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Catalysis by Gold: Recent Advances in Oxidation Reactions

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4.1. INTRODUCTION

The discovery in the 1980s that finely supported divided nanoparticles of gold could act as catalysts for reactions at low temperatures has to be one of the most fascinating recent observations in chemistry, since most consider gold to be an unreactive metal. Gold for a long time had been considered to be a relatively inert material and particularly unpromising as a catalyst. In particular, due to its stability under most conditions it is really surprising that it can be a highly effective oxidation catalyst. Consequently, a large number of experimental and theoretical studies are being undertaken to try to elucidate the nature of this interesting catalytic activity. This recent research has been reviewed by Haruta,[1–5] Bond and Thompson,[6,7] Bond,[8] Thompson,[9] Freund and coworkers,[10] Cortie,[11] Hashmi,[12] Hutchings[13–15] and Hutchings and Scurrell.[16] It should be noted that copper and silver (both in the same triad of the periodic table as gold) are used in many large scale catalytic processes, and it has been known for many years that the preparation of active catalysts with copper and silver requires the metal to be well dispersed on a support. Hence, there should not be so much surprise when the same is observed for gold, but because gold was considered to be inert few experimental studies explored this area until the seminal studies of Haruta[17] who discovered the high activity of gold for CO oxidation at sub-ambient temperature. This new discovery brings with it the opportunity that gold, in an appropriate form, is perhaps the most interesting metal in the Periodic Table with respect to *table its potential* to act as a catalyst.

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Bond and coworkers[18] in early studies demonstrated that very small gold particles supported on silica could give interesting catalytic performance for hydrogenation, but until very recently the use of gold as a selective hydrogenation catalyst has received little attention.[19] In the 1980s there were two significant observations that completely changed this perception and highlighted the special attributes of gold as a heterogeneous catalyst:

- the discovery that supported Au catalysts are very active for low temperature CO oxidation.[17]
- the prediction that Au would be best catalyst for ethyne hydrochlorination.[20]

Since the 1980s publications involving gold as a catalyst have increased exponentially and even when normalized as a proportion of all scientific publications the number of papers concerning catalysis by gold has seen a 400% increase during this period.[12] In this chapter, these early studies will be considered, and against this background some recent research concerning the use of gold as a selective oxidation catalyst will be described and discussed as a way of providing a brief introduction into this fascinating new field to those interested in catalysis by nanoparticles.

4.2. BACKGROUND: EARLY WORK ON GOLD CATALYST

4.2.1. Ethyne Hydrochlorination

In the early 1980s one of the routes to the synthesis of vinyl chloride was based on ethyne hydrochlorination using mercuric chloride supported on carbon as a catalyst. This catalyst suffers from deactivation due to sublimation of the active component and so a replacement catalyst that was more stable was an important research goal. Based on a detailed study by Shinoda[21] it was observed that a range of metal chlorides supported on carbon could give a spectrum of activities for this reaction (Fig. 4.1). The data show a wide spectrum of activities and Shinoda attempted to correlate these data with the electron affinity. However, it is apparent that the $ZnCl_2$/carbon and the $HgCl_2$/carbon catalysts gave low and high activities respectively, yet Zn^{2+} and Hg^{2+} have virtually the same electron affinity. It was considered unlikely that the process of hydrochlorination involved a one-electron transfer in the rate limiting step and therefore it was considered equally unlikely that the catalytic activity could be correlated with a one-electron process represented by the electron affinity. In addition, there was no correlation with cations capable of forming metastable acetylides (represented by the filled symbols in Fig. 4.1). Furthermore, the data set out in Fig. 4.1 could not be used predictively, and consequently further experiments would be required to find an improved catalyst. It was considered more appropriate that the ethyne hydrochlorination reaction involved at least two electrons and most of the catalysts examined by Shinoda were based on divalent cations. Subsequently, the key observation was that the catalyst activity for ethyne hydrochlorination was correlated with the standard electrode potential (Fig. 4.2). The plot of conversion against the standard electrode potential gives a smooth curve and this predicts that gold, and more importantly Au^{3+}, will be the best catalyst for this reaction. This prediction[20] was subsequently confirmed experimentally.[22–24]

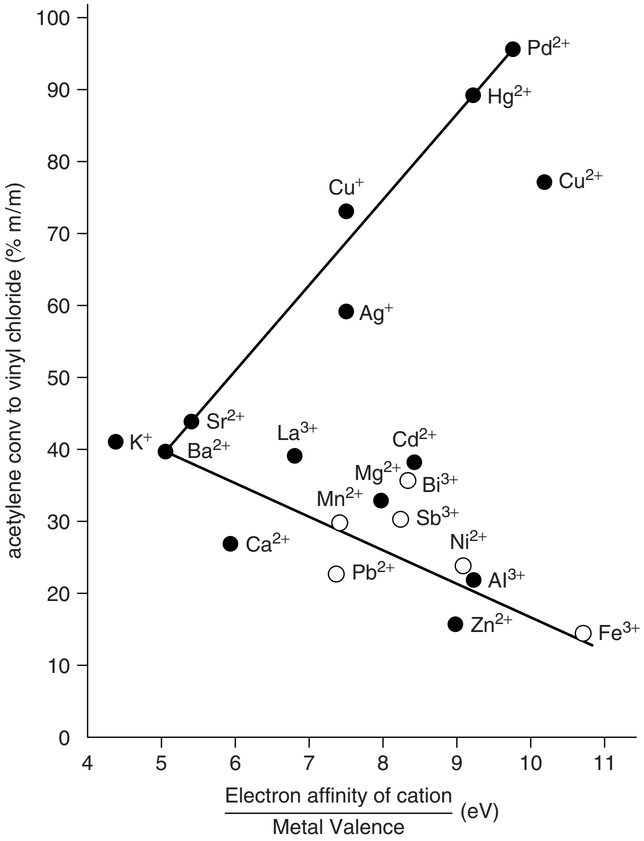

FIGURE 4.1. Correlation of activity for ethyne hydrochlorination with the electron affinity of the cation divided by the metal valence.[21]

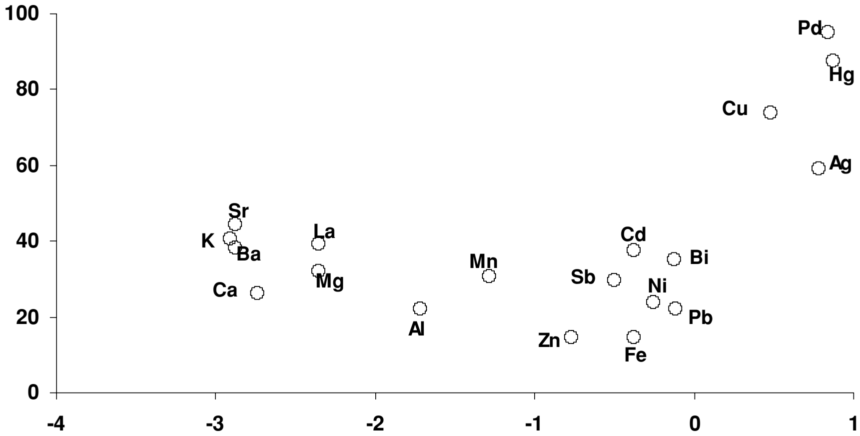

FIGURE 4.2. Correlation of activity for ethyne hydrochlorination with the standard electrode potential.[20]

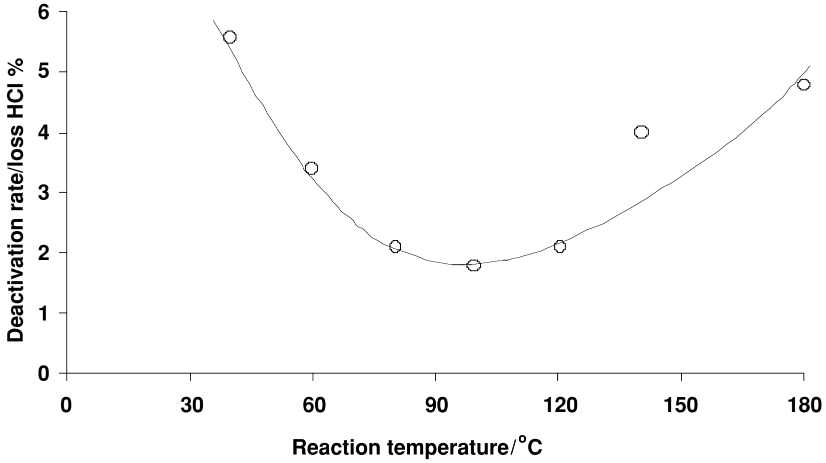

FIGURE 4.3. Deactivation rate of Au/carbon catalysts for ethyne hydrochlorination as a function of temperature (0.0005 mol Au/100 g catalyst, C_2H_2:HCl = 1:1.2).[23]

Although the gold catalysts were much more stable than the supported mercuric chloride catalysts, they still deactivated slowly with time and the rate of deactivation is dependent on temperature (Fig. 4.3). 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° as shown by detailed ^{197}Au Mössbauer spectroscopy (Fig. 4.4). This was a key observation and meant that the deactivation could be arrested by *in situ* reactivation by cofeeding dilute NO in with the reactor feedstock. This had no effect on catalyst selectivity but did stop deactivation (Fig. 4.5). 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. In this early study it was predicted, and subsequently verified, that gold was the catalyst of choice for this reaction. It was also recognized that Au^{3+} was the active form of gold. One interesting observation is that the catalysts could be easily prepared by a simple impregnation onto activated carbon of a gold solution in aqua regia; subsequently, it was observed that boiling deactivated catalysts in aqua regia restored the activity of the catalyst totally. This clearly demonstrates aspects of the unique robustness of supported gold catalysts. In this early study no emphasis was placed on the manner in which the supported gold catalysts were prepared. Effective catalysts could readily be prepared by impregnation and this led to the formation of relatively large gold nanoparticles. However, the spectroscopy studies detailed above clearly show that the enhanced activity is associated with cationic gold, although there is a sustained activity, albeit at a lower level, when the catalyst was deactivated following reaction for some time (Fig. 4.5). This may imply that metallic gold may play a role or that a low steady-state concentration of cationic gold was sustained during the catalytic cycle and this gives rise to the sustained catalytic performance. Since these early studies no further work

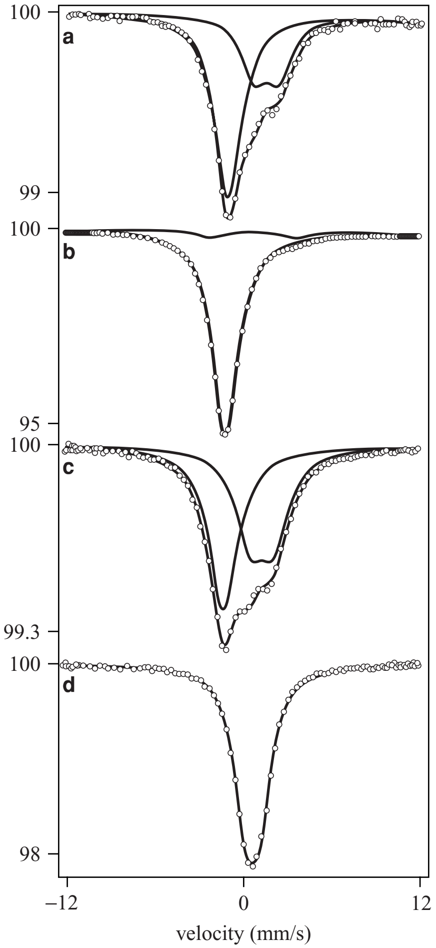

FIGURE 4.4. ^{197}Au Mössbauer spectra of: (a) 2% $HAuCl_4/C$ adsorbed on activated carbon from an aqua regia solution, (b) the same catalyst after deactivation at 180°C for 6 h (GHSV = 1140 h^{-1}, C_2H_2:HCl = 1:1.1), (c) a sample of the same type after reactivation by boiling in aqua regia, and (d) crystalline $HAuCl_4 \cdot xH_2O$.[24]

has been published on ethyne hydrochlorination using gold catalysts, but the catalysts would prove interesting for *in situ* spectroscopic investigation to determine the relative roles played by Au^0 and Au^{3+}.

4.2.2. Carbon Monoxide Oxidation

Also in 1980s Haruta[16,25] recognized that supported gold nanocrystals can be highly effective catalysts for the oxidation of CO at very low temperatures (Fig. 4.6) and in particular at temperatures below 0°C. This is a surprisingly high activity and is not replicated by other metals. Haruta recognized that the method of preparation

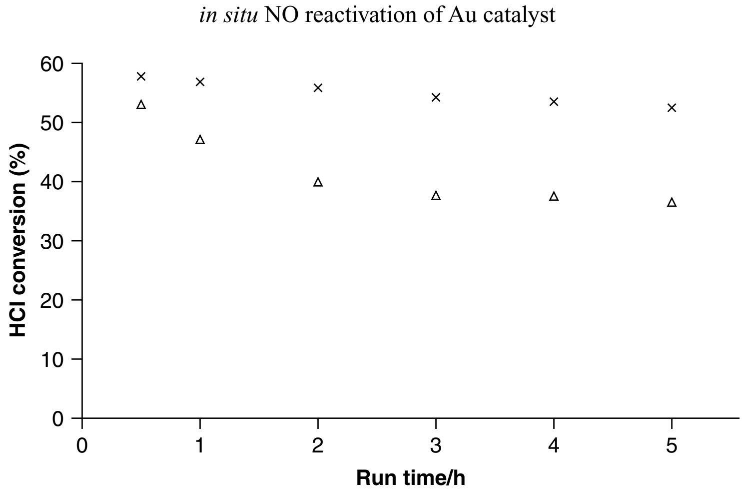

FIGURE 4.5. Effect of *in situ* reactivation of 2 wt.% Au/C catalyst at 180°C. Key: △ C_2H_2/HCl/N_2, × 0.42 vol.% NO cofed with reactants.[24]

was crucial to observe this high catalyst activity. For example, finely divided gold in a non-supported form only becomes active at *ca.* 280°C, whereas preparing α-Fe_2O_3-supported gold nanocrystals by impregnation produced a catalyst that was active at *ca.* 60°C. However, preparing the α-Fe_2O_3-supported gold nanocrystals by coprecipitation followed by calcination at 400°C produced a catalyst that was active at temperatures as low as −76°C. Haruta recognized that the very active catalysts comprised small gold nanoparticles *ca.* 2 to 4 nm in diameter. This amazing activity has now been replicated by many researchers, but it should be noted that each group appears to have their own techniques associated with preparing high activity catalysts. These early studies

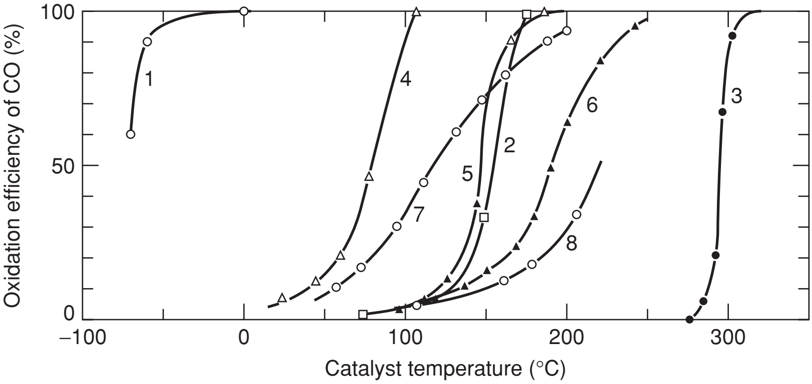

FIGURE 4.6. CO conversion over various catalysts as a function of temperature. 1, Au/α-Fe_2O_3 (Au/Fe = 1/19, coprecipitation, 400°C); 2, 0.5 wt.% Pd/γ-Al_2O_3 (impregnation, 300°C); 3, Au fine powder; 4, Co_3O_4 (carbonate, 400°C); 5, NiO (hydrate, 200°C); 6, α-Fe_2O_3 (hydrate, 400°C); 7, 5 wt.% Au/α-Fe_2O_3 (impregnation, 200°C); 8, 5 wt.% Au/ γ-Al_2O_3 (impregnation, 200°C).[25]

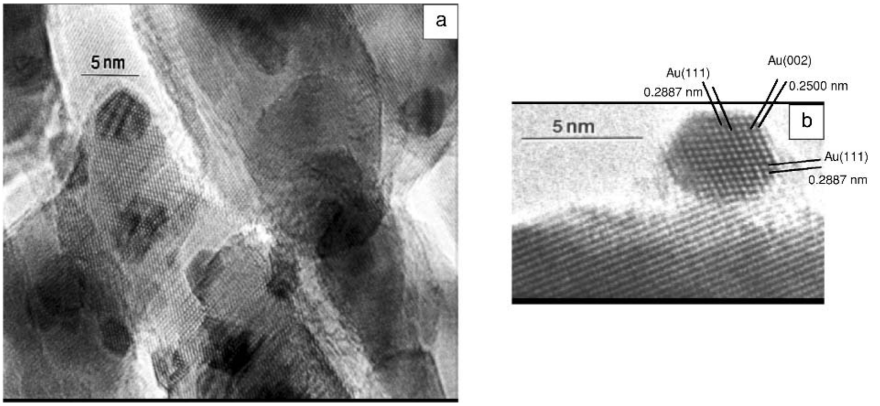

FIGURE 4.7. TEM micrographs for Au/ZnO catalyst calcined at 400°C showing the presence of 2 to 5 nm cuboctahedral gold particles.

also showed that the nature of the support was important and inferior catalysts are produced using γ-Al_2O_3 as support. However, it is the observation by Haruta that low temperature activity is feasible with supported gold nanocrystals that has spurred a great deal of the current research interest in gold today.[1–15] More recent studies have shown that low concentrations of water vapor are important for the observed catalysis and that TiO_2 is also an effective support.[26]

4.3. LOW TEMPERATURE CO OXIDATION: NATURE OF THE ACTIVE SITE

The early research indicated that catalysts must be prepared in a particular way using precipitation. Many of the active catalysts are typically found to comprise small crystallites, 2 to 4 nm in diameter, of gold supported on an oxide. There has been much debate concerning the nature of the active site for these catalysts and, recently, Bond and Thompson[7] have proposed a model where Au atoms at the interface between the Au particle and the oxide are the active oxidation centers. For example, Fig. 4.7 shows cuboctahedral gold nanoparticles supported on ZnO that is a very active CO oxidation catalyst. The periphery of the particle in association with the support is clearly visible and it is these peripheral atoms that have been the focus of much of the mechanistic debate. However, it remains unclear whether Au^{3+} or Au° is the active form of gold, and Bond and Thompson[7] have suggested that these peripheral atoms could be cationic gold and it is these atoms that are responsible for the activation of dioxygen in the catalytic process. Later Kung and coworkers[27] have also used this as the basis for their mechanistic discussion. However, it should be noted that this is an intense area of study at present, but although there has been much research using model systems a definitive study has not been published concerning the relative roles of Au^0 and Au^{n+} in the catalytic oxidation of CO. For example, Goodman and coworkers[28] using a combination of STM and spectroscopy considered that the unusual reactivity could be due to quantum size effects of the very small gold particles.

Indeed, the catalyst activity correlated with the transition of the electronic state of gold. As noted by Haruta,[5] this observation is questionable as far as CO oxidation is concerned, since the transition of the electronic state of gold was determined for one specific gold cluster of a defined diameter using STM under very controlled conditions, whereas the catalysis was determined using an entire Au/TiO_2 sample with a range of gold cluster diameters for which the mean diameter correlated with the observed STM electronic transition. Subsequently, Boyen *et al.*[29] concluded that Au particles containing 55 atoms, which are 1.4 nm in diameter, are extraordinarily stable and these Au_{55} particles could be active site for CO oxidation. Nørskov and coworkers[30] showed using DFT calculations that the activation of CO was energetically favored reaction path on Au particles with 10 atoms. However, others have focused on the role of Au^{3+}. In particular, Baker[31] noted that trying to explain the enhanced reactivity of small gold nanocrystals on the basis of size alone neglects the importance of the underlying support. Consequently, it is the interface between the small gold particles and the support that is important and this re-emphasizes the key part of the Bond Thompson mechanistic proposal.

However, it must be stressed that the model of the active site proposed by Bond and Thompson[7] or Kung and coworkers[26] has yet to be experimentally verified. A recent model study by Goodman and coworkers[32] has tried to address the role played by these peripheral atoms by designing well-ordered monolayers and bilayers of gold atoms that completely cover the TiO_2 support that clearly does not comprise any of these peripheral sites. They found that the bilayers were more active than the monolayers indicating that the catalysis can proceed on the extended gold surface so created. However, in this study no technique was used that could distinguish between cationic or metallic gold and consequently the effect on the electronic state of gold by the TiO_2 support cannot be ruled out.

Other researchers have used spectroscopic techniques in which cationic forms of gold can be observed, namely X-ray photoelectron spectroscopy and Mössbauer spectroscopy. Hutchings and coworkers[33] showed that Au^{3+} in Au / Fe_2O_3 was an important component of very active catalysts for the oxidation of CO. In 2003, Flytzani-Stephanopoulos and coworkers[34] demonstrated that the cationic form of gold was an important factor in obtaining high activity water gas shift catalyst based on Au added by deposition precipitation onto nanocrystalline 10% La-doped CeO_2 ($\sim$5 nm). The catalysts were subsequently leached with 2% NaCN removing 90% of the gold and, importantly, no Au particles remained after NaCN leaching. However the catalytic activity was not only retained but also significantly enhanced. CO oxidation can be viewed as an elementary reaction in the water gas shift reaction and so the observations by Flytzani-Stephanopoulos may be of general significance.

In a recent review, Haruta[5] has reassessed the mechanism of CO oxidation on the basis of the Bond and Thompson and Kung models, i.e. that the CO is activated by adsorption on Au^0 on the surface of the gold nanoparticles and that dioxygen is activated by the atoms at the periphery between the support and the gold nanocrystals (Fig. 4.7). The atoms at the periphery are proposed by Haruta to be cationic in nature, possibly $Au(OH)_3$ or Au(OH) formed by the presence of water vapor that is essential for the observed high activity catalysts.[26] It is clear that the debate will continue for the immediate future. There are two reasons why finding an answer to the key question of the nature of the active site in gold catalysts for CO oxidation. The first is purely scientific in that the problem poses a significant challenge and it is worthy of close analysis and reflection. Secondly, the oxidation of CO is seen as a crucial aspect of using methanol or hydrocarbons as fuels for fuel cells. At present the reformate from these materials contains traces of CO that must be removed as they poison the electrodes, and gold catalysts may provide a mechanism of removing these trace amounts; this is addressed in the next section.

4.4. COMPETITIVE OXIDATION OF CARBON MONOXIDE IN THE PRESENCE OF HYDROGEN

As noted in the preceding two sections, in recent years there has been considerable interest in the oxidation of CO at relatively low temperatures using gold as a catalyst. One particular application is in fuel cells, especially polymer electrolyte fuel cells (PEFC), which are used in electric vehicles and operate at *ca.* 80 to 100°C. PEFCs operate by the oxidation of hydrogen produced from methanol by steam reforming and water gas shift reactions. Residual CO can poison the Pt anode at the low operating temperature and hence trace amounts of CO have to be removed from the H_2 in the presence of water to ensure long cell lifetimes. Although conceptually simple, the oxidation of CO in the presence of excess moist H_2, without oxidizing the hydrogen, is a particularly difficult reaction which is now attracting considerable research effort. An alternative strategy is to design PEFCs that can tolerate the residual CO, but to date this has also proved to be unsuccessful, so both approaches are being actively pursued at this time.

Considerable effort has been applied to the design of suitable catalysts for the competitive oxidation of CO in the presence of H_2, and the most commonly used partial oxidation catalysts (alumina-supported Pt, Ru and Rh) are unsuitable since they require temperatures in the range 150 to 200°C to be effective,[35–37] and even then significant conversion of H_2 is observed. Haruta and coworkers[38,39] first demonstrated that supported Au nanoparticles could be active at much lower temperatures, but again H_2 was oxidized together with CO at temperatures >70°C. Au/Fe_2O_3 catalysts have also been studied and Kahlich *et al.*[40] used catalysts calcined at 400°C but found that significant H_2 oxidation occurred at 80°C. Most recently, Qiao and Deng[41] have shown that noncalcined Au/Fe_2O_3 catalysts, dried only at 120°C, were very selective for CO oxidation in the presence of H_2 at 25°C, but the selectivity was lost at higher temperatures. To date, some of the best results for this demanding reaction have been reported by Grigorova *et al.*[42] for a Au/CeO_2 catalyst promoted with SnO_2, but even this catalyst gives significant (*ca.* 5%) H_2 conversion at temperatures >70°C with CO conversions of *ca.* 40 to 60%. Recently, Corma and coworkers[43] have reported a nanocrystalline CeO_2-supported gold catalyst that gave appreciable selectivity at 60°C for a dry CO/H_2 mixture. Unfortunately, all these previous studies use dry reactants and consequently are not applicable to the humid conditions prevailing in the fuel cell application which in addition also contains significant quantities of CO_2. However, recently Schubert *et al.*[44] have shown that a calcined Au/Fe_2O_3 can operate under realistic fuel cell conditions in which CO_2 and H_2O are present and reasonable selectivity can be achieved. Given these promising results we can anticipate further progress with this fascinating reaction in the future.

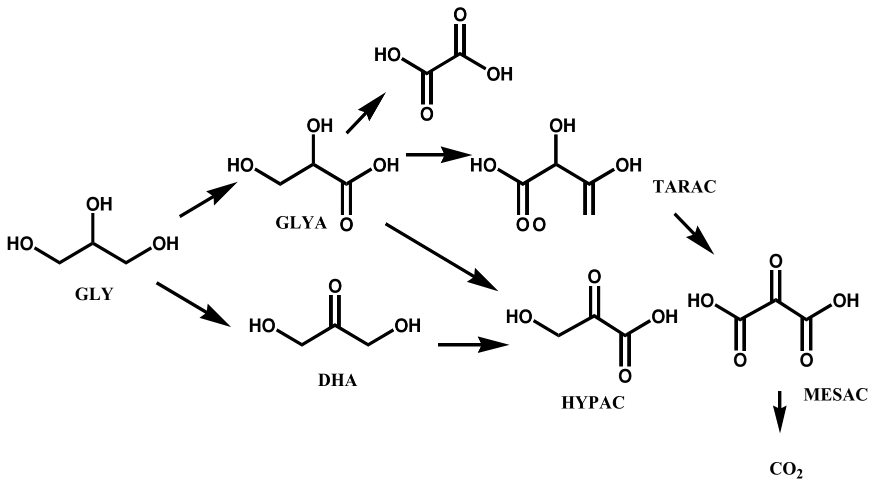

FIGURE 4.8. Reaction scheme for the oxidation of glycerol.

4.5. OXIDATION OF ALCOHOLS

The oxidation of alcohols and polyols to chemical intermediates represents a demanding target. Supported platinum and palladium nanoparticles are generally acknowledged as effective catalysts for the oxidation of polyols, for example in carbohydrate chemistry for the oxidation of glucose to glucinic acid. Glycerol is a highly functionalized molecule that is readily available from biosustainable sources, for example it can be obtained as a by-product of the utilization 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 (Fig. 4.8). One of the key problems is the potential complexity of the products that can be formed and so control of the reaction selectivity by a careful design of the catalyst is required. Glycerol oxidation, in aqueous solution, has been extensively studied and in general, palladium catalysts were found to be more selective than platinum, but in all these previous studies using Pt and Pd, mixtures of most of the potential products were formed in addition to nonselective products such as formic acid and carbon dioxide. Hence, glycerol has remained an elusive starting point for the synthesis of chemical intermediates.

Prati and coworkers[45–48] have shown in their seminal studies that supported gold nanoparticles can be very effective catalysts for the oxidation of alcohols, including diols. Recently, the use of supported gold catalysts has been extended to show that Au supported on graphite can oxidize glycerol to glycerate with 100% selectivity using dioxygen as the oxidant under relatively mild conditions (Table 4.1).[49,50] The oxidation of alcohols was recognized by Prati and coworkers to require a base[45–48] which is considered to be essential for the first hydrogen abstraction.[50] Hence NaOH has to be added to observe reaction with supported gold catalysts. This is not the case for supported Pd and Pt catalysts which are active in acidic as well as in alkaline media, but these catalysts are, in general, much less selective when compared with the supported gold catalysts

TABLE 4.1. Oxidation of glycerol using 1 wt.% Au/C catalysts.[a]

Catalyst	Glycerol (mmol)	P_{o2} (bar)	Glycerol/ metal (mol ratio)	NaOH (mmol)	Glycerol Conversion (%)	Selectivity (%)		
						Glyceric Acid	Glyceraldehyde	Tartronic Acid
1 wt.% Au/activated carbon	12	3	538[b]	12	56	100	0	0
1 wt.% Au/graphite	12	3	538[b]	12	54	100	0	0
"	12	6	538[b]	12	72	86	2	12
"	12	6	538[b]	24	58	97	0	3
"	6	3	540[c]	12	56	93	0	7
"	6	3	540[c]	6	43	80	0	20
"	6	3	214[d]	6	59	63	0	12
"	6	3	214[d]	12	69	82	0	18
"	6	6	214[d]	6	58	67	0	33
"	6	6	214[d]	12	91	92	0	6
"	6	6	214[d]	0	0			

[a] 60°C, 3 h, H_2O (and 20 ml), stirring speed 1500 rpm.
[b] 220 mg catalyst.
[c] 217 mg catalyst.
[d] 450 mg catalyst.

used under basic conditions (Table 4.1). It is apparent that the selectivity to glyceric acid and the glycerol conversion are 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. For comparison, the 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. In a final set of experiments, catalysts with lower Au concentrations were investigated. 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. The previous studies for diol oxidation by Prati and coworkers[45–48] 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. As noted earlier in this chapter, for gold as a CO oxidation catalyst, it has been shown that the activity is highly dependent on the particle size, and the optimum size is *ca.* 2 to 4 nm.[1–5] 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 wt.% 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. The catalysts that were active and selective for glycerol oxidation were not found to be active for the CO oxidation reaction. Consequently, we consider that different active sites are involved in these two contrasting reactions and this opens up the mechanistic debate still further.

4.6. SELECTIVE OXIDATION OF HYDROGEN TO HYDROGEN PEROXIDE

At present there is significant interest in the design of new heterogeneous catalysts for selective oxidation under ambient conditions, and these typically use hydrogen peroxide as the oxidant.[51–53] At present, hydrogen peroxide is produced by the sequential hydrogenation and oxidation of alkyl anthraquinone[54] and global production is *ca.* 1.9×10^6 tonnes per annum. This process is currently only economic on a large scale ($4–6 \times 10^4$ tpa), whereas it is often required practically on a much smaller scale. Consequently, there is considerable interest in the direct manufacture of hydrogen peroxide from the catalyzed reaction of hydrogen and oxygen.[55,56] At present, some success has been achieved using Pd as a catalyst, especially when halides are used as promoters.[57,58] Supported Au catalysts have been investigated for the oxidation of propene to propene oxide using O_2/H_2 mixtures,[59] and it is considered that a surface hydroperoxy species may be formed as the oxidant. Hutchings and coworkers have found that supported Au catalysts can be very effective for the synthesis of hydrogen peroxide[60,61] and, furthermore, the rate of hydrogen peroxide formation can be significantly enhanced by the use of a supported Au/Pd alloy.

The initial research approach for the design of a direct hydrogen oxidation process for the synthesis of hydrogen peroxide, was to use supercritical CO_2 as a reaction medium. This is because earlier studies with Pd catalysts have indicated that H_2 diffusion is a significant problem and this can be expected to be largely overcome by using supercritical media due to the enhanced solubility of H_2. Au/ZnO, Pd/ZnO and Au:Pd/ZnO catalysts containing 5 wt.% metal were evaluated for the synthesis of hydrogen peroxide using supercritical CO_2 (35°C, 9.7 MPa). The Au/ZnO and Au:Pd/ZnO catalysts exhibited some hydrogen peroxide synthesis, albeit at a low rate. However, the Pd catalyst only generated water as a product. At this temperature it was considered that the hydrogen peroxide formed was relatively unstable with respect to decomposition or hydrogenation (Fig. 4.9). Hence, although using supercritical CO_2 as the reaction medium may have overcome the diffusion limitation, the inherent instability of hydrogen peroxide at the elevated temperature required to achieve supercritical conditions mitigates against the use of this medium.

Subsequently, experiments were conducted at significantly lower temperatures (2°C) and the results, shown in Fig. 4.10, indicate that hydrogen peroxide can be formed at a high rate for the supported Au catalyst. The selectivity for H_2O_2 for the Au/Al_2O_3 catalyst was determined to be 53%. In this case, the catalysts were prepared by impregnation and they were tested for hydrogen peroxide formation at 2°C using methanol as a solvent. The supported Au:Pd (1:1 by wt) catalyst produces significantly more than the pure Au catalyst or the Pd catalyst. It was found that the addition of just a small amount of Pd gave much better effects than the Au:Pd (1:1 by wt) catalyst (Fig. 4.10). This indicates a synergistic effect of Pd acting as a promoter for the Au catalyst. A detailed analysis using STEM-EDX confirmed that the catalysts comprised

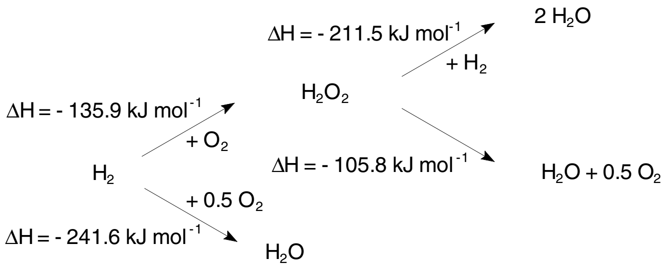

FIGURE 4.9. Reaction scheme for the oxidation of hydrogen to hydrogen peroxide.

Au–Pd alloys with compositions close to that of the bulk components and that particle sizes were *ca.* 25 to 50 nm in diameter. The catalysts that were effective for H_2O_2 synthesis were found to be wholly inactive for CO oxidation at ambient temperature, and catalysts that were effective for low temperature CO oxidation were inactive for H_2O_2 synthesis. This shows that selective oxidation reactions active may utilize very different sites than those for the oxidation of CO.

This preliminary work demonstrates that supported Au catalysts are effective for the direct synthesis of hydrogen peroxide from hydrogen and oxygen. In particular, Au catalysts may provide a significant improvement over Pd catalysts that have been investigated previously.[54–58] This clearly represents an exciting new reaction for which nanocrystalline gold is a highly effective catalyst.

4.7. CONCLUDING COMMENTS

The field of catalysis by gold is now well established. Although most effort to date has been focused on the oxidation of CO it is apparent that this research might

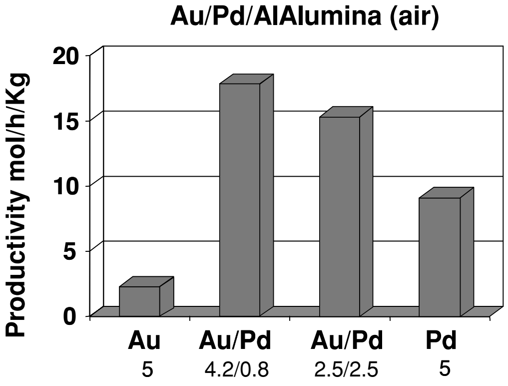

FIGURE 4.10. Production of hydrogen peroxide from the reaction of H_2 and O_2 over Au and Au/Pd catalysts at 2°C in an autoclave reactor using aqueous methanol (CH_3OH,5.6 g; H_2O 2.9 g) as solvent with catalyst (0.05 g), the reactor was purged three times with CO_2 (3 MPa) and then filled with 5% H_2/CO_2 and 25% O_2/CO_2.

find application in fuel cells. There is enormous potential for the use of supported gold nanocrystals for selective oxidation reactions and it is here where we can anticipate the greatest progress in the future.

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