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Supported gold and gold palladium catalysts for selective chemical synthesis

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ABSTRACT

Catalysts based on gold are now well established as very active and selective for broad ranges of redox reactions. Although primarily known for selective and preferential oxidation reactions, gold catalysts are also highly effective for selective hydrogenation. Hydrogenation reactions provide the focus for this perspective paper that is based on a François Gault lecture given at the Sabatier Conference in 2007. In particular, two reactions will be discussed; namely, the use of supported gold catalysts for selective hydrogenation of α,β-unsaturated aldehydes to unsaturated alcohols, and the use of supported gold palladium alloys for the direct hydrogenation of molecular oxygen to form hydrogen peroxide in preference to water.

1. Introduction

Two contemporaneous discoveries made in the 1980s demonstrated that supported gold materials could be the catalysts of choice [1,2]. Prior to these observations a number of studies had been carried out using gold catalysts but invariably they were found to be much less reactive or effective when compared with other catalysts [3,4]. One key early paper was the observation by Bond and co-workers [5] that gold could be an effective hydrogenation catalyst for butadiene. Of particular significance was their observation that very small particles of gold were effective. This has become the key facet with supported gold catalysts since now it is apparent that for many applications very small nano-sized gold particles are required for the observation of high activity. Since the 1980s there has been an enormous amount of research concerned with gold catalysis, and much of this has been extensively reviewed [6–16] and gold nano-particles are now recognised as a hot area for research. Supported gold catalysts are now known to be effective for the low temperature oxidation of CO [6–8,12,17], the preferential oxidation of CO in the presence of H_2 [18–23], the oxidation of alkenes [24–26], the oxidation of alcohols [24–32], the hydrogenation of α,β-unsaturated aldehydes [33–35], selective hydrogenation of nitro groups [36–38] and the direct formation of hydrogen peroxide [39–45]. This paper is based on a François Gault lecture delivered at the Sabatier Conference in September (2007) on the subject of selective catalysis using supported gold and gold palladium nano-particles. The topic of selective hydrogenation will be discussed and, in particular, the hydrogenation of α,β-unsaturated aldehydes, and the direct formation of hydrogen peroxide will be discussed.

2. Selectivity problems associated with hydrogenation

A problem associated with many catalysed reactions concerns the control of selectivity so that an intermediate product can be obtained in high yield. In these reactions kinetic control is required and this problem is often encountered in selective oxidation of hydrocarbons where CO_2 and H_2O are the thermodynamically preferred products. It is also commonly encountered in hydrogenation. However, fortunately, selective catalytic hydrogenation is less complex than oxidation, since molecular hydrogen has to be activated on the surface of a catalyst, since otherwise it cannot take part in the hydrogenation process. Hence, background homogeneous hydrogenations with molecular hydrogen do not play a role in the reactions and any observed activity can be associated with catalysis. The same is not true for oxidations with molecular oxygen, since in its ground state it is a di-radical and consequently does not require activation by a catalyst to induce activity. Consequently, non-catalysed homogeneous oxidation reactions can play a major role alongside catalytic oxidation, and in the extreme can dominate the observed reactivity. This is one of the reasons why selective hydrogenation has been studied in greater detail than oxidation.

The two hydrogenation reactions selected for comment in this paper have selectivity problems where a reactive intermediate is required. In addition, they both exhibit parallel and consecutive reaction pathways and hence represent genuine challenges for selectivity control.

The first reaction, the hydrogenation of α,β-unsaturated aldehydes has been studied by many researchers [35,46]. The

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particular challenge is to obtain high selectivity for the unsaturated alcohol rather than the saturated aldehyde or saturated alcohol (Fig. 1). Many approaches have been utilised in addressing this challenge particularly using supported metal catalysts, bimetallic catalysts and the use of sulfur-poisoned catalysts. Recently [33–35] supported gold catalysts have been found to be very effective for this reaction. The second reaction, the direct formation of hydrogen peroxide by the hydrogenation of molecular oxygen has been less well studied by academic researchers, but has been extensively studied in industry for almost a century [47–60]. In this reaction (Fig. 2) H_2O_2 can be readily hydrogenated to water in a consecutive hydrogenation reaction, as well as the competing decomposition reaction. We have recently shown that supported gold palladium nano-particles can be very effective for this selective hydrogenation reaction [39–45].

3. Hydrogenation of α,β-unsaturated aldehydes

A number of early studies showed that supported gold could be active as a hydrogenation catalyst [5,61] and, in particular, gold nano-crystals were found to be very effective for the hydrogenation of alkenes. For example, as early as 1973, Bond et al. [61] were the first to show that with gold on silica, γ-alumina or boehmite an efficient hydrogenation is possible at temperatures as low as 100 °C for the hydrogenation of 1-pentene. This was observed with as little as 0.01 wt.% gold on the SiO_2 support. They subsequently showed that the hydrogenation was sensitive to both the support and the particle size of the gold nano-crystals [5]. Despite all these early indications that supported gold nano-crystals could be effective as hydrogenation catalysts, most research at present concerns mainly both selective and total oxidation reactions. Consequently, much less attention has been given to the activity and selectivity of gold catalysts for hydrogenation reactions. Even today there are few groups working on selective hydrogenation as compared with the extensive research activity presently devoted to the oxidation of CO. However, supported gold catalysts are now finding application in selective hydrogenation, as evidenced by the recent striking example by Corma and co-workers [35–37] that Au/CeO_2 was a very selective catalyst for the challenging reaction of selective hydrogenation of nitro compounds.

In the last ten years there has been renewed interest in selective hydrogenation catalysts using supported gold catalysts. Bailie et al. [33,34] were the first to demonstrate that Au/ZrO_2 and Au/ZnO catalysts were highly selective for the formation of crotyl alcohol from the hydrogenation of crotonaldehyde and selectivities up to 81% at conversions of 5–10% could be observed, i.e. these supported gold catalysts preferentially hydrogenated the C=O bond rather than the C=C double bond. They also showed that the addition of low amounts of sulfur from thiophene promoted this selective hydrogenation (Fig. 3). This is one of the few examples of promotion for a gold catalyst, and it can be anticipated that this will become a useful research approach for the design of improved catalysts. The observation of a promotional effect of sulfur is analogous to that observed for Cu [47] catalysts. Two effects were apparent in these studies. First, the selectivity for crotyl alcohol was enhanced by sulfur only for relatively small particles (*ca.* 2 nm). For larger particle sizes the promotional effect decreased. However, the selectivity for crotyl alcohol increased with the Au particle size. This was demonstrated by the calcination of a 5 wt.% Au/ZnO at temperatures between 250 and 400 °C and the crotyl alcohol selectivity increased dramatically (Table 1 and Fig. 4).

Subsequently, the hydrogenation of acrolein has been extensively studied by Claus and co-workers [62–68] using Au/SiO_2, Au/ZrO_2, Au/TiO_2, Au/ZnO and Au–In/ZnO. The studies by Claus and co-workers for the hydrogenation of acrolein have been comprehensive and have concentrated on designing catalysts comprising gold nano-

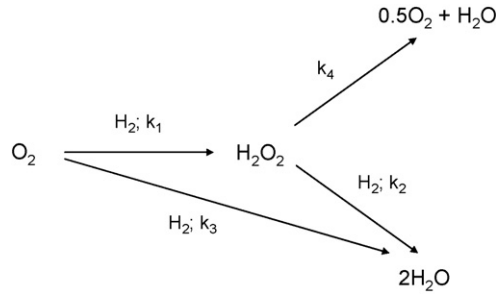

Fig. 2. Reaction scheme for the hydrogenation of molecular oxygen to form hydrogen peroxide.

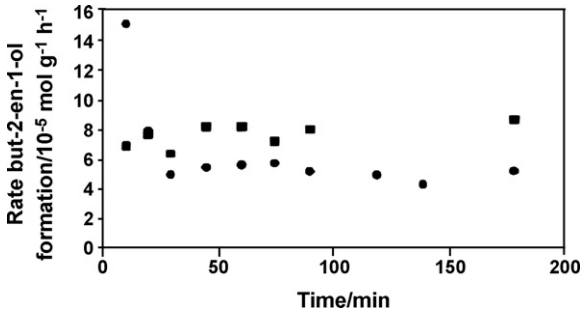

Fig. 3. Effect of thiophene-modification on the rate of but-2-en-1-ol formation over 5 wt.% Au/ZnO at 250 °C. Key: (●) Au/ZnO; (■) thiophene-modified Au/ZnO [34].

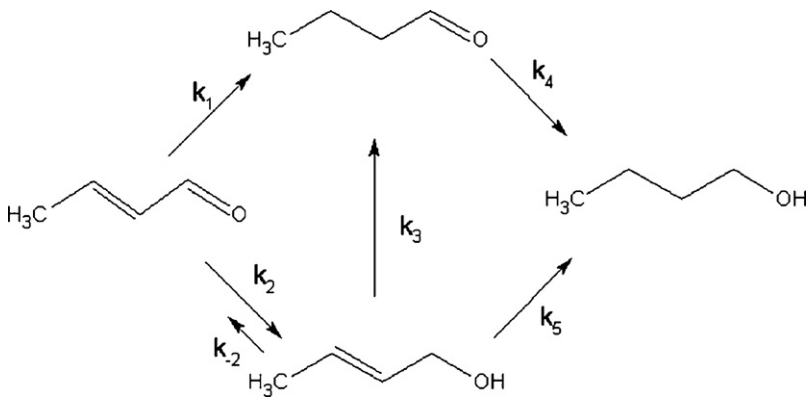

Fig. 1. Reaction scheme for the hydrogenation of crotonaldehyde [46].

Table 1
Effect of reduction temperature on the performance of 5 wt.% Au/ZnO for but-2-enal hydrogenation at 250 °C [34]

Reduction temperature (°C)[a]	Reaction time (min)	Conversion (%)	Product selectivity (%)			
			But-2-en-1-ol	Butanal	Butanol	Others[b]
250	20	13.1	50.2	32.5	0	17.3
	60	8.9	51.7	35.1	0	13.2
300	20	28.6	60.1	28.6	0	11.3
	60	27.9	56.0	27.9	0	16.1
350	20	6.7	63.8	26.1	0	10.1
	70	4.5	61.2	28.4	0	10.4
400	20	6.1	76.5	18.9	0	4.6
	60	6.3	79.2	17.4	0	3.4

[a] Catalysts calcined at 400 °C, 4 h; treated with from ambient temperature to the specified reduction temperature prior to cooling to the H_2 reaction temperature of 250 °C.
[b] Others: 2-ethyl hexanal, 2-ethyl-2-hexenal, butane and C_3 molecules.

particles (*ca.* 5 nm). They have found that the support influences the morphology of the gold nano-particle and more rounded particles were present on TiO_2 as compared with ZnO which were highly faceted. The higher activity observed with the Au/TiO_2 catalysts was associated with the more rounded morphology of the particles accompanied by a higher relative amount of low coordinated surface sites [66]. Claus and co-workers have also investigated bimetallic catalysts, e.g. Au–In/ZnO, and have found that the bimetallic catalyst can also give enhanced selectivity for C=O hydrogenation in acrolein. This example demonstrates that the selectivity of supported gold catalysts can be finely tuned by the addition of a second component, in this case a metal. Transmission electron microscopy studies have shown that the In decorates gold faces on the nano-particle and this is considered to be the origin of the enhanced selectivity. In this way it can be considered that the effect of In addition is analogous to the selectivity effects induced on Pt catalysts by the addition of Bi which is known to decorate specific sites [69], and the effects observed by Bailie et al. [33,34] with sulfur on small gold nano-crystals may have a similar origin.

4. Direct hydrogenation of molecular oxygen to form hydrogen peroxide

The direct formation of hydrogen peroxide represents one of the grand challenges for selectivity in catalysis today. It has fascinated many for decades. It is complicated by the observation that most compositions of molecular hydrogen and oxygen are explosive, and therefore it is only safe to work with dilute mixtures below the lower explosion limit, so that as the hydrogen is consumed the reaction mixture cannot become explosive. Reaction mixtures that start above the higher explosion limit could stray into the explosion region as the hydrogen is consumed, and this hazard should be avoided.

Hydrogen peroxide is produced currently on an annual scale of *ca.* 2 M tons by the sequential hydrogenation and oxidation of an alkyl anthraquinone, which avoids explosive mixtures of hydrogen and oxygen [70]. This process has in the main replaced all its competitors and has remained largely unchanged for decades.

The first reported study for the direct formation of hydrogen peroxide was in 1914 [47] using a Pd catalyst. Since then, there have been a number of investigations and virtually all of these have been pioneered in industrial laboratories [47–60]. It is reported that the hydrogen peroxide yield is improved by the addition of acid and bromide [52,53], and solutions of over 35 wt.% hydrogen peroxide have been made by reacting H_2/O_2 over Pd catalysts at elevated pressures [53]. Hence, until our studies, previous work on the direct hydrogen peroxide synthesis has focused on the use of Pd as a catalyst.

The recent discovery of the catalytic efficacy of gold has given a renewed impetus to the search for selective redox catalysts [6–16], and new discoveries are being uncovered at an amazing rate. Gold has also been found effective for the selective oxidation of alkenes [24–32] and alcohols [71]. Recently, we have shown that supported gold–palladium alloys are very active and selective for the oxidation of alcohols [72], being 25 times more active than the corresponding gold or palladium monometallic catalysts. Furthermore, we have shown that the addition of Au–Pd increases the catalytic efficiency for the direct formation of hydrogen peroxide [39–45]. The increase in activity is significant on the addition of gold to palladium and the nature of the support is found to be important. In all our studies to date we have used a non-complex method of catalyst synthesis in which the support is impregnated with an aqueous solution of $HAuCl_4$ and $PdCl_2$ in the appropriate ratio (typically 1:1 by wt., or Au:Pd = 1:2 molar ratio). The catalysts required calcination at 400 °C to ensure they were stable and catalysts calcined at lower temperatures tended to be unstable and leach Au and Pd during reaction. Consequently, they could not be reused. However, we have found that catalysts that are calcined at 400 °C are stable and can be reused several times. The effect of the addition of Pd–Au using this method of preparation is shown for several supports in Table 2. In all cases, the pure Au catalysts generate H_2O_2 but at very low rates, and at an insufficient level to enable the hydrogen selectivity to be determined with any reasonable accuracy. It is apparent that for the Au monometallic catalysts TiO_2 is far more effective a support when compared with silica and carbon. For the Pd monometallic catalysts, silica was found to be the best support with the order of activity being: $SiO_2 > C > TiO_2 > Al_2O_3$. The addition of Pd–Au, to give catalysts comprising 2.5 wt.% Au–2.5 wt.% Pd, dramatically enhances the catalytic performance for the synthesis of H_2O_2 for all the catalysts, irrespective of the support. The highest rates of hydrogen peroxide formation and hydrogen selectivities are observed for the Au–Pd/carbon catalyst and the Au–Pd/silica catalysts, both materials yielding very similar performances in terms of activities and H_2 selectivities.

We have carried out detailed X-ray photoelectron spectroscopy (XPS) and scanning transmission electron microscopy studies together with X-ray energy dispersive spectroscopy (STEM–XEDS) of the Au–Pd (2.5 wt.% Au–2.5 wt.% Pd) catalysts supported on carbon, TiO_2 and Al_2O_3 calcined at 400 °C (Fig. 5). XEDS maps of the larger particles show that the Au–M_2 and the Pd L_α signals are spatially coincident, indicating that the metal nano-particles in the field of view are in fact Au–Pd alloys in all these samples. Using multivariate statistical analysis (MSA) on the XEDS spectrum image data sets we have found that there is a tendency for Pd surface segregation to occur in the alloy particles supported on

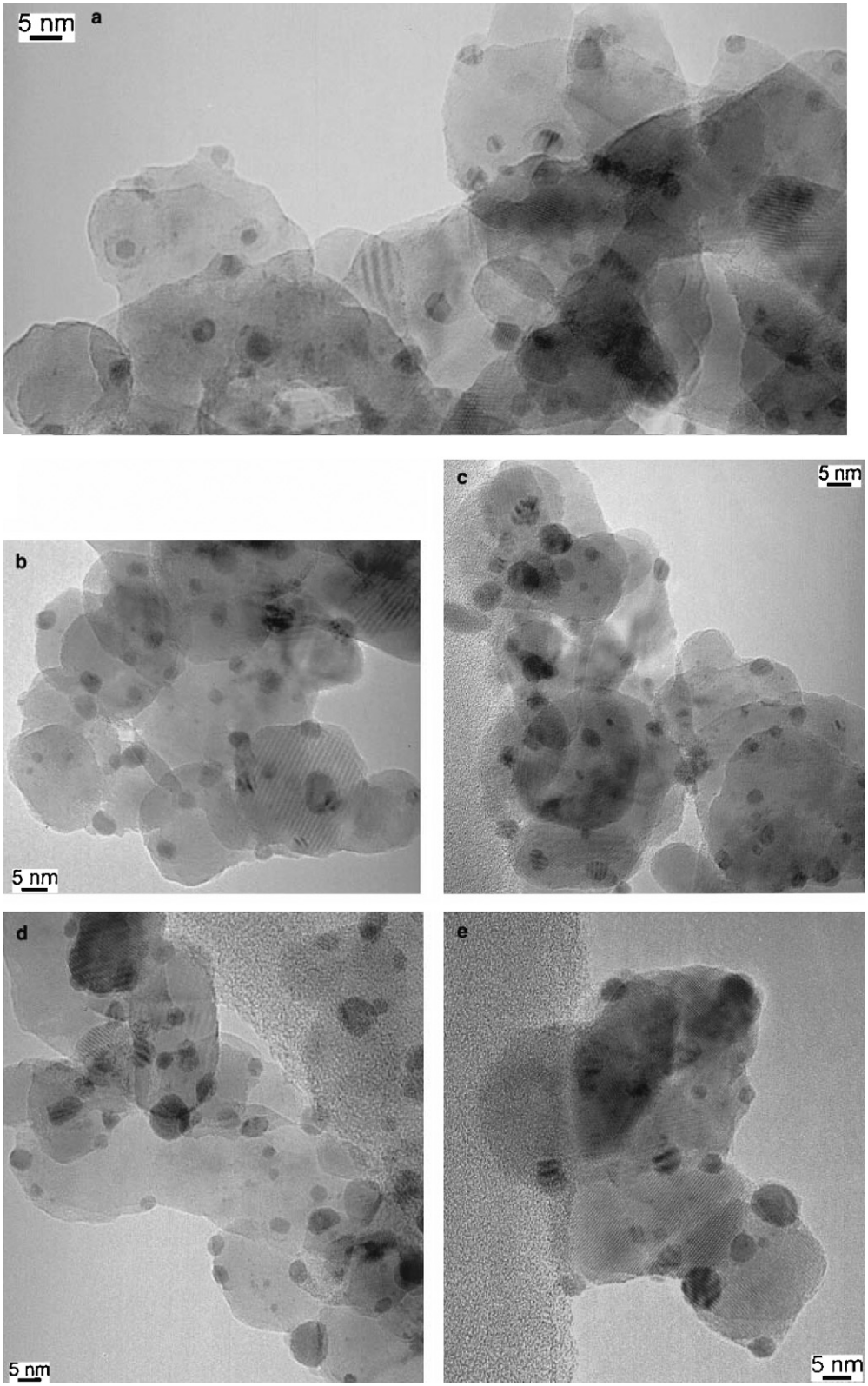

Fig. 4. Transmission electron micrographs of fresh calcined 5 wt.% Au/ZnO catalysts. (a) The unreduced material, whereas the others are reduced at (b) 250 °C, (c) 300 °C, (d) 350 °C and (e) 400 °C, respectively, showing the increase in Au particle size [34].

TiO_2 and Al_2O_3, and this is consistent with XPS analysis. We consider that it is presumably brought about by the preferential formation of Pd–O bonds at the alloy surface since in this temperature range palladium oxidizes more readily than gold. However, the structure of the Au–Pd nano-particles supported on carbon is significantly different, since the core-shell morphology is not observed and, rather, homogeneous Au–Pd alloys are now observed in Fig. 5 and again this is consistent with the XPS

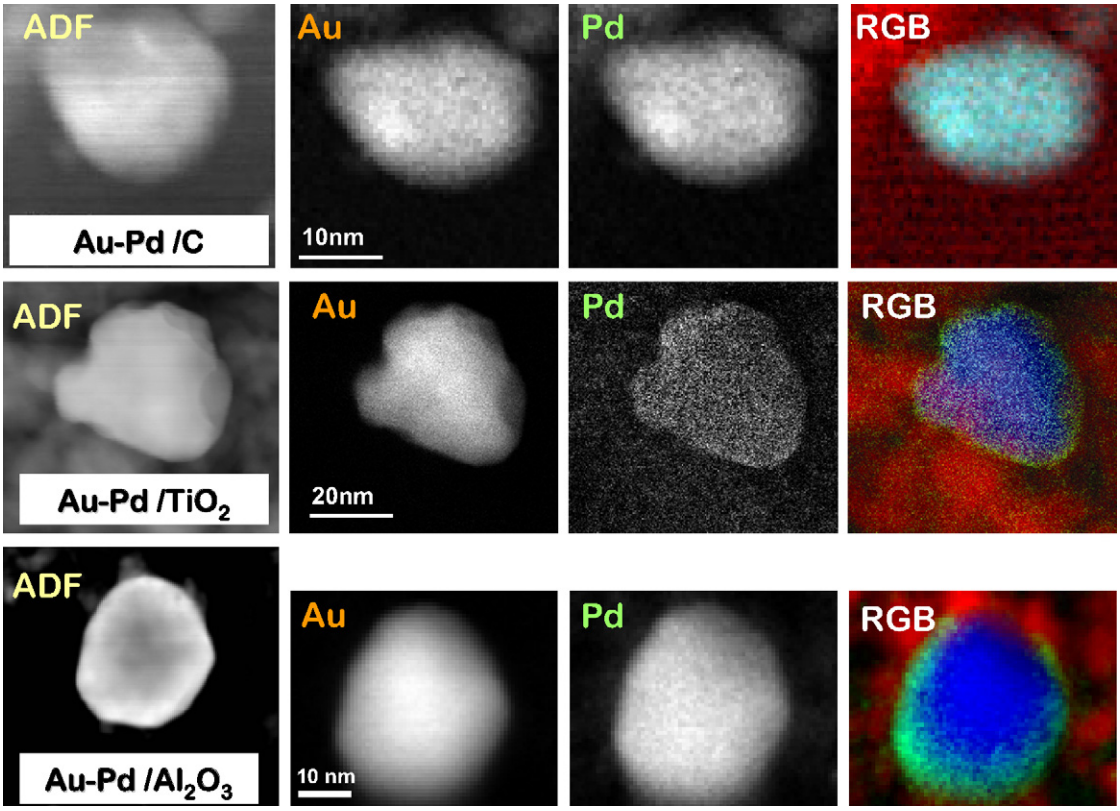

Fig. 5. Montage of HAADF image (*column 1*), Au map (*column 2*), Pd map (*column 3*) and RGB reconstructed overlay map (*column 4*) [(Au-blue: Pd-green)] for calcined AuPd/C (*row 1*), calcined AuPd/TiO_2 (*row 2*) and calcined AuPd/Al_2O_3 (*row 3*). Note that the calcined AuPd particles on TiO_2 and Al_2O_3 supports show a Au rich-core/Pd-rich shell morphology, whereas calcined AuPd particles on activated C are homogeneous alloys [44] (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article).

evidence. Furthermore, we have found that the composition of the Au–Pd alloy nano-crystals changes markedly with the particle size [73] and the amount of gold present in the nano-crystals increases with the particle diameter. These observations indicate that the core-shell structures, which spontaneously form on TiO_2 and Al_2O_3 supports Fig. 6, are not essential for the observation of high activity for the direct synthesis of hydrogen peroxide. At present we have not been able to determine if the bimetallic particles on SiO_2 are core-shell or homogeneous alloy structures. At present we are actively pursuing the nature of the active species in these bimetallic catalysts, but we consider that particle size may be a crucial factor in determining both activity and selectivity.

Table 2
Formation of hydrogen peroxide using Au, Pd and Au–Pd supported catalysts [45][a]

Catalyst	Hydrogen peroxide formation (mol H_2O_2/kg_{cat} h)	Hydrogen selectivity (%)
5%Au/silica	1	nd
2.5%Au–2.5%Pd/silica	108	80
5% Pd/silica	80	80
5%Au/Carbon	1	nd
2.5%Au–2.5%Pd/Carbon	110	80
5%Pd/Carbon	55	34
5%Au/Al_2O_3	2.6	nd
2.5%Au–2.5%Pd/Al_2O_3	15	14
5%Pd/Al_2O_3	9	nd
5%Au/TiO_2	7	nd
2.5%Au–2.5%Pd/TiO_2	64	70
5%Pd/TiO_2	30	21

nd = Not determined as the yield is too low for reliable measurement.

[a] Catalyst testing was performed using a stainless steel autoclave which was charged with the catalyst (0.01 g), solvent (5.6 g MeOH and 2.9 g H_2O), purged three times with 5%H_2/CO_2 (3 MPa) and then filled with 5%H_2/CO_2 and 25%O_2/CO_2 to give a hydrogen–oxygen ratio of 1:2 at a total pressure of 3.7 MPa. Stirring (1200 rpm) was commenced on reaching the desired temperature (2 °C), and experiments were carried out for 30 min.

5. 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 focused 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 catalysts that can be suitable for chemical synthesis. In particular, there are opportunities to develop very selective hydrogenation catalysts based on gold as a central catalyst component. In this paper two examples are examined and both show that gold-based catalysts can provide interesting and effective control of reaction selectivity so that the partial hydrogenation product can be obtained in high yields.

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