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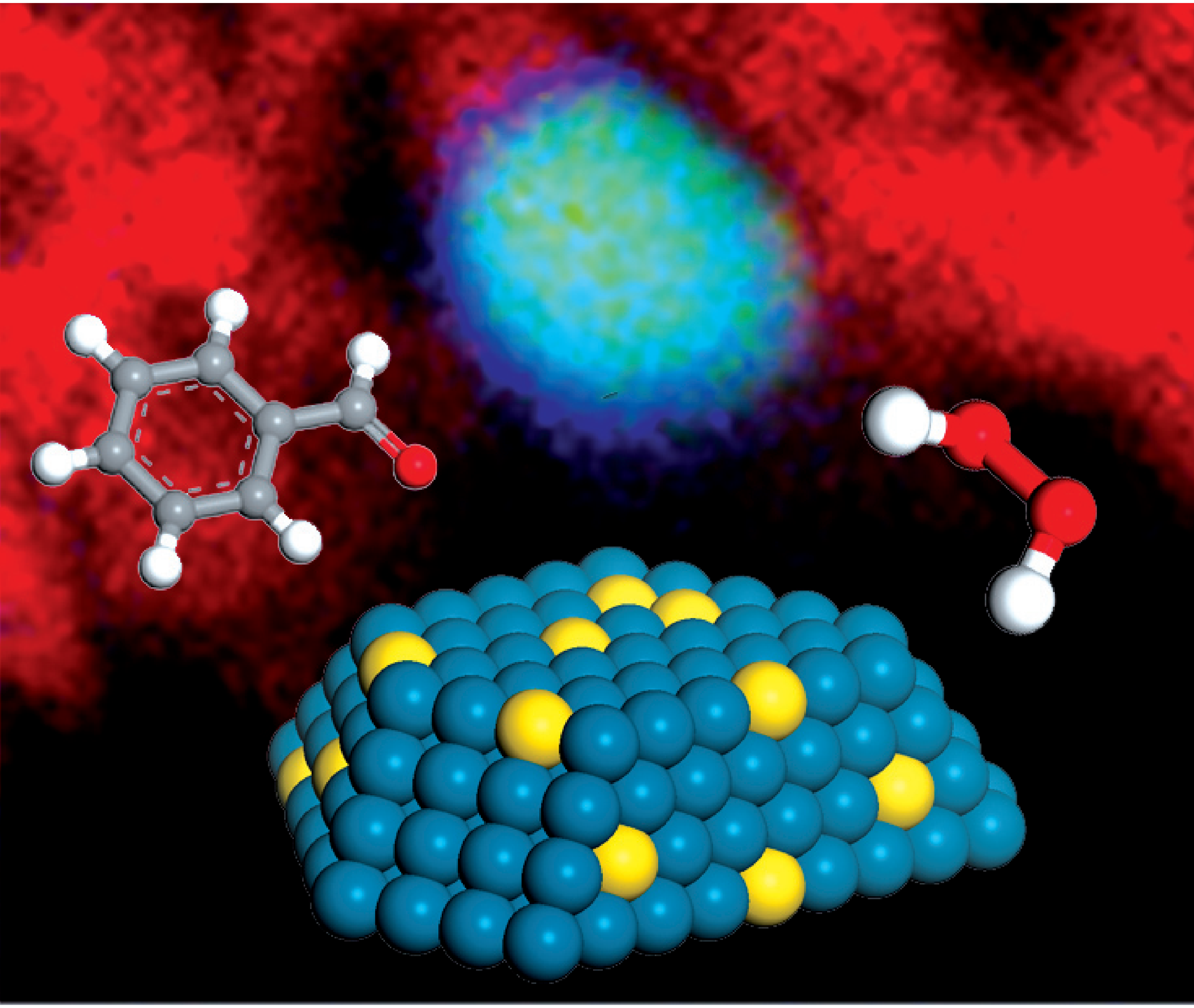

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FEATURE ARTICLE
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Nanocrystalline gold and gold palladium alloy catalysts for chemical synthesis

Graham J. Hutchings

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Catalysis by gold has become one of the most studied new topics in chemistry in recent years, and yet for many gold acting as a catalyst is, perhaps, a most unlikely possibility since bulk gold is a relatively non-reactive, immutable, ductile metal that is prized for its great beauty and value rather than for the depth of its chemistry. However, when prepared in nanocrystalline form, as a collection of a few hundreds of atoms, it displays remarkable activity as a heterogeneous catalyst for a broad range of redox reactions. Of particular note is the ability of gold, either alone or alloyed with palladium, to catalyse selective oxidation reactions, *e.g.* alkene epoxidation, alcohol oxidation, and the direct synthesis of hydrogen peroxide by the hydrogenation of molecular oxygen. In this article the recent advances in this exciting new field are explored.

Introduction

Heterogeneous catalysis plays a major role worldwide, not only with respect to an economic viewpoint, but it also provides the necessary infrastructure for the well being of society as a whole. Without effective heterogeneous catalysis the manufacture of many materials, pharmaceuticals and foodstuffs would not be possible. It is not surprising, therefore, that as it is a subject that spans chemistry, chemical engineering and materials science, there is intense and broad interest in the design of new catalysts as well as seeking to understand how these materials function as catalysts. With respect to current industrial processes many of these are based on acid–base catalysts, *e.g.* catalytic cracking of hydrocarbons for the production of transportation fuels, and hydrogenations with molecular hydrogen typically using metal catalysts, *e.g.* the Fischer–Tropsch synthesis. In addition, selective oxidation remains one of the key synthetic steps for the activation of a broad range of substrates for the production of either finished products of intermediates for the preparation of pharmaceuticals, agrochemicals, as well as commodity chemicals. However, in contrast to hydrogenation reactions which are often carried catalytically with molecular hydrogen, there are relatively few selective oxidation reactions that are catalysed using molecular oxygen. Often selectivity in these processes can only be achieved if stoichiometric oxygen donors, *e.g.* manganates, or activated forms of oxygen, *e.g.* hydrogen peroxide, are utilised; this increases the costs as well as significantly decreasing the atom efficiency of the overall process. While many would consider hydrogenation with a heterogeneous metal catalyst and molecular hydrogen as a commonplace laboratory procedure, most would not consider doing a similar oxidation process with molecular oxygen as a standard laboratory procedure. Why is this the case? There is one essential difference between catalytic hydrogenation and oxidation. Under most reaction conditions, the hydrogen molecule has to be activated by chemisorption on a catalyst surface before it can be reacted with a substrate for hydrogenation to occur. At the relatively low temperatures at which catalytic hydrogenation reactions are carried out, activation of hydrogen *via* a competing radical pathway is not feasible. This is not the case with selective oxidation. Dioxygen in its ground state is a diradical triplet species. This opens up the possibilities of competing non-catalysed gas or liquid phase reactions in which triplet dioxygen reacts directly with the substrate without the intervention of a catalyst. Fortunately, most organic substrates of interest are in singlet states in their ground states and so this effect can be minimised. However, it is a competing factor that complicates oxidation reactions, and necessarily makes them far more complex and demanding to study. However, even with this added complication, given its central importance, it is surprising that there have been few new approaches in the design of selective oxidation catalysts using molecular oxygen in the past forty years.[1] Indeed, the major advances in selective oxidation were marked out over 50 years ago; since then there have been the remarkable developments of the titanium silicalite TS-1 for the

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epoxidation of alkenes and iron-doped ZSM-5 zeolite for the oxidation of benzene to phenol. Both of these oxidations are complex and difficult and had previously eluded many talented researchers; however, both processes use activated forms of oxygen, namely H_2O_2 for TS-1 and N_2O for Fe-ZSM-5, and both catalysts are totally non-selective with molecular oxygen.

There is, therefore, a real need for new catalytic processes that use molecular oxygen, especially since environmental factors are of paramount importance and we need to develop atom efficient green processes. It is against this background that recent developments in selective oxidation reactions using supported gold and gold–palladium nanocrystals are beginning to make an impact. In this feature article the discovery of gold as a catalyst and the recent advances concerning selective oxidation reactions will be described and discussed.

Gold as a catalyst: discovery and fascination

While the current fascination with gold catalysis for both homogeneous and heterogeneously catalysed systems continues, we should perhaps ponder how this change in fortune for gold has come about. For many years researchers had tried to use gold as a catalyst but it was found to be relatively inactive. Indeed, in 1972 Bond stated[2] "Although the catalytic properties of gold are surpassed by those of the Group VIII metals, especially palladium and platinum, possible applications of gold in catalytic processes have been widely studied", and even as late as 1985 Schwank concluded[3] "in spite of its low intrinsic activity, gold can influence the activity and selectivity of group VIII metals". This was for many scientists, at that time, the general conclusion concerning the catalytic prospects for gold, at best it might improve the activity of other more active metals. To some extent this is a comfortable conclusion, after all gold is a very stable element and the chemistry of gold as represented in the inorganic texts of the time was severely limited, especially when contrasted with the far richer chemistry and catalysis displayed by copper and silver, the two elements with which gold shares a triad in the periodic table. Although Bond and co-workers[4] subsequently showed that nanocrystalline gold could be effective for the hydrogenation of dienes, gold was not shown to be more effective than well dispersed palladium or platinum and as these catalysts were well established, gold was not viewed as a viable alternative.

In the early to mid 1980s there were two significant observations that completely changed this perception and highlighted the special attributes of gold as a heterogeneous catalyst. These discoveries were made independently by Haruta and Hutchings,[5] namely the discovery that supported Au catalysts are very active for low-temperature CO oxidation,[6] and the prediction that Au would be the best catalyst for ethyne hydrochlorination[7] and the subsequent verification of this prediction.[8–11] In both these cases gold was observed to be the most active catalyst, by far, and these discoveries lay at the heart of the new impetus on gold catalysis. However, as noted in an analysis of the literature by Hashmi[12] real interest in gold catalysis did not materialise until the late 1990s, *i.e.* not until over a decade after the initial discoveries; but after the late 1990s the publications and patents concerning gold catalysis have been growing exponentially even when normalised against the general growth in all scientific publications. The reasons for the delay in the development of this new field may be complex. For example, ethyne hydrochlorination is a difficult reaction to study in the laboratory, and with inexpensive oil prices persisting until recently, interest in this reaction has been waning industrially. It is only now that coal is once again competitive with oil that interest in the production of VCM by ethyne hydrochlorination again becomes commercially viable. Also, the preparation of supported gold catalysts can present difficulties and the introduction of standard reference catalysts[13] has eased this situation.

There is now a general fascination with this new found reactivity in nanocrystalline gold, but virtually most of the research still concerns CO oxidation. The research in this field has been the subject of many reviews.[14–22] The reason that many give for this fascination is that CO oxidation is an essential goal for fuel cell technology where residual traces of CO have to removed from the H_2 that is used as the fuel source. Indeed this is a topic that has received significant recent attention.[23–26] However, this requires preferential oxidation of CO in the presence of CO_2, H_2O and a massive excess of H_2;[27,28] and the design of a catalyst for this duty is far removed from a supported gold nanocrystalline catalyst that exhibits high activity for CO oxidation at sub-ambient temperatures.[28] However, the reason is probably, for many researchers, far less complex, it is a relatively facile reaction to study requiring inexpensive equipment to get impressive catalytic results. There is another more noble reason. There is a quest to understand why gold is such an effective catalyst for the oxidation of CO. It is active at temperatures as low as -76 °C, and is therefore active at temperature some 200 °C lower than supported well dispersed palladium and platinum catalysts. This observation has continued to fascinate most active in the field of gold catalysis and as yet there are no agreed answers to two key questions: (a) what is the mechanism by which supported gold nanocrystals oxidise CO? and (b) what is the nature of the active site and is it the same for all supported gold catalysts? Indeed, this is an area of immense controversy. Proposals have included the size and morphology of the gold particle and its interface with the support,[20,29] the metal oxidation state,[30] and support effects.[20] Most of the fundamental insights for the nature of the active site for this reaction have come from well-defined model studies,[17,31,32] in which specific structures are tailor made and their reactivity examined.[32] One aspect of the problem is demonstrated by considering the relative reactivity of Au/Fe_2O_3 and Au/ZnO catalysts which show interesting differences (Fig. 1). Au/Fe_2O_3 that is prepared by coprecipitation and drying at *ca.* 100 °C is an exceptionally active catalyst and has very small clusters of gold ≤ 1 nm, whereas the same material calcined at 400 °C is relatively inactive under comparable condition of reactant flow rate and concentration and this material comprises very distinct cuboctahedral nanocrystals of gold *ca.* 5 nm in diameter

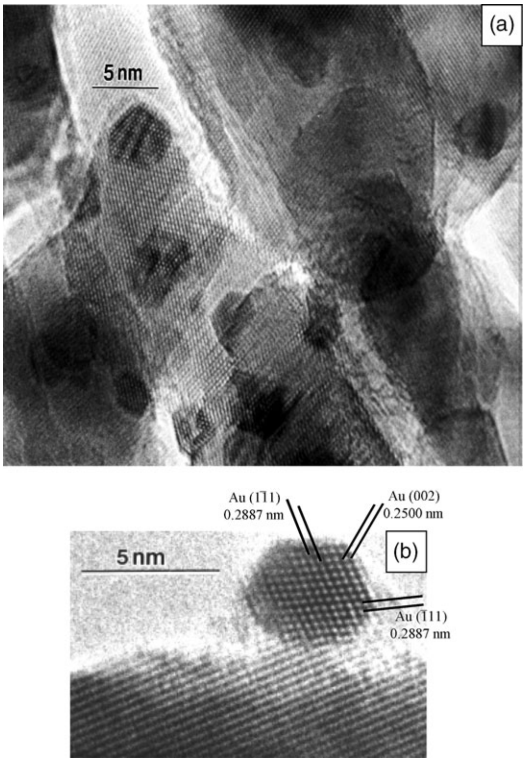


Fig. 1 Transmission electron micrographs of (a) Au/Fe_2O_3 which is inactive for CO oxidation at ambient temperature, and (b) Au/ZnO which is active for CO oxidation at ambient temperature.[35]

(Fig. 1(a)). For the Au/ZnO catalyst prepared in a similar manner the dried material is inactive, whereas the material calcined at 400 °C is extremely active for CO oxidation and comprises very distinct cuboctahedral nanocrystals of gold *ca.* 5 nm in diameter (Fig. 1(b)). This could demonstrate a very strong support effect; however, there are reports that many supports are effective for this reaction. In his initial work Haruta showed that α-Fe_2O_3 was active,[6] and subsequently, he also showed that TiO_2 was equally effective,[16] and since then many supports have been found to be effective. Considerable emphasis has been placed on the nature of the support and most researchers agree that high activity catalysts can be observed with α-Fe_2O_3[23,24,26–28,33,34] and TiO_2[35–44] and recently with CeO_2[45,46] as support. Most detailed studies have concentrated on TiO_2. However, recently, Lahr and Ceyer[47] have extended the temperature range at which activity for CO oxidation is observed to as low as −203 °C using a Au/Ni(111) surface questioning the potential role of the oxide supports. Above all, though, one thing is clear, gold catalysts do have a unique catalytic activity for the oxidation of CO at particularly low temperatures.

The efficacy of gold for CO oxidation may well find commercial application, and a recent review by Thompson and co-workers[48] highlights that this may occur both in the removal of CO[49,50] in respiratory protection as well as in fuel cells.[51] However, there exist possibilities for gold to be used as catalysts in chemical synthesis rather than in total or preferential oxidation, and this is the topic that will be explored in the next sections of this article. While this article will concentrate mainly on the use of gold and gold palladium alloys in selective oxidation reactions, it should be noted that supported gold catalysts are also highly effective for selective hydrogenations. Following on from the early work by Bond and co-workers,[4] where gold was found to be effective for the hydrogenation of dienes, gold has been found to selectively hydrogenate an α,β-unsaturated aldehyde to the unsaturated alcohol, in preference to the saturated aldehyde.[52–54] Indeed, very high specificities can be achieved of *ca.* 85%.[53] Recently, there have been some remarkable developments in which α,β-unsaturated nitro-compounds are hydrogenated with molecular hydrogen to give oximes.[55–57] This is an application where previously only non-catalytic stoichiometric reactions using bulky hydrogen donors had been found useful. In particular the synthesis of cyclohexanone oxime is of central importance in the manufacture of nylon,[55] and this new application of gold catalysis is of significant interest for this application.

Early work on selective chemical synthesis

Alkyne hydrochlorination

The earliest example of chemical synthesis using gold-based catalysts concerns the reactions of alkynes, most notably for the production of vinyl chloride[7–11] and vinyl acetate.[58–60] Vinyl acetate is currently produced commercially using a supported gold palladium alloy in which the gold is a minor component. In contrast, gold alone has been found to be the best catalyst for vinyl chloride production. Vinyl chloride is still widely used as a polymer for applications where stability against biodegradation is required. For many years the preferred route is based on ethene oxidative hydrochlorination, since ethene is widely available from the steam cracking of oil derivatives. However, a far simpler method of preparation is ethyne hydrochlorination which does not require the introduction of molecular oxygen, which can introduce additional hazards. Ethyne is readily available in coal-based processing, but in most parts of the world ethyne hydrochlorination has been replaced by the ethene as a feedstock due to the differential costs of the feedstock. However, in the last few years with rising energy costs coal based processes are now becoming economic and it is therefore worth reconsidering potential processes based on ethyne.

When ethyne hydrochlorination has been practised commercially it has used a relatively inexpensive mercuric chloride supported on carbon as catalyst.[61,62] This catalyst is decidedly non-green, both in its manufacture and its application. This, therefore, represents one of the paradoxes of catalysis. Catalytic processes are often, if not exclusively, viewed as green processes. The introduction of a catalyst to a stoichiometric process is viewed as making the process greener. However, often the materials used as catalysts or the manner in which they are fabricated are distinctly non-green. This is particularly true of mercuric chloride which is a toxic and hazardous material at all stages of its use, *i.e.* catalyst manufacture, utilisation and disposal. Furthermore, the mercuric chloride catalyst suffers from deactivation due to sublimation of the active component[61,62] and so it readily loses the active component, thereby contaminating the production unit and environment. Work carried out in the early 1980s focussed on the identification of potential improvements in catalysts, especially with respect to activity. Earlier, Shinoda[63] had demonstrated that a range of metal chlorides supported on carbon could give a spectrum of activities and that there was a correlation with the electron affinity of the cation. Subsequently, the author[7] reasoned that the reaction was not a one-electron process, as defined by the electron affinity, but was more likely to involve two π electrons of the ethyne and hence, as most of the cations in the data set were divalent; the standard electrode potential was a more viable parameter with which to correlate the data. On this basis it was predicted that gold would be the best catalyst and this was subsequently confirmed,[8–11] and indeed supported gold catalysts were found to be the catalysts of choice for this reaction (Fig. 2) and exhibited excellent stability, being much more stable than the supported mercuric chloride catalysts However, gold catalysts still deactivated very slowly with time and the rate of deactivation was found to be dependent on temperature. The deactivation rate was at a minimum at 100 °C, but at this temperature the catalyst was not sufficiently active and temperatures of *ca.* 180 °C are preferred. At temperatures below 100 °C the deactivation was caused by deposition of polymeric carbonaceous materials and at higher temperatures the deactivation was caused by reduction of Au^{3+} to Au^0 as shown by detailed ^{197}Au Mössbauer spectroscopy.[10] This was a key observation and meant that the deactivation could be arrested by *in situ* reactivation by co-feeding dilute NO in with the reactor feedstock. This had no effect on catalyst selectivity but did stop deactivation. This was the first demonstration of *in situ* reactivation of gold catalysts and also the first clear demonstration that cationic gold can be an effective heterogeneous catalyst. However, we have recently[64] shown that the supported gold catalyst can be reactivated by treatment with *aqua regia*. We were prompted to study the effect of *aqua regia* on catalysts when we observed that gold is particularly difficult to remove from carbon supports using this solvent. In particular, we found that a 24 h treatment of the fresh catalyst with *aqua regia* with stirring at room temperature leads to relatively little removal of gold, and less than 3% of the total gold present could be removed from a standard 1 wt% Au/C. A deactivated catalyst was treated with boiling *aqua regia* for 20 min. This treatment led to less than 1% of gold present being dissolved in the *aqua regia*, so it is considered that the sample used for the second test has the same total loading as the original catalyst, *i.e.* 1 wt% gold. The catalyst was recovered and dried and reused as a catalyst. After treatment with *aqua regia*, the catalytic activity was fully recovered, and both fresh and regenerated catalysts display quite similar activity.

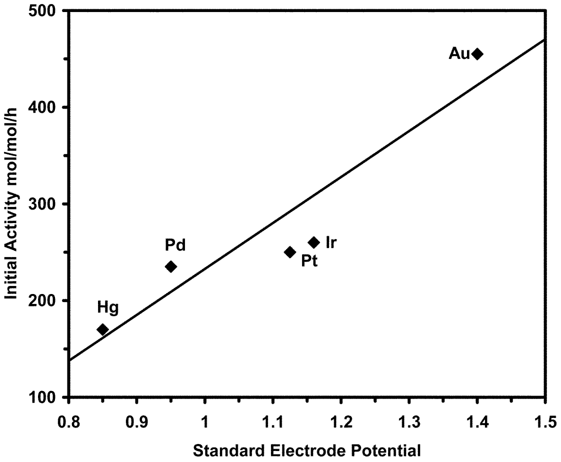
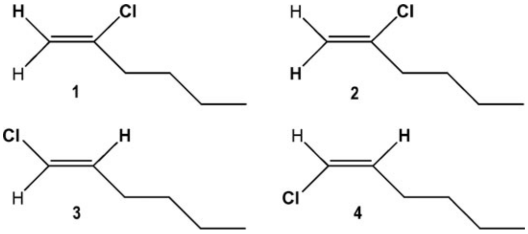


Fig. 2 Correlation of catalysts activity for ethyne hydrochlorination with the standard electrode potential (180 °C, gas hourly space velocity = 1140 h^{-1}, catalysts contain 0.0005 mol metal/100 g catalysts).[7]

Gold-catalysed ethyne hydrochlorination is very selective with VCM selectivity >99.9%. This is much more selective than the mercuric chloride catalyst which also produces small amounts of ethane dichloride, the product of a sequential hydrochlorination reaction. The reason for this enhanced specificity is that the gold catalyst shows no activity for the reactions of ethene, indeed if ethene is added to the reactants it behaves as an inert diluent. This interesting observation can be expected to be exploited since selection between alkynes and alkenes as reactants is a major target in many chemical transformations.

In a recent study we have shown[65] that gold supported on carbon can be effective for the hydrochlorination of higher alkynes. We found that the reaction of higher alkynes is affected by steric factors with the trend in activity being: acetylene ≫ hex-1-yne > phenylacetylene > hex-2-yne. Concerning product selectivity there are four products that can be formed from the hydrochlorination of higher alkynes due to *syn* and *anti* addition together with Markovnikov and *anti*-Markovnikov addition. For hex-1-yne the four reaction products are shown in Scheme 1. Using ^{1}H NMR spectroscopy it was found that for hex-1-yne and phenyl acetylene the *anti*-Markovnikov product is formed by *anti* addition of HCl. However, the Markovnikov products are equivalent for *syn*- and *anti*-addition of HCl, and hence we investigated the reaction using deuterated substrates and confirmed the products are formed by the *anti* addition of HCl. It therefore appears that supported gold catalysts can be generally effective for the chemical synthesis of several chlorohydrocarbons of commercial importance. Given that energy costs are considered to remain high in coming years, and the era of relatively cheap oil is considered to be past, we can expect interest in the use of coal as a feedstock to be rekindled. Of course a major pathway for its use will be gasification to produce synthesis



Scheme 1 Possible regioselectivity and stereochemistry of the addition of HCl to hex-1-yne: **1** Markovnikov with *syn* HCl addition, **2** Markovnikov with *anti* HCl addition, **3** *anti*-Markovnikov with *syn* HCl addition and **4** *anti*-Markovnikov with *anti* HCl addition.

gas, a very flexible feedstock, but perhaps we can expect ethyne-based processes to, once again, be of interest in chemical syntheses.

Alkene epoxidation

In the previous section the relative non-reactivity of alkenes with cationic gold catalysts was viewed as a key feature underpinning catalyst specificity. However, supported gold catalysts comprising nanocrystalline metallic gold have been found to be particularly effective for the epoxidation of alkenes as long as a sacrificial reductant, typically H_2 is present to aid the activation of molecular oxygen. Most research has focussed on the oxidation of propene to propene oxide which is a major research target, as this is a commodity chemical used in the manufacture of polyurethane and polyols. Although the epoxidation of ethene with dioxygen is a commercial process operating with selectivities in excess of 90% using a supported Ag catalyst[66] the oxidation of propene has proved to be much more problematic and typically selectivities lower than 10% are observed with many catalysts. However, very recently Lambert and co-workers[67] have shown that supported catalysts can give selectivities of *ca.* 50% at 0.25% conversion, in the absence of a sacrificial reductant, but the selectivity declines rapidly with increasing conversion. At present, the most promising commercial route for the synthesis of propene oxide is based on the reaction between propene and hydrogen peroxide (and this has spurred great interest in the manufacture of hydrogen peroxide which is discussed in the next section) using the titanium silicalite TS-1 as catalyst. However, the relative costs of hydrogen peroxide and molecular oxygen make a process based on molecular oxygen far more preferable, but this requires the solution to the major problem of reaction selectivity since propene can be readily activated by the formation of allylic species which lead to non-selective oxidation and do not result in the formation of the epoxides which requires the electrophilic addition of an oxygen intermediate to the carbon–carbon double bond.

Haruta and co-workers were the first to demonstrate the potential of supported gold catalysts for the epoxidation of propene with dioxygen in the presence of H_2 as a sacrificial reductant. H_2 permits the activation of O_2 at relatively low temperatures permitting the selective oxidation of propene to occur.[68,69] Haruta found that Au/TiO_2, prepared using the deposition precipitation, was selective for propene epoxidation and the catalysis was associated with an intimate contact between hemi-spherical gold nano-crystals (2–5 nm in diameter) and the TiO_2 support. Initial selectivities were low but promising and improvement were made by using different titanium-containing supports including TS-1, Ti-zeolite β, Ti-MCM-41 and Ti-MCM-48.[70–83]

It is clear that all these studies confirm that with H_2 as a sacrificial reactant Au/TiO_x catalysts are very effective for this epoxidation. Many of the early studies concentrated on the use of TS-1 as a support as it is known that this material is selective for the epoxidation of propene with H_2O_2 as the oxidising species.[70] Haruta and co-workers[71] found the Au/TS-1 catalysts produced more propanal than propene oxide. In contrast, Moulijn and co-workers[72] clearly showed that Au/TS-1 catalysts could be very selective to the formation of propene oxide, and that the catalysts were stable under reaction conditions. Recent mechanistic studies by Nijhuis *et al.*[73,74] show that a bidentate propoxy species is formed as an intermediate, and that the role of the gold nanoparticles in the catalytic reaction is not only to provide the peroxy species but is also involved in establishing the bidentate propoxy intermediate.[74] Nijhuis and Weckhuysen[75] have also recently shown that water plays a role in decreasing the deactivation of these gold catalysts. Studies by Delgass and co-workers[76,77] have confirmed the findings concerning the role of the bidentate propoxy species. In particular, it has been observed that the gold loading requires careful tuning, as had previously been noted by Haruta and co-workers,[78] to obtain high selectivities and activities[84] and when normalised for gold content propene oxide yields of 350 g $(\mathrm{h\ g_{Au}})^{-1}$ are achievable at 200 °C for a 0.01 wt% Au/TS-1 catalysts with Si/Ti ratio of 500. In these catalysts the active species are considered to be gold species with diameters much smaller than 2 nm.

Very recently, trimethylamine has been identified as a gas-phase promoter for the epoxidation of propene with supported gold catalysts.[81] This is an important observation, since the epoxidation of ethene is greatly enhanced by a complex mixture of gas-phase promoters and so this could provide a very valuable new line for research activity.

Haruta and co-workers have met the challenge of poor H_2 utilisation and have shown that using mesoporous titanosilicates as a support[84] reasonably efficient H_2 consumption was attained together with high propene oxide yields (93 g $(\mathrm{h\ kg_{cat}})^{-1}$ at 160 °C) and observing propene oxide selectivities of $>90\%$, at propene conversions of *ca.* 7% together with a hydrogen efficiency of 40%.[80] Although these catalysts showed relatively short lifetimes they could be reactivated and these catalysts are of commercial potential.

Oxidation of alcohols

The investigation of a range of oxidation reactions using gas or liquid phase reagents to produce valuable intermediates or products for the chemicals industry has become a major research target. The reasons for this are many, but, in particular, it is the drive for greener processes based on the realisation that reaction selectivity is the most important factor in chemical synthesis, as making non-desired by-products can now be very costly. There has therefore been a drive to identify atom-efficient oxidation reactions that can be carried out with molecular oxygen, rather than an activated form of oxygen, using mild solvent-free reaction conditions. There are many catalytic processes operated today that rely on oxidation, but, significantly, very few of these are used in the fine chemicals industry. Unfortunately, many reactions are still carried out using stoichiometric oxygen donors often with particularly non-green components. This is a field where we can expect a number of advances with gold and gold palladium catalysts. The oxidation of alcohols and polyols to chemical intermediates represents a demanding target.

Rossi, Prati and co-workers[85–87] were the first to clearly demonstrate in their seminal studies that supported gold nanoparticles can be very effective catalysts for the oxidation of alcohols, including diols to the corresponding acid, for example 1,2-propanediol formed lactic acid by oxidation of the primary alcohol group rather than the secondary alcohol group, which might have been expected to be more reactive. The presence of base (typically NaOH) was found to be essential for the observation of activity, and consequently sodium salts of the acids were formed as products. The base was considered to be essential for the first hydrogen abstraction, and this is a significant difference between the supported gold catalysts and Pd and Pt catalysts that are effective in acidic as well as basic conditions. The catalysts were Au/C and they were observed to be effective for a range of substrates, including alcohols, diols and polyols such as sugars. In addition, the catalysts were shown to be effective with gas-phase reactants and in this case no base addition is required.[88] However, in this case the products formed were aldehydes rather than the sodium salt of the acids that was the dominant product when NaOH was added as the base. These researchers have extended their studies to the oxidation of sugars and similar high catalytic efficiency for the oxidation of glucose and sorbitol has been observed[89,90] In recent studies they have reported the synergistic effect of the addition of Pd or Pt to the Au/C catalysts for the selective oxidation of D-sorbitol to gluconic and gulonic acids.[91] In many catalytic studies the support–catalyst interaction is a crucial factor controlling reactivity. Interestingly, Rossi and co-workers[92] have shown that "naked" gold colloidal particles can be very effective catalysts for the oxidation of glucose to gluconic acid. They demonstrated that the initial rates for these non-supported particles were identical to the rates observed with Au/C catalysts operated under the same conditions; hence, confirming that the support is of limited importance in the origin of the catalyst activity in these oxidation reactions. The support–catalyst interaction is, however, essential for the observation of a stable catalyst system. Subsequently, Mertens *et al.*[93,94] have also shown that colloidal gold can catalyse the oxidation of 1,2-diols. Recently, Tsunoyama *et al.*[95] have shown that benzyl alcohol can be oxidised using oxygen in aqueous media with gold nanoclusters stabilised on polymers.

Christensen and co-workers[96,97] have made a number of significant advances in the direct oxidation of primary alcohols using supported gold nanocrystals and they have concentrated on decreasing the amount of base present in these oxidations. They have shown that gold can catalyse the oxidation of aqueous solutions of ethanol to give acetic acid in high yields.[96] This provides a potential new route to a key commodity chemical that is based on a bio-renewable feedstock suing a substantially green technology approach. Recently, this group have shown that methyl esters of a broad range of primary alcohols can be produced using a similar approach.[97]

The use of Au/C catalysts were extended by Carrettin *et al.*[98–100] for the oxidation of glycerol. Glycerol is a highly functionalised molecule that is readily available from biosustainable sources, for example it can be obtained as a by-product of the utilisation of rape seed and sunflower crops. This makes glycerol a particularly attractive starting point for the synthesis of intermediates, and a large number of products can be obtained from glycerol oxidation and this potential complexity represents both an opportunity and a problem and so control of the reaction selectivity by careful design of the catalyst is required. In particular, it was found that Au supported on graphite can oxidise glycerol to glycerate with 100% selectivity using dioxygen as the oxidant under relatively mild conditions with yields approaching 60%.[98–100] Under comparable conditions, supported Pd/C and Pt/C always gave other C_3 and C_2 products in addition to glyceric acid and, in particular, also gave some C_1 by-products. For the Au/C catalyst, it was observed that the selectivity to glyceric acid and the glycerol conversion were very dependent upon the glycerol/NaOH ratio. In general, with high concentrations of NaOH, exceptionally high selectivities to glyceric acid can be observed. However, decreasing the concentration of glycerol, and increasing the mass of the catalyst and the concentration of oxygen, leads to the formation of tartronic acid *via* consecutive oxidation of glyceric acid. Interestingly, this product is stable with these catalysts. It is apparent that, with careful control of the reaction conditions, 100% selectivity to glyceric acid can be obtained with 1 wt% Au/C. The activity is dependent on the gold loading. For catalysts containing 0.25 or 0.5 wt% Au supported on graphite, lower glycerol conversions were observed (18 and 26%, respectively as compared to 54% for 1 wt% Au/graphite under the same conditions) and lower selectivities to glyceric acid were also observed. This was observed to be consistent with the earlier studies for diol oxidation by Prati and co-workers[85–87] which have also shown that the conversion is dependent on the Au loading upon the support. This is possibly due to a particle size effect of the Au nanoparticles on the support. However, the Au supported catalysts that were selective for glycerol oxidation comprised Au particles as small as 5 nm and as large as 50 nm in diameter. The majority, however, were about 25 nm in size and were multiply twinned in character. Decreasing the loading to 0.5 or 0.25 wt% did not appreciably change the particle size distribution; the particle number density per unit area was observed to decrease proportionately however, which may be correlated to the decrease in glycerol conversion and selectivity to glyceric acid. Recently, we have used cyclic voltammetry to study Au catalysts supported on graphite,[101] since in this case the support is conducting and this very incisive technique can be used. Four catalysts were investigated, namely two samples with 1 wt% Au, one of which was inactive and the other giving 100% specificity to glycerate, and two less selective catalysts containing lower gold loadings (0.25 and 0.5 wt% Au/graphite). In the absence of glycerol, the active gold catalysts show two features in the CV experiments (labelled A and B in Fig. 3(a)), the feature denoted B is observed with bulk gold metal, *e.g.* the gold sample holder (Fig. 3(b)), whereas feature A is absent with bulk gold and is associated with nanocystalline gold. The CV experiments were also carried out with the Au/graphite catalysts in the presence of glycerol, air and NaOH, thereby studying the behaviour *in situ* under reaction conditions (a typical voltamogram is shown Fig. 3(c)). In the forward potential sweep, all catalysts showed a broad signal associated with the electrooxidation of glycerol at *ca.* 0.9–1.3 V (labelled C) and a narrower feature on the reverse sweep (labelled D). Peak D corresponds to the situation in which the gold surface is being stripped of bulk oxide leaving behind only the Au–OH species (peak A) with a minimal amount of

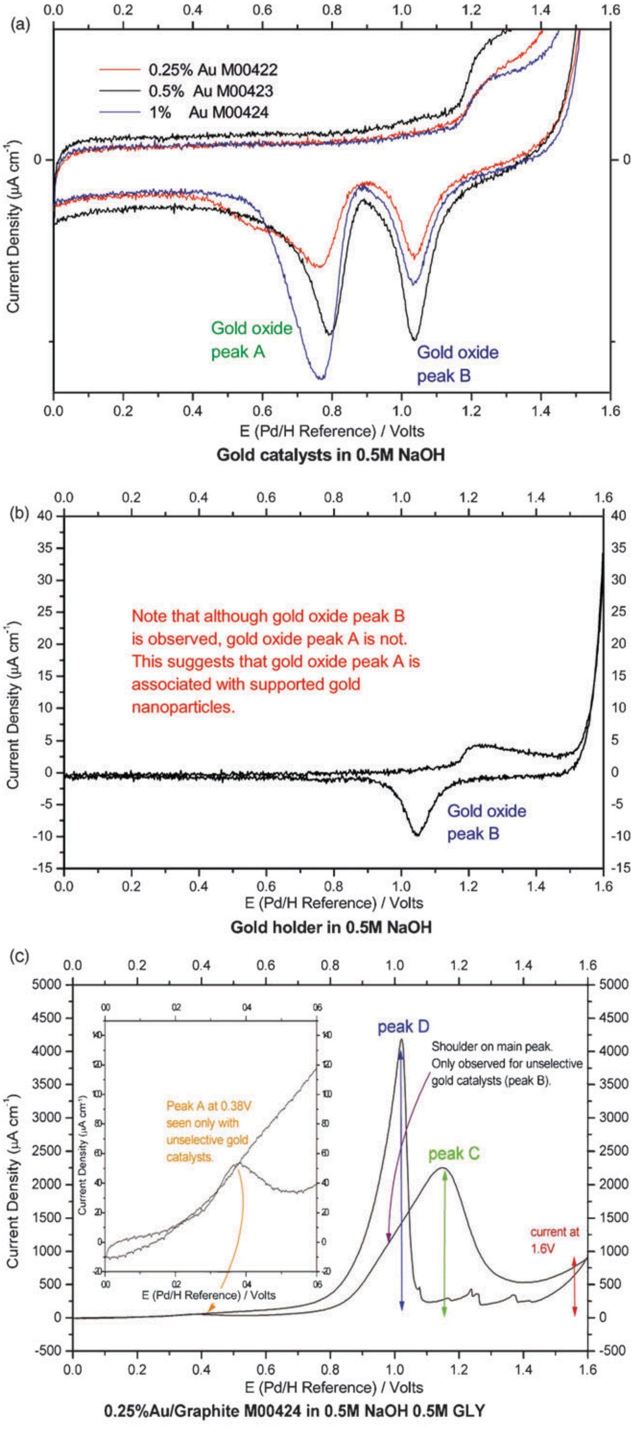


Fig. 3 Cyclic voltametry of gold supported on graphite: (a) Au/C in NaOH (0.5 mol l^{-1}), (b) gold sample holder in NaOH 0.5 mol l^{-1}), (c) 0.25 wt% Au/C in NaOH (0.5 mol l^{-1}) and glycerol (0.5 mol l^{-1}).

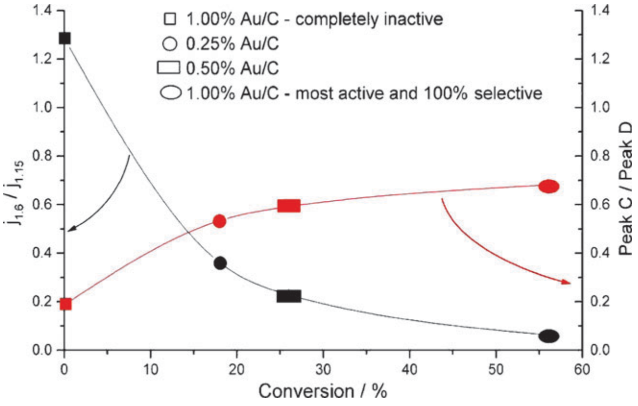


Fig. 4 Plot of current density at 1.6 V (*j*1.6)/current density at 1.15 V (*j*1.15) and ratio of peak C/peak D *vs.* percentage conversion for various supported Au/C catalysts used for glycerol oxidation.[97]

molecular fragments adsorbed (since these have been oxidised during the previous positive potential sweep). This situation leads to peak D being the most intense and the catalyst being in its most active state. Peak C corresponds to the same situation although the relative amounts of strongly adsorbed molecular fragments is increased (since these have not yet been oxidised) and hence a smaller concentration of Au–OH species due to site-blocking *via* glycerol decomposition. Both of these factors lead to peak C being smaller than peak D. This behaviour also emphasises the poisoning effect on the reaction of bulk gold oxides which quench reaction at potentials >1.3 V on the forward sweep and also down to 1.1 V on the negative sweep due to hysteresis in the "irreversible" formation/desorption of the bulk oxide phase.[102] This suggested that there should be a strong correlation between activity and the relative intensities of peaks C and D. In addition, it should be noted that the 0.25 and 0.5% Au/C catalysts gave rise to two minor peaks at 0.38 and 1.0 V. For the active catalyst displaying total specificity to glycerate (1 wt% Au/graphite) the minor peaks are both absent and we also considered this to be important. Furthermore, current density positive of 1.3 V associated with the electrooxidation of strongly adsorbed glycerol fragments increases in the order:

1% Au/C < 0.5% Au/C < 0.25% Au/C < 1% Au/C (inactive)

indicating that this factor could also be used to rank catalyst performance. In this way, the CV study revealed key differences between all four the catalyst samples. In particular, two features were identified that appeared to correlate with catalyst activity: (a) the relative insensitivities of specific peaks observed in the CV and (b) the amplitude of the current density at >1.3 V. Fig. 4 shows a plot of these two parameters *vs.* catalyst activity, namely (i) the ratio of current densities (*j*) of peak C/peak D and (ii) the ratio of current density at 1.6 V/the current density of peak C. Both these parameters express the rates of surface blocking (poisoning) relative to oxidation by adsorbed Au–OH species. It is apparent that there exists a smooth correlation between activity and both of these parameters and this observation may have significance in the design of improved oxidation catalysts, certainly we can expect the use of this technique to become more widely used in aiding the design of improved graphite-supported gold catalysts.

Direct H_2O_2 synthesis using gold palladium alloy catalysts

The direct synthesis of hydrogen peroxide from the oxidation of molecular hydrogen by molecular oxygen is considered to be of immense current interest. Hydrogen peroxide is an important green oxidant that is useful in many large scale processes such as bleaching and as a disinfectant. Its use in the fine chemical industry accounts for a much lower consumption but since it is viewed as a green oxidant with water being the only by-product, it is recognized to have significant potential in chemical synthesis, particularly in the production of propene oxide.

At present, hydrogen peroxide is produced by the sequential hydrogenation and oxidation of an alkyl anthraquinone, and global production is *ca.* 1.9 × 10^6 tonnes per annum. It is therefore a major commodity chemical, yet its method of manufacture has remained unchanged for decades. The current indirect process is only economic on a large scale (4–6 × 10^4 tpa), whereas hydrogen peroxide is often required practically on a much smaller scale. An additional complication arises because of the scale of manufacture, and this relates to the concentration at which it is prepared as a final product and shipped. To make this process economic hydrogen peroxide is produced at high concentrations (50–70 vol%) to minimize transport costs. However, when used, as a disinfectant or as a bleach, it is required at a strength of only *ca.* 3–5 vol%. For the indirect process to be viable it is required that the material is manufactured at a central location and shipped to its point of use. This means that highly concentrated hydrogen peroxide, a very hazardous material, is shipped and this has not been without consequences.[102] Hence, there is a significant mismatch between the current scales at which it is made and used and the concentration at which it is provided and utilized. The direct small scale production of hydrogen peroxide at the site where it is used would offer many advantages, not least that this will negate the need to transport concentrated solutions of hydrogen peroxide. Such a direct process could not be expected to replace, or indeed be desirable for, all manufacture of hydrogen peroxide, since there are applications for which highly concentrated hydrogen peroxide is required, *e.g.* as a propellant for rockets. At present, no commercial process exists for the direct formation of H_2O_2, but it is currently being evaluated at pilot plant scale in the Degussa Headwaters collaboration.[103] The direct reaction has been the subject of significant interest for over 90 years especially,[104] and, indeed, almost exclusively, in industrial laboratories.[105–117] Indeed, it can be viewed as one of the dream reactions (along with the direct oxidation of methane to methanol). However, the direct synthesis is a notoriously difficult reaction, since the product is unstable with respect to both hydrogenation and decomposition, and the non-selective combustion of hydrogen is a facile competing reaction (Fig. 5).

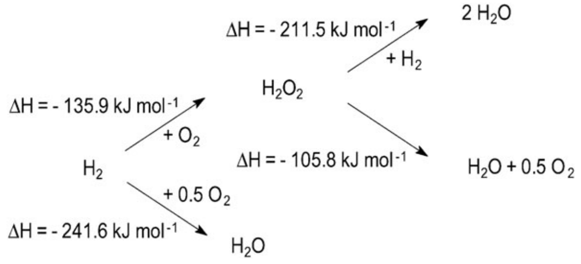


Fig. 5 Synthesis and decomposition of hydrogen peroxide.

Until very recently, the catalysts used in the investigation of direct hydrogen peroxide synthesis have been based on Pd, since it is a highly effective hydrogenation catalyst. Since many researchers have concluded that it is important to try to achieve the highest rate of product formation most of these earlier studies used H_2/O_2 mixtures in the explosive region; solutions of over 35 wt% hydrogen peroxide have been made by reacting H_2/O_2 over Pd catalysts at elevated pressures.[109] However, operating in the explosive region with H_2/O_2 mixtures can be considered extremely dangerous, and more recently, studies have concentrated on carrying out the reaction with dilute H_2/O_2 mixtures well away from the explosive region.[118,119] This has been the area in which we have concentrated and observed that the addition of gold to palladium can increase both its activity selectivity.[118–123]

We have evaluated a number of supports, TiO_2, Al_2O_3, Fe_2O_3 and carbon, in detail, using very dilute reactant gases below the lower explosive limit and at low reaction temperatures (2 °C). In general, we find that the best, most active catalysts are prepared by a relatively simple impregnation procedure, and catalysts prepared sing deposition precipitation or coprecipitation are much less active. For the catalysts calcined at 400 °C prepared by impregnation, the pure Au catalysts all generate H_2O_2 but at low rates. The addition of Pd to Au significantly enhances the catalytic performance for the synthesis of H_2O_2, and moreover it is interesting to note that there is an optimum Pd–Au composition where the rate of H_2O_2 production is much higher than for the pure Pd catalyst, which in itself is significantly more active than pure gold. Our initial studies concerned Al_2O_3 as a support and it was observed that the optimum catalysts were gold rich (Fig. 6). Subsequent studies with TiO_2 and carbon all showed that the highest rates are observed for the 2.5 wt% Au–2.5 wt% Pd catalysts (Table 1). The rates of hydrogen peroxide formation

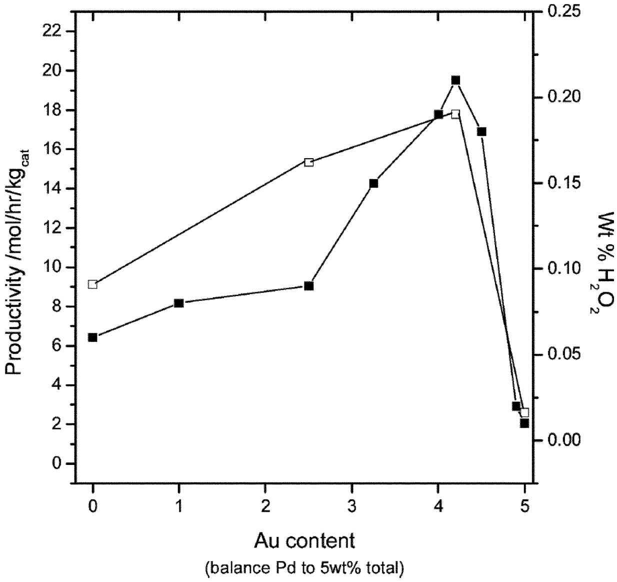


Fig. 6 Effect of addition of Au to supported Pd/Al_2O_3 catalysts for the synthesis of hydrogen peroxide. Catalysts calcined at 400 °C in air (■) or calcined in air at 400 °C and reduced at 500 °C with hydrogen (□). Mass of catalyst = 50 mg.[120]

Table 1 Formation of hydrogen peroxide using Au, Pd and Au–Pd supported catalysts[a,123]

Catalyst	Hydrogen peroxide formation/mol H_2O_2 (h kg_{cat})$^{-1}$	Hydrogen selectivity (%)
5% Au/C	1	nd
2.5% Au–2.5% Pd/C	110	80
5% Pd/C	55	34
5% Au/Al_2O_3	2.6	nd
2.5% Au–2.5% Pd/Al_2O_3	15	14
5% Pd/Al_2O_3	9	nd
5% Au/TiO_2	7	nd
2.5% Au–2.5% Pd/TiO_2	64	70
5% Pd/TiO_2	30	21

[a] Standard reaction conditions, nd = not determined as the yield is too low for reliable measurement.

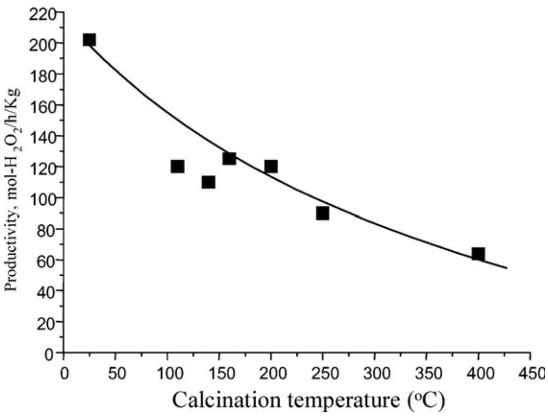


Fig. 7 Influence of the calcination temperature of 2.5 wt% Au–2.5 wt% Pd/TiO_2 catalysts on the productivity to hydrogen peroxide. Reaction time 30 min, using standard reaction conditions at 2 °C.[122]

with the carbon-supported catalysts are almost a factor of two higher than the corresponding TiO_2-supported catalysts, and almost an order of magnitude greater than the Al_2O_3-supported catalysts, demonstrating that the nature of the support plays an important role in the direct oxidation reaction. However, the synergistic effect observed for the rate of hydrogen peroxide formation on addition of Au to Pd is similar for the carbon- and titania-supported catalysts, being roughly a factor of two, and the synergistic effect is less marked in the alumina-supported catalysts (Table 1).

In our initial studies with TiO_2-supported catalysts we found that catalysts that were not calcined were much more active and selective than those calcined at 400 °C (Fig. 7). This observation made us investigate these catalysts in considerable more detail, particularly with respect to catalysts stability and reuse. For any catalyst that is used in a batch process it is important to determine if the catalyst can be successfully re-used: with precious metal catalysts it is essential that the metals are not lost from the catalyst during use. Indeed, the possibility has to be investigated whether active components can leach into the reaction mixture, thereby leading to catalyst deactivation or, in the worst case, leading to the formation of an active homogeneous catalyst. We have investigated the effect of calcination on the stability of catalysts used in the direct synthesis reaction since, in general, catalysts that are not calcined prior to use are highly active *e.g.* 2.5% Au–2.5% Pd/TiO_2 dried at 25 °C, gives a rate of H_2O_2 synthesis of 202 mol H_2O_2 (kg_{cat} h)$^{-1}$, H_2 conversion of 46% and H_2O_2 selectivity of 89%. This rate is significantly higher than that observed for calcined catalysts (Fig. 7). However, the non-calcined materials are highly unstable due to loss of metals during use and representative data for Al_2O_3- and TiO_2-supported catalysts are shown in Table 2. In contrast, catalysts that are pre-calcined at 400 °C prior to use are very stable and do not leach any Au or Pd into solution. Data for consecutive reuse of the carbon and TiO_2-supported catalysts are shown in Fig. 8 and it is apparent that these catalysts can be re-used many times. It is important to note that the way in which the calcination is carried out is critical. Both the temperature and gas environment need to be carefully controlled to achieve the stable catalysts that we report in this study. Use of lower temperatures than 400 °C, even for a longer time, leads to catalysts that leach Au and Pd on use.

To determine the nature of the supported Au–Pd catalysts a detailed structural and chemical characterization was carried out using scanning transmission electron microscopy (STEM) and X-ray photoelectron spectroscopy. The combined Au(4d) and Pd(3d) spectra for a 2.5 wt% Au–2.5 wt% Pd/C, 2.5 wt% Au–2.5 wt% Pd/TiO_2 and 4.2 wt% Au–0.8 wt% Pd/Al_2O_3 catalysts are shown following drying (Fig. 9(a)) and calcination at 400 °C (Fig. 9(b)). For the dried samples, we observe clear spectral contributions from both Au and Pd leading to severe overlap of peaks. After calcination at 400 °C, for the TiO_2- and Al_2O_3-supported catalysts there is a dramatic decrease in the intensity of the Au(4d) peaks, and for the TiO_2-supported catalyst the Au($4d_{3/2}$) feature is not readily apparent. It is clear that for these materials the surface has

Table 2 Reuse of catalysts and catalyst stability[123]

Catalyst	Pre-treatment	Run	Au remaining[a] (%)	Pd remaining[a] (%)
2.5 wt% Au–2.5 wt% Pd/TiO_2	Air, 25 °C	1	20	10
	Air, 25 °C	2	8	5
2.5 wt% Au–2.5 wt% Pd/TiO_2	Air, 400 °C	1	100	100
	Air, 400 °C	2	100	100
2.5 wt% Au–2.5 wt% Pd/Al_2O_3	Air, 25 °C	1	25	21
	Air, 25 °C	2	20	15
2.5 wt% Au–2.5 wt% Pd/Al_2O_3	Air, 400 °C	1	100	100
	Air, 400 °C	2	100	100

[a] [(Au or Pd after run 1 or 2)/(Au or Pd in fresh catalyst)] × 100.

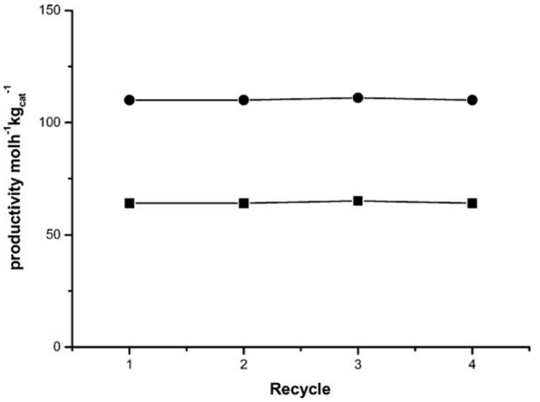


Fig. 8 The effect of the number of uses on the productivity for H_2O_2 formation: (●) 2.5 wt% Au–2.5 wt% Pd/C catalyst calcined in air at 400 °C; (■) 2.5 wt% Au–2.5 wt% Pd/TiO_2 catalyst calcined in air at 400 °C.[123]

become enhanced in Pd on calcination at 400 °C. Such an observation is consistent with the formation of a core–shell structure. In contrast, the carbon catalyst shows almost no differences in the surface Pd : Au ratio which remains close to the bulk value of 1 : 1 by weight. This shows that the carbon-supported material, which is by far the most active catalyst for the direct synthesis reaction, is significantly different from the oxide supported catalysts.

The calcined, *i.e.* stable, catalysts have been examined in detail using STEM characterisation. High-angle annular dark field (HAADF) images of the calcined Au–Pd/TiO_2 and the Au–Pd/C (2.5% Au–2.5% Pd) catalysts have been obtained and the measured particle size distributions are shown in Fig. 10 in which the emphasis is placed on the particles in the 1–10 nm size range. It is apparent that both catalysts comprise mainly small particles (*ca.* 2–10 nm), but both also contain larger particles and it is clear that the carbon-supported material, which is the more effective catalyst, has a higher number density of the larger particles (Fig. 10). This finding may be significant with respect to the origin of enhanced catalytic activity, *i.e.* that higher catalytic activity in calcined catalysts is associated with the presence of larger particles. This is consistent with our earlier observations concerning the relationship between the particle size distribution and activity of Au–Pd/Al_2O_3 catalysts.[120] There it was observed that fresh catalysts comprised Au–Pd nanoparticles with a 3–10 nm size distribution, whereas, the same catalysts that had aged on storage at ambient temperature exhibited a bimodal size distribution with some larger particles (> 10 nm) being observed. Most significantly, the aged Au–Pd/Al_2O_3 catalysts that contained the larger particles showed an enhancement in activity by a factor of three.

X-Ray energy dispersive spectroscopy (STEM-XEDS) of the larger particles has also been carried out for the Au–Pd (2.5 wt% Au–2.5 wt% Pd) catalysts supported on carbon, TiO_2 and Al_2O_3 calcined at 400 °C and the results are shown in Fig. 11. XEDS maps of the larger particles show that the Au–M_2 (9.712 keV) and the Pd L_α (2.838 keV) signals are spatially coincident, indicating that the metal nanoparticles in the field of view are in fact Au–Pd alloys in all these samples.

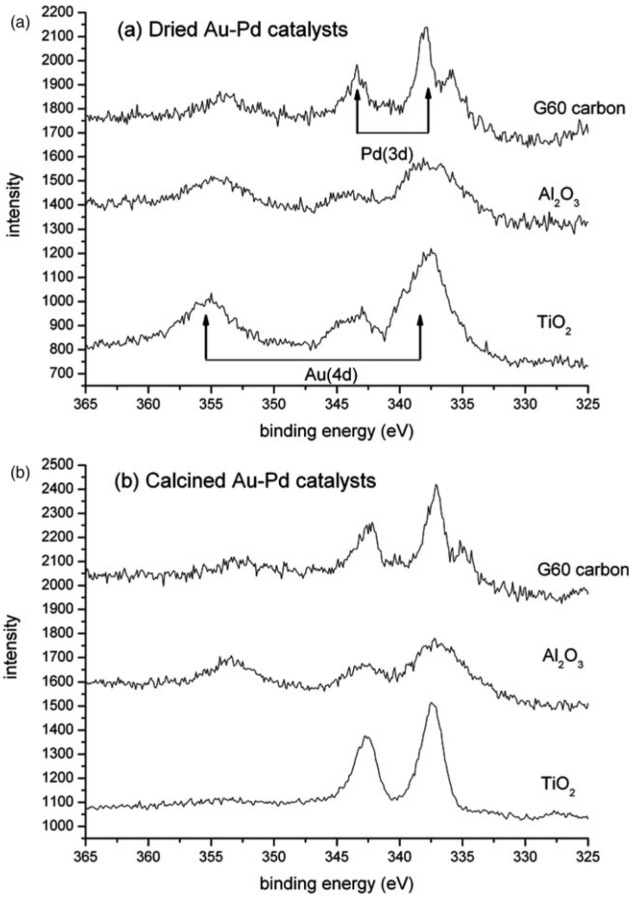


Fig. 9 Au (4d) and Pd (3d) spectra for 2.5 wt% Au–2.5 wt% Pd catalysts after different heat treatments: (a) uncalcined, (b) calcined at 400 °C in air.[123]

This suggests that there is a tendency for Pd surface segregation to occur in the alloy particles supported on TiO_2 and Al_2O_3, as indicated by the XPS analysis discussed earlier. The strong tendency for palladium surface segregation, observed in this study and for bulk alloys,[124] is not expected. We consider that it is presumably brought about by the preferential formation of Pd–O bonds at the alloy surface since in this temperature range palladium oxidizes more readily than gold.

However, the structure of the Au–Pd nanoparticles supported on carbon is significantly different, since the core–shell morphology is not observed and, rather, homogeneous Au–Pd alloys are now observed (Fig. 11). Again, this is wholly consistent with the XPS evidence (Fig. 9(b)). Furthermore, the composition of the Au–Pd alloy nanocrystals changes markedly with the particle size (Fig. 12) and the amount of gold present in the nanocrystals increases with the particle diameter. These are significant observations, since they demonstrate that the core–shell structures, which spontaneously form on Fe_2O_3, TiO_2 and Al_2O_3 supports,[120–122] are not essential for the observation of high activity for the direct synthesis of hydrogen peroxide. Rather, we have suggested that the particle size of the Au–Pd alloy is the important factor,[120–123] with larger particles appearing to be associated with high activity and in this respect the variable composition of the Au–Pd particles may be an important factor. Given these factors, the active sites for the direct formation of

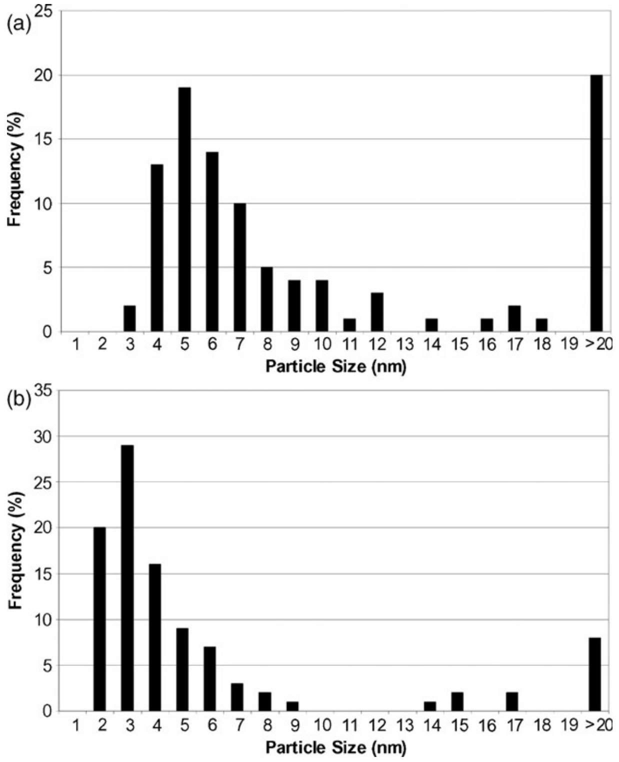


Fig. 10 Particle size distributions for Au–Pd catalysts: (a) Au–Pd/C, (b) Au–Pd/TiO_2[123]

hydrogen peroxide may well be very different from the isolated sites described by Chen *et al.*[125] for Au–Pd alloy catalysts that are effective for the acetoxylation of ethene in the production of vinyl acetate. The question arises as to why core–shell structures form spontaneously on the oxide supports but not on carbon. This may be due to the oxidation efficacy of the support surface, since carbon is a reducing support. As noted earlier, the formation of palladium shell structures may be due to the surface of the nanocrystals being oxidised and PdO, therefore, phase separates to the surface. This process is hindered by the reducing nature of the carbon support. Indeed, carbon is used in the extraction of Au^{3+} salts during the commercial production of gold and during this process the Au^{3+} is reduced to metallic gold. This process may also occur during the preparation of the Au–Pd alloys used in this study and this may stabilise the random alloys rather than core–shell structures.

Using our dilute reaction conditions we can generate hydrogen peroxide at significant rates in the stirred batch autoclave reactor. However, the reaction time and amount of catalyst used are important variables in the direct synthesis reaction since there are a number of competing processes that lead to the decomposition of hydrogen peroxide, even at 2 °C, the temperature at which we have carried out our experiments. The effect of increasing reaction time in the autoclave is shown in Fig. 13 for the 2.5% Au–2.5% Pd/TiO_2 catalyst calcined at 400 °C. Separate experiments were conducted for each reaction time and so the data present the amount of H_2O_2 formed as an average over the reaction period. It is apparent that as the yield of H_2O_2 increases steadily with reaction time so the rate of formation decreases, and under our reaction conditions we have concluded that 30 min gives a reasonable compromise

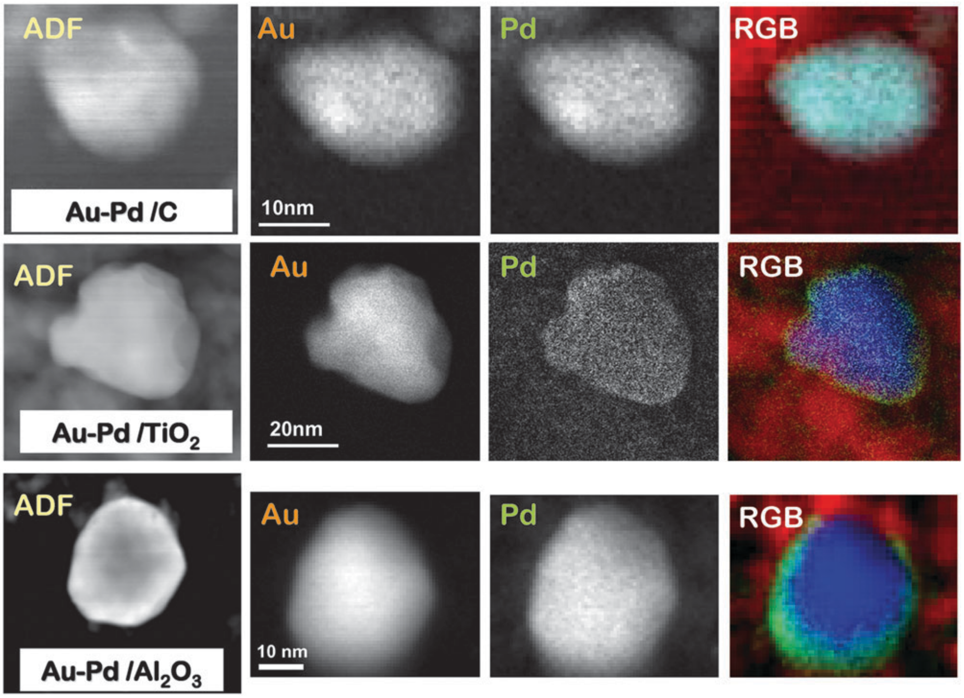


Fig. 11 Montage of HAADF image (*column 1*), Au map (*column 2*), Pd map (*column 3*) and RGB reconstructed overlay map (*column 4*) (Au – blue, Pd – green) for calcined AuPd/C (*row 1*), calcined AuPd/TiO_2 (*row 2*) and calcined AuPd/Al_2O_3 (*row 3*). Note that the calcined AuPd particles on TiO_2 and Al_2O_3 supports show a Au rich-core/Pd-rich shell morphology, whereas calcined AuPd particles on activated C are homogeneous alloys.[123]

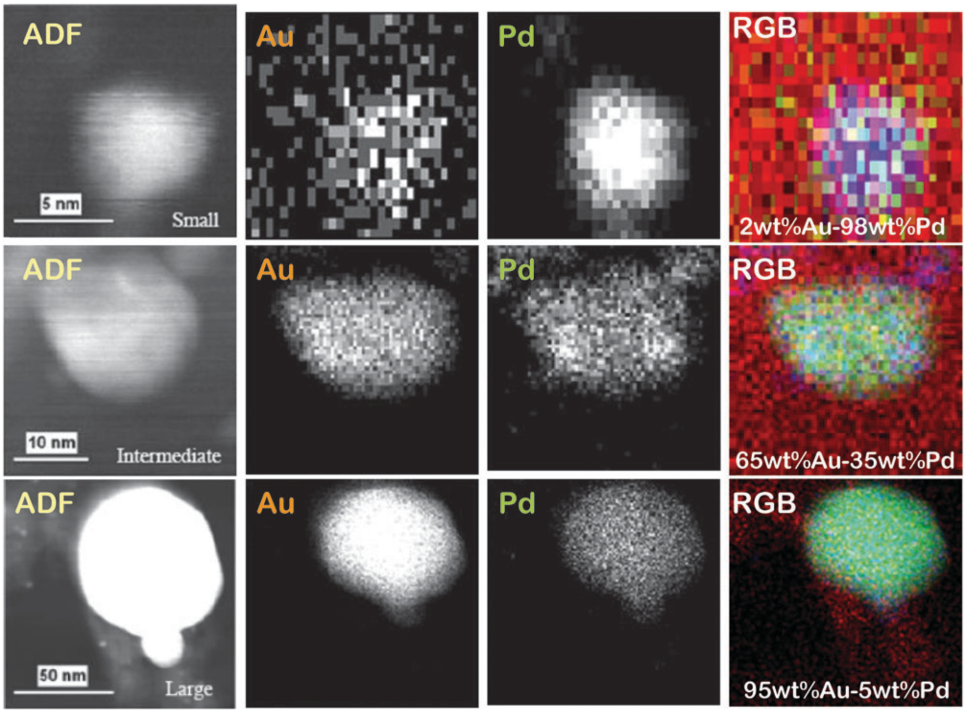


Fig. 12 Montage of (a) ADF image, (b) Au L_α XEDS map, (c) Pd L_α XEDS map and (d) RGB overlays (C – red, Au – green, Pd – blue) from small (row 1), intermediate (row 2) and large (row 3) particles found in a AuPd/C catalyst.[133]

between rate and overall yield of H_2O_2 for the purposes of comparing the catalytic performance of these catalysts. Of course the optimal conditions will vary with other conditions such as temperature and pressure, and so it can be reasonably anticipated that at higher temperatures and reaction pressures much shorter reaction times will be preferred. For example we have conducted virtually all of our studies at one fixed solvent composition (methanol/water), and we have recently shown that the rate of hydrogen peroxide synthesis is dependent on the solvent composition (Fig. 14), and even water alone can be successfully used as a solvent. At first sight the use of diluted reactants, that avoid the potential for explosion hazards, might imply that the direct synthesis method will only produce relatively dilute solutions and hence the methodology may be better suited to *in situ* utilisation in chemical syntheses in which the H_2O_2 is used as soon as it is formed. However, our catalyst can produce hydrogen peroxide at significant rates (Table 1) and if flow reactors are considered then we anticipate that the target concentrations required for the direct synthesis reaction (*i.e.* 6–8 vol% H_2O_2) can be achieved using the intrinsically safe dilute conditions we have pioneered, indeed it is the synergy between Au and Pd that leads to enhanced activity that permits the real possibility of a commercial direct synthesis process.

Alcohol oxidation revisited

In the initial studies with supported gold catalysts it was noted that alcohol oxidation could be achieved under mild conditions when base was present.[87] Although, it was also apparent that raising the temperature and using gas-phase reactants the

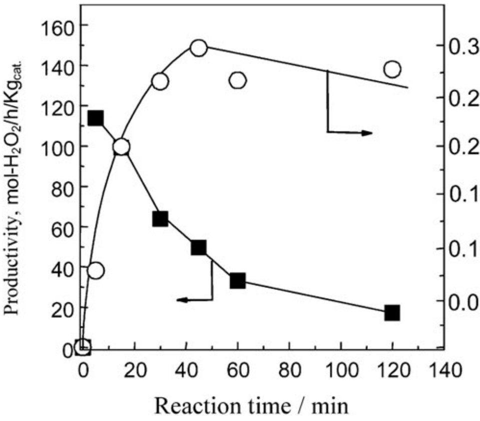


Fig. 13 Effect of reaction time on the synthesis of hydrogen peroxide (catalyst 20 mg, standard reaction conditions at 2 °C).[122]

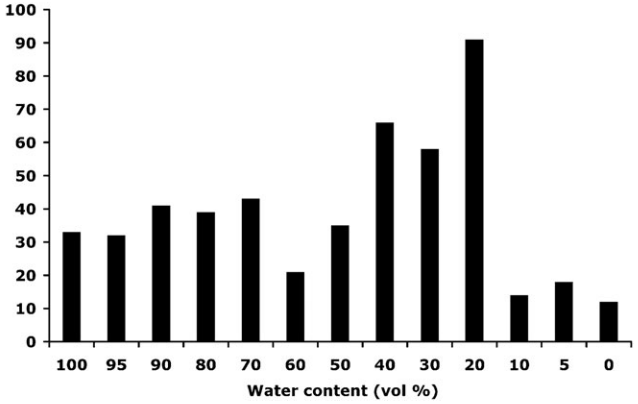


Fig. 14 Effect of water–methanol ratio on the rate of synthesis of hydrogen peroxide under standard reaction conditions at 2 °C.[134]

Table 3 Comparative data for benzyl alcohol oxidation and hydrogen peroxide synthesis[a,131]

	Benzyl alcohol oxidation					
	Conversion (%)		Benzaldehyde selectivity (%)			
Catalyst	0.5 h	8 h	0.5 h	8 h	Benzaldehyde productivity[c]/ mol (h kg_{cat})$^{-1}$	H_2O_2 productivity/ mol (h kg_{cat})$^{-1}$
2.5% Au–2.5% Pd/Al_2O_3	2.6	83.3	90.5	86.6	174	23
2.5% Au–2.5% Pd/TiO_2	3.7	74.5	95.2	91.6	165	64
2.5% Au–2.5% Pd/SiO_2	3.6	35.7	97.3	88.0	76	80
2.5% Au–2.5% Pd/Fe_2O_3	3.6	63.4	74.9	66.4	102	16
2.5% Au–2.5% Pd/C	2.9	69.2	53.9	46.4	78	30
2.5% Au/TiO_2	0.6	15.3	96.7	63.9	24	(<2) nd[b]
2.5% Pd/TiO_2	13.4	60.1	51.3	54.4	79	24

[a] Comparative results obtained for the oxidation of benzyl alcohol after 8 h reaction and for H_2O_2 synthesis for 0.5 h. The oxidation of benzyl alcohol was carried out at 373 K temperature, 0.2 MPa O_2 pressure and 1500 rpm stirrer speed. The H_2O_2 synthesis was carried out under the conditions described in refs. 26 and 27. [b] Very low rate <2 mol H_2O_2 (h kg_{cat})$^{-1}$. [c] Calculated for 8 h reaction.

activation of the alcohol could be achieved, but now the product was the aldehydes rather than the sodium salt of the mono-acid.[126] However, it has been known for some time that highly dispersed metal catalysts, *e.g*. Pd and Ru could effectively catalyse the oxidation of alcohols to aldehydes and ketones. One of the most significant advances in the field of alcohol oxidation has been the observations of Corma and co-workers[127,128] showing that an Au/CeO_2 catalyst is active for the selective oxidation of alcohols to aldehydes and ketones and the oxidation of aldehydes to acids. In these studies the catalysts are active at relatively mild conditions, without the addition of a solvent, using O_2 as oxidant without the requirement for the addition of NaOH to achieve high activity. This last factor is most significant and the omission of NaOH permits the use of green reaction conditions for these oxidation reactions. The results were shown to be comparable to, or higher than, the highest activities that had been previously observed with supported Pd catalysts.[129] The catalytic activity was ascribed to the Au/CeO_2 catalyst stabilising a reactive peroxy intermediate from O_2. We have previously shown that supported Au–Pd alloys are efficient catalysts for the direct synthesis of H_2O_2 from H_2 oxidation by O_2 at low temperatures.[112–118] In particular, Au–Pd/TiO_2 catalysts were very selective for hydrogen peroxide synthesis. Hydroperoxy species are considered to be involved in this H_2O_2 formation process, and because hydroperoxy species are key reagents/intermediates in the oxidation of alcohols,[130] we reasoned that these catalysts should also be effective for the oxidation of alcohols. This we found to be the case[131] (Table 3), and the catalysts previously found to be effective for hydrogen peroxide synthesis were all effective for the oxidation of benzyl alcohol, which we used as a test reactant. TiO_2-supported catalysts were found to be the most selective and these were examined in greater detail for the oxidation of benzyl alcohol at 100 °C with O_2 as oxidant in the absence of solvent (Fig. 15). The Au–Pd/TiO_2 catalysts were very active for this reaction, and the selectivity to benzaldehyde was >96%, with the only by-product being benzyl benzoate. In contrast, Pd/TiO_2 also produced toluene and benzene as by-products, and the Au/TiO_2 catalyst produced a significant amount of an acetal product. The selectivity of the Au/TiO_2 catalyst for benzaldehyde decreased with the time on line, but further oxidation of the acetal by-product led to an increase of the final selectivity in benzaldehyde. The effect of adding Au to a Pd/TiO_2 catalyst is apparent in these initial studies. Although the Pd/TiO_2 catalyst has a high initial activity, and the addition of Au decreases the activity, the Au–Pd/TiO_2 catalyst retained high selectivity to benzaldehyde at high conversion rates, a feature not observed with the supported pure-Au and pure-Pd catalysts. Carbon mass balances were 100%, and no carbon oxides were formed for Au–Pd/TiO_2 or Au/TiO_2 catalysts, but carbon oxides were formed with the supported Pd catalysts. Most importantly, no leaching of gold or palladium was observed with these catalysts, and it should be noted that these reactions were carried out using the catalysts prepared by calcination at 400 °C which had been shown to be totally stable during the direct formation of hydrogen peroxide and to possess a core–shell structure (Fig. 11).

The Au–Pd/TiO_2 catalysts were investigated with a range of substrates and conditions (Table 4). It is clear that these catalysts are highly reactive for a very broad range of alcohols. As noted previously, both Kaneda and co-workers[129] and Corma and co-workers[127] have shown that supported Pd

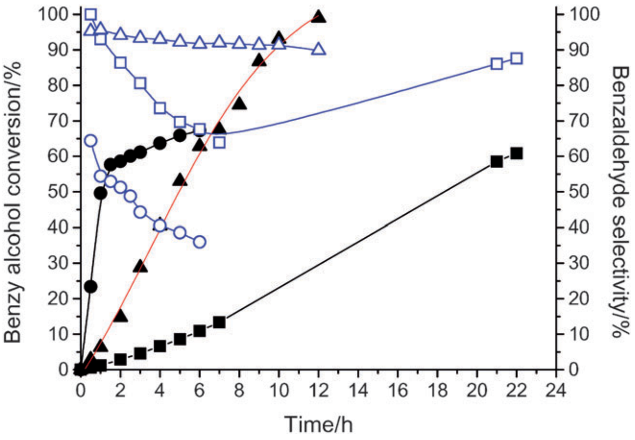


Fig. 15 Benzyl alcohol conversion and selectivity in benzaldehyde with the reaction time at 373 K, 0.1 MPa O_2 pressure: (■) Au/TiO_2, (●) Pd/TiO_2, (▲) Au–Pd/TiO_2; solid symbols – conversion, open symbols – selectivity (benzyl alcohol (40 ml), catalyst (200 mg), 100 °C, 0.2 MPa O_2).[131]

Table 4 Comparison of the catalytic activity for alcohol oxidation to the corresponding aldehyde. Catalyst is 2.5% Au–2.5% Pd/TiO_2 unless noted otherwise; substrates oxidised without solvent unless specified; catalyst mass varied to give metal concentrations indicated; TOF measured after first 0.5 h reaction[131]

		Reaction conditions		10^5[metal]/mol l^{-1}		
Entry	Alcohol	T/K	$10^{-5}P$/Pa	Au	Pd	TOF/h^{-1}
1	Benzyl alcohol	373	2	63.5	118	607
2	Benzyl alcohol[a]	373	2	63.5	0	213
3	Benzyl alcohol[b]	373	2	0	118	2200
4	Benzyl alcohol	373	1	2.1	3.9	6190
5	Benzyl alcohol	373	2	2.1	3.9	6440
6	Benzyl alcohol	373	5	2.1	3.9	6190
7	Benzyl alcohol	373	10	2.1	3.9	5950
8	Benzyl alcohol	383	1	2.1	3.9	14 270
9	Benzyl alcohol	393	1	2.1	3.9	26 400
10	Benzyl alcohol	433	1	2.1	3.9	86 500
11	1-Phenylethanol	433	1	1.8	3.2	269 000
12	3-Phenyl-1-propanol	433	1	2.1	3.9	2356
13	Vanillyl alcohol[c]	363	1	21.6	40.6	10
14	Cinnamyl alcohol[d]	363	1	21.6	40.6	97
15	Octan-1-ol	433	1	2.5	4.7	2000
16	Octan-2-ol	433	1	2.5	4.7	0
17	Octan-2-ol/Octan-1-ol	433	1	2.1	3.9	0
18	Octan-3-ol	433	1	2.1	3.9	10 630
19	1-Octen-3-ol	433	1	2.1	3.9	12 600
20	Crotyl alcohol	433	5	2.1	3.9	12 600
21	Butan-1-ol	433	5	2.1	3.9	5930
22	1,2-Butanediol	433	1	2.1	3.9	1520
23	1,4-Butanediol	433	1	2.1	3.9	104 200
24	Benzyl alcohol[e]	433	1	2.1	3.9	12 500
25	Benzyl alcohol[f]	433	1	2.1	0	12 400
26	Benzyl alcohol[g]	433	1	0	3.9	24 800
27	Benzyl alcohol[h]	433	1	2.4	4.5	36 500
28	Benzyl alcohol[i]	433	1	0	3.6	37 600
29	1-Phenylethanol[i]	433	1	0	3.1	11 600

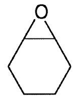
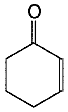
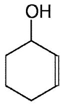
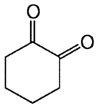
[a] 2.5% Au/TiO_2. [b] 2.5% Pd/TiO_2. [c] 0.2 mol l^{-1} in toluene as solvent. [d] 0.2 mol l^{-1} in water as solvent. [e] 2.5% Au–2.5% Pd/HAP prepared by impregnation of HAP with $HAuCl_4{\cdot}3H_2O$ and $PdCl_2$. [f] 2.5% Au/HAP prepared by impregnation of HAP with $HAuCl_4{\cdot}3H_2O$. [g] 2.5% Pd/HAP prepared by impregnation of HAP with $PdCl_2$. [h] 2.5% Au–2.5% Pd/TiO_2 prepared with the method of Kaneda[129] using TiO_2 as support. [i] 0.2% Pd/HAP prepared using the method of Kaneda[129] using HAP as support.

and Au monometallic catalysts are highly effective for the oxidation of 1-phenylethanol under solvent-free conditions at 160 °C with a pO_2 of 0.1 MPa. Under these conditions, the Pd/HAP and Au/CeO_2 catalysts gave TOFs of 9800 and 12 500 h^{-1} for 1-phenylethanol. Under these conditions, the Au–Pd/TiO_2 catalyst, gave a TOF of 269 000 h^{-1}. This represents a significant enhancement on the TOFs of the single metals. The Au–Pd/TiO_2 catalyst is also effective for a range of straight-chain, benzylic, and unsaturated alcohols (Table 4) and, in particular, for the oxidation of primary alcohols, such as butan-1-ol and octan-1-ol, and high TOFs are observed. Interestingly, the Au–Pd catalysts are more reactive for the oxidation of 1-alcohols, which again contrasts with the Au and Pd monometallic catalysts which are more reactive for the oxidation of secondary alcohols.

Alkene epoxidation revisited

As noted earlier, supported gold catalysts, and, in particular gold supported on titania or titanium silicalites are very active for the oxidation of propene to propene oxide as long as a sacrificial reductant, typically hydrogen, was present.[68,69] As gold supported on carbon was shown to be effective for the oxidation of glycerol to glycerate under mild conditions using molecular oxygen[98] as the oxidant, we considered that it was worth investigating the activity of this catalyst system for alkene oxidation.[132] The initial experiments investigated the oxidation of cyclohexene using 1% Au/C with oxygen using polar solvents (for example, water) in a stirred autoclave reactor or a stirred non-pressurized glass reactor. Even under relatively mild conditions (60–80 °C, 4–24 h), only CO_2, formic acid and oxalic acid were formed with up to 100% cyclohexene conversion (Table 5), but, crucially, no C_6 products were observed. Experiments involving the potential reaction of expected C_6 products with water as solvent under identical conditions indicated that had these been formed they would have been observed. It is therefore clear that in polar solvents the oxidation of the alkene does not proceed *via* the epoxide. It was at this stage that we carried out a key experiment in the absence of solvent but in the presence of molecular oxygen, in a stirred autoclave reactor. In this case, 2-cyclohexene-1-one and 2-cyclohexen-1-ol were observed. This demonstrates that the Au/C catalyst was able to selectively oxidise an alkene, although the products observed are those of allylic oxidation, and are not associated with electrophilic epoxidation. We subsequently investigated apolar solvents and found that selective oxidation could be observed, provided a small catalytic amount of a peroxy initiator was added at the start of the reaction. In the absence of the gold catalyst, but in the presence of the catalytic amount of the radical initiator, again

Table 5 Effect of solvent on selective oxidation of cyclohexene using 1% Au/C[132]

Solvent	Conv. (%)	Product selectivity 				$\sum C_6$ Sel.[a] (%)	Yield[b] (%)
Water	100[c]	0	0	0	0	0	0
Methanol	27.1[c]	0	0	0	0	0	0
THF	5.8[c]	0	0	0	0	0	0
Hexane	26.1	tr	tr	tr	0	0	0
Toluene	29.1	tr	35.1	25.1	0	60.2	17.5
1,4-Dimethylbenzene	53.5	0	12	0	43.5	55.5	29.7
1,3,5-Trimethylbenzene	8	tr	78.1	Tr	0	78.1	6.2
1,2,3,5-TMB[d]	29.7	50.2	26.3	0	0	76.3	22.7
1,2,4,5-TMB[d]/1,4-Dimethylbenzene	23.1	26	42	9.1	0	77.1	17.8
Quinoline	33.2	0	10.5	0	0	10.5	3.5
1,4-Difluorobenzene	29.1	0	47.1	26.8	0	73.9	21.5
Hexafluorobenzene	15.8	8.9	36.1	2.5	0	47.5	7.5

Reaction conditions: 1% Au/C (0.22 g), C_6H_{10} (0.012 mol), 80 °C, 24 h, solvent (20 ml). For apolar solvents *tert*-butyl hydroperoxide (5 mol% based on C_6H_{10}) was added.[a] Total selectivity to C_6 partial oxidation products. [b] Total yield of C_6 partial oxidation products. [c] Products exclusively CO_2, HCOOH and oxalic acid. [d] Tetramethylbenzene.

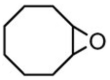
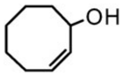
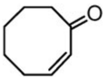
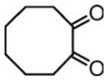
no conversion was observed, confirming that the nanocrystalline gold catalyst is necessary. We also found that small amounts of Bi could promote the selectivity for the partial oxidation products.[132] This opens up an interesting possibility in the design of supported nanocrystalline gold catalysts; as yet this is a subject area that has received very little attention, but is a topic that could produce new exciting discoveries.

The use of d_8-deuterotoluene as solvent did not lead to any discernable change in the rate of reaction, nor did we observe the incorporation of deuterium into the products. This indicates that the solvent is not involved intimately with the reaction, and the absence of a kinetic isotope effect indicates that the solvent was not acting as a sacrificial source of hydrogen in the rate-determining step, in contrast to the way in which sacrificial hydrogen is required in previous studies for propene oxidation.[68,69]

One of the remarkable features of the preliminary results on the gold-catalysed oxidation of alkenes was the large solvent effect on the reaction rate and the observation that only in aromatic solvents was oxidation controllable so that the alkene (cyclohexene) was not converted into carbon dioxide, formic acid and oxalic acid (Table 5). Indeed the solvent can be used it can be used to tune or control the selectivity to a range of products (Table 5). Among a range of aromatic solvents, where the absence of an effect of solvent deuteriation precludes chemical involvement, the solvent effect on rate was large, even comparing conversions in solvents with very similar molecular structures (epoxide selectivities in parentheses), *e.g.* *p*-xylene, 53.5 (0); mesitylene, 8 (trace); 1,2,3,5-tetramethylbenzene, 29.7 (50); hexafluorobenzene, 16 (9), and epoxide selectivities were clearly not simply related to overall reactivity. We are currently exploring the origins of this reactivity.

We investigated the oxidation of *cis*-cyclooctene under solvent-free conditions (Table 6). We found that with *cis*-cyclooctene (Table 6) as substrate, high selectivities can be achieved even when the amount of the peroxy initiator (TBHP) was decreased to as low as 0.002 g per 10 ml substrate, representing a cyclooctene : TBHP molar ratio of 300 : 1 and a molar ratio of epoxide to peroxide of 32 : 1. With our non-optimized system, yields of 35 mol product per mol Au per h (1.9 mol per kg catalyst per h) can be achieved, which is comparable to the previous reports for propene epoxidation by Haruta and co-workers.[81] The high selectivity for the epoxide, particularly for cyclohexene and *cis*-cyclooctene, demonstrates that direct oxidation of the carbon–carbon double bond is occurring with this catalyst system. At present, our results show the gold catalyst to have significant potential for selective epoxide formation rather than the competing allylic oxidation. This characteristic is promising and worthy of further evaluation.

Table 6 *cis*-Cyclooctene oxidation with molecular oxygen in the absence of a solvent[a,132]

Catalyst	TBHP/g	Conv. (%)	Selectivity (%) 				$\sum_{\mathrm{sel}} C_8$
1% Au/graphite	0.12	7.9	81.2	9.3	4.1	0.5	95.1
1% Au/graphite	0.02	7.1	79.2	6.8	3.0	0.5	89.5
1% Au/graphite	0.002	1.3	82.6	7.4	2.1	0.6	92.7
No catalyst	0.008	2.0	Trace	0.0	0.0	0.0	—
Graphite	0.008	2.3	Trace	0.0	0.0	0.0	—

[a] *Reaction conditions*: 0.12 g catalyst, *cis*-cyclooctene (10 ml, 0.066 mol), 80 °C, 24 h, in a stirred autoclave with O_2 3 bar. TBHP = *tert*-butylhydroperoxide.

Concluding remarks

During the last ten years there has been a transformation in the field of gold chemistry. The popular and well established principle that gold was an unreactive metal with very limited chemistry has been overturned, and there is general acceptance that supported nanocrystalline gold can be extremely reactive for both oxidation and reduction reactions. In many cases, either alone or alloyed with palladium, gold possesses unique activities and at present provides the highest activities for a number of selective reactions. Indeed, it appears that gold can act as an effective catalyst for virtually every reaction it is applied to. However, this cannot be the case, and although gold may show activity in many cases, this is not in itself a new finding. It had been known for many decades that gold could be used as a catalyst; it was just that virtually every other metal was better. We should, therefore, try to concentrate on the reactions for which gold surpasses other metals, and at present these include, CO oxidation, ethyne hydrochlorination, alcohol oxidation and the selective hydrogenation of α,β-unsaturated nitro-compounds. In addition, gold catalysts have significant potential in alkene epoxidation, but it has yet to be seen whether they can surpass other approaches to epoxidation since at present the gold catalysts either require sacrificial hydrogen or a peroxide initiator. The synergistic effect of the addition of gold to palladium for the direct synthesis of hydrogen peroxide is another area, where although the activity of the gold palladium alloy is not unique, the enhancement in activity and selectivity are pronounced and enable the use of dilute and inherently safe reaction conditions to be employed. It can be confidently expected that for these reactions, where significant advantages are demonstrated by supported gold and gold palladium alloys, we can expect to see commercial activity in the near future. We can, of course, expect further significant discoveries where gold is found to possess unique features and activity, after all its scope in hydrogenation reactions has yet to be fully explored. However, in the future what is urgently required are detailed mechanistic studies aimed at understanding the reasons why gold can display these unique features of catalytic activity. In recent years such mechanistic studies have not been large in numbers and for this reason we still do not know the nature of the active site and the reaction mechanism for the most well studied reaction with gold catalysis, namely low-temperature oxidation of CO. Armed with such mechanistic knowledge we can be sue that further advances is the relatively young and new field of catalysis by gold can be achieved, for without them progress will be much slower.

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