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Catalysis by gold

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Abstract

The recent interest in gold catalysis provides the focus for this perspectives paper. Until recently gold has been overlooked as a key component of both homogeneous and heterogeneous catalysts. Two observations in the 1980s showed that gold could be a catalyst of choice, but it is only relatively recently that gold has been shown to be a very versatile redox catalyst. In this paper aspects of both the background to this interest and some of the recent work on gold will be discussed.

Keywords: Catalysis; Gold; Nanoparticles

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. Typically chapters on gold chemistry in the standard textbooks are relatively thin in comparison to those for other noble metals. For example platinum and palladium are both extensively used as catalysts, in addition copper and silver (both in the same triad of the periodic table as gold) are used in many large scale processes, and it has been known for many years that the preparation of active catalysts with these metals 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 it had been long considered that gold was unreactive and consequently its chemistry was particularly unexciting. However, just as with the other metals it is nanocrystalline gold supported on oxides has been found to be most reactive in many reactions [1–5]. This has been led by the seminal work of Haruta et al. [1] who discovered the high activity of gold for CO oxidation at subambient temperature. The new discoveries bring the opportunity that gold, in an appropriate form, is perhaps the most interesting metal in the periodic with respect to table its potential to act as a catalyst.

Bond and co-workers [6] 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 selective hydrogenation catalyst has received little attention [7]. 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 [1];
- the prediction that Au would be best catalyst for ethyne hydrochlorination [8].

In this paper 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 discussed as a way of providing a brief introduction into this fascinating new field.

2. 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 catalyst. This

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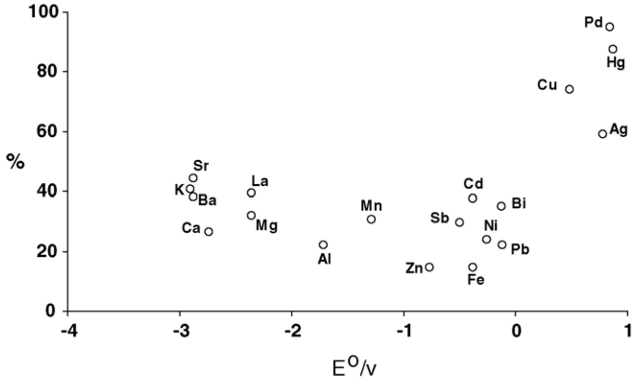

Fig. 1. Correlation of activity for ethyne hydrochlorination with the standard electrode potential [4].

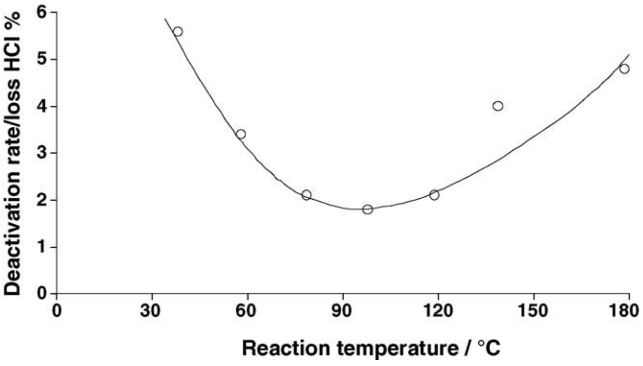

Fig. 2. Deactivation rate of Au/carbon catalysts for ethyne hydrochlorination as a function of temperature (0.0005 mol Au/100 g catalyst, C_2H_2:HCl = 1:1.2) [6].

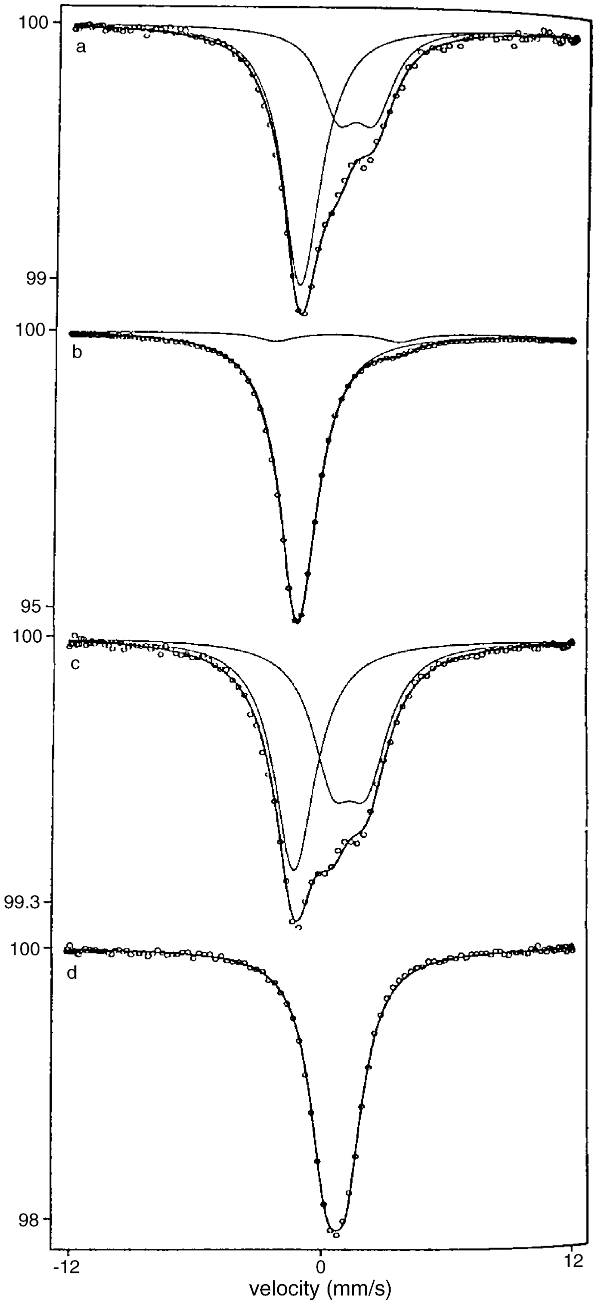

Fig. 3. ^{197}Au Mössbauer spectra of: (a) 2% $HAuCl_4$/C adsorbed on activated carbon from an aqua regia solution, (b) the same catalyst after deactivation at 180 °C for 6 h (GHSV = 1140 h^{-1}, C_2H_2:HCl = 1:1.1), (c) a sample of the same type after reactivation by boiling in aqua regia, and (d) crystalline $HAuCl_4 \cdot xH_2O$ [7].

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 [9] it was observed that a range of metal chlorides supported on carbon could give a spectrum of activities for this reaction. The key observation was that the activity was correlated with the standard electrode potential (Fig. 1). 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, and this was confirmed in subsequent research [10–12]. 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. 2). 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. 3). 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). 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 recognised that Au^{3+} was the active form of gold. One interesting observation is that

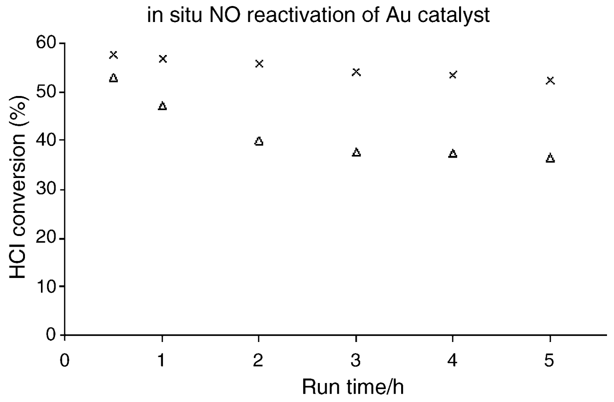

Fig. 4. Effect of in situ reactivation of 2 wt.% Au/C catalyst at 180 °C. Key: (Δ) C_2H_2/HCl/N_2, (×) 0.42 vol.% NO cofed with reactants [7].

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.

2.1. CO oxidation

Also in the early 1980s Haruta et al. [1] recognised that supported gold nano-crystals can be highly effective catalysts for the oxidation of CO at very low temperatures (Fig. 5) and in particular at temperatures below 0 °C. This is a surprisingly high activity and is not replicated by other metals. This low temperature activity has spurred a great deal of the current research interest in gold today.

CO oxidation is now being used by many researchers as a standard test reaction, and this early work has been extensively reviewed [2–5]. This early research indicates that catalysts must be prepared in a particular way using precipitation. Many of the active catalysts are typically found to comprise small crystallites, 2–4 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 [3] have proposed a model where Au atoms at the interface between the Au particle and the oxide are the active oxidation centres. However, it remains unclear whether Au^{3+} or Au is the active form of gold. There has been much research using model systems but as yet there has not been a definitive study published. For example, Goodman and co-workers [13] 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. Subsequently, Boyen et al. [14] 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 co-worker [15] showed using DFT calculations that the activation of CO was energetically favoured reaction path on Au particles with 10 atoms. However, others have focussed on the role of Au^{3+}. In particular Baker [16] 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-emphasis 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 has yet to be experimentally verified.

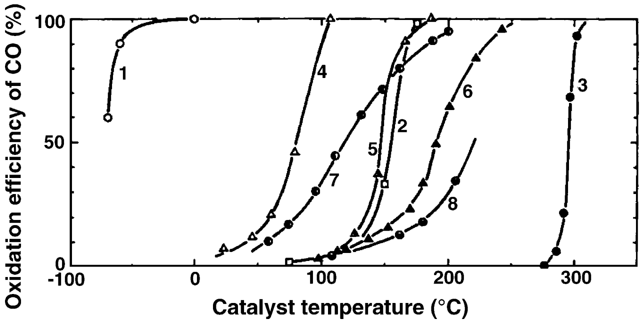

Fig. 5. CO conversion over various catalysts as a function of temperature. (1) Au/(-Fe_2O_3 (Au/Fe = 1/19, co-precipitation, 400 °C); (2) 0.5 wt.% Pd/(-Al_2O_3 (impregnation, 300 °C); (3) Au fine powder; (4) Co_3O_4 (carbonate, 400 °C); (5) NiO (hydrate, 200 °C); (6) (-Fe_2O_3 (hydrate, 400 °C); (7) 5 wt.% Au/(-Fe_2O_3 (impregnation, 200 °C); (8) 5 wt.% Au/(-Al_2O_3 (impregnation, 200 °C) (Haruta et al., Journal of Catalysis 115 (2) (1989) 301).

Hutchings and co-workers [17] 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 co-workers [18] 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 nano-crystalline 10% La-doped CeO_2 (~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 it was 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.

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 to removing these trace amounts.

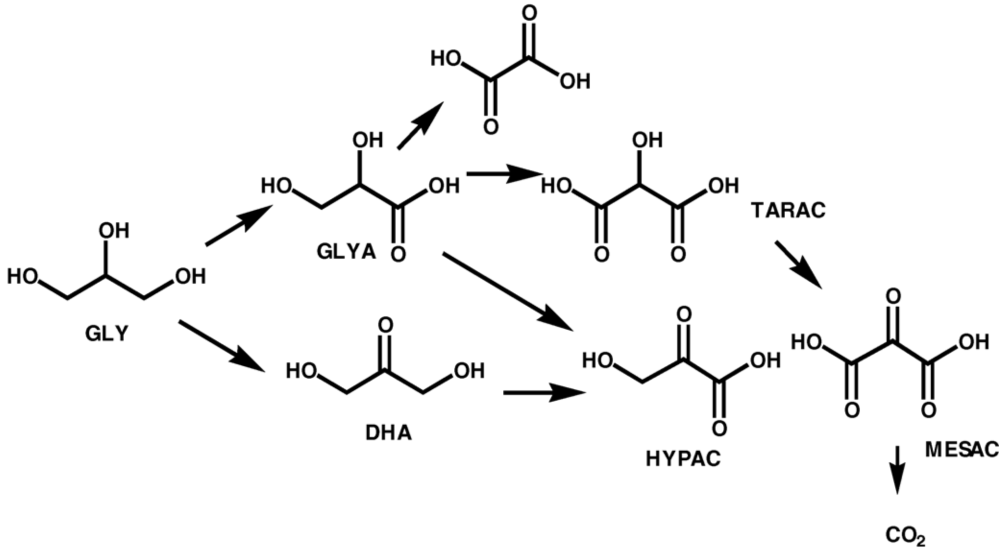

Fig. 6. Reaction scheme for the oxidation of glycerol.

3. Selective oxidation: oxidation of alcohols

In recent years, the investigation of a range of oxidation reactions using gas or liquid phase reagents to produce valuable intermediates or products for the chemicals industry has been a major research target. There are many catalytic processes operated today that rely on oxidation, but very few of these are used in the fine chemicals industry. Unfortunately, many reactions are still carried out using stoichiometric oxygen donors often with particularly non-green components. This is a field where we can expect a number of advances with gold as a catalyst.

In particular, 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 functionalised molecule that is readily available from biosustainable sources, for example it can be obtained as a by-product of the utilisation of rape seed and sunflower crops. This makes glycerol a particularly attractive starting point for the synthesis of intermediates, and a large number of products can be obtained from glycerol oxidation (Fig. 6). One of the key problems is the potential complexity of the products that can be formed and so control of the reaction selectivity by 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 non-selective products such as formic acid and carbon dioxide. Hence, glycerol has remained an elusive starting point for the synthesis of chemical intermediates.

Table 1
Oxidation of glycerol using 1 wt.% Au/C catalysts

Catalyst	Glycerol (mmol)	Po$_2$ (bar)	Glycerol/metal ratio (mol)	NaOH (mmol)	Glycerol conversion (%)	Selectivity (%)		
						Glyceric acid	Glyceraldehyde	Tartronic acid
1 wt.% Au/activated carbon	12	3	538[a]	12	56	100	0	0
1 wt.% Au/graphite	12	3	538[a]	12	54	100	0	0
	12	6	538[a]	12	72	86	2	12
	12	6	538[a]	24	58	97	0	3
	6	3	540[b]	12	56	93	0	7
	6	3	540[b]	6	43	80	0	20
	6	3	214[c]	6	59	63	0	12
	6	3	214[c]	12	69	82	0	18
	6	6	214[c]	6	58	67	0	33
	6	6	214[c]	12	91	92	0	6
	6	6	214[c]	0	0			

60 °C, 3 h, H_2O (and 20 ml), stirring speed 1500 rpm.

[a] 220 mg catalyst.

[b] 217 mg catalyst.

[c] 450 mg catalyst.

In recent years, there has been immense interest in the use of gold catalysts for oxidation reactions. Prati and co-workers [19–22] have shown that supported gold nanoparticles can be very effective catalysts for the oxidation of alcohols, including diols. Recently, we have extended these studies to show that Au supported on graphite can oxidise glycerol to glycerate with 100% selectivity using dioxygen as the oxidant under relatively mild conditions [23,24].

The oxidation of glycerol with dioxygen was also investigated using 1 wt.% Au/C catalysts in an autoclave and the results are given in Table 1. NaOH was added as a base since, in the absence of NaOH, no glycerol conversion was observed. In addition, as noted earlier, the carbon supports were also inactive for glycerol oxidation under these conditions, even when NaOH was present. For all the data presented in Table 1, the carbon mass balance was 100% indicating that, under these conditions, supported Au/C catalysts are extremely selective for this reaction and no C_1 or C_2 by-products were detected. In addition, 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,

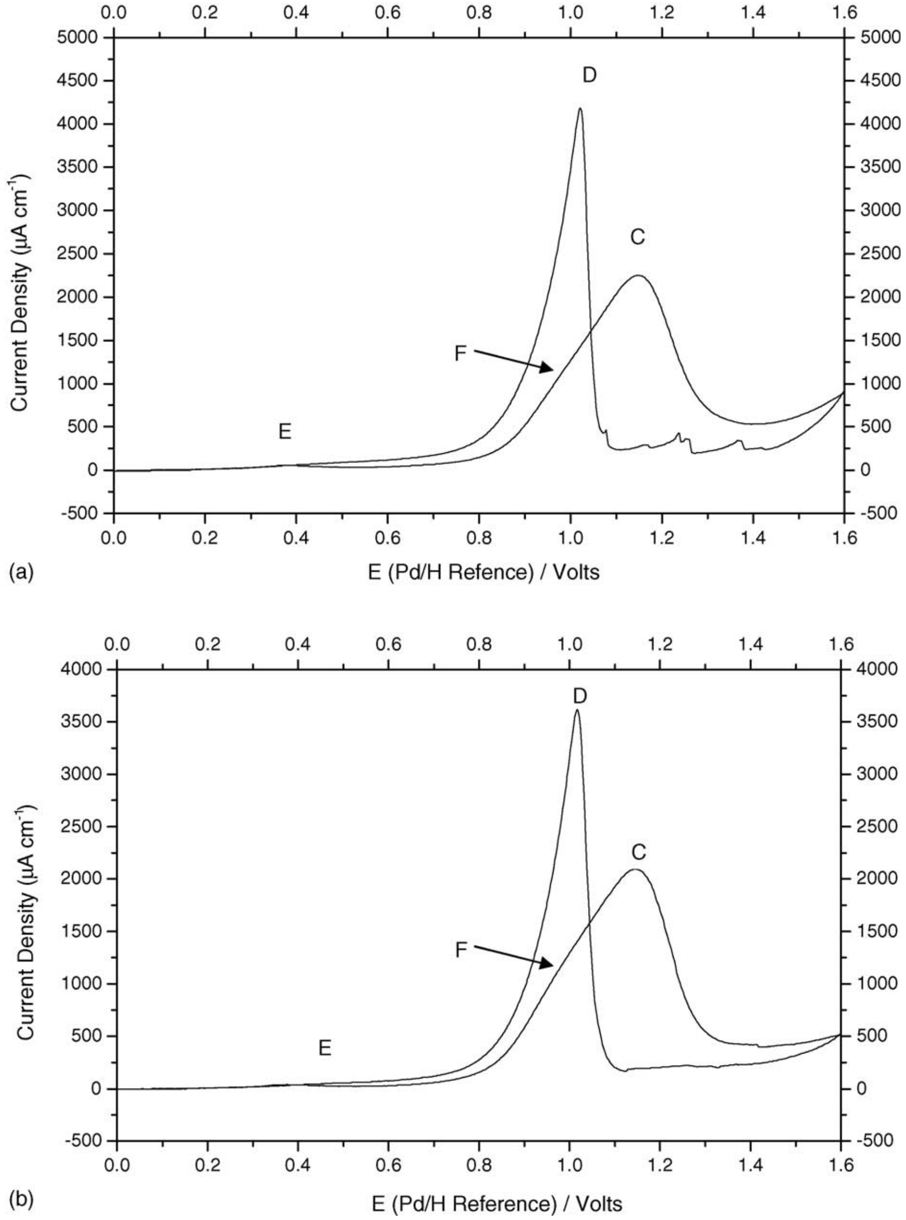

Fig. 7. Cyclic voltammetry of Au/graphite catalysts in aqueous NaOH (0.5 mol/l) and glycerol (0.5 mol/l). (a) 0.25 wt.% Au/graphite; (b) 0.5 wt.% Au/graphite.

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 co-workers [19–22] 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 paper, 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. 2–4 nm [1,2]. However, the Au supported catalysts that were selective for glycerol oxidation comprised Au particles as small as 5 nm and as large as 50 nm in diameter. The majority, however, were about 25 nm in size and were multiply twinned in character. Decreasing the loading to 0.5 or 0.25 wt.% did not appreciably change the particle size distribution; the particle number density per unit area was observed to decrease proportionately however, which may be correlated to the decrease in glycerol conversion and selectivity to glyceric acid. 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. Subsequently, we have shown that catalysts comprising relatively large gold nanocrystals supported on oxides are very active and selective for the direct oxidation of molecular hydrogen to hydrogen peroxide [25,26]. Again these catalysts are inactive for CO oxidation indicating that catalysts for selective oxidation probably have significantly different active sites than those of the catalysts that are active for CO oxidation.

Recently, we have used cyclic voltammetry to study the Au catalysts supported on graphite [27], since in this case the support is conducting and this very incisive technique can be used. A set of CV experiments were carried out with the Au/graphite catalysts in the presence of glycerol, air and NaOH, thereby studying the behaviour in situ under reaction conditions (Fig. 7). In the forward potential sweep, all catalysts showed a broad signal associated with the electrooxidation of glycerol at ca. 0.9–1.3 V (labelled C) and a narrower feature on the reverse sweep (labelled D). Peak D corresponds to the situation in which the gold surface is being stripped of bulk oxide leaving behind only the Au-OH species (peak A) with a minimal amount of molecular fragments adsorbed (since these have been oxidised during the previous positive potential sweep). This situation leads to peak D being the most intense and the catalyst being in its most active state. Peak C corresponds to the same situation although the relative amounts of strongly adsorbed molecular fragments is increased (since these have not yet been oxidised) and hence a smaller concentration of Au-OH species due to site-blocking via glycerol decomposition. Both of these factors lead to peak C being smaller than peak D. This behaviour also emphasises the poisoning effect on the reaction of bulk gold oxides which quench reaction at potentials >1.3 V on the forward sweep and also down to 1.1 V on the negative sweep due to hysteresis in the "irreversible" formation/desorption of the bulk oxide phase [28]. This suggests that there should be a strong correlation between activity and the relative intensities of peaks C and D. This proposition is explored below. In addition, it should be noted that the 0.25 and 0.5% Au/C catalysts gave rise to two less intense peaks labelled E (0.38 V) and F (1.0 V). For the active catalyst displaying total specificity to glycerate (1 wt.% Au/graphite) peaks E and F are both absent and we also considered this to be a key finding. Furthermore, current density positive of 1.3 V associated with

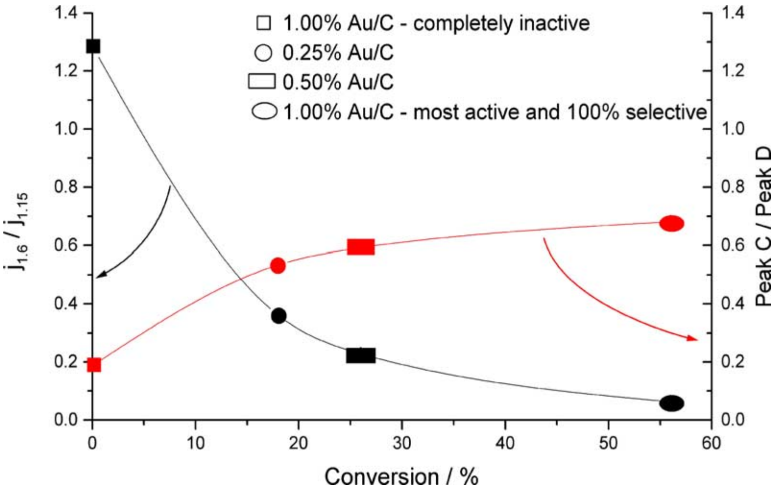

Fig. 8. Plot of current density at 1.6 V ($j_{1.6}$)/current density at 1.15 V ($j_{1.15}$) and ratio of peak C/peak D vs. percentage conversion for various supported Au/C catalysts used for glycerol oxidation.

the electrooxidation of strongly adsorbed glycerol fragments increases in the order:

$$1\%\mathrm{Au/C} < 0.5\%\mathrm{Au/C} < 0.25\%\mathrm{Au/C} < 1\%\mathrm{Au/C}\ (\text{inactive})$$

In this way, the CV study, however, revealed differences between all four the catalyst samples we investigated. In particular, two features were identified that appeared to correlate with catalyst activity (a) the relative intensities of specific peaks observed in the CV and (b) the amplitude of the current density at >1.3 V. Therefore, in Fig. 8, these two parameters are plotted versus catalyst activity, namely (i) the ratio of current densities (j) of peak C/peak D and (ii) the ratio of current density at 1.6 V/the current density of peak C. Both these parameters express the rates of surface blocking (poisoning) relative to oxidation by adsorbed Au-OH species. Inspection of Fig. 8 demonstrates a smooth correlation between activity and both of these parameters and we consider this observation may have significance in the design of improved oxidation catalysts.

4. Concluding comments

The field of catalysis by gold is just starting to show the potential that exists. At present a large amount of effort is focussed on the well documented oxidation of CO at ambient temperature. However, it is clear that supported gold catalysts can provide the basis for an exciting new class of oxidation catalysts and we can expect many new developments in this area in the near future.

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