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H2O2 Synthesis

Palladium and Gold–Palladium Catalysts for the Direct Synthesis of Hydrogen Peroxide**

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gold · heterogeneous catalysis · hydrogen peroxide · nanoparticles · palladium

Dedicated to the Catalysis Society of Japan on the occasion of the 50th anniversary

Today hydrogen peroxide is produced by an indirect process in which an alkyl anthraquinone is sequentially hydrogenated and oxidized. In this way hydrogen and oxygen are kept separate during the manufacturing process. A process where molecular oxygen is directly hydrogenated could be preferred if control of the sequential hydrogenation can be achieved, particularly if high rates can be attained under intrinsically safe, non-explosive conditions. Herein we describe recent progress in the direct synthesis of hydrogen peroxide using supported palladium and gold–palladium alloy catalysts and consider some of the problems that have to be overcome.

1. Introduction

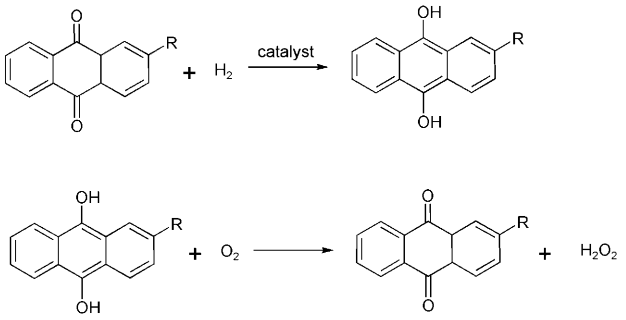
Hydrogen peroxide (H_2O_2) is an important commodity chemical with extensive applications within the fine chemical industry and the home. It is a chemical that the wider public regularly comes into contact with in their everyday lives. Bleaches and hair dyes typically contain around 5 wt% H_2O_2 and in lower concentrations (around 3 wt%) it can be used medically to clean wounds. Around 2.2 million metric tonnes of H_2O_2 are produced annually.[1] In the pulp and paper industry[2] H_2O_2 is used in place of chlorine containing bleaching agents, that is, chlorine dioxide or sodium chlorate, and, by 1994, this application used 40% of the H_2O_2 produced globally. Further industrial uses for H_2O_2 include wastewater treatment, because H_2O_2 can oxidize hydrogen sulfide to elemental sulfur liberating water, and in the chemical industry for the synthesis of fine and bulk chemicals.[3–6] One of the benefits of using H_2O_2 for such oxidations is that the only by-product from the oxidation is water. Thus the processes are considered to be inherently green, especially if H_2O_2 can be used in place of bulky stoichiometric oxygen donors (e.g., sodium perborate, sodium percarbonate, metallic peroxides, organic hydroperoxides, percarboxylic acids), which inherently exhibit poor atom efficiency.[7–10]

2. Synthesis of H_2O_2

Indirect H_2O_2 Synthesis Using Anthraquinones

The indirect anthraquinone process, developed by Riedl and Pfleiderer in 1939,[11–14] involves the hydrogenation of a substituted anthraquinone using a nickel or palladium catalyst, forming the diol. The subsequent oxidation of anthraquinol in air (or oxygen-enriched air) reforms the original anthraquinone, and produces H_2O_2. The process is summarized in Scheme 1.

This process was developed from work carried out previously by Manchot who noted in 1901 that hydroquinone



Scheme 1. The anthraquinone process.

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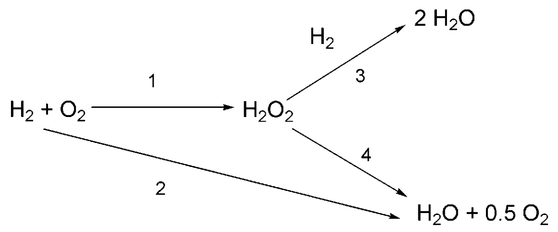
and hydrazobenzenes undergo auto-oxidation under alkaline solutions producing peroxides.[15] The first anthraquinone pilot plant produced around 30 metric tonnes of H_2O_2 per month.[16] Initially, concentrations of H_2O_2 between 0.8–35 wt% could be obtained using this method, depending on the solvent system and the choice of hydrogenation catalyst, and, after refinement, H_2O_2 concentrations can now exceed 70 wt%. Currently the anthraquinone process accounts for around 95% of the global H_2O_2 production[17] and is characterized by large plants producing up to 120000 tonnes of concentrated H_2O_2 per annum.

The indirect process has been commercialized for many years and as a result is now highly energy efficient. There are, however, a number of problems associated with the anthraquinone route to H_2O_2. The process is only economically viable on a relatively large scale and this necessitates the transportation and storage of concentrated solutions of H_2O_2, which can be hazardous,[18] but with care these concentrated solutions can be stable and transported. Although the process operates at relatively mild temperatures (30–60 °C) and prevents the contact of O_2 and H_2 during the reaction, the irreversible formation of anthraquinone derivatives which do not participate in the formation of H_2O_2 requires the constant addition of the original anthraquinone. The reaction of the anthraquinone over a highly reactive palladium catalyst in during the hydrogenation step also results in anthraquinone decomposition. However, recent increases in scale and overall process efficiency have ensured that anthraquinone losses are minimized. As this process is neither 100% carbon or H_2 efficient there is room for an improved technology, and this could be from the development of a new direct process.

Direct Synthesis of H_2O_2

The direct combination of hydrogen and oxygen without the need of a bulky hydrogen carrier would provide a much greener route to H_2O_2. However, there are problems associated with the direct-synthesis route, not least the non-selective formation of water via the combustion or hydrogenation reactions (Scheme 2) which represents the biggest technical problem facing the discovery and design of catalysts for this reaction.

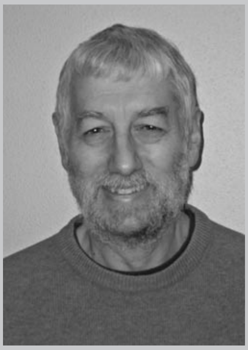


Scheme 2. Reaction pathways involved in the direct reaction; synthesis (1), combustion (2), hydrogenation (3), and decomposition (4).

It is important to note that as H_2O_2 is an unstable compound, much care must be taken when designing experiments for its synthesis. Catalysts active for the direct-synthesis reaction will also be active for its subsequent hydrogenation. There are a number of ways in which to overcome the selectivity problems associated with the direct-synthesis route, for example, decreasing the reaction temperature and the addition of chemical additives can help prevent the unselective formation of water and the subsequent decomposition and hydrogenation of H_2O_2. A further problem associated with the direct route is the inherent hazard associated with mixing high-pressure H_2 and O_2 over a supported nanocrystalline metallic oxidation catalyst. The flammability limits of H_2 in O_2 are 4–94%[19] at ambient temperature and hence for safe working practice H_2 concentrations below 4 vol% should be employed, and this can result in lower yields of H_2O_2. For these reasons there is at present no commercialized direct H_2O_2 process, although plans have been announced by Degussa–Headwaters[20] for such a plant, there are no announcements concerning active commercialization and all new plants are still based on the indirect process.

Direct Synthesis Using Palladium Catalysts

The direct synthesis of H_2O_2 has remained a demanding research target for over 90 years, with the earliest patent being filed in 1914,[21] for a palladium catalyst. Indeed, until very recently the catalysts used in the investigations into the direct synthesis of H_2O_2 have been based on palladium. Since it is important to try to achieve the highest rate of product formation, most of these earlier studies used H_2/O_2 mixtures in the explosive region, and solutions of over 35 wt% H_2O_2 have been made by allowing H_2 and O_2 to react over palladium catalysts at elevated pressures.[22] However, the



Graham Hutchings is currently Professor of Physical Chemistry at Cardiff University having recently completed nine years as Head of the School of Chemistry. His early career was spent in industry, in ICI at Teeside, and then in AECI, South Africa, where he made his initial discoveries concerning catalysis with gold. He moved to academia in 1984, and he has been mainly interested in the discovery of catalysts for oxidation and enantioselective reactions. He has held chairs in the University of Witwatersrand and the University of Liverpool before moving to Cardiff in 1997.

Jennifer Edwards received her BSc degree in chemistry with bioscience and her PhD in chemistry from Cardiff University in 2003 and 2006, respectively. The focus of her PhD thesis was the preparation of gold-based catalysts for hydrogen peroxide synthesis. She has remained in Cardiff for Post-doctoral work and is currently researching the application of gold catalysts for a number of oxidation reactions.

commercial operation of such a process in the explosive region would be extremely dangerous, and more recently studies have concentrated on carrying out the reaction with dilute H_2/O_2 mixtures well below from the explosive regime.[23,24] Alternatively, a catalytic membrane can be employed to prevent the contact of hydrogen and oxygen during the reaction, and in this case pure gases can be used thus obtaining higher yields of H_2O_2.[25,26]

The seminal studies by Pospelova in 1961[27–29] showed that supported palladium catalysts work well in the presence of cyanides in an aqueous acidic reaction medium (HCl, HNO_3) as a result of the decreased decomposition of H_2O_2. The acidity of the support also played a role producing catalysts active for the direct-synthesis reaction, acidic catalysts (Pd/SiO_2) were found to be more active than basic catalysts (Pd/Al_2O_3). The activity of the catalysts was also highly dependent on the H_2:O_2 composition and the reaction temperature. Fu et al.[30] showed that the direct synthesis of H_2O_2 using a fluorinated, hydrophobic palladium/carbon catalyst could be achieved in a stirred autoclave. Low temperature, high pressure, and the presence of a stabilizer in the reactant all lead to improved yields of H_2O_2. The most active catalyst had very low selectivity to H_2O_2 (8.7 %) although the conversion was high (41 %). In this case, H_2SO_4 was used as a stabilizer.

The recent extensive work of Lunsford and co-workers[31–37] has shown that supported palladium catalysts can be highly active for the direct formation of H_2O_2. However, in common with all studies involving supported palladium, the catalysts are only selective when halides are present in the reaction medium as these prevent the prevalent combustion reaction. Detailed studies by Lunsford and co-workers have attempted to explain the roles of stabilizers, both halides and acids, in the direct reaction. Initially high concentrations of HCl (0.1–1 M) were used in the reaction medium leading to the formation of $[PdCl_4]^{2-}$ and colloidal Pd when $PdCl_2$ or reduced Pd/SiO_2 were used as a catalyst.[35,37] Indeed, high concentrations of HCl led to dissolution of Pd from the supported catalyst,[35] and the high activity was attributed to the formation of colloidal Pd as, the reaction medium remained active for the formation of H_2O_2 on removal of the catalyst (Figure 1).

Decreasing the acid content of the solution to 10^{-4} M minimized the dissolution of Pd. A recent study from Lunsford and co-workers using a Pd/SiO_2 catalyst has elucidated many of the controlling factors for H_2O_2 synthesis.[31] The presence of Br^- ions in the acidified reaction medium limited the dissolution of Pd from the support and led to catalysts that are highly selective for the direct-synthesis reaction. For example, the effect of the addition of Br^- ions is shown in Figure 2 as when it is present very high selectivities to H_2O_2 can be attained (ca. 90 %) compared with only 60 % in the absence of halide.

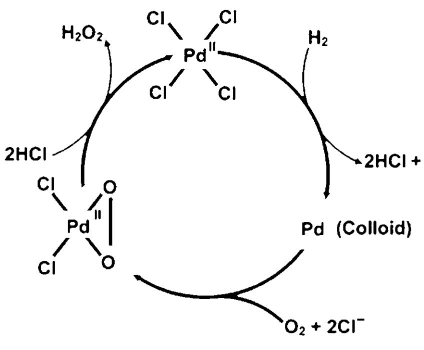


Figure 1. Formation of colloidal Pd and $[PdCl_4]^{2-}$ from a heterogeneous Pd/SiO_2 catalyst during the direct-synthesis reaction.[36]

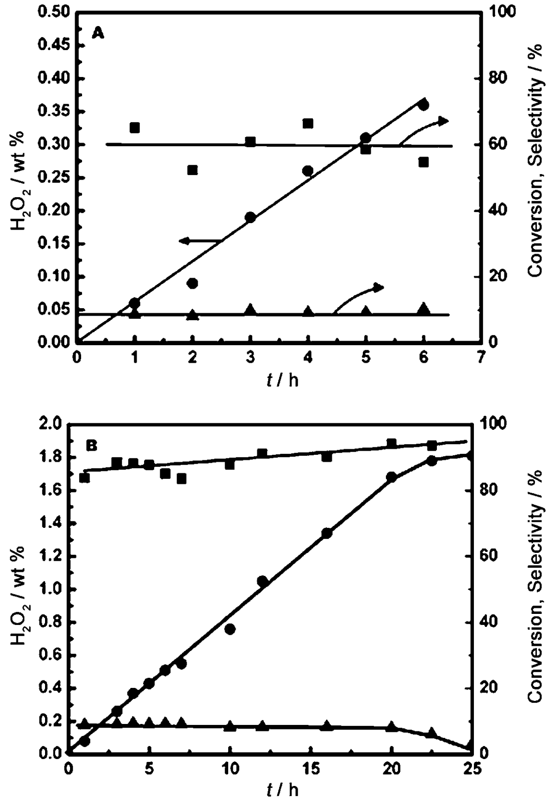


Figure 2. Formation of H_2O_2, A) in the absence of Br^- ions and B) in the presence of Br^- ions (0.01 M); (●) wt% H_2O_2, (▲) H_2 conversion, and (■) selectivity for H_2O_2. The solution was 0.1 N in HCl and the O_2/H_2 gas ratio was 4:1.[36]

The effect of temperature was also found to be important, although H_2 conversion decreases at low temperature, the selectivity is higher and is maintained over a 5 h reaction time. In aqueous acidified ethanol, containing 4×10^{-4} M Cl^- ions, with $O_2/H_2 = 15$, 60 % selectivity towards H_2O_2 was achieved. Addition of Br^- ions to this system reduced hydrogen conversion but increased the selectivity to 80 %, indicating that Br^- ions reduce the combustion/hydrogenation activity of the catalyst. The reaction was found to be first order with respect to H_2 and zero order with respect to O_2, and was not mass-transport limited under the batch-reactor conditions used. Lunsford and Liu also showed that the role of chloride ions is to prevent O–O cleavage.[32] This property is advantageous for two reasons; it prevents the initial combustion of H_2 and O_2 and also helps prevent the decomposition of H_2O_2 after it has formed. The nature of the solvent system is also important. In the absence of an alcohol (e.g. ethanol) the synthesis reaction does not proceed, even if the water is acidified.[38] This effect was also observed by Thompson et al.[39] and is thought to be due to mass transport, as both hydrogen and oxygen are less soluble in water than in water/alcohol mixtures. In H_2SO_4:ethanol it is proposed that acetate ions form on the Pd(110) surface from the reaction of ethanol with O_2, and these species block the sites responsible for the combustion reaction, namely Br^- ions.[38]

Choudhary et al. have also studied supported Pd catalysts for the direct synthesis of H_2O_2.[40–48] Initial studies with a range of supports found that reduced Pd catalysts were inactive for the direct synthesis of H_2O_2 with the combustion reaction being prevalent under these conditions (H_2 conversion $> 50\,\%$). Subsequent treatment of these catalysts with an oxidizing agent resulted in much higher H_2O_2 yields owing to higher selectivity towards H_2O_2.[40] The decomposition of H_2O_2 was studied over the reduced and oxidized Pd catalysts and it was observed that catalysts most active for the direct reaction showed the lowered decomposition activity. The higher activity of the oxidized Pd catalyst was attributed to the presence of PdO on the surface.[47,48] It was subsequently observed that an increase in selectivity could be achieved by bromination of the reduced catalyst,[45] which was achieved by impregnation of the calcined Pd with the corresponding ammonium bromide, followed by drying. As observed with other studies with Pd, an aqueous acidic reaction medium is required for high catalytic activity, and the presence of halides is essential. For Al_2O_3- or carbon-supported Pd catalysts the roles of the promoters (both acid and halides) was to decrease the hydrogenation of the H_2O_2, resulting in a net increase in H_2O_2 yield. A recent study investigating the kinetics of H_2O_2 decomposition/hydrogenation over Pd/Al_2O_3 concluded that Cl^- and Br^- ions interact with the Pd and in turn switch off the rapid decomposition of H_2O_2, a finding that is in agreement with the detailed studies by Lunsford and co-workers.[34,36] Br^- ions showed the highest rate of reduction, their affinity to bind to Pd is not too high (I^- poisoned the catalyst). The presence of H^+ ions in the reaction medium facilitates the adsorption of halide onto the support by lowering the pH value to that below the isoelectric point of the support (X-ray photoelectron spectroscopy (XPS) showed Br^- ion incorporation in the used catalyst). Choudhary concluded that the homolytic fission of H_2O_2 ($H_2O_2 + 2\,Pd^0 \rightarrow 2\,Pd^0{\cdot}OH$) over Pd^0 is inhibited by halides. Choudhary demonstrated catalysts containing PdO were more active than their reduced counterparts, with higher H_2 conversion for direct synthesis of hydrogen peroxide.[47,48] However, these catalysts were much less selective, indicating that the presence of reduced Pd in the catalyst is detrimental to activity in the direct-synthesis reaction. The oxidized catalysts were also less active for the decomposition of hydrogen peroxide when compared to the reduced catalysts. Hence, the formation of metallic Pd on catalysts during on-stream testing could be responsible for catalyst deactivation. However, the assignment of PdO as the active species is in direct contrast to the work of Burch and Ellis who demonstrated that metallic Pd was responsible for high selectivity and conversion.[49]

Direct Synthesis Using Gold and Gold–Palladium Catalysts

Hutchings and co-workers were the first to show that gold containing catalysts (in this case Au/Al_2O_3) were active for the direct synthesis of H_2O_2. However, the key discovery was the observation that the direct synthesis of H_2O_2 was markedly enhanced by using Au–Pd alloys supported on alumina and these catalysts gave significant improvements in the rate of H_2O_2 formation when compared with the Pd or Au only catalysts.[23,24] However, in common with pure Pd catalysts, these Al_2O_3-supported Au–Pd alloys gave low selectivity based on H_2 and in these initial studies selectivities of only about 14 % were observed. Choudhary et al. also studied the effect of precious-metal additives to Pd. The addition of Au to the catalyst increased the H_2O_2 yield when compared to the Pd-only catalyst. This effect was also observed for Pt, but was not as pronounced.[40] Subsequently, Haruta and co-workers[50] have shown that Au/SiO_2 catalysts were also effective for this reaction using temperatures of 10 °C. They concluded that the activity of the catalyst was related to the size of the metal particles, and larger Au nanocrystals that formed on calcination were less active.

Ishihara and co-workers[51] have also demonstrated that gold could be effective for the direct synthesis of H_2O_2, although the activity of the catalyst was dependent on the support used. Addition of Pd to the Au again was found to increase the rate of H_2O_2 formation, and the maximum selectivity achieved using an $Au–Pd/SiO_2$ catalyst was 30 %.

The observation that Au–Pd bimetallic catalysts were more active than either Pd or Au monometallic catalysts was initially reported by Hutchings et al.[23,52–61] and has initiated extensive studies of the nature of this effect.[53–55,57–60,62] Au–Pd catalysts supported on a series of oxides (Al_2O_3,[58] Fe_2O_3[60] SiO_2,[54] and TiO_2[59]) have all shown to be more active for the direct-synthesis reaction than the Pd counterparts at 2 °C. Typically, the addition of Au to Pd leads to a more selective catalyst with a lower H_2 conversion that gives a significantly enhanced rate of H_2O_2 synthesis (Table 1).

A key observation is that the heat pretreatment of the catalyst is essential for catalyst stability (see Table 2 for data on $Au–Pd/TiO_2$ catalysts). For all of the oxide supported catalysts (Pd and Au–Pd) the uncalcined materials were far

Table 1: Activity of supported Pd, Au, and Au–Pd catalysts for the direct synthesis of hydrogen peroxide.[a]

Catalyst	Rate [mol H_2O_2/kg_{cat} h]	H_2 Conversion [%]	H_2O_2 Selectivity [%]
5 % Au/TiO_2	7.1	nd	nd
5 % Pd/TiO_2	31	29	21
2.5 % Au–2.5 % Pd/TiO_2	64	21	70
2.5 % Au–2.5 % Pd/Carbon	110	41	80
2.5 % Au–2.5 % Pd/SiO_2	108	41	80

[a] Reaction carried out under standard conditions; 5 % H_2/CO_2 and 25 % O_2/CO_2, 1:2 H_2/O_2 at 3.7 MPa, 5.6 g MeOH, 2.9 g H_2O, 0.01 g catalyst and 1200 rpm; nd = not determined as too low.

Table 2: Effect of heat treatment on 2.5 wt% Au–2.5 wt% Pd/TiO_2 catalyst.

Pre-treatment	Metal present Au (wt%)	 Pd (wt%)	Use	TOF [h^{-1}]
Dried 25 °C	2.5	2.5	1	564
Dried 25 °C	0.5	0.25	2	2298
Dried 25 °C	0.2	0.125	3	2966
Dried 200 °C	2.5	2.5	1	330
Dried 200 °C	2.22	2.5	2	216
Dried 200 °C	2.18	2.5	3	158
Dried 400 °C	2.5	2.5	1	176
Dried 400 °C	2.5	2.5	2	176
Dried 400 °C	2.5	2.5	3	176

[a] Reaction carried out under standard conditions; 5% H_2/CO_2 and 25% O_2/CO_2, 1:2 H_2/O_2 at 3.7 MPa, 5.6 g MeOH, 2.9 g H_2O, 0.01 g catalyst, and 1200 rpm; TOF: turn over frequency based on metal content of the catalyst.

more active for H_2O_2 synthesis, with very high H_2 conversions observed for the 5% Pd/TiO_2 catalyst (86%). The conversion over the Au–Pd/TiO_2 catalyst is lower, but the selectivity towards H_2O_2 is almost 90%. However, these catalysts are inherently unstable and upon a second use lose approximately 90% of the total metal content which corresponds to a reduction in activity. Catalysts which have been calcined in air at 400 °C are shown to be stable for a number of uses (Table 2). It is interesting to note that the activity of the uncalcined Au–Pd/TiO_2 catalyst, which has been used three times and lost $>95\%$ Au + Pd (Table 2) is still highly active, indicating the presence of some highly active species on the catalyst surface.

The direct synthesis was carried out at low temperature (2 °C) and using dilute H_2 well below the lower flammability limit in a water/methanol solvent system free of any stabilizers. It has also been observed that pure methanol or water can be used as solvents although lower rates of synthesis are observed owing to the relative solubilities of H_2 and O_2 under reaction conditions. The choice of diluent for the H_2, in this case CO_2, proved to be crucial in the early studies. Although there are no additional promoters in the reaction medium it has been shown that carbonic acid forms in situ, and acts as a stabilizer. Substitution of CO_2 for He and Ar resulted in a marked decrease in activity for the calcined 2.5 wt% Au–2.5 wt% Pd/carbon catalyst from 110 to 10 $mol\,h^{-1}\,kg_{cat}^{-1}$.[54] Hence, the choice of CO_2 as diluent was fortuitous, since it was made on the grounds of safety (CO_2 as diluent produces the narrowest flammability limits for H_2 in O_2). Further experiments showed that the addition of stabilizers, such as Br^- ions and H_3PO_4, were deleterious for the Au–Pd catalysts, in marked contrast to the Pd monometallic catalysts, further underlining the differences in reactivity between Au–Pd and Pd catalysts.

For oxide-supported Au–Pd catalysts, the metallic particles were found to be alloys with a core–shell morphology consisting of an gold-rich core surrounded by a palladium-rich shell. This core–shell morphology forms during calcination of the oxide-supported Au–Pd alloys which transform from homogenous alloys for the dried materials to core–shell structures when calcined (Figure 3).

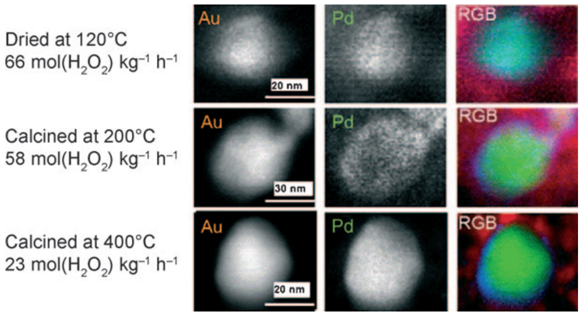


Figure 3. HAADF (high angle annular dark field) image showing development of the core–shell structure in 2.5 wt%Au–2.5 wt%Pd/Al_2O_3 catalyst. Individual Au and Pd maps are combined in the red/green/blue (RGB) image: Au green, Pd blue, Al_2O_3 red. Top row: dried at 120 °C (rate = 66 $mol(H_2O_2)\,kg^{-1}\,h^{-1}$); middle row: calcined at 200 °C (58 $mol(H_2O_2)\,kg^{-1}\,h^{-1}$); bottom row: calcined at 400 °C (23 $mol(H_2O_2)\,kg^{-1}\,h^{-1}$).[63]

Interestingly, the homogenous alloys present in the uncalcined sample are most active, but for oxide-supported Au–Pd catalysts these are unstable, as discussed previously, and hence on oxide supports the stability obtained by calcination at 400 °C is related to the formation of a core–shell structure. However, for carbon-supported Au–Pd catalysts random homogenous alloys were retained on calcination as shown by detailed STEM shown in Figure 4. Additionally the Au:Pd ratio is dependent on the particle size with larger particles containing higher concentrations of Au. The activity of the calcined 2.5 wt% Au–2.5 wt% Pd/carbon catalyst was found to be stable and higher than that of any metal oxide supported Au–Pd catalyst The origin of the enhanced activity for the carbon supported catalysts is a result of higher H_2 selectivity (ca. 80%) for the formation of H_2O_2 which was attributed to surface composition and size distribution of the nanoparticles.[63] Recent studies using sol-immobilized Au–Pd nanoparticles show enhanced activity when compared with catalysts prepared by wet impregnation,[52] and currently it is

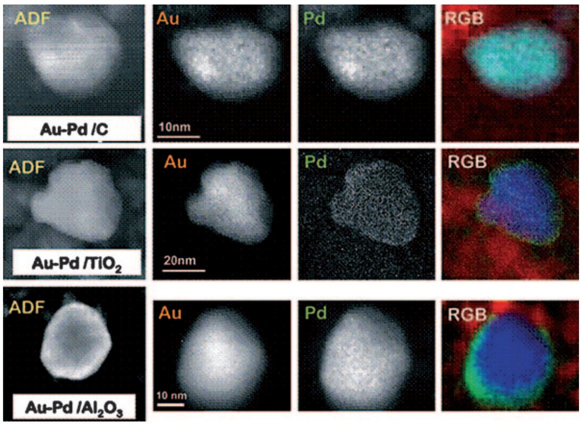


Figure 4. Montage of HAADF image (column 1), Au map (column 2), Pd map (column 3), and RGB reconstructed overlay map (column 4; Au blue, Pd green) for calcined AuPd/C (row 1), calcined AuPd/TiO_2 (row 2), and calcined AuPd/Al_2O_3 (row 3).[55]

considered that the most active and selective catalysts comprise small[64] (ca. 2 nm) Au–Pd nanoparticles that are homogeneous alloys. The enhancement in activity and selectivity induced by the addition of Au to Pd is most likely to result from electronic modification of the metals, and future studies are aimed at understanding the origin of this effect so that improved catalysts can be designed.

3. Conclusions and Outlook

It is apparent, as described in this Minireview, that there has been significant progress in the design of catalysts for the direct synthesis of H_2O_2. The key problem identified concerns the nonselective utilization of H_2 which leads to water formation. Given the cost of H_2 it is clear that H_2 utilization has to be higher than that achieved by the currently used indirect anthraquinone process, this being typically $>95\%$. This has yet to be achieved and will remain a key area of research, but there are promising leads since high selectivities ($>80\%$) are being achieved with Pd and Au–Pd catalysts. While Pd catalysts are both effective and well-studied for the direct reaction, Au–Pd catalysts offer a key advantage over Pd monometallic catalysts, namely, they are effective without the addition of halides and acids and so are able to produce H_2O_2 that require very little clean-up following synthesis. Given that H_2O_2 is used in many applications where the presence of halides would be deleterious (e.g. the epoxidation of propene) this represents a significant advantage. The hazards associated with using H_2/O_2 mixtures is readily overcome by using dilute reactants and many studies have shown that rates of H_2O_2 synthesis can be appreciable, especially when using flow reactors.[36] At present the indirect process is only economic at a large scale, which necessitates the transport of high tonnages of hazardous highly concentrated H_2O_2 to the point of use. Given the recent surge in the costs of fuel this makes the indirect process unattractive in the modern world. The direct method can offer the prospects of smaller scale production of H_2O_2 at the site at which it is used and at the concentration required for most applications (typically 3–8%). The H_2 required for small-scale uses for this local generation could be obtained from water by electrolysis, thus negating the need to transport H_2. However, for larger scale use, location of a plant adjacent to a H_2 generating plant would be beneficial as this would ensure a source of CO_2 which has been shown to be the preferred diluent. The overall objective of research on direct H_2O_2 generation is to design a process with a much lower specific investment than the anthraquinone process and, in the end, to be able to generate H_2O_2 at a lower cost. Given the advantages we can anticipate that this can be achieved and the direct process will be favored once the key problem of H_2 selectivity is fully and successfully addressed.

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