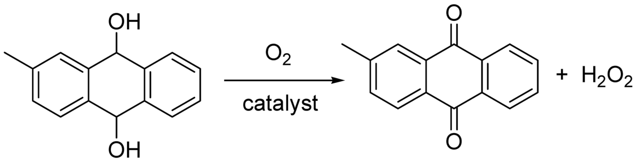
**Scheme 42** Product distribution and differences in the selectivity for the hydrogenation of α,2-dinitrostyrene using supported metal nanoparticles (taken from ref. 262).

that illustrates the large differences in the chemoselectivity of the process depending on the nature of the noble metal catalyst is β-2-dinitrostyrene. Neither Pt nor Pd are able to produce the aromatic nitrophenyl oxime due to the occurrence of simultaneous reduction of the C=C double bond and the reduction of one or two nitro groups to amines (Scheme 42). Thus, indole was the main product using Pt or Pd catalyst in contrast to the high selectivity to 2-(2-nitrophenyl)oxime using $Au/TiO_2$ as catalyst. $Au/TiO_2$ was also selective towards the formation of aliphatic oximes, as for instance in the reduction of 1-nitrocyclohexene.

One of the reasons for this notable selectivity of supported gold nanoparticles is that the formation of condensation products during the hydrogenation of aromatic nitro compounds in the presence of $Au/TiO_2$ catalyst does not occur.[258] Kinetic experiments. and *in situ* IR measurements have shown that nitrosobenzene is generated in only small amounts. and that hydroxylamine and nitrosobenzene interact strongly with the $Au/TiO_2$ catalyst surface.[258]

### Formation of hydrogen peroxide

Hydrogen peroxide is currently obtained at industrial scale by the oxidation of anthrahydroquinone (Scheme 43). Although this process is highly efficient, transport of this hazardous chemical to the site where this chemical is to be used may make competitive the *in situ* generation of this oxidizing reagent from oxygen.



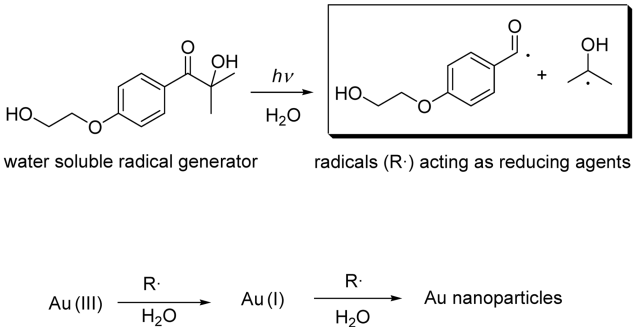
**Scheme 43** Industrial preparation of hydrogen peroxide.

The most direct process for generation of $H_2O_2$ is the oxidation of dihydrogen (or reduction of oxygen). However, this process is extremely hazardous since the mixture of $H_2$ and $O_2$ can be close to the explosion limit. A possibility that can compete with the direct reaction of $H_2$ and $O_2$ is the use of other chemicals as alternatives to hydrogen. In this context, it has been reported that gold nanoparticles supported on rare earth oxides $La_2O_3$ or $Gd_2O_3$ or on MgO can be suitable catalysts for the *in situ* generation of $H_2O_2$ from oxygen and hydroxylammonium sulfate or chloride in water or by the reaction of hydroxylamine and oxygen in methanol, close to ambient conditions (eqn (2)).[263] Thus, hydroxylamine will act as a hydrogen equivalent for oxygen reduction to hydrogen peroxide. The use of hydroxylammonium salt in aqueous solutions requires, however, previous neutralization of the acid by alkali, since in the absence of neutralization only water is formed.[263] It has to be, however, noted that although hydroxylamine is produced in large quantities for ε-caprolactam formation in polyamide fibers, its synthesis is not straightforward and hydroxylamine is an expensive commodity compared to industrial $H_2O_2$. So the real advantages of their use as reducing agent may be limited to certain applications. After all, hydroxylamine has a similar structure to hydrogen peroxide.

$$2H_2N{-}OH + O_2 \xrightarrow{\text{Au catalyst}} H_2O_2 + 2H_2O + N_2 \qquad (2)$$

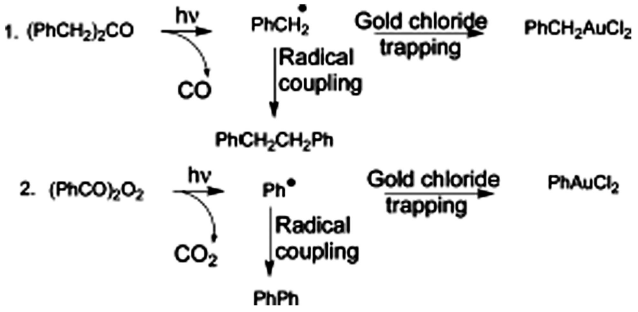
## X. Radical reactions initiated by gold nanoparticles

One of the intriguing properties of gold chemistry is the interplay between gold and radicals. The two aspects to be considered is the interaction of gold salts with radicals and the ability of gold nanoparticles to generate radicals. A new procedure to produce *naked* gold nanoparticles (free from S- or P-ligands) based on the photochemical generation of radicals has been recently reported.[61] Although some precedents on the photochemical generation of gold nanoparticles were already reported, the main contribution in this field arises from understanding that gold ions are efficient quenchers of excited states and, therefore, in order to shorten irradiation times for the generation of nanoparticles from hours to seconds, it is convenient to use radical precursors whose excited states are short-lived, giving rise promptly to C-centred radicals.[61] Ketyl radicals are strong reducing agents that can carry out the reduction of Au(III) to Au(II).[61] The latter disproportionates to form Au(III) and Au(I). Au(I) disproportionation to Au(III) and Au(0) is the actual precursor of gold nanoparticles. Scheme 44 depicts the process of the formation of gold nanoparticles using a photochemical radical initiator as reducing agent. A certain degree of particle size control (from 7 to 40 nm) can be achieved varying light flux and irradiation time, but it can be expected that smaller particles sizes could also be equally formed under appropriate conditions. Particularly, the fact that there is inverse relationship between the photon flux and particle size may open the way to produce monodisperse particles of average size below 10 nm. Since light allows spatial and temporal resolution in nanoparticle formation, it can be anticipated that this procedure can serve to develop systems of interest in catalysis.



**Scheme 44** Photochemical formation of unprotected, stable gold nanoparticles in water using photogenerated radicals as reducing agents (based on ref. 61).

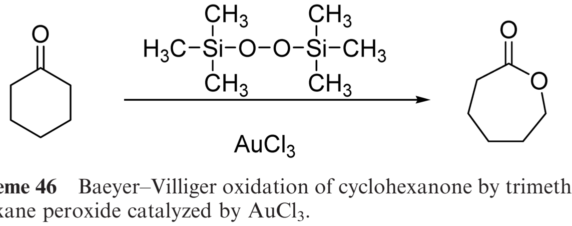
To gain understanding on the interaction of Au salts with radicals a combined experimental and theoretical study on the reaction of C-centred radicals with gold chloride species has been undertaken.[182,185] Radicals were generated by photolysis of



**Scheme 45** Formation of organogold compounds by benzyl (1) and phenyl (2) radical trapping (from ref. 185).

dibenzyl ketone or the thermal decomposition of benzoyl peroxide (Scheme 45). Benzyl radicals can be easily detected in time-resolved optical spectroscopy. It was observed that the lifetime of the benzyl radicals decreases in the presence of gold salts, indicating that gold reacts with the photogenerated benzyl radicals. In addition of the mechanistic evidence monitoring the reaction intermediate, products formed when Au becomes bonded to benzylic groups were also characterized. A parallel process takes place when the C-centred radicals are generated thermally. In this regard, azobis(isobutyronitrile) (AIBN) is one of the most widely used radical initiators. All together, these results indicate that analogously to copper ions, gold cations can also trap radicals. The ability of copper to control C-centred radical polymerization through the atom transfer polymerization mechanism is well established. Since gold nanoparticles also appear concomitantly when gold chlorides are exposed to carbon centred radicals, it is of interest to know if the formation of organogold compounds is a competing process or is involved somehow in the formation of the nanoparticles. These organogold species are interesting species *per se* since it has been proposed that they intervene in those oxidation reactions catalyzed by gold nanoparticles in which minor quantities of hydroperoxides or radical initiators are added.[182]

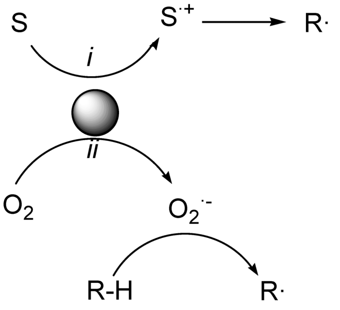
Besides oxygen, hydroperoxides are also considered suitable *green* oxidizing reagents.[159,160,194] *tert*-Butyl and cumyl hydroperoxides are currently used at industrial scale in the production of propylene oxide. In this context, liquid phase epoxidation of olefins using aqueous or anhydrous organic hydroperoxides as oxidizing agents in the presence of supported gold nanoparticles has also been reported.[264] Actually, gold nanoparticles supported on alumina can be used to promote the decomposition of *tert*-butylhydroperoxide present in stock solutions in organic solvents in concentrations between 5 and 30 wt%.[265] Analogously, trimethylsiloxane peroxide in the presence of $AuCl_3$ is able to catalyze the Baeyer–Villiger oxidation of cyclohexanone into 2-oxapanone in 46% yield at 88% conversion (Scheme 46).[266]



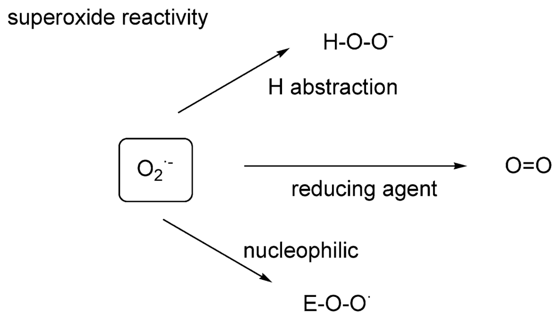
**Scheme 46** Baeyer–Villiger oxidation of cyclohexanone by trimethylsiloxane peroxide catalyzed by $AuCl_3$.

Concerning the ability of gold nanoparticles to generate radicals, EPR measurements have shown that phosphine- and amine-protected gold nanoparticles are able to generate radical species at near ambient temperature and to promote air oxidation of organic substrates containing active hydrogen atoms.[267–270] These radical species have been unambiguously determined by trapping them with dimethyl *N*-oxypyrrolidine. Nanoparticles protected by stronger bound ligands (*e.g.*, thiols) were inactive in these reactions.

It was also found that gold nanoparticles are able to abstract a halogen atom from the halogenated compounds, presumably due to the high affinity of gold metal for halogens.[267] Two possible mechanisms, either electron transfer with the intermediacy of radical cations or hydrogen abstraction to active oxygen species (superoxide) present at the surface of the gold nanoparticles under aerobic conditions, have been proposed as ways to generated C- and N-centred radicals (Scheme 47).[271] In the presence of oxygen, superoxide can render catalytic the formation of radicals from the point of view of gold. Superoxide could also give rise to other processes besides hydrogen abstraction (Scheme 48). In contrast, electron transfer processes with gold nanoparticles as electron acceptors could generate radicals even in the absence of oxygen. This aspect of the new radical chemistry on gold nanoparticles deserves a more comprehensive exploration and exploitation. Given the importance and the wealth of knowledge on radical chemistry,



**Scheme 47** Two possible mechanisms that can operate to generate organic radicals by gold nanoparticles: (i) direct electron transfer from low-oxidation potential organic substrates to gold, and (ii) hydrogen abstraction to superoxide radical bound to the gold nanoparticles surface.



**Scheme 48** General reactivity of superoxide anions. Superoxide can be generated on the surface of gold nanoparticles.

the practical use of the ability of gold nanoparticles to generate radicals under mild conditions remains to be developed.

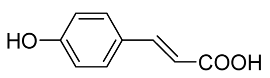
## XI. Gold in environmental catalysis

The catalytic oxidation of volatile organic compounds (VOCs) present in low concentration in effluent gases is an important technique to control air quality and avoid atmospheric pollution. Supported platinum and palladium are generally considered the most effective catalysts and are widely used in commercial systems. More recently the activity of supported gold nanoparticles for VOC oxidation has attracted considerable attention. Several authors have reported that the activity of gold nanoparticles supported on $Co_2O_3$, $Fe_2O_3$ or $MnO_2$ can surpass that of $Pt/Al_2O_3$, the benchmark catalyst for VOC oxidation.[37,38,272,273] Au adsorbed on zeolites can also serve to promote the ozone oxidation of effluents containing organic matter and ammonia.[274]

Gold supported on ceria has been used to carry out the catalytic oxidation of representative volatile organic compounds, which are hard to degrade, including methanol, 2-propanol and toluene.[275] It was found that the activity of ceria is largely promoted by gold and that the preparation procedure, either co-precipitation or deposition–precipitation, largely influences the catalytic activity.[275] It was assumed that the reaction mechanism follows a Mars–van Krevelen mechanism[171] that assumes the reversible incorporation–vacancy of lattice oxygens of ceria and it was proposed that the promotion of gold nanoparticles on the activity of ceria derives from the ability of gold to weaken the Ce–O bonds adjacent to the Au atoms.[275]

The effect of calcination pre-treatment on the catalytic activity of $Au/Fe_2O_3$ for the combustion of representative organic compounds such as 2-propanol, ethanol, methanol, acetone and toluene has been studied.[276] It was observed that the activity of the supported gold nanoparticles decreases upon increasing the calcination temperature.[276] XPS, XRD and BET surface area characterization of the samples has been used to rationalize the negative influence of increase of the calcination temperature. It is proposed that Au oxidation state, particle size and iron oxide phase play a role explaining the influence of the calcination temperature.[276]

Olive milling is one of the traditional industrial activities in Mediterranean countries that causes environmental problems with the residual products. The polyphenolic compounds present in the pulp and seeds of olives are biologically recalcitrant compounds hardly degradable by natural degradation mechanisms. Using *p*-coumaric acid as a model compound (Scheme 49), the activity for the wet air oxidation at 80 °C and 2 MPa air pressure of gold nanoparticles supported on ceria was compared to that of ceria support or ceria supported platinum.[277] It was observed, however, that in contrast to the effect of platinum that enhances significantly the mineralization of *p*-coumaric acid to $CO_2$, the presence of Au nanoparticles does not promote the activity of $CeO_2$.



**Scheme 49** Structure of *p*-coumaric acid.

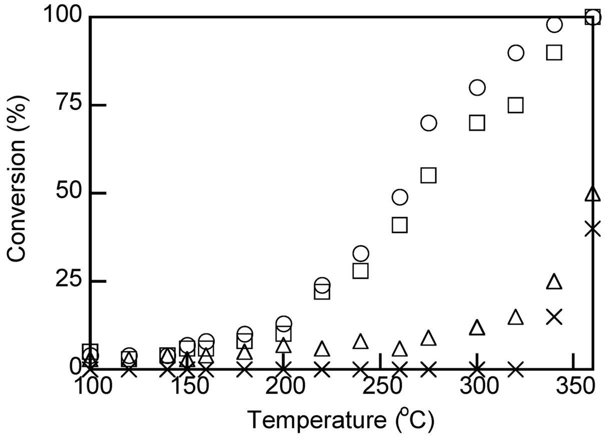


**Fig. 9** Conversion of *n*-hexane as a function of temperature without catalyst (×) in the presence of $TiO_2$ (□) or using $TiO_2$ supported gold nanoparticles either treated with hydrogen (□) or with oxygen (○) (data taken from ref. 36).

The activity of $TiO_2$ and $MnO_2$ supported gold nanoparticles towards the complete oxidation of *n*-hexane as a model has been studied by Gaigneaux *et al.*[36] In the case of titania it was found that the presence of gold decreases the onset temperature to carry out *n*-hexane oxidation from 320 to 200 °C, complete oxidation being achieved at 360 °C (Fig. 9). Moreover, it was observed that thermal treatment at 300 °C as the final step of the deposition–precipitation procedure with oxygen rather than hydrogen renders a more active $Au/TiO_2$ catalyst.[36] This effect is not due to differences in the oxidation state of gold nanoparticles, since essentially coincident XPS Au $4f_{7/2}$ peaks were recorded after hydrogen or oxygen treatment. Based on the difference in the C/Ti atomic ratios, a very interesting concept has been proposed in which the differences in activity depending on the hydrogen or oxygen treatment arises from the low-temperature combustion during the treatment of carbonaceous contaminants under oxygen activation that otherwise will lower the inherent catalytic activity of gold if the pretreatment is carried out under hydrogen.[36] Comparing $Au/TiO_2$ samples of different gold loading and monitoring gold dispersion by XPS plotting the Au/Ti atomic ratio, a linear relationship between catalytic activity and the surface area occupied by gold nanoparticles was observed.

$NO_2$ is among the gases responsible for the greenhouse effect and it can be produced during the combustion of fossil fuels. Nitrogen oxides and residual hydrocarbons and O-rich organic compounds present in flue gases from gas fuel combustion can be removed efficiently by a series of noble metal catalysts including gold nanoparticles supported on porous inorganic oxides.[278,279]

In those places in which $NO_2$ is being produced in large concentrations, it could be possible to couple its decomposition with use as an oxidizing reagent.[280] It has been reported that gold can act as a catalyst for the gas-phase oxidation of organic compounds by $NO_2$. Alcohols are oxidized to aldehydes and ketones while cyclohexane is dehydrogenated to benzene.[281] This reaction is not only the basis for new and general organic reactions, but also can be used to develop selective sensors coupling $NO_2$ reduction with the selective detection of NO.[281]

Considering the importance of environmental protection, it can be anticipated that processes dealing with the complete oxidation of organic pollutants using gold nanoparticles as catalysts will continue to attract attention in the near future.

## XII. Concluding remarks and future prospects

Preparing solid catalysts with single isolated sites is one way to bridge the gap between homogeneous and heterogeneous catalysis and we have been actively working on this. The synthesis of stable nanoparticles of metals and oxides introduces new possibilities for catalysis since their properties are neither those of the bulk materials nor of the isolated atoms. Moreover such nanoparticles can strongly interact with the support and an electron transfer may occur within either directions. This interaction can stabilize surface charged species that can work as Lewis acids in a similar way as the corresponding salts in solution or in the corresponding transition metal complexes.

We have seen along the review that very small gold particle can strongly interact with some supports, up to the point that different spectroscopies indicate the presence of charged gold species and, what it is even more interesting, they are able to catalyze a variety of reactions that require the presence of charged gold. In other words, even if one could be reluctant to accept the presence of cationic gold on some supports, one has to accept that in some supports there must be some highly unsaturated gold atoms that are able to polarize reactants in a similar manner as Au(III) and Au(I) do in solution. Because of this, we can see the catalytic applications of gold expanding to new reactions. Moreover, these highly unsaturated systems can be ideal to achieve chiral gold active sites through the interaction with chiral ligands.[282] Another research direction we see possibilities for is in the preparation of bifunctional or even multifunctional gold based catalysts that lead either to new products or to existing products in one-pot multistep reactions.

Finally, it would be a great boon for those working on catalysis to stabilize and control the formation of Pt, Ir, Rh, Pd, *etc.* surface charged species. Then, concepts and reactions developed with homogeneous catalysis could be directly transferred to solid catalysts and consequently into heterogeneous catalysis. We believe that this could be one bridge to communicate both types of catalysis.

Concerning the commercial applicability of gold catalysts in industrial process, gold is a precious metal whose price is dependant upon market fluctuations and pressure from external economic considerations besides availability. However, the main issue in many industrial applications is catalyst productivity, based on activity and selectivity. This productivity is related to the stability and durability of the supported gold catalysts. For this reason, platinum, palladium and other precious metals can be used when the impact of catalyst cost in the process is affordable and has advantages over less efficient transition metal catalysts. Of course, precious metals present in exhausted catalysts can be recovered and recycled. It has also to be noted that gold is considerably more abundant and its price more stable than other noble metals, such as platinum. Thus, as it is the case of other noble metal catalysts currently used, the use of gold in large industrial processes could be economically feasible.

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