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Gold-Catalysed Reactions

J.A. Moma, T.A. Ntho and Michael Scurrell

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Abstract

In recent years, there have been three significant pieces of research which helped propel gold catalysis research into the forefront: the discoveries that gold/silica can catalyse the hydrogenation of pentene, that gold on carbon can be used in the hydrochlorination of acetylene and that deposition-precipitation (DP) methods can be used to prepare nanogold on titania capable of enabling the oxidation of CO at very low temperatures. The synthesis of small gold particles, their characterisation and peculiar properties are considered together with their behaviour as heterogeneous catalysts for a variety of reactions. Some of the issues concerning the practical application of gold catalysts are also discussed.

Keywords: gold, catalysis, nanogold, CO oxidation, VOC oxidation, fuel cells, deactivation, regeneration, emissions control

1. Synthesis of gold nanoparticles

Nanosized gold particles are conveniently synthesised for practical applications in solution or on surfaces. In the latter case the use of supports to derive supported gold catalysts is the most widespread approach. An intermediate method comprises the use of polymerisation to accompany the development of metallic gold from gold salts exemplified by the use of simultaneous polymerisation of polyaniline where very fine control over the mean gold particle size in the range 3–10 nm can be exerted [1].

For solution, an excellent summary was recently published [2]. Examples of the synthesis include the formation of well-defined gold clusters, small nanoparticles of direct interest for catalysis and especially shaped particles such as polyhedra, rods, wires and plates. Very often protecting organic layers are used [3–7] such as thiols, citrate and polyvinylpyrrolidone (PVP)

and can act as capping agents. For gold, reduction is relatively easy, so mild reducing agents such as citrate, ascorbic acid or diols can be used. The use of sodium borohydride is also found as well as cases where no additional reductant is used, such as the simultaneous polymerisation of aniline where the hydrogen atoms released by polymerisation effectively do the work [8]. The growing polymer is thereby in intimate contact with the nanogold particles being formed and so electronic effects and nanoparticle stability are considerably enhanced.

The final size distribution often reflects the transport control mechanisms that occur and these have been well discussed [9, 10]. A degree of additional control can be provided by the use of photochemical, electrochemical or sonochemical methods as well as the use of microwave synthesis [2].

The vast majority of work has employed hydrogen tetrachloroaurate as the gold source.

The use of silica-coated gold has been discussed [11–13]. Use is made of tetraethyl orthosilicate and the method is a useful way of preparing unsupported heterogeneous catalysts. The nanoparticles are present in an essentially homogeneous environment by the silica shell, which also assists in providing a physical barrier to particle agglomeration. For solids, much use has been made of the deposition-precipitation (DP) method adopted by the Haruta group. A solution of $HAuCl_4$ is adjusted to the desired pH and gold precipitated onto a slurried support material by controlled addition of a base, usually sodium hydroxide. The point of zero charge of the support is critically important in controlling the interaction with the gold anions, so that the interactions with titania and silica, for example, are very different. Anionic gold entities are easy to adsorb onto titania at pH values above 7–8, for example. Again, a recent review summarises a lot of the essential information [14]. For materials capable of ion exchange, an alternative approach is to use gold in a cationic form and AuHY zeolites have been successfully synthesised in this way [15]. These zeolites have demonstrated activity in CO oxidation and ethylene hydrogenation, depending on the extent of the reduction of the gold, gold in higher oxidation states favouring the olefin hydrogenation reaction [15]. A degree of autoreduction has been observed, and as the ethylene hydrogenation falls, the CO oxidation increases. Once gold forms small particles, these are no longer stabilised as much by electrostatic forces and the gold moves out of the constraints of the ion-exchange sites. The state of gold in the DP samples in the case of titania as support is not simple. Gold in the +3, +1 and 0 oxidation states are found to coexist, revealed by using Mössbauer effect spectroscopy, even when no external reducing conditions have been applied [16]. The +1 state appears to correlate best with CO oxidation activity. The careful retention of all gold in the +3 state has been demonstrated using titania, as evidenced by EXAFS work [17]. The simultaneous reduction of gold and development of activity for CO oxidation has been demonstrated using a combination of reactor studies, EXAFS and TPR, and again Au(+1) seems to be implicated in catalysis, though a role for Au(0) cannot be ruled out entirely.

After DP the samples are typically hot water washed. It has been shown that extraneous anions and cations can exert an effect on gold catalysis [18]. Anions in particular appear to promote catalysis via some sort of electronic effect and exert an electron-withdrawing effect on the gold centres [18, 19]. The use of urea to give a gradual rise in pH during DP has been recorded [20, 21] and examples of high gold loadings up to about 8 mass% have been given [14]. In studies

by the Gates group, the use of organometallic gold precursors under dioxygen-free conditions is used to give a controlled formation of ligand-free small clusters on oxide supports [22, 23]. Further, a simple preparative method was reported by Haruta group who ground supports with solid gold acetylacetonate to yield solid samples [24].

Co-precipitation methods have not been entirely neglected and have been applied to the synthesis of transition metal oxide-supported gold [25–28]. Sol-gel methods have also been used, but appear to result in solids with rather large Au particles [14] when tetraethoxysilane or tetrabutoxytitanate is used.

Very recently the incorporation of gold into nanorods of rutile, especially prepared in a flower-like structure, has been reported as having very high thermal stability (of the gold), presumably due to substantially reduced gold-gold nanoparticle interactions [29]. Particles as small as 8 nm can be found even after extended exposure to 800°C. This appears to reopen the debate about whether gold-based catalysts could be used for auto emission control catalysts [30]. The addition of relatively small amounts of platinum to gold renders them less liable to sintering [31] and this aspect may also auger well for future high-temperature gold catalysis, particularly in environmental applications. The use of rutile rather than anatase avoids the debilitating effects of the anatase to rutile phase transition which can be expected to take place at about 500°C, though the phase transition temperature is itself raised in the presence of gold, a result, it is assumed, of gold-containing entities being pinned at defect sites which are the seat of the phase transition process.

2. Characteristics of nanogold particles

The effects of increased surface/volume ratio on catalysis are well known. Additionally, the presentation of a relatively high proportion of corner, edge, and misplaced surface atoms is also well known. Rates of CO oxidation, expressed as the turnover frequency, are remarkably increased at low gold particle diameters [32]. It seems that other reactions such as hydrogen oxidation to hydrogen peroxide, organic oxidation and hydrogenation may follow a similar pattern. Relativistic effects have also been discussed for gold [33]. Au-O bonds can be significantly strengthened by the linear O-Au-O structures. The Au-O bond is always stronger when embedded in common surroundings. The result is assigned to the spatial extent of d orbitals of gold, due to the strong relativistic effects. The wider spatial extension of d orbitals of gold leads to two influences. First, gold atoms in clusters or particles with smaller coordination numbers are active due to the ease in forming strong Au-O bonds, especially for the O-Au-O bond. Second, gold atoms in bulk with larger coordination numbers are chemically inert, because the strong suppression by neighbouring gold atoms destabilises the O-Au-O structures. Other discussions based on theoretical treatments have been presented for gold systems [34]. Shell closing aspects can explain the behaviour of clusters of certain sizes and the formation of ligand-protected clusters can provide a basis for the synthesis of nanocatalysts. Ligand engineering may offer the potential to tune the electron states and thereby control catalytic activity. Although tightly bound ligands may act as catalyst modifiers in a negative

sense, behaving as catalytic poisons, partial removal by mild thermal treatment may be sufficient in practice to expose active sites. The use of planar model systems to monitor and understand surface structures in gold systems has been well discussed very recently [35]. Electron spectroscopy, low-energy ion scattering, secondary ion mass spectrometry, high-resolution electron loss spectroscopy, infrared spectroscopy, low-energy electron diffraction, small angle X-ray scattering and scanning tunnelling and atomic force microscopies have been particularly useful. These studies help to understand why small clusters of gold behave in a very different manner to bulk gold. Substrate effects can also be monitored with the aid of these methods and underlying film influences can be used to understand how metal-support effects may manifest themselves in practical catalysts. Spectroscopic methods have also been widely used to monitor surface plasmon effects in gold [36], Raman effects, especially en-hanced Raman scattering [37] and infrared methods in studying chemisorption and surface reactivity of IR-active molecules such as CO and NO [38, 39]. X-ray photoelectron spectroscopy has often been used to assess gold oxidation states [40, 41], but beam-induced decomposition is well known to result in a gradual drift toward a zero-valent gold states regardless of the nature of the original sample. Low beam energies and short exposure times seem to be the key to help overcome these effects. The example of simultaneous presentation of gold in various oxidation states [16] serves to illustrate that gold may not be homogeneously present in solid catalysts. Careful studies have argued that the activity of gold is proportional to the gold content of gold-titania catalysts for CO oxidation [41] but elsewhere it has been shown that unit gold activity can be made to increase as the gold content falls by removal of less active gold by reaction with cyanide solutions [42]. Cyanide removal of gold from gold-ceria also seems to result in the retention of almost all the original activity for the water-gas shift reaction [43], an observation considered to reveal the importance of Au(+1) entities in catalysis. Cyanide treatment might therefore be useful in the thrifting of gold, but the interaction of cyanide with gold is undoubtedly multifaceted. Cyanide may bind to the gold; rendering active sites useless, it may preferentially dissolve metallic gold (an oxidative process), or it may react preferentially with Au(+1) centres since no oxidation is then required. Indeed the use of cyanide in the absence of dioxygen may be a useful way of enhancing interaction selectively with Au(+1) species [44]. Partial or total removal of cyanide after cyanidation treatments by thermal means seems to be necessary for the resulting solids to display catalytic activity [45]. The complicated action of cyanide makes it difficult to unambiguously decide on the nature of the gold entities being removed or deactivated and hence makes interpretation of the results difficult.

Several studies [46, 47] have suggested that anionic gold species on titania are essentially pinned to defect sites associated with oxygen loss from the oxide lattice. Thus gold inhibits the anatase to rutile phase transition by an appreciable amount. Nevertheless for high-temperature applications, it seems sensible to avoid anatase or anatase-containing samples as supports [29]. A lot of the titania-based gold catalysts examined for low-temperature reaction are predictably unstable at higher temperatures due to the gross structural changes encountered.

A compilation of data [48, 49] for the specific activity of gold systems for the CO oxidation reaction reveals that Au/titania is particularly active. Steyn et al. [50] have recently shown that gold-perovskites can exhibit activities essentially equal to those shown by Au/titania for CO

oxidation, depending on the nature of the A and B elements in the Au/ABO_3. Perovskites are interesting because they themselves tend to exhibit some oxidation activity and their properties can be tuned by choice of A and B elements.

3. Oxidation of carbon monoxide

One reaction that has attracted a lot of research interest in the catalysis by gold is the oxidation of carbon monoxide to carbon dioxide at ambient or lower temperatures. Although the pioneering discovery of the catalytic activity of Au for CO oxidation was based on Fe, Ni and Co oxides as support for Au [51], over the years Au supported on TiO_2 has been extensively studied because although neither Au nor TiO_2 is active independently, their combination generates surprisingly high scatalytic activity for CO oxidation [52–54]. Several factors influence the activity of this class of catalysts which include the type and nature of the support, the gold crystallite size and the method of preparation [53, 55]. Although the Au/TiO_2 catalyst is known to be very active for CO oxidation, a major setback is that the catalyst tends to deactivate with storage and/or time on-line at low temperatures [56]. Also controversial is the nature of the active species. Various authors have claimed different states of Au to be responsible for catalytic activity in CO oxidation. Some have claimed ionic gold to be responsible for the active sites [57, 58], whilst some report metallic gold to be the active species [59, 60]. Another group of authors claim that a combination of both ionic and metallic gold is necessary for catalytic activity [61]. We draw attention to these uncertainties concerning the active metal species and deactivation mechanisms resulting from both storage and time on-line as well as to areas involving the support such as use of promoters, mixed metal oxides supports, various types of TiO_2 and some unconventional supports (e.g. zeolites and perovskites). We also look at some parameters involved in the preparation of the catalysts and how these influence the activities of the catalysts. Some practical applications of gold catalysts in carbon monoxide oxidations can also be expected.

3.1. Nature of support

Although it is generally agreed that the role of the support of gold-supported catalysts is to stabilise the active gold particles, the nature of the interaction between the support material and the gold particles is very important for catalytic activity [55, 62–64]. For example, for the oxidation of carbon monoxide, exceptionally high activities have been reported for reducible metal oxide supports such as TiO_2, Fe_2O_3 and CeO_2 suggesting that the support supplies oxygen to form active oxidic gold sites [64]. It has also been suggested that sites at the gold-support interface are responsible for the activity in CO oxidation [57, 65].

Taking these into account, we have been tempted to assume that the contact structure between Au particles and the support is the most important factor for the origin of the activity of gold catalysts and have studied CO oxidation on gold-supported catalysts over a number of supports with different properties.

3.1.1. Mixed metal oxide supports

Although TiO_2 has been one of the most investigated supports for Au for CO oxidation, the catalyst tends to lose its activity with time on stream. This deactivation process has been ascribed to various factors such as the change in the oxidation state of Au [61, 66] and ag-glomeration/sintering of the gold nanoparticles [67], the presence of moisture [68] as well as other structural changes that may occur on both the support and the metal [69]. Carbonaceous (carbon containing) species such as carbonates, bicarbonates and formates formed as inter-mediates during the reaction may also accumulate on the catalyst surface causing deactivation [70]. Many studies have been performed not only to improve the activity but also the stability of the catalyst with time on stream. Many transition metal oxides have also been studied as supports for Au for CO oxidation. The use of binary mixed oxide supports has been reported as a possible solution for stabilising the Au nanoparticles and preventing them from sintering, thus preventing catalyst deactivation resulting from sintering. It has also been suggested that increasing the basicity of the support may improve the stability of the catalyst by minimising deactivation resulting from the formation of adsorbed CO, carboxylate and carbonate species on the catalyst surface [71]. Au/TiO_2 catalysts modified by Al_2O_3, CaO, ZnO, NiO, ZrO_2 and rare earths were found to be beneficial to the reaction for CO oxidation whereas MoO_3 and WO_3 had a negative effect on the stability [72]. Moreau and Bond also reported a lowering of the rate of deactivation of Au supported on TiO_2, SnO_2 and CeO_2 when iron was added in the preparation [73].

Au/TiO_2 and Au/FeO_x-TiO_2 catalysts were examined in order to get a thorough understanding of the effect of Fe on the Au/TiO_2 catalyst and link it to the differences observed in their activities for CO oxidation. The Fe-containing supports were either only dried at 120°C or dried at 120°C followed by calcination at 300°C or 500°C prior to Au addition. Activity depended of the support pretreatment temperature. The Au/FeO_x-TiO_2 catalysts were more active than the Au/TiO_2 catalyst with the catalyst containing FeO_x-TiO_2 calcined at 300°C showing the highest activity. The FeO_x-containing catalysts showed smaller Au particles on average; hence they have higher metal surface area which could possibly lead to the superior activities observed. Our study went further than considering particle size effects alone and examined other effects that the FeO_x brought to improve activity. For example, although all the FeO_x-containing catalysts had similar Au particle sizes, there were clear differences in the Au-normalised activity shown. From the CO and CO_2 desorption profiles of the samples, the activation energy of desorption of CO and CO_2 from the samples was quantified using the Redhead method (Eq. (1)) [74]:

$$\frac{E_d}{RT_p} = \ln\left\{\frac{\nu T_p}{\beta}\right\} - 3.64 \tag{1}$$

where E_d is the activation energy of desorption, T_p is the temperature at peak maximum, β is the heating rate or ramp rate dT/dt in units of degrees K per unit time and ν is the frequency factor approximated for first order kinetics to be 10^{13}/s. The calculated desorption activation

energies showed a significant difference (ca. 24% difference) in the activation energy of desorption for CO between the samples that contain FeO_x and those that do not. This difference could manifest itself in the observed reaction rates during CO oxidation. For all intents and purposes, the E_d's for CO_2 of all the tested samples were identical.

XPS data indicated that Au/FeO_x-TiO_2 catalysts all have similar Fe^{3+} and Fe^{2+} ratios implying that they contain similar FeO_x species. TPR data however shows that the FeO_x species distribution is different in the catalysts. The total acid sites in the Brønsted to Lewis site ratio amongst the Au/FeO_x-TiO_2 catalysts are also distinctly different. Part of the observed activity trend results from the final speciation of the FeO_x that seems to be dominated by a mixture of FeO and Fe_3O_4 with small amounts of Fe_2O_3 present. The activity and stability increase for the series as the absolute amount of Brønsted acid sites increases. The Au/FeO_x-TiO_2 (support calcined at 300°C) which shows the highest activity and stability has small Au particles, a high total acid site amount and the highest Brønsted to Lewis site ratio. It is suggested that the increased Brønsted acidity destabilises carbonate species and prevents them from building up on the surface of the catalyst. The activity trend may also be related to the Au particle size on the FeO_x-TiO_2 supports as it is noted that amongst the three Au-FeO_x-TiO_2 catalysts the most active are the ones with the smallest Au particles. In particular, the catalyst with FeO_x-TiO_2 calcined at 500°C has a high activity and stability and the smallest Au particles size but has the lowest amount of acid sites. Thus it is not possible to fully discriminate the effect of the acidity from the Au particle size influence on the activity of this series of catalysts [75].

3.1.2. Perovskite supports

Perovskites (ABO_3 structures where A and B represent metals in the 12- and 6-coordinated sites, respectively) are promising catalyst materials due to their low cost, thermal and mechanical stability at relatively high temperature, great diversity and excellent redox properties [76, 77]. They can be manipulated by partial or complete substitution of the cations A and B and are known to be active for CO oxidation, but only at high temperatures for potential use in automobile exhaust catalysts, with no activity being shown at temperatures below 200°C [78–81]. Besides, it is generally known that the addition of a metal to oxides can modify the intrinsic catalytic properties of the oxides themselves, possibly increasing the activity, selectivity or stability of the resulting catalytic systems [82, 83]. Palladium-perovskites have been the subject of studies for potential use in automotive exhaust systems and appear to offer the property of self-generation, associated with palladium's ability to move in or out of the perovskite structure depending on the oxidising/reducing characteristics of the atmosphere [76, 78]. To the best of our knowledge, only a few reports on the preparation of Au-perovskite catalysts have been seen in the literature. Addition of Au to $LaBO_3$ perovskite catalysts (B = Cr, Mn, Fe and Ni) showed significant enhancement in the rate of CO oxidation with 2 wt%Au-$LaNiO_3$ showing the best performance with CO conversion at temperatures below 150°C [84]. A comparison of the CO oxidation activities of $LaCoO_3$, the mixture of La_2O_3 and Co_3O_4 and the Au-supported Au/La-Co-O catalysts showed that the gold catalyst supported on the perovskite had higher catalytic activity and stability than that of the simple oxides or the perovskite [85]. Three-dimensionally ordered macroporous (3DOM) $LaFeO_3$-supported Au

also showed superior performance for the oxidation of soot compared to the corresponding perovskite [86]. Despite these, the state of knowledge about Au-perovskite systems is still limited. In particular, very little characterisation of these systems has been done, being limited to XRD, textural studies and some XPS work. More detailed characterisation work as well as the exploration of the powerful ability of perovskites to be modified by substituting other cations in gold systems for CO oxidation is necessary. We have addressed these issues here.

Two perovskite systems, $CaTiO_3$ and $LaCa_xFeO_3$, have been selected to check if any major differences are displayed for different perovskites when used as a support for gold in catalysis. The systems investigated include Au-supported $LaFeO_3$, $LaMnO_3$, $LaCuO_3$ and $CaTiO_3$. However, only catalysts supported on $CaTiO_3$ and $LaFeO_3$ showed activity for CO oxidation for reaction temperatures below 100°C and the other systems were eliminated from the study.

3.1.3. Modified titania supports

Titania is amongst the most effective supports for gold for carbon monoxide oxidation [51–53, 55, 56, 59, 61, 65–68, 71–73]. The biphasic Degussa P25 (75% anatase and 25% rutile TiO_2) is commonly used as support material. The phase structure, crystal size, surface and textural properties are important parameters on the catalytic performance of Au/TiO_2 for CO oxidation [87]. We have therefore modified TiO_2 with the aim of modifying its properties as support for Au for CO oxidation.

3.1.3.1. Nitrogen doping of TiO_2

Nitrogen doping of TiO_2 results in $TiO_{2-x}N_x$ which contain more oxygen vacancies than pure TiO_2. According to density functional theory (DFT) calculations, N doping of TiO_2 favours the formation of oxygen vacancies [88] and this finding was confirmed by real-time transmission electron microscopy (TEM) [89]. The computed energy cost to create oxygen vacancies is drastically reduced from 4.2 eV in pure TiO_2 to 0.6 eV in N-doped TiO_2 [89].

In our work [90], we confirm that nitrogen doping of anatase TiO_2 creates oxygen vacancies (point defects). These play an essential role as metal cluster nucleation sites. Theoretical studies show that electron transfer from defects to the Au clusters facilitates CO oxidation. Centeno et al. [91] reported that Au/TiO_2 catalysts showed higher activity than $Au/TiO_{2-x}N_x$, though our work shows that care must be taken over the pretreatment conditions used, as we find that for catalysts pretreated in an oxidising atmosphere, the $Au/TiO_{2-x}N_x$ catalyst clearly shows superior activity over Au/TiO_2. Although the $Au/TiO_{2-x}N_x$ samples contain smaller Au particles, they were generally less active than the Au/TiO_2 catalysts showing no direct positive correlation of activity with Au specific surface area. However, for catalysts pretreated reductively in hydrogen, the Au/TiO_2 catalysts showed an increase in activity by about three fold whereas the nitrided catalysts showed only a very slight increase.

Moisture plays a major role in promoting the CO oxidation activity of the Au/TiO_2 catalyst as well as inhibits its deactivation when introduced from the start of the reaction. This effect is not seen for $Au/TiO_{2-x}N_x$ where moisture did not either promote the catalytic activity or prevent

deactivation suggesting that even small amounts of nitrogen doping of TiO_2 inhibit any positive role that moisture might play in the reaction.

3.1.3.2. Potassium titanate: $KTiO_2(OH)$

Titanate materials have been synthesised recently and used in catalytic applications [92–94]. However, only few reports exist where these have been exploited as support for Au for CO oxidation. We find that gold supported on potassium titanate can, under some circumstances, exhibit superior performance for CO oxidation relative to that obtained with titania as a support [95]. The specific surface area of the titanate material $KTiO_2(OH)$ was three times more than that of the commercial TiO_2 (Degussa P25), whilst the average Au particle sizes for the Au-supported catalysts were 4.7 and 5.1 nm, respectively. An oxidative pretreatment of both catalysts Au/TiO_2 (P25) and $Au/KTiO_2(OH)$ generally results in $Au/KTiO_2(OH)$ being significantly more active than Au/TiO_2 (P25). $Au/KTiO_2(OH)$ catalyst pretreated in a reducing atmosphere was also more active than the Au/TiO_2 (P25) catalyst treated under the same conditions but it was noted that deactivation of the Au/TiO_2 (P25) was more rapid. In general, the treatment conditions that a catalyst is subjected to ultimately affect its composition and in this case the contribution of ionic Au species may have played a significant role. Although we have not fully established whether the enhancement in activity with the titanate support is due to a particle size effect or chemical effects, the fact that both catalysts show similar Au particle size distributions makes it more likely that chemical effects have a major contribution to the differences in activity observed. Generally, $KTiO_2(OH)$ is a more basic support than TiO_2 and the basicity of the support has to be taken into account as well. Basic oxides such as magnesia have been shown to be particularly active for supported gold for CO oxidation [55, 96, 97], and more acidic supports such as zeolites, for example, are generally less active [16]. Modification of TiO_2 by the addition of Group 1 metal ions has been shown to either increase or decrease the activity of the resulting Au-supported catalysts subsequently prepared from the treated support depending on the amount of the Group 1 metal ions added. This effect appears to be related to the electronic environment of the Au in the catalysts [18]. A further factor may well be the detailed structure of the support at the nanoscale. Nanosized ceria, for example, appears to lead to a higher activity when used to support gold [98] than other forms of ceria. Nevertheless, our work adequately demonstrates that titanate materials may well be used in offering a further support system for gold-mediated catalysis.

3.1.3.3. Rutile nanorod dandelion structures

The stabilisation of gold nanoparticles is of immense importance when nanogold catalysts are considered, as catalytic activity is directly related to gold particle size [51–55, 59, 61, 72]. For example, gold catalysts for potential use in the automotive industry must be able to withstand high temperatures from exhaust gases, where sintering of the gold nanoparticles results in catalyst deactivation. Sintering of gold particles not only occurs at high temperatures but occurs slowly over time at ambient temperatures that can result in the deactivation of the catalysts over extended time [55, 99]. Very few gold catalysts have the durability to withstand temperatures over 400°C for extended periods of time without complete loss of activity [100–

103]. Almost all of these catalysts, whilst showing activity after exposure to moderately high temperatures, are not durable enough for long-term catalytic applications. If gold catalysts are to be used in applications above 400°C, such as in automotive catalysts, thermal stability of not only the gold nanoparticles but also of the support is crucial for long-term stability. We carried out a thorough search of the literature to understand the reasons for deactivation of catalysts at high temperatures and used the information gained to develop a support that can combat the deactivation processes.

We have been able to synthesise titanium dioxide catalyst support material comprising rutile nanorods extending radially from a central point, each rod having a free end spaced from adjacent nanorods [104]. The material has a high surface area of ca. 100 g/m^2. When gold nanoparticles are deposited on the support, they preferentially locate at or near the free ends of the nanorods. At low gold loadings on the support, the orientation of the gold particles on the support prevents sintering of the particles when heated at high temperatures. The catalysts exposed to temperatures of 550°C for up to 120 hours show very insignificant changes in the catalyst activity for CO oxidation as opposed to a standard Au/TiO$_2$ (P25) catalyst which almost completely loses its activity after exposure to 550°C for only 24 hours as a result of sintering of the gold nanoparticles. When CO oxidation is carried out at 250°C, the heated catalysts show similar performance with the fresh catalysts. Storage of the catalysts at ambient conditions for several months showed no effect on the Au particle sizes demonstrating the long-term stability of the catalyst.

3.1.3.4. Modification of TiO$_2$ with ions

The interface between gold and the support in gold-supported catalysts is crucial for catalytic activity in CO oxidation [105, 106]. Charge transfer between the support, particularly involving negatively charged defect sites, and the Au particles has also been connected with catalytic performance [107]. The addition of anions and cations has been reported to act as promoters for some heterogeneous. The poisoning effect of residual chloride ions on gold-supported catalysts prepared using HAuCl$_4$ solution is well documented [108, 109]. Residual chloride is found to affect activities by facilitation agglomeration during heat treatment and also poisoning the active sites. The addition of low levels of nitrate ions to Au/TiO$_2$ catalyst has been shown to enhance the catalytic activity towards CO oxidation, with high levels leading to a decrease in activity [19]. Our comprehensive study on the effects of the incorporation of varying levels of a number of anions and cations into Au/TiO$_2$ catalysts for CO oxidation [18, 110] reveals activity enhancement in some cases, whilst in others activity is depressed. The effect seen depends on the concentration levels of the ions added and the manner in which they are added. In order to gain an understanding into the nature of the effects operating between the added ions and the support and/or Au, we incorporated these ions into the support before gold introduction and into the catalyst after catalyst preparation. For the sulphate-modified sample, there is a direct evidence that entities containing both Au and S exist on the surface of the final catalyst and it may well be that the promoting effect of sulphate is due, at least in part, to a direct interaction occurring between gold centres and sulphate or sulphate-derived entities. The evidence points strongly to the fact that the enhancement is associated with gold centres

having a relatively high electron deficiency. For the anions and cations other than sulphate, it appears that these exert an influence on catalytic activity via the interaction with the support, rather than by direct interaction with the gold centres. Our findings here generally support the idea that the performance of gold catalysts can be extremely sensitive to parameters involved in the catalyst preparation which may include exposure to "foreign" ions [19] and at the same time suggests that the specific activity of gold can be improved through the judicious use of such ions.

3.1.4. Zeolites

An important feature of gold-based catalysts for CO oxidation is the size of the gold particle of which 3 nm is reported as optimum [111]. Various methods have been used for controlling the size of the gold nanoparticles amongst which is to embed the Au nanoparticles within the pores of zeolites. The strong confinement of the nanopores of zeolites can result in a very uniform size distribution of gold nanoparticles. Zeolites have the advantages of high surface area (typically 1000 m^2/g) [111], tunable uniform pores (2–10 nm) which can be used to stabilise the small gold particles by inserting them into the small cages and also ion-exchange ability. However, traditionally zeolites are considered to be an "inert" support resulting in poor catalytic activity for gold nanoparticles [64]. This poor activity was generally considered to be due to sintering of the gold nanoparticles as SiO_2 is known to have a relatively weak metal-support interaction with Au [112]. We however showed that partial reduction can lead to higher activity of gold-zeolite-Y [16] consistent with the work of Chiang et al. [113]. For gold-HY zeolites, in which gold is initially introduced as Au(III) by ion exchange from $[Au(en_2)]^{3+}$, samples become catalytically active only after a considerable induction period has been exceeded. The induction period is substantially shortened by carrying out a mild reductive pretreatment of the AuHY with reducing agents such as sodium borohydride. This significantly also increases the activity of the catalyst. This behaviour is consistent with the suggestion that gold in a partly reduced state is required for activity. The reduction of Au(3+) in AuHY would result from a sufficiently long exposure of the catalyst to the reacting CO mixture. There is however compelling evidence that the majority species in most active catalysts is in the zero-valent state, the obvious conclusion being that most of the gold might well be considered as a spectator species and do not take part in the catalysis. This has been shown for gold-ceria catalysts where after removing a large fraction of the gold present in the catalysts by oxidative cyanide leaching, no fall in activity for the water-gas shift reaction was observed and that the remaining gold was essentially present as Au(1+) [43].

3.2. Influence of the preparation method

Since the activities of gold-supported catalysts for CO oxidation can be ascribed to a significant metal-support interaction, the degree of interaction and thus the method of preparation of the catalysts will largely affect the properties of the resulting catalysts. Numerous papers have been published describing various methods to incorporate gold nanoparticles on various metal oxide supports including TiO_2, Al_2O_3, CeO_2, Fe_2O_3, Co_3O_4, ZrO_2 and SiO_2. Depending on the choice of the metal oxide support, the main synthesis methods include deposition-precipita-

tion, co-precipitation, colloidal dispersion, chemical vapour deposition and photodeposition. Conventional incipient wetness impregnation yields large Au nanoparticles due to weak interaction of the most commonly used Au precursor ($HAuCl_4$) with the metal oxide support. This method also results in a large amount of residual chloride in the catalyst which promotes sintering of the Au nanoparticles and may poison the catalyst active sites [59, 60]. Deposition-precipitation has been most widely used especially for support metal oxides with high IEP, such as TiO_2, Fe_2O_3, CeO_2 and Al_2O_3. Deposition-precipitation is however not suitable for incorporating Au nanoparticles onto supports with low IEP such as SiO_2, because under the high pH conditions required to hydrolyse the $HAuCl_4$, which is the most common Au precursor used, there is weak interaction between the negatively charged support surface and the $[Au(OH)_nCl_{4-n}]$ species which hinders the gold adsorption and facilitates the mobility of the Au nanoparticles. This can lead to the Au nanoparticles sintering easily during the synthesis process, yielding low gold loadings and inactive catalysts [114]. Particular attention has also been given to TiO_2 since Au supported on this oxide has been found to be more active for CO oxidation than many other supports.

It has been shown that the acidity of TiO_2 can be strongly increased by treatment with sulphate ions, with the formation of S-O and O-S-O bonds in bulk and surface, creating unbalanced charge on Ti and vacancies and defects in the TiO_2 network [115, 116]. Au/TiO_2 samples prepared from $TiCl_4$ were inactive up to 100°C, but when sulphated with 2.5 mass%SO_4^{2-}, the CO oxidation initiation temperature was lowered to 30°C. In the case of the Au/TiO_2 when the titania support was prepared from titanium isopropoxide, the CO oxidation activity started at 30°C and gradually increased to 40% at 150°C. But when the sample was impregnated with 2.5 mass%SO_4^{2-}, the CO conversion increased to 98% at the same temperature. The sample prepared in the presence of sodium dodecyl sulphonate containing sulphate (1.5 mass%) showed 84% conversion without further addition of sulphate. However, the CO conversion is reduced to 42% when loaded with 2.5 mass%SO_4^{2-}. This showed that low amount of sulphate is responsible for enhancing the activity of the Au/TiO_2 catalyst and high amount of sulphate is detrimental for CO oxidation. An examination of a series of low sulphate-loaded 1 wt%Au/TiO_2 samples revealed a dramatic effect of sulphate treatment on CO oxidation activity recorded at room temperature where an over 5-fold higher activity was found for relatively low sulphate loadings. The promotional effect of sulphate on CO oxidation was found to be unlikely due to physical or textural changes in the catalyst but more likely that chemical effects are responsible. The source of TiO_2 was also found to have a considerable influence on the CO oxidation activity of gold-supported catalysts on the supports [117].

One of the practical routes used to prepare gold catalysts especially for CO oxidation, which achieves high activity and a high gold dispersion, is the deposition-precipitation method [52]. Deposition-precipitation, usually a two-step procedure of deposition of the gold precursor in aqueous phase onto the support, followed by reduction of the gold precursor using a reducing agent is typically carried out at a controlled pH (usually in the range 6–10) and uses $HAuCl_4$ as gold source. The $HAuCl_4$ is often added at a carefully controlled and low rate with vigorous stirring and with pH control, and frequently solutions are heated to 60–70°C to affect the process. A key aspect of the use of high pH appears to be associated with the removal of

chloride entities from the coordination sphere of the Au atom which would otherwise tend to deactivate the gold centres and contribute to sintering of the gold nanoparticles during catalytic operation and/or heat treatment. A simple single-step method for preparing Au/TiO$_2$ was reported which proceeds without pH control during the contacting of the support with the gold source HAuCl$_4$ solution, followed by washing with water only, and leads to a highly active and stable CO oxidation catalyst. The method makes use of a suitable reducing agent such as an aqueous solution of sodium borohydride and the number of variables involved in the catalyst preparation is drastically reduced and there is no need to rigorously control the pH. The particle diameters of the gold in the catalyst are in the range 2–5 nm as obtained by the deposition-precipitation method, and no residual sodium- or boron-containing species are present in the vicinity of the gold particles in these catalysts as any residual sodium borohydride is easily washed out during the washing procedure. It is however noted that an excess of the sodium borohydride calculated on the reductive stoichiometry of sodium borohydride undergoing conversion to sodium metaborate and all the gold in HAuCl$_4$ being reduced to the zero-valent state is used. The pH of the system upon the sodium borohydride addition rises to over 8 and so the beneficial effects of an alkaline medium on chloride removal from the coordination sphere of the gold may still be achieved [118].

3.3. Active metal species

Although there is a general agreement on the high activity of gold catalysts for CO oxidation, the need for small Au nanoparticles, and the catalyst preparation methods, the nature of the active Au species in relation to its oxidation state has been quite controversial. Determination of the active oxidation state (Au^0, Au^I and Au^{III}) or establishing whether some combination of them is needed turns out to be very difficult because of the extreme sensitivity of supported gold catalysts to their surroundings and the fact that the mere act of examining them may change their composition. Examining the state of the catalyst before and after a catalytic reaction may not necessarily reveal its state during the reaction [119]. This is made even more complicated by the fact that sometimes most often the active sites are present in very low amounts on the catalyst surface as most of the atoms present in the solid sample are located in the bulk. This makes it more difficult to understand the nature of the active sites and has led to the design of model systems using single crystals and well-defined surfaces as these can be interrogated using modern surface spectroscopy. Such surfaces may not be representative of a working catalyst [120]. Another difficulty lies in the fact that gold catalysts contain a multiplicity of Au species in one catalyst and their activation under different conditions can lead to various distributions of the various species. This makes it possible that working with the same catalyst under different conditions will lead to the activation of different sites. It is therefore important to consider which active sites are activated in a given catalyst under applied conditions and not just what the nature of the active sites is, in the catalyst. So, in some cases probably the results of different groups do not contradict but supplement each other [121].

A number studies [17, 122–126] have concluded that just the metallic form of gold is active. On the other hand, gold cations have been found to be the catalytically active sites for CO

oxidation [127–130]. Other studies reveal that a combination of both metallic and cationic gold is necessary for CO oxidation activity. Using EXAFS and XANES, it was reported that for Au/MgO catalyst under reaction conditions, both Au^+ and Au^0 were present and that higher concentrations of cationic Au resulted in higher catalytic activity [131]. Similar results were reported for Au/Fe_2O_3 where both Au^+ and Au^0 coexisted upon exposure to the reaction gas mixture with the conclusion that the cationic Au species was more active but less stable than the metallic Au [132]. Different electronic states of ionic and metallic Au species were detected in Au/H-mordenite (zeolite)—Au^+ and Au^{3+} ions, charged $Au_n^{\delta+}$ and neutral nanoparticles Au_m and catalytic tests in CO oxidation revealed the coexistence of several types of active species; gold clusters <1.5 nm were responsible for low-temperature activity whilst gold nanoparticles were responsible for high-temperature activity [121].

The oxidation state of Au can be characterised by several experimental and theoretical techniques, amongst which spectroscopic methods are most commonly used. These include diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), X-ray photoelectron spectroscopy (XPS), X-ray absorption near-edge structure spectroscopy (XANES), extended X-ray absorption fine structure spectroscopy (EXAFS), infrared (IR) spectroscopy and Mössbauer spectroscopy. Temperature-programmed oxidation and reduction (TPO and TPR) can also provide quantitative oxidation state information by determining the uptake of oxidising (e.g. O_2) or reducing (e.g. H_2, CO) agents.

For Au/TiO_2 catalyst system for CO oxidation, DRIFTS was used to show a synergy between positively charged and metallic gold nanoparticles whereby, on the reduced catalyst, CO is weakly adsorbed on Au^0 species and, in the presence of oxygen, CO is adsorbed on the Au particle associated with oxygen. Metallic Au particles are believed to be activating an oxygen molecule into two oxygen atoms [133]. In a separate study, using XAS (X-ray absorption spectroscopy) and FTIR (Fourier transform-infrared spectroscopy), it was found that during CO oxidation on Au/TiO_2, the activity of the catalyst increased with the degree of reduction up to 70% reduction and then decrease slightly beyond 80% reduction due to an increase in the Au particle size and changes in particle morphology consistent with metallic Au being responsible for catalytic activity [17].

From the suggestions found in the literature, one might conclude that the choice of the nature of the active Au species for CO oxidation on gold-supported catalysts depends on the technique used for the determination and that different supports may have different active gold species as defect formation is more facile in some supports than others.

3.4. Catalyst deactivation and regeneration

One of the major drawbacks of gold catalysts is the fact that they tend to lose their activity during reaction (on-line) [48, 68, 71, 98, 109, 122, 126, 134–138] as well as during storage [139, 140].

3.4.1. On-line deactivation

The main reason for the loss of activity during reaction is a growth of the gold particles (agglomeration/sintering) [135, 136, 140]. Prior to the reaction, the agglomeration of gold particles may also occur from the conditions of thermal treatment used to reduce Au^{III} to Au^0. The removal of hydroxyl groups from the active sites during thermal treatment may also be responsible for deactivation during thermal treatment [48, 137]. It was found for Au/TiO_2 that a lowering of the pretreatment gas flow rate as well as an increase in the amount of sample being pretreated may lead to the gold particle size increasing. Also pretreatment in air instead of hydrogen or argon led to an increase in the gold particle size [140]. Residual chloride in catalysts prepared using $HAuCl_4$ as Au precursor may also promote the sintering of the Au particles during thermal treatment [99].

Intermediate carbonate formation during the formation of CO_2 also results in loss of catalyst activity by blocking some of the catalyst active sites [135–137].

The on-line deactivation characteristics of Au/TiO_2 were studied in an unconventional PROX system using dry, cylinder-stored CO-contaminated hydrogen for fuel cell applications. The results obtained suggest that as opposed to CO removal from air, the accumulation of carbonate species and surface hydration have minor, if any, effect on the on-line deactivation of the catalyst. The deactivation is more likely to be due to an intrinsic transformation in the catalytic properties of the catalyst, by distorting the balance between Au^0 and Au^{x+} through reducing Au^{x+} to Au^0 [50].

3.4.2. Deactivation during storage

The main reasons purported for the loss of activity of gold catalysts during storage are gold particle sintering and change in oxidation state. Indoor light has been reported to cause the slow reduction of ionic gold to metallic gold in Au/TiO_2 catalysts during storage. A substantial drop in the gold content on the TiO_2 surface was also observed, as light causes the migration of gold on the Au/TiO_2 surface into TiO_2 solid. However, no growth in the gold nanoparticles was observed in this case. It was recommended that the catalysts be stored in a well-defined dark environment under ambient conditions to preserve catalytic performance even after 5 months [139]. In addition to light, water in ambient air is also reported to lead to deactivation of gold catalysts by causing the reduction of unreduced gold and the sintering of metal gold nanoparticles with a proposal for the catalysts to be stored in a desiccator under vacuum and in the dark [140]. Impurity gases in air or occasionally the accumulation of products on their surface during ambient storage may also lead to deactivation of gold catalysts [141].

In a systematic study of the effect of various storage conditions on Au/TiO_2 (refrigeration, vacuum, light, dark and inert gas storage) stored over 12 months, we found that a number of factors contribute to the deactivation of the catalysts. These factors include reduction of ionic gold, agglomeration of Au nanoparticles, loss of hydroxyl groups and moisture as well as formation and accumulation of carbonate and formate species on the catalyst surface. When the catalyst was stored in the refrigerator, the extent of Au reduction and Au particle agglomeration as well as the formation of carbonate species was reduced compared to catalysts stored

at ambient temperature in light or dark conditions. Storing the catalyst in vacuum accelerated catalyst deactivation quite drastically caused by Au reduction and agglomeration of the Au nanoparticles, loss of surface hydroxyls and moisture as well as accumulation of carbonates and formates. From the findings of the work, we recommended that gold catalysts be thoroughly purged with inert gas to remove all the atmospheric and adsorbed CO_2 from the catalyst and the catalysts stored in a refrigerator or at least a cool and dark place to minimise the effects of temperature and light [142].

3.4.3. Catalyst regeneration

Deactivation caused by the adsorption of CO and its accumulation as carbonates and formates may be reversed by heating the catalyst to evolve CO_2 from the surface [135, 136]. Activity loss caused by the depletion of hydroxyl groups from the active sites may be restored by treatment with hydrogen or water [48, 137]. Deactivation caused by agglomeration of Au particles is weak but however irreversible. Deactivation of Au/TiO_2 catalysts in selective oxidation of CO in the presence of hydrogen caused by a distortion of the balance between Au^0 and Au^{x+} through reducing Au^{x+} to Au^0 was reversed by exposing the catalysts to oxidising atmospheres [50].

An atmospheric pressure non-thermal plasma method using oxygen plasma and O_3 injection has been reportedly applied to regenerate Au/TiO_2 catalyst deactivated by the adsorption of VOCs. Deactivation of Au/TiO_2 exposed to environmental conditions resulting in the blocking of the active sites for CO adsorption was regenerated by irradiation of light (photo-cleaning) without heat treatment [141].

3.5. Practical applications of Au catalysts

Gold has come up to take a place alongside the other precious metals (platinum group metals and silver) as a key catalyst in a range of industrial processes and uses. Project AuTEK hosted by Mintek in South Africa is the leading organisation in the commercialisation of important new catalytic applications for gold. Project AuTEK makes kilogram quantities of gold catalysts under the trade name AUROlite™ (1 wt% gold on titania, alumina and zinc oxide supports). The advantages of these Au catalysts over other precious metal catalysts are being demonstrated by achieving high activities and selectivities in both liquid- and gas-phase reactions which have commercial potential. This is likely to result in new industrial applications for gold catalysts in chemical processing and pollution control. Selective oxidation of carbon monoxide in the hydrogen streams used for fuel cells has been achieved using AuTEK catalysts, as is the use of this ambient temperature oxidation process for use in gas masks for protection from CO poisoning and for CO removal from room atmospheres [143, 144].

3.5.1. Chemical processing

Vinyl acetate monomer is used in emulsion-based paints, wallpaper paste and wood glue and has a worldwide annual production of 5 million tonnes. 80% of this is produced by the

acetoxylation route employing Pd:Au/SiO$_2$ catalysts. The presence of Au leads to a fourfold increase in space time yield compared with use of Pd alone [144].

Gluconic acid is used as a food and beverage additive, metals cleaning and applications in pharmaceuticals with a worldwide production of 100,000 t/a. It is produced catalytically from glucose.

Au/Al$_2$O$_3$ shows stable activity and selectivity for up to 110 days using a continuous stirred tank reactor. Four tonnes of gluconic acid were produced per gram of Au with no significant deactivation observed [145]. Au has greater activity, selectivity and resistance to deactivation compared to PGM systems. It is also more environmentally friendly and economical compared to the biological, chemical and electrochemical methods [145].

3.5.2. Pollution control

The low-temperature CO oxidation ability of gold catalysts makes them ideal for air-quality applications. Industrial Technology Research Institute (ITRI), Taiwan, has developed a nanogold catalyst for use in CO oxidation fire escape hood [146]. This is available commercially from Taiwan-based Novax Material and Technology.

Project AuTEK's Au/TiO$_2$ catalysts tested under typical EN403 (fire escape mask) test conditions are more active and durable than the established commercial technology, namely, Hopcalite (CuMnOx). The activity of the catalyst is amplified by the presence of moisture, unlike Hopcalite which experiences rapid deactivation.

Nanostellar has developed an oxidation catalyst for cleaning diesel exhaust gas based on Au-Pt-Pd catalysts. The material increases hydrocarbon oxidation by 40% compared with conventional platinum converters at equivalent precious metal cost.

3.5.3. Fuel cells

Project AuTEK has developed a new system for hydrogen purification for PEM fuel cells trademarked AuroPureH$_2$ designed to purify cheap hydrogen on board vehicles, drawing the hydrogen feed for fuel cell directly from a cylinder. The system makes use of Au/TiO$_2$ catalyst which is very selective for CO oxidation and can remove high levels from the hydrogen. The low operating temperature gives high selectivity and no additional energy is required to heat the reactor. Fuel efficiency is essentially maintained. The AuroPureH$_2$ system outperforms the PtRu and PtMo CO-tolerant technologies [144].

4. Gold catalysts for the oxidation of volatile organic compounds (VOCs)

Palladium and platinum catalysts are generally more active for the complete oxidation of hydrocarbons. However, due to the high activity of gold catalysts for CO oxidation at low temperatures and the fact that catalytic performance can be tuned by the choice of the support, a number of reports now exist attempting to develop Au catalysts for the complete oxidation

of VOCs. A large number of metal oxides have been reported as support for gold in various VOC oxidation reactions.

Formaldehyde is one of the most common and most noxious indoor gaseous pollutants commonly emitted from materials used for building construction as well as decorative materials. Long-term exposure to indoor air containing formaldehyde even at low concentrations is adverse to human health. Supported base metals and precious metals have been applied for catalytic oxidation of formaldehyde. However, base metals require high temperatures [147]. Noble metal catalysts can, however, completely oxidise formaldehyde at ambient temperatures. Fe_2O_3-, ZrO_2- and CeO_2-supported Au catalysts have been found to be able to completely oxidise formaldehyde, but at temperatures above 100°C [148, 149]. Room temperature removal of formaldehyde has been reported over Au/TiO_2 and Au/CeO_2 [147]. For Au/CeO_2, it was found that the method of preparation played an important role on the catalyst performance with deposition-precipitation using urea offering a more active system than using NaOH.

Hydrocarbons are amongst the most prevalent environmental VOC emissions due to their use as transportation fuels as well as being essential feedstocks for chemical production. For hydrocarbons, Co_3O_4 as support for gold has shown the highest catalytic activity amongst other supported metals [150]. Addition of gold to CoO_x, MnO_x, CuO_x, Fe_2O_3 and CeO_2, which on their own catalyse the oxidation of alkanes, but at high temperature, was found to increase the activity of the catalysts by reducing the temperature at which the reaction occurred. The most effective catalyst for alkane oxidation was Au/CoO_x which retained a constant high activity for a 48-h test period; the highest activity catalysts were prepared by coprecipitation rather than impregnation [27]. A detailed study of methane combustion over transition metal oxide-supported gold catalysts prepared by coprecipitation also concluded that the best catalytic performance was obtained with Co_3O_4 as the support [151].

Au/V_2O_5 supported on titania and zirconia were used for the oxidation of benzene and a strong synergistic effect was observed between Au and V_2O_5 especially with titania. In this case, activation of oxygen was thought to occur on the gold nanoparticles whilst benzene was activated on vanadium oxide surface [152]. High-surface area ceria prepared by precipitation and calcined at only low temperatures showed surface reducibility and high activity for benzene oxidation at low temperatures. The high-surface area ceria stabilised gold at high dispersion and gold promoted the oxidation of benzene [153].

Au supported on ceria or ferric oxide was found to be very active for oxygenated VOCs, e.g. methanol, ethanol, 2-propanol and acetone as well as for aromatic molecules like toluene although for toluene, gold catalysts showed lower activity compared to oxygenated compounds due to the much lower strength of the organic substrate adsorption on the catalyst [154]. The use of various forms of manganese oxide materials in combination with gold for the target total or partial oxidation of 2-propanol, 2-butanol and toluene and the direct comparison made with gold catalysts from the AUROlite™ series (based on the use of alumina, zinc oxide or titania supports) with a further examination of Au-ceria systems has been reported [155]. Amorphous manganese oxides prepared by co-precipitation showed excellent activity due to the mixed oxidation states present. The surface structure of the support was found to play a
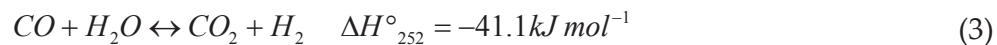
role in the oxidation reaction. Au//γ-MnO$_2$ was found to be a more superior catalyst than the Au/β-MnO$_2$ catalyst. The gold-based catalysts proved to be superior to Ce/MnO$_2$ catalysts. Ce-based catalysts were less active for the oxidation of 2-propanol than the Au-based samples. Overall, it was determined that the catalytic activity of gold-based catalysts depends on the nature of the support and the nature of the VOC. The order of reactivity observed over the same catalyst was 2-butanol > 2-propanol > toluene. The Au/CeO$_2$ catalyst was found to exhibit superior catalytic activity towards aromatic VOC oxidation. Au/MnO$_x$ catalysts showed better CO$_2$ selectivity than Au/Al$_2$O$_3$ and Au/ZnO catalysts.
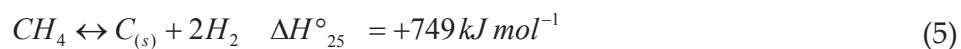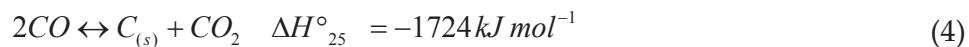
5. Automotive applications

One of the applications for which low-temperature oxidation is important is automotive pollution abatement. The three major pollutants emitted by internal combustion engines are carbon monoxide, non-methane hydrocarbons and nitrogen oxides (NOx). Environmental legislation governing the emission of these pollutants is becoming increasingly stringent. To comply with these regulation standards, highly efficient catalysts for complete elimination of these compounds are needed. Catalysts that are capable of removing these pollutants simultaneously are generally referred to as three-way catalysts (TWCs) and the design of these catalysts is continually evolving to meet lower emission requirements. For the cleaning of exhaust from diesel engines, particulate matter, especially carbonaceous particulates, also needs to be considered. The platinum group metals (platinum, palladium and rhodium) are the essential constituents of automotive catalysts in the catalytic converter. The support consists of zirconia-stabilised ceria, zirconia and γ-Al$_2$O$_3$ with barium oxide and zinc oxide as promoters [102]. However, low-temperature start-up of catalysts remains an area in which there is need for improvement. PGM-based TWCs are not very efficient during low-temperature start-up and prolonged idling mainly because the catalyst monolith does not operate until light-off temperature (~300°C) required for oxidation of hydrocarbons is attained. Gold-based catalysts have the ability to be active at relatively low temperatures and be used in conjunction with the TWCs in automotive catalysts systems to overcome the cold engine problem. In addition, Au-based catalysts have shown activity for the lean-burn reduction of NOx, at both high and relatively low temperatures.

6. Hydrogen economy

The most common industrial-scale process for the production of hydrogen and synthesis gas is steam-methane reforming (SMR) [156]. The main products of SMR are CO, CO$_2$ and H$_2$, which are produced according to Eqs. (2) and (3). The hydrogen and syngas obtained from SMR are used as raw materials in the ammonia, methanol and Fischer-Tropsch syntheses, as well as reducing feed in steel production [156–158].

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad \Delta H^{\circ}_{25} = +206 \, kJ \, mol^{-1} \tag{2}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H^{\circ}_{252} = -41.1 \, kJ \, mol^{-1} \tag{3}$$

The reaction represented in Eq. (2) is a composite reaction: first, methane is dissociated on the surface of a catalyst leading to hydrogen formation; second, the remaining carbon is oxidised by water to form additional molecular hydrogen and carbon monoxide [158]. This multistep process is highly endothermic and hence is favoured by high temperatures. It has been reported that with H_2O/CH_4 feed ratios in the range 3–4, up to 80% of methane conversion can be achieved at 850 °C [159]. However, although these elevated temperatures are desirable for improved reaction rates without being limited by thermodynamics, simultaneous disproportionation of carbon monoxide (Boudouard reaction) and CH_4 decomposition can take place [160]. The disproportionation reaction is highly thermodynamically favoured. These two processes are represented by Eqs. (4) and (5), respectively.

$$2CO \leftrightarrow C_{(s)} + CO_2 \quad \Delta H^{\circ}_{25} = -1724 \, kJ \, mol^{-1} \tag{4}$$

$$CH_4 \leftrightarrow C_{(s)} + 2H_2 \quad \Delta H^{\circ}_{25} = +749 \, kJ \, mol^{-1} \tag{5}$$

These reactions are undesirable because they lead to the formation of whisker carbon and other kinds of carbon deposits which are detrimental to the activity of SMR catalysts [161]. A lot of research has been done in the past three decades in trying to solve the problem of coke formation over SMR catalysts [158, 162–167]. Most of these studies focused on Ni-based catalysts since Ni exhibits high activity for SMR and Ni is cheaper (albeit less active) compared to the traditional platinum group (Pt, Ru, Rh and Pd) metals.

Several ways of alleviating the problem of coking of Ni surfaces have been explored experimentally and theoretically. Based on density functional theory (DFT) calculations, boron was proposed as a viable promoter for improving coking resistance of Ni-based catalysts [168]. The addition of alkali metal salts also improves coking resistance, although at the expense of reforming rate [169–171]. Alloying Ni with slight amounts of Au was proposed to be another viable method of improving resistance towards graphitic carbon formation [171, 172]. Bengaard et al. [171] concluded that there are at least two kinds of active sites with different reactivities for SMR on a Ni-based catalyst: a more active site associated with defect (step) sites and a less active one associated with close-packed facets. The step sites were suggested to be the nucleation sites for graphite formation and these sites could be blocked by additives such as K, S and Au, which preferentially bind to the step sites of Ni.

In order to elucidate how Au can influence the reactivity of Ni catalysts, we have used carbon monoxide as a probe molecule in both Monte Carlo simulations and combined quantum mechanical (QM) and molecular mechanics (MM) force field calculations on a Ni particle with

close-packed facets and defect (step) sites. The Ni nanocluster used to mimic a Ni catalyst was made up of 393 atoms (diameter $\cong$ 2.5 nm) with pyritohedral symmetry (T_h). The cluster was alloyed with 24 gold atoms on the step sites without distorting the T_h symmetry. **Figure 1** shows the Ni_{393} cluster as well as the alloy $Au_{24}Ni_{369}$ cluster. In this geometry the clusters have three possible adsorption sites: the step site and two low index close-packed, (1 1 1) and (1 0 0), facets.
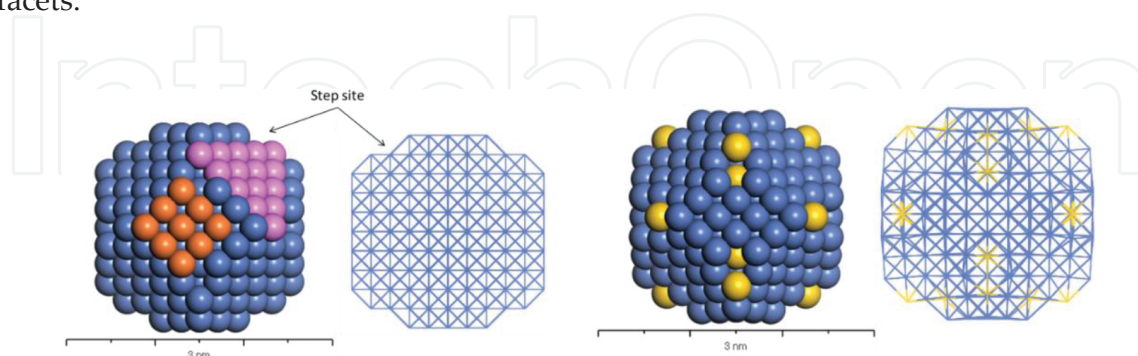
Figure 1. CPK and wire-frame models of Ni_{393} (left) and $Au_{24}Ni_{369}$ (right). All the atoms on the Ni_{393} cluster are Ni—the different colours are just for illustration purpose: brown atoms show (1 0 0); pink atoms show the (1 1 1) facet. The step sites are also shown.

All calculations were done using commercially available software programs from Dassault Systèmes Biovia Corp. and graphical displays generated with Materials Studio. The Forcite module in Materials Studio was used to optimise the geometry of the clusters (and CO) prior to the Monte Carlo simulations and QM/MM calculations. The universal force field was used in all calculations to describe approximately the potential energy hypersurface on which the atomic nuclei move. In order to find low-energy adsorption sites on the clusters, the meta-heuristic simulated annealing algorithm, which uses a canonical Monte Carlo sampling of the search space, was applied using the Adsorption Locator module within Materials Studio. The annealing simulation predicted the step site as the preferred adsorption site for CO on both clusters. The QMERA module, at fine setting, was used to further optimise the geometry of the adsorbed CO molecule. QMERA employs DMol³ as the QM server and GULP for the MM calculations. The CO ligand was treated at LDA/PWC level of theory (with DNP basis set) as the QM part of the calculation. All the metal atoms were treated as the MM part of the calculation with the universal force field. **Figure 2** shows the final configuration of the adsorbed CO ligand as optimised by the QM/MM settings in QMERA.
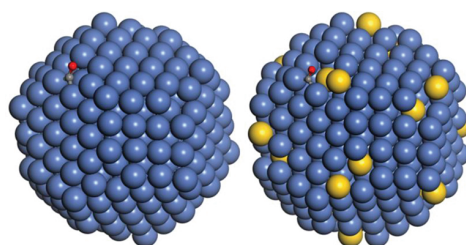

Figure 2. Optimised configuration of CO on step (bridge) site of Ni_{393} (left) and $Au_{24}Ni_{369}$ clusters.

The binding energy and vibrational frequency of CO are summarised in **Table 1**. Binding energy was described as

$$BE = E_{tot} - (E_{cluster} + E_{CO}) \tag{6}$$

where BE is the binding energy and E_tot is the total energy of the fully relaxed CO adsorbed on the cluster. The binding energy results indicate that CO binds slightly more strongly on the step site of the pure Ni_{393} cluster than on the same site of the $Au_{24}Ni_{369}$ alloy. However, the DFT that predicted stretch vibrational frequency of CO (ω_{CO}) adsorbed on the step site of the $Au_{24}Ni_{369}$ alloy is less than that of its counterpart on the pure Ni_{393} cluster by 31 cm^{-1}. The implication is that the C–O bond is weaker when it is adsorbed on the step site of the $Au_{24}Ni_{369}$ alloy than when the molecule is adsorbed on pure Ni_{393} cluster. This result, where the same ligand exhibits different electronic characteristics as a result of adsorption site modification, indeed indicates that Au can influence the reactivity of Ni if the two metals are alloyed where Au is more of a promoter (i.e. only small amounts of Au used).

	Adsorption site	Ni–CO bond Å	C–O bond Å	ω_{CO} (cm^{-1})	Binding energy (kcal/mol)
Ni_{393}	Step (twofold)	1.722 (bond 1)	1.203	1905	176
		1.763 (bond 2)			
Au_{24}	Step (twofold)	1.892 (bond 1)	1.211	1874	174
Ni_{369}		1.892 (bond 2)			

Table 1. Binding energy and C-O stretch vibrational frequency.

Indeed, Nørskov and co-workers [172–174] have carried out surface science, theoretical and microkinetic studies whose findings suggested that alloying Ni with Au was the main reason for the observed suppression of graphite formation in their systems. The recent work of Lazar and co-workers [175–177] has further strengthened the argument that alloying Ni with Au leads to improved CH_4 conversion, higher selectivity to CO_2 and an improved H_2 yield at low temperature ($T < 873$ K). At a higher temperature, ca 973 K, the Au additive had no significant effect in H_2 production and deactivation was accelerated under their testing conditions. This result is in agreement with the earlier findings of Chin et al. [178], who found a lower initial activity and deactivation rate resulting from Au promotion of their Ni catalyst. Our QM/MM findings in this work have shown that alloying Ni with Au on the step sites weakens the CO bond (relative to pure Ni) and this system might accelerate CO disproportionation (Eq. 3) at high temperatures, which would explain the negative effect of high temperature on AuNi systems for SMR. In conclusion, a lot of studies report positive effects of Au promotion of Ni-based SMR catalysts; however, only a few report negative results which can be linked to accelerated graphite formation as a direct consequence of Au presence. Our conclusion is that whether or not Au acts as a promoter for SMR or a catalyst for accelerating the competing disproportionation reaction is partly dependent on the process conditions.

7. Concluding remarks

The research efforts in gold catalysis continue at an impressive level. It is true that a more sober view is now being taken concerning the commercial exploitation of gold catalysts as issues such as cost, longevity, stability in storage and others are being more seriously considered. Our increasing understanding of the way in which gold catalysts operate and our ability to manipulate particularly the activity and stability of nanogold could pave the way for realising improved commercialisation. An ever widening array of support materials is now being studied together with very important aspects such as the promotion of gold and also the use of gold in bi- or multi-metallic systems. The debate as to whether high-temperature uses of gold catalysis can be realised continues and it is suggested that recent advances in arriving at formulations that are catalytically active and that exhibit very high thermal stability have thrown this field wide open again for critical examination and further exploration.

Author details

J.A. Moma[1], T.A. Ntho[1] and Michael Scurrell[2*]

*Address all correspondence to: scurrms@unisa.ac.za

1 Advanced Materials Division, MINTEK, Randburg, South Africa

2 Department of Civil and Chemical Engineering, University of South Africa, Florida Campus, Roodepoort, South Africa

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