Strategies for Designing Supported Gold−Palladium Bimetallic Catalysts for the Direct Synthesis of Hydrogen Peroxide

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CONSPECTUS

Hydrogen peroxide is a widely used chemical but is not very efficient to make in smaller than industrial scale. It is an important commodity chemical used for bleaching, disinfection, and chemical manufacture. At present, manufacturers use an indirect process in which anthraquinones are sequentially hydrogenated and oxidized in a manner that hydrogen and oxygen are never mixed. However, this process is only economic at a very large scale producing a concentrated product. For many years, the identification of a direct process has been a research goal because it could operate at the point of need, producing hydrogen peroxide at the required concentration for its applications. Research on this topic has been ongoing for about 100 years.

Until the last 10 years, catalyst design was solely directed at using supported palladium nanoparticles. These catalysts require the use of bromide and acid to arrest peroxide decomposition, since palladium is a very active catalyst for hydrogen peroxide hydrogenation. Recently, chemists have shown that supported gold nanoparticles are active when gold is alloyed with palladium because this leads to a significant synergistic enhancement in activity and importantly selectivity. Crucially, bimetallic gold-based catalysts do not require the addition of bromide and acids, but with carbon dioxide as a diluent its solubility in the reaction media acts as an *in situ* acid promoter, which represents a greener approach for peroxide synthesis. The gold catalysts can operate under intrinsically safe conditions using dilute hydrogen and oxygen, yet these catalysts are so active that they can generate peroxide at commercially significant rates.

The major problem associated with the direct synthesis of hydrogen peroxide concerns the selectivity of hydrogen usage, since in the indirect process this factor has been finely tuned over decades of operation. In this Account, we discuss how the gold−palladium bimetallic catalysts have active sites for the synthesis and hydrogenation of hydrogen peroxide that are different, in contrast to monometallic palladium in which synthesis and hydrogenation operate at the same sites. Through treatment of the support with acids prior to the deposition of the gold−palladium bimetallic particles, we can obtain a catalyst that can make hydrogen peroxide at a very high rate without decomposing or hydrogenating the product. This innovation opens up the way to design improved catalysts for the direct synthesis process, and these possibilities are described in this Account.
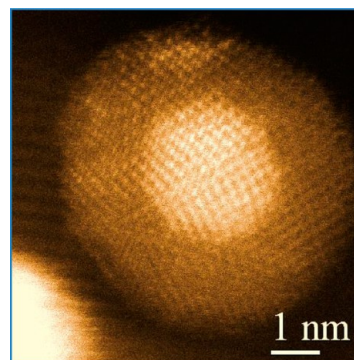
Introduction

Supported gold-based bimetallic nanoparticles have become increasingly important as catalysts.[1,2] Until recently[3,4] gold has been ignored as a component of catalysts, and indeed some researchers considered that the slight indications that gold could be acting as a catalyst were due to impurities in the gold. The perception was that because gold was the most noble of metals it was not likely to provide any chemical reactivity. However, supported gold nanoparticles and in particular gold nanoalloys are now considered to be extremely effective redox catalysts. A key reaction for which supported gold containing bimetallic particles are

effective catalysts is the direct synthesis of hydrogen peroxide from molecular hydrogen and oxygen. In this reaction hydrogen has to be activated but the oxygen needs to retain the oxygen−oxygen bond, otherwise water is rapidly formed. This imposes clear constraints on the materials that can be used in the catalysts.

Hydrogen peroxide is an important commodity chemical, and 4 million tons per annum are manufactured globally. It has major applications in bleaching and disinfection, as well as being used as an oxidant in chemical manufacture.[5] The current method of manufacture is by an indirect process that has been optimized significantly over the last 50 years. Substituted anthroquinones are sequentially hydrogenated and then oxidized leading to the synthesis of hydrogen peroxide, and the original substituted anthraquinone is recovered. This cyclic process has very high efficiencies based on hydrogen, which is the most expensive reagent. However, it is only economic at a large scale and consequently the hydrogen peroxide has to be concentrated (50−70 vol %) and then transported to the point of use, where it is diluted to the required concentration (6−8 vol %), and hence the indirect process has a high energy usage. For this reason a direct process would be attractive, since if it is feasible it could be used to make hydrogen peroxide at the desired concentration at the point of use. Interest in a direct process has occupied researchers for almost a century, and until recently most studies have focused on supported palladium catalysts.[6] While the activity of palladium catalysts is good and high yields of H_2O_2 can be achieved when operating under batch reaction conditions, generally acid

and halide promoters have to be added to suppress the nonselective water forming reactions such as hydrogen peroxide decomposition and hydrogenation and achieve high hydrogen selectivity. Indeed, without the addition of such promoters, H_2O_2 formation is undetectable under some conditions, for example, after 120 min in a glass reactor at atmospheric pressure using a Pd/SiO_2 catalyst, no H_2O_2 can be detected whereas the same reaction with acid additives shows detectable amounts of H_2O_2.[7] However, alloying gold with palladium leads to a substantial improvement in both the overall activity and critically the hydrogen selectivity, and this opens up new possibilities in the design of effective catalysts for this challenging reaction. In this Account, we describe the steps we have taken in designing gold−palladium bimetallics for the direct synthesis of hydrogen peroxide to achieve a catalyst that can make hydrogen peroxide without at the same time decomposing or hydrogenating the peroxide once it has been made.

Getting the Reaction Conditions Right: Safety First

One route that has to be avoided when reacting hydrogen and oxygen is their reaction to form water explosively. Early work on the direct synthesis of hydrogen peroxide involved the use of reaction mixtures within the explosive region (Figure 1), since this can readily lead to the formation of concentrated hydrogen peroxide.[8] Unfortunately, such conditions are exceptionally dangerous and lead invariably to explosions; while this can be contained on a small scale in the laboratory by appropriate risk analysis and mitigation,
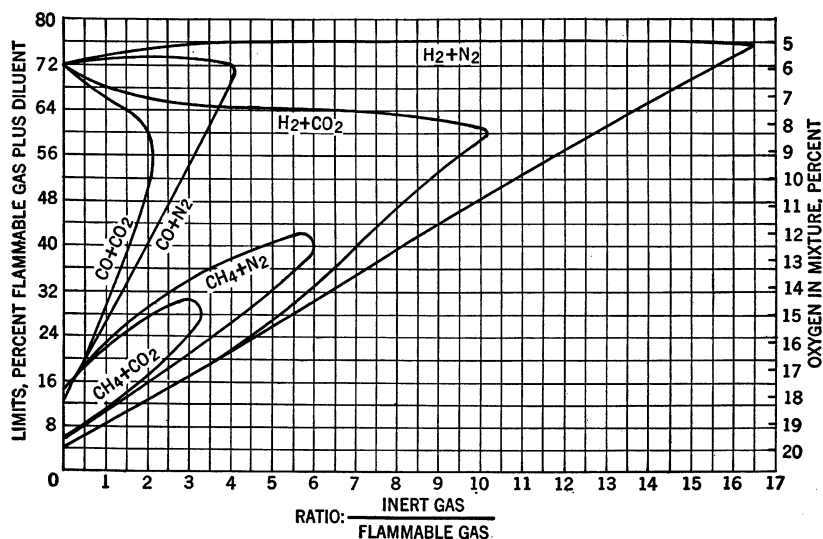
FIGURE 1. Limits of flammability of hydrogen, carbon monoxide, and methane with CO_2 and N_2 as diluents. Taken from ref 10, 1952 U.S. Bureau of Mines.

TABLE 1. Effect of CO_2 Diluent on the Synthesis[a] of Hydrogen Peroxide[9]

catalyst	gas used	H_2O_2 productivity[a] (mol kg_{cat}^{-1} h^{-1})
2.5% Au/2.5% Pd/C	5% H_2/CO_2, 25% O_2/CO_2	110
2.5% Au/2.5% Pd/C	5% H_2/N_2, 25% O_2/CO_2	10
2.5% Au/2.5% Pd/TiO$_2$	5% H_2/CO_2, 25% O_2/CO_2	64
2.5% Au/2.5% Pd/TiO$_2$	5% H_2/N_2, 25% O_2/CO_2	29

[a]Hydrogen peroxide synthesis conditions: 5% H_2/CO_2 (2.9 MPa) and 25% O_2/CO_2 (1.1 MPa), 8.5 g of solvent (2.9 g HPLC water, 5.6 g MeOH), 0.01 g catalyst, 2 °C, 1200 rpm, 30 min.

TABLE 2. Formation of Hydrogen Peroxide Using Au, Pd, and Au−Pd Supported Catalysts with Various Supports[12]

catalyst[a]	H_2O_2 productivity[b] (mol kg_{cat}^{-1} h^{-1})	H_2 selectivity (%)
5% Au/carbon	1	[c]
2.5% Au/2.5% Pd/carbon	110	80
5% Pd/carbon	55	34
5% Au/Al$_2$O$_3$	2.6	[c]
2.5% Au/2.5% Pd/Al$_2$O$_3$	15	14
5% Pd/Al$_2$O$_3$	9	[c]
5% Au/TiO$_2$	7	[c]
2.5% Au/2.5% Pd/TiO$_2$	64	70
5% Pd/TiO$_2$	30	21

[a]It should be noted that 2.5 wt % Pd/2.5 wt % Au is equivalent to 0.023 mol % Pd−0.013 mol % Au (that is, there is a 77% molar excess of Pd relative to Au). [b]H_2O_2 synthesis conditions given in Table 1. [c]Not determined.

it cannot be countenanced for a full scale plant. In view of this, we selected from the outset conditions below the lower explosive limit so that as the hydrogen was consumed, the reaction mixture moved further away from the explosive region. We view such conditions as intrinsically safe. Of course this still requires the use of dilute hydrogen and we use typically 2 vol % H_2 and 4 vol % O_2. Selection of the diluent for the remaining 94% was also made on the basis of safety considerations since CO_2 as a diluent has the smallest explosive region (Figure 1). Hence in a typical experiment, we use an autoclave reactor (50 mL volume) with methanol/water (5.6 g of methanol and 2.9 g water) as a solvent in which to suspend the catalyst. The choice of CO_2 was fortuitous, since had we selected N_2 as a diluent we would not have observed the high reactivities[9] (Table 1). CO_2 dissolves in the reaction medium to form carbonic acid which acts as an *in situ* acid promoter that stabilizes the hydrogen peroxide that is formed.

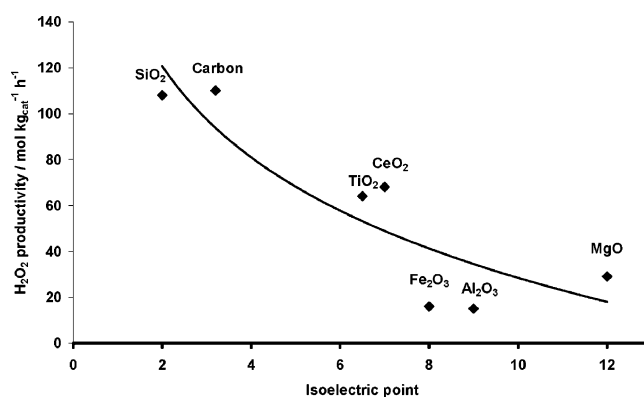## Direct Hydrogen Peroxide Synthesis Using Gold and Gold−Palladium Nanoparticles

Our initial studies were conducted using a monometallic gold catalyst prepared by impregnation, using Al$_2$O$_3$ as a support, and we observed some activity for the direct synthesis reaction.[11] However, we found that by alloying gold with palladium we could dramatically enhance the activity through a synergistic effect; the Au−Pd combination was far more effective than the Au- or Pd-only catalysts. A series of catalysts, prepared by either impregnation or coimpregnation using incipient wetness with carbon, TiO$_2$, and Al$_2$O$_3$ as supports, were investigated for the direct synthesis of hydrogen peroxide, and the results for reaction at 2 °C are shown in Table 2.[12] Prior to testing, all the catalysts were calcined at 400 °C. In all cases, the pure Au catalysts generate H_2O_2 but at low rates and at an insufficient level to enable the hydrogen selectivity to be determined with any accuracy. The addition of Pd to Au, to give catalysts comprising 2.5 wt % Au−2.5 wt % Pd, significantly

FIGURE 2. H_2O_2 productivity over Au−Pd catalysts as a function of the isoelectronic point of support.[13] H_2O_2 synthesis conditions given in Table 1.

enhances the catalytic performance for the synthesis of H_2O_2, and the rate of H_2O_2 production is much higher than that for the pure Pd catalyst, which in itself is significantly more active than pure gold. The highest rates of hydrogen peroxide formation and hydrogen selectivities are observed for the 2.5 wt % Au/2.5 wt % Pd/carbon catalyst, and these are significantly higher than those observed with the other supports. Furthermore, the rates of hydrogen peroxide formation with the carbon-supported catalysts are almost a factor of 2 higher than the corresponding TiO$_2$-supported catalysts, and almost an order of magnitude greater than the Al$_2$O$_3$-supported catalysts, demonstrating that the nature of the support plays an important role in the direct oxidation reaction (Table 2).

The catalytic performance for the direct synthesis of hydrogen peroxide under these dilute reaction conditions was observed to be correlated with to the isoelectronic point of the support (Figure 2).[13] This can be rationalized in terms of the stability of H_2O_2 on the surface of the support since acidic surfaces stabilize hydrogen peroxide. Hence, the best

TABLE 3. Effect of Heat Treatment on Gold and Palladium Remaining on the Catalysts after Multiple Reaction Cycles as Determined by Atomic Adsorption Spectroscopy[12]

| catalyst	pretreatment	run	Au remaining (%)	Pd remaining (%)
2.5% Au/2.5% Pd/TiO$_2$	25 °C air	1	20	10
	25 °C air	2	8	5
2.5% Au/2.5% Pd/TiO$_2$	400 °C air	1	100	100
	400 °C air	2	100	100
2.5% Au/2.5% Pd/Al$_2$O$_3$	25 °C air	1	25	21
	25 °C air	2	20	15
2.5% Au/2.5% Pd/Al$_2$O$_3$	400 °C air	1	100	100
	400 °C air	2	100	100
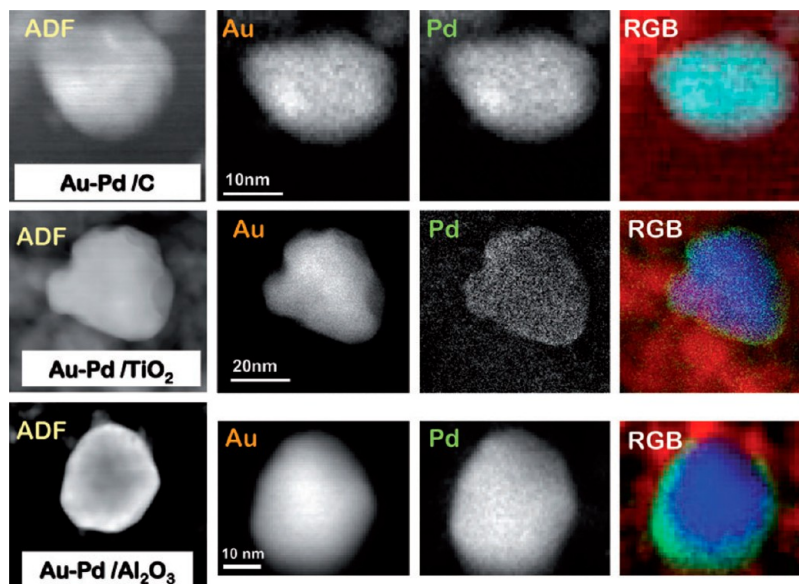
FIGURE 3. Montage of high angle annular dark field (HAADF) images (column 2), Au map (column 3), Pd map (column 4), and RGB reconstructed overlay map (column 4; Au blue, Pd green) for calcined AuPd/C (row 1), calcined AuPd/TiO$_2$ (row 2), and calcined AuPd/Al$_2$O$_3$ (row 3).[12]

catalysts can be obtained using acidic supports in combination with the formation of an *in situ* acidic promoter from using CO$_2$ as a diluent.

For the supported Au–Pd catalysts, we observed that the heat treatment of the catalyst during preparation was very important[12] (Table 3); catalysts calcined at 400 °C were observed to be fully stable and could be reused several times without loss of performance.[12,14] If the catalysts were calcined at lower temperatures, they were found not to be stable, and this was due to the loss of both Au and Pd during use. STEM with X-ray elemental mapping of the oxide-supported catalysts calcined at 400 °C revealed that they comprised core–shell structures with a Pd-rich shell and a Au-rich core (Figure 3). Indeed, this core–shell structure was formed during the calcination process (Figure 4), and as the core–shell structure is formed, the catalysts simultaneously become less active and more stable.[15] We have found that the heat treatment at all stages of the catalyst preparation is the essential feature controlling stability.[15] On the basis of
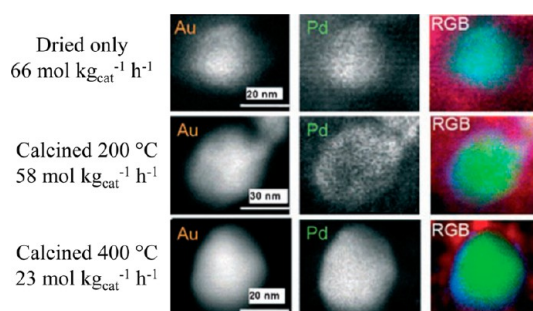
FIGURE 4. HAADF image showing development of the core–shell structure in 2.5 wt %Au–2.5 wt %Pd/Al$_2$O$_3$ catalyst.[15] Individual Au and Pd maps are combined in the red/green/blue (RGB) image: Au green, Pd blue, Al$_2$O$_3$ red. Top row, dried at 120 °C; middle row, calcined at 200 °C; bottom row, calcined at 400 °C with respective H$_2$O$_2$ productivities. H$_2$O$_2$ synthesis conditions given in Table 1.

these results, we questioned whether the core–shell structures were an essential requirement for selective hydrogen peroxide synthesis, but this is not the case because the most active Au–Pd carbon-supported catalysts comprised
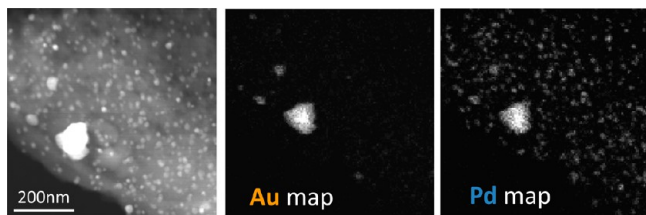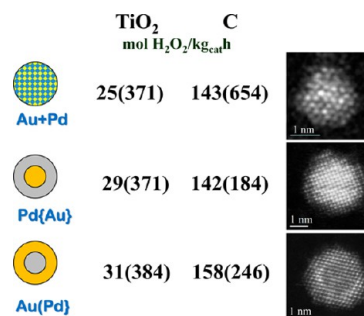
FIGURE 5. HAADF STEM image and Au and Pd STEM XEDS maps showing the spatial and chemical distribution of alloy particles in the uncalcined 2.5 wt % Au−2.5 wt % Pd/carbon sample.[12]

FIGURE 6. Hydrogen peroxide synthesis (H_2O_2 synthesis conditions given in Table 1) and hydrogenation (hydrogen peroxide hydrogenation conditions: 2.9 MPa 5%H_2/CO_2, 8.5 g of solvent (2.22 g of H_2O, 5.6 g of MeOH, and 0.68 g of 50% H_2O_2), 0.01 g of catalyst, 2 °C, 1200 rpm, 30 min) activity for 1 wt % AuPd/C catalysts (the nominal Au/Pd ratios for all these sol-immobilized samples was 1:1 wt %) prepared by sol-immobilization with varying particle morphology.[17] The micrographs in the right-hand column show representative HAADF images of the various morphologies fabricated by sol-immobilization. The schematic diagrams in the left-hand column illustrate how the contrast variations in the HAADF images relate to elemental distributions.

homogeneous random alloys (Figure 4) and no core−shell structures were observed in this latter case.

Analysis of the carbon-supported Au−Pd catalysts using transmission electron microscopy revealed that they comprised a bimodal distribution of nanoparticles, all of which were alloys. A small amount of the metal was present as nanoparticles in the range 2−15 nm, but most of the metal was present as larger nanoparticles >20 nm in diameter (Figure 5). The nanoparticles also showed a composition variation with the particle size; the small particles were always Pd-rich whereas the larger nanoparticles were consistently Au-rich. Hence, with this impregnation preparation method there are a large range of nanostructures present in the catalyst, and these could all contribute to the activity we observe. This prompted us to study the effect of using catalysts comprising exclusively small nanoparticles, and the effect of these is discussed in the next section.

Initial Thoughts on the Nature of the Active Nanoparticles

It was apparent to us that the catalysts prepared by wet impregnation coupled with calcination produced a wide spectrum of potentially active catalyst species, yet the TiO_2- and carbon-supported Au−Pd nanoparticles did display significant selectivity to hydrogen peroxide based on H_2 usage (Table 2) of 70% and 80%, respectively. We initially reasoned, on the basis of the prevailing logic of gold catalysis,[4] that the smaller nanoparticles were possibly the origin of the observed activity. On this basis, we investigated the use of supported Au−Pd alloys prepared by a sol-immobilization method, which involves the initial preparation of a colloidal sol from the reduction of a solution of gold and palladium salts that is stabilized in our case by poly(vinyl alcohol).[16] This method produces a very narrow particle size distribution and therefore allows the hypothesis that small particles are the important catalyst species to be evaluated. Indeed, using a variation of the sol-immobilization technique[17] it is possible to make supported bimetallic particles

that are either homogeneous random alloys or core−shell structures with approximately the same particle size distribution. Homogeneous alloy nanoparticles originate from simultaneous addition and reduction of the metal salts, whereas core−shell structures are formed when one metal is reduced first and the second added later. However, investigation of these structures for the direct synthesis of hydrogen peroxide showed that although these materials were active for the formation of hydrogen peroxide, they were far more active for its subsequent hydrogenation/ decomposition, since very high hydrogenation rates were observed with these catalysts (Figure 6). In addition, because the nanoparticles prepared using impregnation demonstrated a systematic composition variation with size, we investigated the effect of varying the Pd/Au content of a set of random alloy catalysts prepared using sol-immobilization. We found that the addition of Au to Pd, and *vice versa*, led to a significant enhancement in activity for the direct synthesis of hydrogen peroxide; however, this same trend was also observed for the hydrogenation of the hydrogen peroxide that was formed (Figure 7). Because there are no significant differences in the particle size distribution and particle morphology for these Au−Pd nanoalloy catalysts prepared using different Pd/Au ratios, we can conclude that the positive effects observed with alloying are caused by an electronic effect where the addition of a small amount of Au affects the electronic nature of Pd. Consequently, we concluded that although this method can make active catalysts, the selectivity based on H_2 was very poor, and
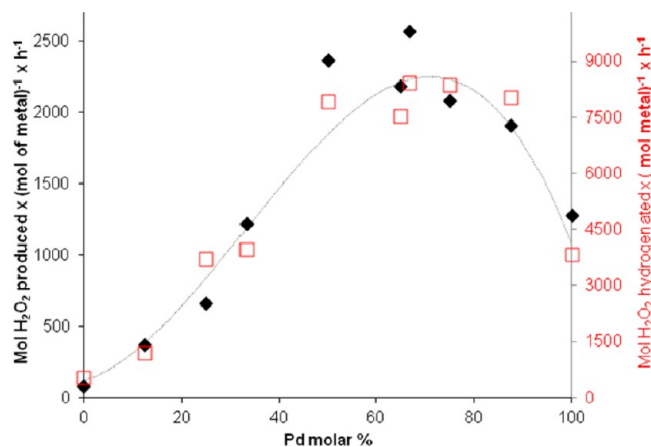
FIGURE 7. Specific activity comparison based on moles of metal present for hydrogen peroxide synthesis (H_2O_2 synthesis conditions given in Table 1) and hydrogen peroxide hydrogenation (H_2O_2 hydrogenation conditions given in Figure 6) with 1 wt % Au−Pd/C prepared by sol-immobilization with various Pd/Au molar ratio (solid black tilted square).[16] H_2O_2 productivity calculated after 30 min (left axis) and rate of H_2O_2 hydrogenation calculated after 30 min (empty red square).

so we concentrated on designing catalysts based on coimpregnation.

The H_2 Selectivity Problem

Some may view the direct reaction between H_2 and O_2 to form hydrogen peroxide as an oxidation reaction, but this is not the case, since it is the H−H bond that is broken and the O−O bond is retained. The competing reaction in which water is directly formed is an oxidation reaction. In this sense, the direct formation of hydrogen peroxide is better viewed as the hydrogenation of oxygen. For this reason, catalysts that are effective for the reaction, for example, supported Pd catalysts, are also effective hydrogenation catalysts, because their primary role is the activation of H_2 at low temperatures. This then leads to a major problem, since catalysts that are effective in the initial hydrogenation of oxygen to give hydrogen peroxide are also equally effective at the hydrogenation of hydrogen peroxide to water in a subsequent hydrogenation reaction (Scheme 1).

In catalytic reactions, it is important to consider the primary selectivity, denoted S_0, for the desired product. S_0 is the selectivity obtained by extrapolating selectivity to zero conversion and is therefore the limiting selectivity of the catalytic system. It is therefore essential that S_0 is high, since if it is not then very little of the desired product can be expected at higher conversions. At very low conversions of H_2, that is, as the conversion approaches zero, the contribution to the overall rate of H_2O_2 synthesis from the sequential hydrogenation of hydrogen peroxide and the sequential

SCHEME 1. Reaction Scheme for the Direct Synthesis of Hydrogen Peroxide
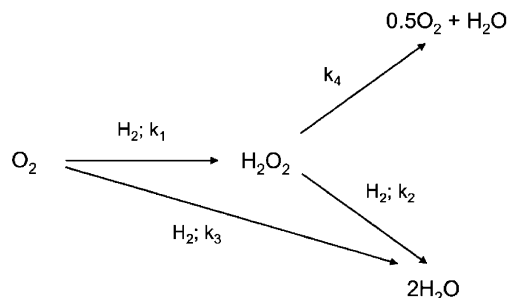
decomposition of hydrogen peroxide both become negligible. In experiments at low conversion and at very short reaction time, we have determined S_0 for both TiO_2- and carbon-supported catalysts to be >99%. Hence, with the supported Au−Pd catalysts, H_2 combustion reaction to form water is not significant, and thus the major loss of selectivity in the direct synthesis reaction with the supported Au−Pd catalysts is associated with the sequential hydrogenation of the hydrogen peroxide. This means that the active sites for the total oxidation reaction, which involves the scission of the dioxygen bond, can be different from the active sites for the selective hydrogenation reaction of dioxygen. This provides key evidence on which catalysts can be designed, since if the reactions of O−O hydrogenation and O−O scission can occur at separate sites, then it should be feasible to design catalysts that can synthesize hydrogen peroxide with total specificity if one can switch-off the sites for hydrogen peroxide hydrogenation.

Switching off Hydrogen Peroxide Hydrogenation

As noted earlier, we observed differences in selectivity for Au−Pd catalysts based on the supports used when prepared using the coimpregnation method (Table 2). We observed that hydrogenation and decomposition of H_2O_2 over oxide supports showed no activity in the absence of the metals, but the carbon support did show some limited reactivity. This shows that carbon is active for this hydrogenation reaction, and this could be associated with metallic impurities in the support. When the metals are impregnated, all show appreciable activity for these nonselective reactions, with the order of activity being broadly in-line with the observed H_2 selectivities in the synthesis reaction (Table 4). The Au−Pd catalysts were prepared by wet impregnation of an acidic solution of the metal salts onto the support, and we considered that the acidic nature of this impregnating solution

TABLE 4. Effect of Acid Pretreatment of the Support on the Hydrogenation and Decomposition of H_2O_2[18]

	support only				Au−Pd catalyst			
	untreated		pretreated		untreated		pretreated	
support	hydrog[a]	decomp[b]	hydrog[a]	decomp[b]	hydrog[a]	decomp[b]	hydrog[a]	decomp[b]
Al_2O_3	0	0	0	0	24	3	16	8
TiO_2	0	0	0	0	12	6	13	4
SiO_2	0	0	0	0	15	8	12	1
carbon	4	1	3	1	5	2	0	0

[a]H_2O_2 hydrogenation in mol kg_{cat}^{-1} h^{-1}; reaction conditions given in Figure 6. [b]H_2O_2 decomposition in mol kg_{cat}^{-1} h^{-1}; reaction conditions 2.9 MPa of 25%O_2/CO_2, 8.5 g of solvent (2.22 g of H_2O, 5.6 g of MeOH and 0.68 g of 50% H_2O_2), 0.01 g of catalyst, 2 °C, 1200 rpm, 30 min.

could be significant. We therefore investigated the effect of an initial acid pretreatment step in which the support was treated with 2% aqueous HNO_3 and dried, prior to addition of the metals. For the Au−Pd catalysts on SiO_2 and TiO_2 supports, this step led to a decrease in combined hydrogenation/decomposition and hence higher H_2O_2 yields are obtained. However, for the carbon support, the Au−Pd catalysts showed no activity for hydrogenation/decomposition when a 4 wt % H_2O_2 solution was reacted.[18] Indeed, we found that we could react even higher concentrations of hydrogen peroxide with this acid pretreated catalyst without any decomposition of the hydrogen peroxide (Figure 8). Pd and Au−Pd catalysts prepared on untreated carbon, as well as the bare support itself, react in a similar manner and give significant sequential hydrogenation. These results show that the support plays a crucial role in the performance of catalysts for the direct reaction because it controls the manner in which the active components are dispersed, as well as providing the sites on which hydrogen peroxide hydrogenation−decomposition, and hence product loss, occur. However, the acid pretreated carbon support shows some reduction in hydrogen peroxide hydrogenation activity relative to the nontreated material, but when it is loaded with Pd the rate of hydrogenation of H_2O_2 becomes identical to that of the corresponding non-pretreated Pd/C catalyst, showing that the nonselective hydrogenation sites have been restored (Figure 8). In total contrast, the acid pretreated Au−Pd alloy catalyst shows no substantial activity for the sequential hydrogenation of H_2O_2, up to 14 wt % H_2O_2, and it is only at a concentration >17.5 wt % that some sequential hydrogenation begins to occur.

When we investigated the carbon-supported Au−Pd catalysts for the direct synthesis reaction, we observed a marked increase in the yield of hydrogen peroxide and selectivity of H_2 utilization (Table 5). Interestingly, no enhancement was observed for similarly pretreated Pd-only catalysts, whereas a slight positive effect is still observed for
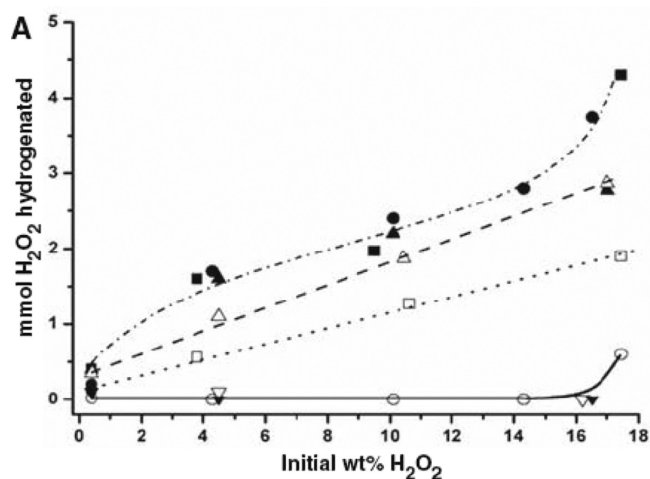
FIGURE 8. Performance of acid-pretreated carbon-supported catalysts compared with nontreated catalysts for the hydrogenation of H_2O_2. Dashed-dotted line: (■) untreated 2.5% Au−2.5% Pd/C; (●) untreated carbon support. Dashed line: (▲) untreated 5% Pd/C; (△) pretreated 5% Pd/C. Dotted line: (□) pretreated support. Solid line: (○) pretreated 2.5% Au−2.5% Pd/C; (▽) pretreated 5% Au/C; (▼) untreated 5% Au/C.[18] For H_2O_2 hydrogenation conditions, see Figure 6

pretreated Au catalysts; hence, the effect is associated with the presence of gold. An enhancement was always observed with the Au−Pd bimetallic catalysts when the acid pretreatment was conducted prior to metal addition and this is the key step; note that the acid pretreatment has to be conducted prior to the addition of the metals. Nitric and acetic acids were the most effective acids investigated; treatments using hydrochloric acid and phosphoric acid both lead to poorer catalysts, and treatment with bases also led to inferior catalysts. Treatment with water alone, or ammonium, sodium, or potassium nitrates had no effect. The materials prepared using acid pretreated supports combined with a calcination at 400 °C were found to give catalysts that could be reused several times without any loss of performance. For each use, the acid pretreated catalyst gave an initial rate of 640 mol of H_2O_2 kg_{cat}^{-1} h^{-1} determined at 2 min reaction time and 160 mol pf H_2O_2 kg_{cat}^{-1} h^{-1}

TABLE 5. Activity and Selectivity of Pretreated and Untreated Carbon-Supported Catalysts for H_2O_2 Synthesis at 2 °C[a]

catalyst	pretreatment	H_2O_2 selectivity (%)	H_2O_2 productivity[b] (mol kg_{cat}^{-1} h^{-1})
2.5% Au/2.5% Pd/carbon	none	80	110
2.5% Au/2.5% Pd/carbon	water	80	112
2.5% Au/2.5% Pd/carbon	2% HNO_3	>98	160
5% Pd/carbon	none	42	50
5% Pd/carbon	water	42	50
5% Pd/carbon	2% HNO_3	42	52
5% Au/carbon	none	[c]	0.4
5% Au/carbon	water	[c]	0.4
5% Au/carbon	2% HNO_3	[c]	0.5

[a]All catalysts were calcined in air 400°C for 3 h.[18] [b]H_2O_2 synthesis conditions given in Figure 2. [c]Not determined.

determined at 30 min reaction time, with 40% hydrogen conversion and almost total hydrogen selectivity. The addition of nitric acid to the reaction mixture prior to H_2O_2 synthesis, which is an established procedure for stabilizing H_2O_2 because peroxide[19] decomposition is known to be a base catalyzed process, also led to an enhancement in the yield of H_2O_2. To some extent, it could be surmised that the effect may be due to acidification of the reaction medium, but the effect of acid addition was not sustained upon subsequent catalyst reuse cycles.[18] Treatment of any of the supports after metal deposition did not enhance catalyst performance and the addition of nitric or hydrochloric acid during the metal impregnation step did not lead to any enhancement; indeed, the use of hydrochloric acid was always deleterious. These results demonstrate the importance of the precise manner in which the acid pretreatment is carried out. However, we observed that neither the acid concentration nor the duration of the acid pretreatment are critical factors, and the same effect can observed with dilute or concentrated nitric acid over a range of treatment times. Additionally, the effect observed could not be linked with the addition or removal of impurities present in the carbon by the acid pretreatment.[18] Interestingly, both the untreated and the acid pretreated Au catalysts also show no activity for sequential hydrogenation, but unfortunately, both these catalysts also show remarkably little activity for hydrogen peroxide synthesis. These results show that Au adsorption onto the surface of the carbon support blocks the sites responsible for loss of H_2O_2 since the catalyst has no activity for the decomposition reaction. Hence, we consider it is the interaction of Au with the pretreated C support that is crucial for observing the effect of switching-off hydrogen peroxide hydrogenation/decomposition. The switch-off phenomenon was also observed after the acid pretreated Au—Pd/C catalysts had been used for the direct synthesis reaction, that is, the effect is relatively long-lived. Hence, the catalysts can be used multiple times without either the loss of activity for
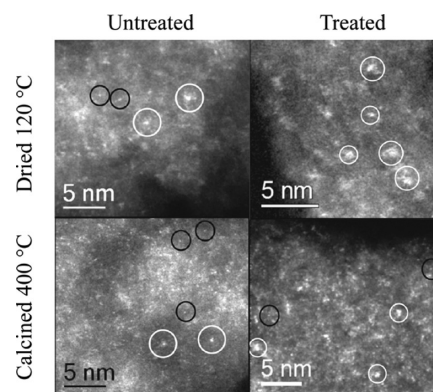

FIGURE 9. STEM—HAADF images of acid pretreated and untreated AuPd/C catalysts calcined at different temperatures; black circles show atomic species; white circles indicate sub-nanometer clusters.[20]

the direct H_2O_2 formation reaction or an increase in activity for H_2O_2 hydrogenation/decomposition.

This is the first time in the numerous investigations of the direct synthesis reaction that hydrogen peroxide decomposition/hydrogenation has been switched-off, thereby permitting essential total specificity of hydrogen peroxide to be achieved. At present, the origin of the effect is under intense investigation. Initially we considered that the effect was due to a difference in the dispersion of the metals of the acid pretreated carbon support.[18] However, a detailed subsequent study[20] showed that this was not the case, and there are no discernible differences in the particle size distributions and particle morphologies for the nontreated and the acid pretreated catalysts (Figure 9). The effect on the oxidation state of the metals and the nature of the surface chloride species was examined using X-ray photoelectron spectroscopy (Figure 10). The effect of switching-off hydrogen peroxide hydrogenation/decomposition is only observed for samples calcined at 400 °C, and samples calcined at lower temperatures all show appreciable hydrogenation activity.[20] At present, it is clear that for high hydrogen peroxide selectivity it is essential that the palladium is present on the surface in a cationic form (Figure 10) and that surface chloride species may
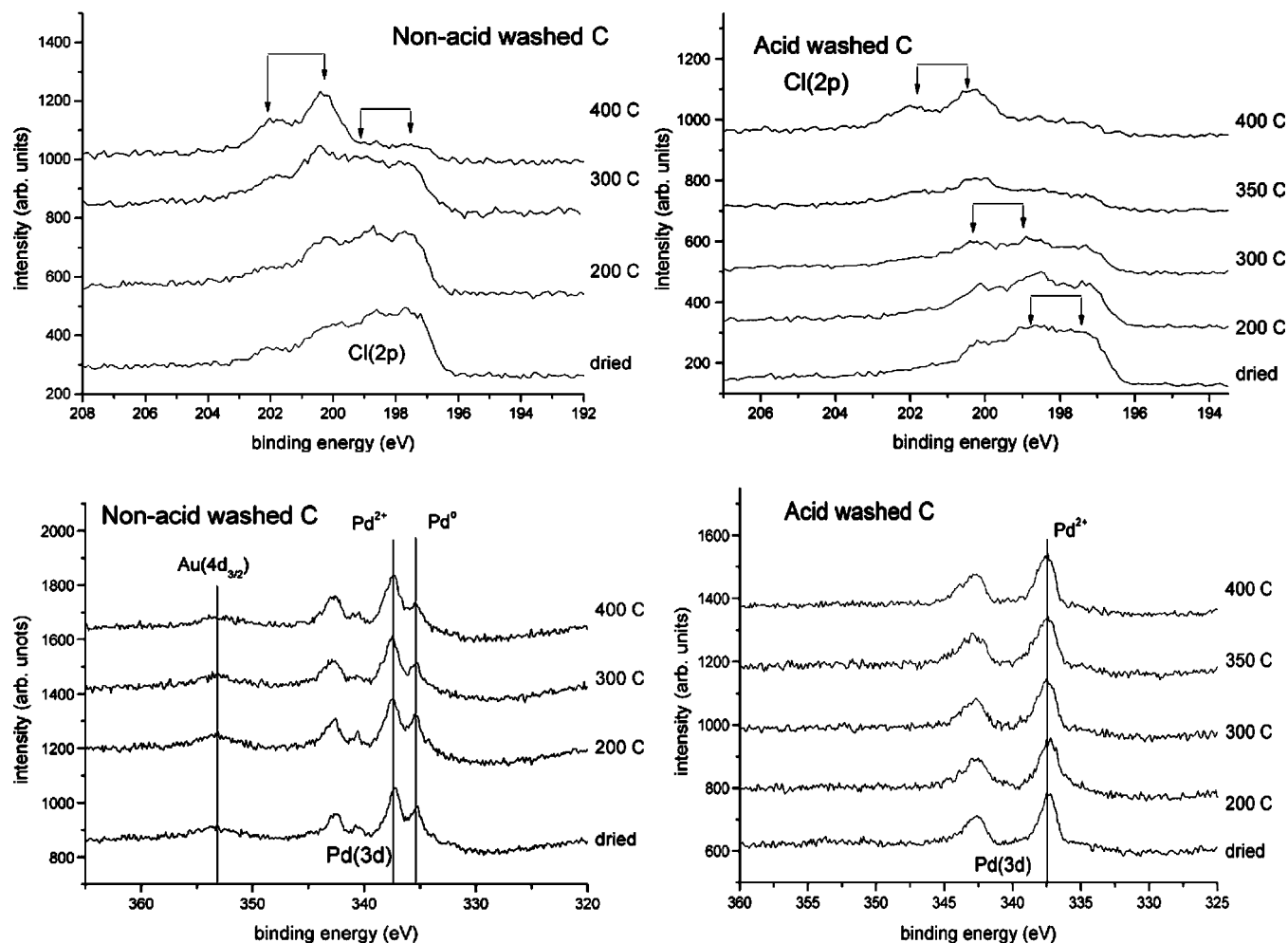
FIGURE 10. Cl (2p) and Pd (3d) XPS spectra observed for the 2.5 wt % Au—2.5 wt % Pd catalysts supported on acid and untreated carbon and calcined at the temperatures indicated.[20]

play a significant role since there are several surface chloride species that are affected by the calcination process (Figure 10).

Future prospects

The direct synthesis of hydrogen peroxide represents one of the grand challenges in catalysis in controlling reaction selectivity. Conceptually it is a very simple reaction in that it involves small molecules and in effect is a simple hydrogenation of molecular oxygen. However, the key problem is that catalysts based solely on palladium, although active for the synthesis of hydrogen peroxide, are also active in its destruction by O—O scission leading to water formation. To some extent, this is overcome by the addition of acids and halides during the reaction, but these additives have to be subsequently removed. We have found that alloying gold with palladium and using calcination to ensure that the palladium is present in the cationic form leads to catalysts that can be totally selective for the direct synthesis reaction.

At present, bimetallic AuPd catalysts can be prepared that give high activities and high selectivities. The current remaining problem to be overcome for these catalysts is that at present the maximum amount of hydrogen peroxide produced is typically <1 vol %, so we need to increase this value by an order of magnitude, since 6—8 vol % hydrogen peroxide is typically required for use in the applications of bleaching, disinfection, and chemical synthesis. This is the challenge to which we are now directing our efforts. Understanding the origin of the fascinating effect by which we have totally decoupled hydrogen peroxide synthesis and hydrogenation will be a critical component in this future work. One of the main considerations will be to devise new synthesis methods since by using the coimpregnation method, we are still only utilizing a small proportion of the total precious metal deposited on the support. It is clear at this stage that it is the larger nanoparticles that are required, and their interaction with the support will be crucial, so the

way in which these active centers can be made is of critical importance. Additionally, the introduction of a third metal could be expected to yield advances as well as increasing the complexity of this catalyst system. We have recently shown that the addition of Pt to AuPd supported nanoparticles can have a significant effect on the selectivity in alcohol oxidation,[21] and it is possible that interesting effects can be achieved by using such trimetallic formulations in hydrogenation reactions.

BIOGRAPHICAL INFORMATION

Jennifer K. Edwards, born in 1982, holds a Chancellor's Research Fellowship in the Cardiff Catalysis Institute. She has worked in Tokyo Metropolitan University with Prof. Haruta through her award of a JSPS fellowship. She has been awarded the Carol Tyler Award in 2011 and Clara Immerwahr award in 2013.

Simon J. Freakley, born in 1987, gained his Masters degree in chemistry from Durham University in 2009, which included a yearlong placement at Johnson Matthey catalysts. He completed his Ph. D. in heterogeneous catalysis in 2012 at Cardiff University, where he continues his research on the direct synthesis of H_2O_2.

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Christopher J. Kiely, born in 1962, was educated at Bristol University. He was Professor of Materials Chemistry in Liverpool before moving in 2002 to Lehigh University and is Professor of Materials Science and Chemical Engineering. His research expertise lies in the application and development of electron microscopy techniques.

Graham J. Hutchings, born in 1951, studied chemistry at University College London. His early career was with ICI and AECI Ltd where he became interested in gold catalysis. In 1984, he moved to academia and has held chairs at the Universities of Witwatersrand, Liverpool, and Cardiff, and currently he is Director of the Cardiff Catalysis Institute. He was elected a Fellow of the Royal Society in 2009.

FOOTNOTES

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