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A review of recent advances in the direct synthesis of H$_2$O$_2$.

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Graphical abstract

The direct synthesis of hydrogen peroxide represents an atom efficient way to make this important commodity chemical. In this mini review we discuss some of the latest advances for this reaction and also point out the challenge that remain to be solved so that this reaction can be considered ready for commercial exploitation; namely the need for increased catalyst activity so that more concentrated solutions can be synthesised.
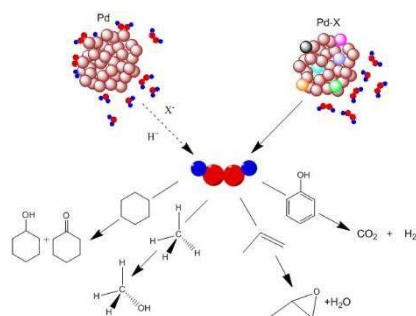
Key words:

Hydrogen Peroxide
Direct Synthesis
Heterogeneous Catalysis
Palladium
In Situ Oxidation

Abstract

Hydrogen peroxide (H_2O_2) is a highly effective, green oxidant that has found application in sectors ranging from the synthesis of fine chemicals and waste stream treatment to the extraction of precious metals and the bleaching of paper pulp and textiles. The growing demand for H_2O_2 has seen it become one of the 100 most important chemicals in the world. The direct synthesis of H_2O_2 from H_2 and O_2 has been a challenge for the scientific community for over 100 years and represents an attractive alternative to the current means of production. Herein we discuss the historical perspective of the direct synthesis process, the recent literature regarding catalyst design and the role of additives as well as the application of H_2O_2 as an in situ oxidant. We discuss the key problems that remain and conclude that although there has been progress with respect to the selectivity of hydrogen utilisation, there is a need to now concentrate on catalyst activity as the key remaining problem requiring a solution is the concentration of H_2O_2 that can be achieved especially in flow reactors.

Introduction.

Hydrogen peroxide (H_2O_2) is a powerful, environmentally friendly, oxidant that can oxidise both inorganic and organic substrates, under mild conditions. The uses of H_2O_2 are predominantly in applications where its efficacy as a bleaching agent are required, or those that utilize the high active oxygen potential, such as the synthesis of fine chemicals. Unlike stoichiometric oxidants, such as tBuOOH, N_2O or permanganate which produce large amounts of waste that requires separation from the desired product, H_2O_2 utilisation results only in the co-production of H_2O.

In recent years, global H_2O_2 production has exceeded 3 million tons per annum[1] and is predicted to rise growing at a rate of approximately 4 % with demand forecast to reach 5.2 million tons per annum by 2020.[2]

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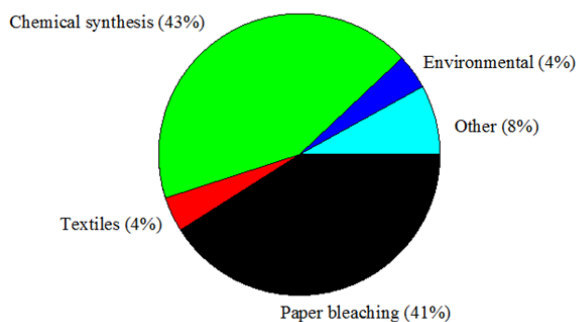
Figure 1. Applications of H_2O_2

The principal industries that utilise H_2O_2 (Figure 1) are the pulp / paper bleaching and textile industries[3-6] as well as water treatment where it is increasingly superseding chlorine containing oxidants,[7-9] primarily due to increasing environmental protection legislation. In particular it is known that H_2O_2 is able to destroy toxic chemicals present in industrial waste water such as thiocyanate, nitrate and hypochlorite.[10, 11]
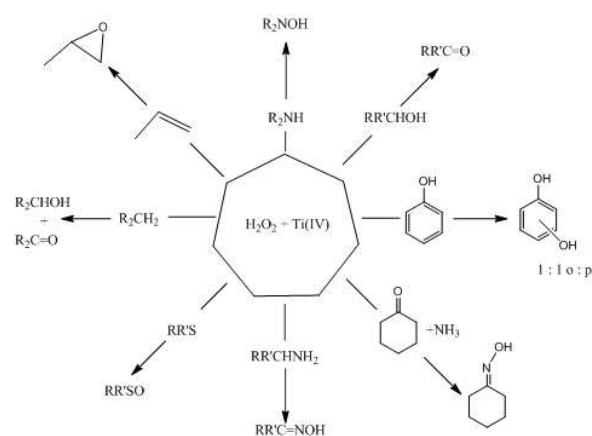
Figure 2. Schematic representation of oxidation reactions catalysed by H_2O_2 in conjunction with TS-1.

More niche uses of H_2O_2 include its use in the mining sector for the extraction of gold and uranium.[10] Further demand for H_2O_2 is driven from its application in chemical synthesis (see Figure 2) with typical applications of H_2O_2 found in the integrated HPPO process[12-19] and the ammoximation of cyclohexanone to cyclohexanone oxime, a key intermediate in the formation of Nylon-6.[20-23] These routes for chemical synthesis have, in-part, been driven by the discovery of

TS-1 by Enichem in 1983.[24] With the utilisation of H_2O_2 in tandem with TS-1 and other titianosilicates,[25-28] finding further application in a number of key processes including, aromatic hydroxylation,[29-31] alkane oxidation[32-34] and alkene epoxidation.[35-37]

Current production of H_2O_2 on an industrial scale is limited to electrolytic production, the partial oxidation of isopropanol and the well-established anthraquinone oxidation (AO) or in-direct synthesis process. The AO process, which accounts for more than 95 % of global H_2O_2 production was first developed by Riedl and Pfleiderer in BASF in 1939,[38] although the production of H_2O_2 can be traced back to its isolation in 1818 by L.J.Thenard.[39] The original process developed by Ridel and Pfleiderer has undergone continual improvement since 1939 and so is highly efficient, although the underlying chemistry has changed little and utilises H_2, O_2 and an anthraquinone derivative, with the latter reduced over a Pd based catalyst to produce the diol. The oxidation of subsequent anthraquinol reforms the original anthraquinone in-tandem with H_2O_2 formation. This highly efficient process is able to produce H_2O_2 concentrations of 1-2 wt. %, through further purification and distillation it is possible to produce H_2O_2 concentrations in excess of 70 wt. % which can be shipped and stored prior to dilution at point of final use. Often on-site application of H_2O_2 will require dilution to a range of 1-10 wt. %

Although the anthraquinone process is highly efficient, there are some concerns regarding its carbon efficiency, with the unselective hydrogenation of the carrier molecule resulting in the need for its periodic replacement. This coupled with the overall complexity of the process, in particular the choice of appropriate solvent, requires production to occur on a large scale, often precluding the synthesis of H_2O_2 at point of use. Furthermore, the instability of H_2O_2, with its rapid decomposition to H_2O in the presence of relatively mild temperatures or weak bases requires the use of stabilizing agents, often acidic stabilizers such as; acetic acid, peracetic acid,[40] dipicolinic acid, quinolinic acid[41] or phosphoric acid[42] are utilised. However, the use of such stabilizing agents often lead to reactor corrosion as well increased costs associated with their downstream removal.

Dr. Richard Lewis received his degree from Cardiff University in 2012 and completed his PhD at the Cardiff Catalysis Institute (CCI) in 2016. He is currently a post-doctoral research associate within the CCI with research interests including the design and synthesis of precious metal based catalysts for liquid phase oxidation and waste-stream treatment.
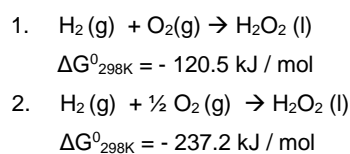
Prof. Dr. Graham Hutchings is Regius Professor of Chemistry and Director of the Cardiff Catalysis Institute. He studied chemistry at University College London. His early career was with ICI and AECI Ltd where he became interested in gold catalysis. In 1984 he moved to academia and has held chairs at the Universities of Witwatersrand, Liverpool and Cardiff. He was elected a Fellow of the Royal Society in 2009, and he was awarded the Davy Medal of the Royal Society in 2013.

The direct synthesis of H_2O_2 as an alternative to the anthraquinone process.

The direct synthesis of H_2O_2 from molecular H_2 and O_2 has the potential to offer a more atomically efficient route than the current industrial process, where the non-selective hydrogenation of the quinone-derivative H_2 carrier molecule neccessitates its periodic replacement. Pd based catalysts have been known to be highly active for the direct syntheiss of H_2O_2 since 1914[43] and have received significant attention in the literature.[44-50] However, a major challenge associated with the direct synthesis of H_2O_2 is associated with catalyst selectivity; often catalysts that offer high activity towards the direct synthesis of H_2O_2 are also active to it's degradation via over hydrogenation or decomposition to H_2O.[47, 51-53] The issue of catalyst selectivity can be understood as the formation of water from H_2 and O_2 is thermodynamically favourable in comparison to the formation of H_2O_2 as summarized by Equations 1-2.

1. $H_2 (g) + O_2 (g) \rightarrow H_2O_2 (l)$
    ΔG^0_{298K} = - 120.5 kJ / mol
2. $H_2 (g) + \frac{1}{2} O_2 (g) \rightarrow H_2O_2 (l)$
    ΔG^0_{298K} = - 237.2 kJ / mol

3

Furthermore, the undesired subsequent H_2O_2 decomposition and hydrogenation reactions are also thermodynamically favourable:

3. H_2O_2 (l) $\rightarrow$ H_2O (l) + ½ O_2 (g)
     ΔG^0_{298K} = - 116.7 kJ / mol

4. H_2O_2 (l) + H_2 (g) $\rightarrow$ 2 H_2O (l)
     ΔG^0_{298K} = - 354.0 kJ / mol

The direct synthesis of H_2O_2, therefore demonstrates the need for catalyst design to balance selectivity and activity carefully, as well as the selection of reaction conditions that inhibit the degradation of H_2O_2. It is known that H_2O_2 is highly unstable at high temperatures or in the presence of basic conditions and it has been demonstrated that through the use of low reaction temperatures it is possible to limit the thermodynamic favourability of the subsequent H_2O_2 degradation reactions.[54]

Although experimental studies have demonstrated that the active site for the direct synthesis of H_2O_2 and its decomposition may be different the exact nature of sites responsible for both the formation of H_2O_2 and its subsequent degradation remains unclear.[51, 55] It is widely accepted that the formation of H_2O_2 proceeds via the addition of hydrogen to O_2*, with O_2 isotope labelling experiments revealing that the irreversible cleavage of the O-O bond prevents the formation of H_2O_2, with a resulting production of H_2O.[56, 57] Thus perhaps the most significant challenge in terms of catalyst design is supressing the formation of thermodynamically favoured intermediates that result in the production of H_2O, namely O* and OH*.[58]

There is significant debate within the literature around whether Pd as a metal or an oxide favours the formation of H_2O_2. Choudhary and co-workers[59] have studied supported Pd catalysts for the direct synthesis of H_2O_2 and have reported that the degradation of H_2O_2 over supported Pd catalysts strongly depends on the presence of Pd^0. Indeed Choudhary and co-workers[60, 61] and others[62] have reported that supported PdO catalysts offer much greater selectivity and activity for H_2O_2 synthesis than corresponding Pd^0 catalysts, and the greater selectivity of PdO or Pd^{2+} compared to that

of Pd^0 can be attributed to the lower H_2O_2 decomposition activity of the PdO catalysts. Alternatively, Burch and Ellis[63] have reported the reduction of supported PdO catalysts prior to use can enhance both H_2 conversion and selectivity towards H_2O_2, with Liu et al. also reporting higher H_2O_2 yields over supported Pd^0 catalysts.[64] Although it should be noted that both Strukul and co-workers[65] and Lunsford[66] have reported a change in Pd oxidation state during the direct synthesis reaction. While studies by Ouyang et al. have revealed the production of H_2O_2 may take place at the interface between Pd and PdO indicating a strong dependence on both phases.[67, 68] The work of Flaherty and co-workers also indicates the need for a proportion of nanoparticles to exist in the reduced state, with a signifcant induction time required for PdO nanoparticles to exhibit activity towards H_2O_2 formation, with no such induction period exisits for Pd nanoparticles.[69]

Although the nature of the active site responsible for the cleavage of the O-O bond and production of H_2O is unkown it is likely that H_2O_2 degradation is promoted by the high energy, low co-ordiaiton Pd centres.[70] Plauck et al. have, through a combination of density functional theory and reaction kinetic studies, reported that both the close-packed Pd (111) and more open Pd (100) facets can represent the active site for H_2O_2 decomposition for supported Pd nanoparticles,[71] this is in keeping with the work of Kim et al.[49] who reported enhanced activity of Pd of the Pd (111) facet towards H_2O_2 synthesis. However, computational studies by Yoshizawa and co-workers have revealed that the Pd (111) surface also has capability to catalyse the non-selective formation of H_2O.[72]

The role of additives in the direct synthesis of H_2O_2.

To overcome limitations around selectivity Pd supported catalysts have often relied on the presence of acid and halide promotors to supress the routes responsible for H_2O_2 degradation. Pospelova et al.[73] were the first to report an inhibition in H_2O_2 decomposition with the addition of inorganic acids, potentially by preventing the deprotonation of H_2O_2 to OOH^- and its subsequent decomposition.[74] Lunsford and co-workers demonstrated the need for careful control of acid

conctrations to prevent leaching of supported Pd, resulting in a loss of catalyst stability and the development of a homoeneous catalytic component.[56, 57, 75]

Despite the majority of research centering around the use of acids within the reaction solution, either in the form of oxyacids, such as phosphoric acid and sulphuric acid, or halogen acids, such as hydrochloric acid[76] the use of solid acid additives such as Cs-exchanged tungstophosphoric acid has also shown promise in the direct synthesis of H_2O_2.[77] Edwards et al. have also demonstrated that a benefiical effect can be achieved through the acid pre-treatment of both oxide[78, 79] and carbon[80] supports prior to metal deposition with a dramatic enhancement in catalytic selectivity over the AuPd / C catalyst in particular. This is ascribed to an enhancement in Au dispersion and a resulting increase in the proportion of smaller (2 to 5 nm) bi-metallic particles at the expense of large (> 50nm) Au-rich nanoparticles. Further investigations by Garcia et al.[81, 82] have also demonstrated that enhanced catalytic selectivity can be achieved through the modification of a mesoporous carbon support, prior to precious metal impregnation, through a similar means to that previoulsy reported by Edwards et al.[76,77]

Recently Wilson and Flaherty[83] have completed a comprehensive mechanistic study of the direct synthesis of H_2O_2 over a Pd supported catalyst and have demostrated that the presence of protons are key for H_2O_2 synthesis, with H_2O_2 yields in protic solvents such as H_2O and CH_3OH much greater than in aprotic solvents, such as acetonitrile (Figure 3). In the same work they report that the presence of protons, from mineral aicds can aid in the the reduction of molecular O_2, a key step in H_2O_2 synthesis and make compelling arguments for the importance of the counterions, such as SO_4^{2-} and Cl^- in determining selectivitiy towards H_2O_2. In particular they conclude the enhancement in H_2O_2 selectivity can be related to a combination of electronic modification of the reaction solution at the liquid-solid interface by these anions as well as their adsorption onto the surface of Pd nanoparticles, which must be displaced prior to O-O bond cleavage. This explanation is in good agreement with the findings already discussed within the literature.[84, 85]
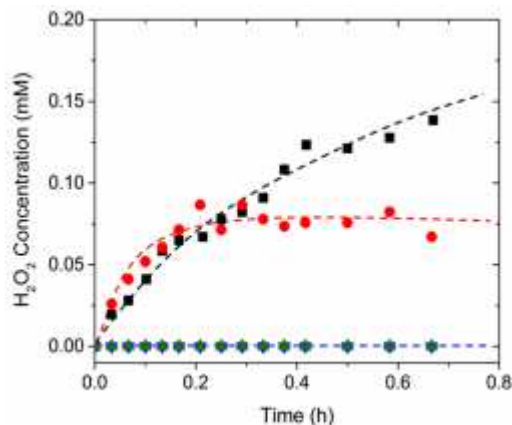
Figure 3. The formation of H_2O_2 as a fucntion of time using protic (methanol (black squares), water (red circles)) or aprotic (dimethyl sulfoxide (green triangles), acetonitrile (blue inverted triangles), propylene carbonate (magenta diamaonds). Reproduced from ref. [83]

Numerous studies have revealed the beneficial role of halides in the direct synthesis reaction, in particular bromide, either incorporated on the support[86-88] or within the reaction solution, often in conjunction with aicds.[89, 90] It is generally considered that halides aid the inhibition of H_2O_2 degradation to H_2O and enhancing catalytic selectivtiy while the role of acids is to aid in H_2O_2 stability by diminishing the base catalysed decompostion of H_2O_2. Previously halides had been purported to enhance catalytic selectivity through binding to sites responsible for the cleavage of the O-O bond,[52, 91] resulting in the formation of H_2O, recent studies have now revealed that the role of halides may be far more complex. Work by Biasi et al. has revealed that through post-synthesis catalytic treatment bromide can enhance catalytic activity through promoting a restrcturing of the metal phase in addition to the previosuly suggested poisoning the highly active sites responsible for H_2O_2 degradation.[92, 93] Furthermore it has been suggested that the promotional effect associated with halide use can be attributed to an inhibition of electron back-donation to O_2 $2\pi^*$ orbitals aiding in the maintenance of the O-O bond.[94] It is therefore likely that a combination of site poisoning and electronic and structural modification all contribute to an enhancement in catalytic selectivity through the addition of halides. Although bromide has been found to be optimal for inhibiting sites responsible for O-O bond cleavage Choudhary et al. have found that the simultaneous use of fluoride or iodide in addition to

bromide is able to inhibit all three routes to H_2O formation (decomposititon, hydrogenation and combustion).[95] However, it should be noted that the addition of one halide, in particular chloride or bromide only results in an inhibition of H_2O_2 decomposition and catalytic activty towards H_2O_2 hydrogenation remains.[96] This observation implies that there may be significant differences between the active sites repsonible for the decomposition and hydrogenation of H_2O_2. Finally, the use of increasing concentrations of halides has been reported to cause an increase in Pd particle size, possibly through the leaching and re-deposition of Pd,[97] with Tian et al. recently elucidating the effect of Pd particle size on activtiy towards H_2O_2 synthesis.[98] Often the utilisation of increasing concentrations of halides, in particular chloride, results in an oxidation of metallic Pd and enhanced dissolution of the support resulting in the formation of soluble Pd^{2+} complexes and a reduction in catalyst lifetime.[99]

The role of secondary metals in the direct synthesis of H_2O_2.

Although Pd based catalysts are highly active towards the formation of H_2O_2 from molecular H_2 and O_2 as noted previously, they often display significant activity towards its subsequent degradation, through the hydrogenation and decomposition pathways. Landon et al. were the first to report the activity of Au supported catalysts for the direct synthesis of H_2O_2.[100] Subsequently Haruta and co-workers reported the activity of Au catalysts supported on a range of supports[101] with Ishihara et al. demonstrating that promising H_2O_2 yields could be achieved, in the absence of halide promoters over a Au / SiO_2 catalyst and that through Pd addition H_2O_2 synthesis rate could be greatly enhanced.[102] With subsequent work by Todorovic and Meyer investigating the catalytic activity of Au, Pd and Pt crystal planes towards the direct synthesis and subsequent degradation of H_2O_2 via DFT calculations.[103] Edwards et al.[104] were the first to report increased catalytic activity towards H_2O_2 formation when alloying Au and Pd, building on these initial findings subsequent investigation of Pd-based, bi- and tri-metallic catalysts for the direct synthesis reaction with numerous combinations of catalysts since reported,

including; Pd-Pt,[105-108] Pd-Ru,[109] Pd-Rh,[59, 110] Pd-Ir[111] and Au-Pd-Pt.[112, 113]

A comprehensive study by Deguchi et al. has investigated the effect of precious metal (Au, Pt, Ru, Rh and Ir) addition to a Pd-polyvinylpyrrolidone colloid, with dramatic enhancements being observed with the addition of very low (0.5 at.%) concentrations of Pt or Ir doubling the formation rate of H_2O_2.[111] Kinetic analysis, supported by DFT studies, indicated that the high H_2 activating abilities of Pt and Ir were responsible for the enhanced H_2O_2 synthesis reaciton rate, while the subsequent H_2O_2 hydrogenation rate remained fairly constant with Pt and Ir incorporation, indicating that the H_2^* activated on Ir or Pt played little role in the degradation of H_2O_2.

Hutchings and co-workers [77, 114-117] and others[118-121] have extensively studied the synergistic effect achieved through the combination of Au and Pd. With the development of Au core- PdO shell nanoparticle morphology upon calcination often reported as key for improvement in catalytic selectivity, with Cybula et al. following the effect of calcination temperature on Au-Pd nanoparticles via HAADF microscopy combined with elemental mapping[122] (Figure 4) and Tiruvalam comparing the nature of Au-Pd nanoparticle structure and morphology for the direct production of H_2O_2.[123]
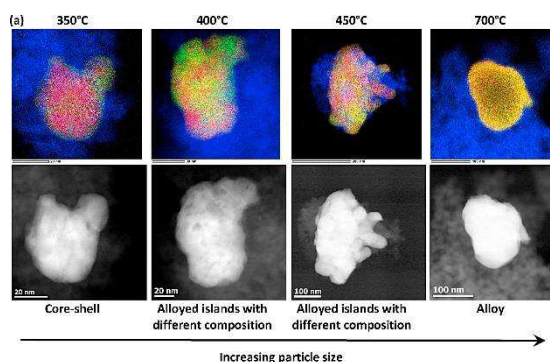
Figure 4. HAADF images combined with elemental mapping of Au-Pd modified TiO_2. Au (red), Pd (green) and Ti (blue) calcined at 350 400 and 700 ^{0}C. Reproduced from ref. [122].

The means by which Au incorporation enhances catalytic selectivity is widely debated with electronic, structural and isolation effects all potential causes for the enhanced activity of Au-Pd supported catalysts. In many cases, the observed synergy is likely to be a combination these factors, but providing conclusive evidence on the nature of the enhancement is

exceptionally challenging. A number of theoretical studies by Yoshizawa and co-workers compared Pd and PdAu surfaces and provided evidence that the presence of Au inhibits the formation of H_2O, compared to that over a Pd (111) surface.[124, 125] This is in good agreement with the work of Han and Mullins who have recently probed the influnce of the surface composition of Au-Pd catalysts for O-O bond dissociation, widely believed to be a key step for the formation of H_2O, and have reported that the extent of O_2 dissociaton is proportional to Pd content, with the increasing development of Pd ensembles attributed as the cause for increased O-O bond cleavage and a resulting increase in H_2O formation.[126] A further study by Li and Yoshizawa[127] into the role of Au in bi-metallic AuPd systems has suggested a more direct involvement of Au in the production of H_2O_2 (Figure 5). They calculated the energetic favourability of O-O bond cleavage that exists over a pure Pd surface is reduced through the introduction of Au, to a state where the maintenance of the O-O bond is favoured, resulting in the high selectivity of AuPd systems reported experimentally in the literature. That is, the presence of Au in Pd-Au interface sites weakens the Pd-O interactions, leading to an enhanced selectivity towards the O-O bond.
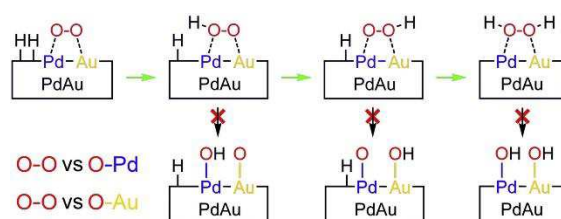
Figure 5. The case for the direct involvement of Au in the direct synthesis of H_2O_2 over AuPd supported catalysts as proposed by Li and Yoshizawa. Reproduced from ref. [127].

Until recently the modification of Pd with other precious metals, including Au, Pt, Rh, Ru and Ir have been the focus of many studies, with the modification of Pd by Au incorporation in particluar widely reported. However, the choice incorporating secondary noble metals such as Au and Pt into supported Pd catalysts can signifcanlty enhance costs, with both Au and Pt being more expensive than Pd which might prohibit the application of such catalysts on an industrial scale. As such replacing secondary noble metals with more abundant, cost effective alternatives is of great improtance. To this

end there is growing interest in the use of base metals as secondary metals in conjunction with Pd. Freakley et al.[128] recently reported a series of supported Pd-base metal catalysts, which are completely selective towards the direct synthesis of H_2O_2. Through successive calcination-reduction-calcination heat treatments of the catalyst it has been shown that the degradation of H_2O_2 can be completely inhibited. The detailed investigation of a Pd Sn/ TiO_2 catalyst that has been exposed to this optimized heat treatment cycle has yielded an approach that is believed to be applicable to a number of other Pd-base metal combinations, including Ni, Zn, Ga, In and Co.[128] It was proposed that as a result of this heat treatment the small Pd-rich nanoparticles responsible for H_2O_2 degradation are encapsulated into an oxide layer of the secondary metal, limiting catalytic activity towards H_2O_2 destruction possibly by reducing the availability of low coordination Pd edge sites (Figure 6).
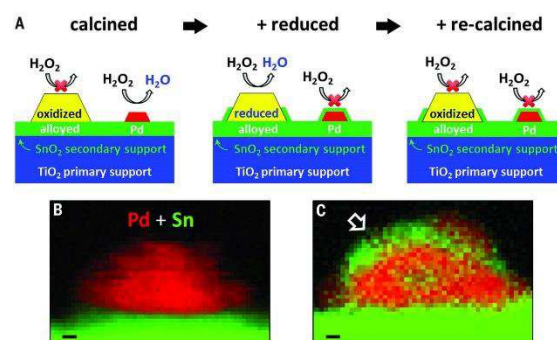
Figure 6. The role of the secondary metal in the inhibition of H_2O_2 degradation over small Pd-rich nanoparticles as proposed by Freakley et al. (A) Proposed mechanism, where the secondary metal encapsulates small Pd nanoparticles as a result of successive heat treatments. (B and C) STEM-EELS mapping of model 5% Pd / SnO_2 catalyst showing partial encapsulation of Pd nanoparticles (red) by SnO_x (green). Reproduced from ref. [128].

Building on this work Li et. al.[129] have demonstrated that through Sn incorporation supported Pd catalysts exposed to rapid thermal treatment can deliver complete inhibition of H_2O_2 decomposition and hydrogenation, with H_2O_2 synthesis activities approaching twice that reported by Freakley et al., with minimal catalyst deactivation over re-use and no structural changes observed via TEM or EDX analysis.

Through a combination of DFT calculations and Sabatier analysis Gao and co-workers have proposed that several base metal dopants, such as W, and Pb, are able to enhance both catalytic activity and selectivity

of Pd-based and bi-metallic Pd-Au catalysts towards H_2O_2. They propose that electronegative elements in particular are able to inhibit O-O bond cleavage through the withdrawal of electron density from Pd.[130] However, further experimental evidence is required to confirm these findings.

Additional investigations by Abate et al. revealed that N doping carbon nanotubes results in increased catalytic activity and stability through increased dispersion of Pd and enhanced acidity of the support.[131, 132] While Melada et al. report an enhancement in catalytic activity through the introduction of sulphate and halide dopants into zirconia supported Pd catalysts.[65] Although the use of dopants can enhance catalytic activity and selectivity in the direct synthesis reaction the leaching and concentration of these elements can lead to catalyst deactivation, reactor corrosion and often the requirement for downstream removal, as such future research should focus on enhancing catalyst lifetime and stability.

 Further studies have investigated the beneficial role of Zn,[133] Ag,[134] Te,[135] Sb[136] and Ni[137] as secondary metals that are able to enhance catalytic selectivity through enhanced stabilization of O_2^-, as a result of a reduction in the amount of contiguous Pd ensemble sites and an enhancement in the number of isolated Pd sites favorable for H_2O_2 formation. Table 1 below highlights the enhancement in catalytic selectivity

towards H_2O_2 that can be achieved through modification of Pd by secondary non-precious metals.

Choice of support for precious metal catalysts.

The nature of the support is a key factor which can affect catalytic activity and selectivity towards H_2O_2. A range of zeolitic,[138-142] oxide, resin,[62, 108, 143, 144] heteropolyacid[45, 145-148] and carbon[80, 134, 149, 150] supports have been investigated to date.

Hutchings and co-workers have extensively studied the use of oxide supports for the direct synthesis of H_2O_2 over bi-metallic AuPd catalysts and correlated catalytic activity with the iso-electric point of the support, with those more acidic supports benefiical for catalytic selectivtiy and hence net yield of H_2O_2.[151, 152] Further study by Menegazzo et al.[153] has reported that it is possible to control Pd nanoparticle size and in turn balance catalytic activity and selectivity towards H_2O_2 through the choice of support. They reported that the use of SiO_2 is superior to that of either ZrO_2 or CeO_2 in tuning these two parameters of catalytic efficiency.

Due to their high acidity numerous studies have investigated heteropolyacids as both catalyst supports[145, 148, 154-156] as well as solid acid additives[77] for the direct synthesis of H_2O_2. Problems concerning their low surface area and high solubility in polar solvents can be overcome through the introduction of

Table 1. Comparison of catalytic selectivity towards H_2O_2 as a function of secondary metal.

Reference	Catalyst	Reactor system	Temp. / °C	Pressure / bar	Time / h	Solvent	Promoter	H_2O_2 selectivity / %
Gu [134]	1% Pd / C	Batch	2	30	0.25	MeOH	0.03M H_2SO_4	54
	Pd-Ag(10) / C[a]	Batch	2	30	0.25	MeOH	0.03M H_2SO_4	72
Wang [133]	1 % Pd / γ-Al_2O_3	Batch	2	30	0.25	MeOH	0.03M H_2SO_4	64
	1%Pd- 5% Zn / γ-Al_2O_3	Batch	2	30	0.25	MeOH	0.03M H_2SO_4	79
Freakley [128]	1% Pd – 4% Sn / TiO_2	Batch	2	40	0.5	H_2O / MeOH	-	95
	3% Pd - 2% Sn / TiO_2	Batch	2	40	0.5	H_2O / MeOH	-	96
Maity [137]	Pd (unsupported)	Semibatch	10	1	1	H_2O	0.1 M HCl + 0.01M KBr	82
	$Ni_{0.4}Pd_{0.6}$ (unsupported)[b]	Semibatch	10	1	1	H_2O	0.1 M HCl + 0.01M KBr	95
Ding [136]	3 % Pd / TiO_2	Semibatch	10	1	0.25	EtOH + H_2SO_4	0.12 M H_2SO_4	54
	$Pd_{50}Sb$ / TiO_2[c]	Semibatch	10	1	0.25	EtOH + H_2SO_4	0.12 M H_2SO_4	73
Tian[135]	3 % Pd / TiO_2	Semibatch	10	1	0.17	EtOH + H_2SO_4	0.12 M H_2SO_4	65
	$Pd_{100}Te_1$ / TiO_2[d]	Semibatch	10	1	0.17	EtOH + H_2SO_4	0.12 M H_2SO_4	100

[a] Pd loading fixed at 1 wt.% with value in parentheses indicating Pd / Ag molar ratio. [b] Subscript values indicate nominal Ni / Pd weight ratio.
[c] Pd loading fixed at 3 wt.% with subscript value indicating Pd / Sb molar ratio. [d] Subscript values indicate atomic Pd / Te ratio.

specific cations, such as Cs^+, K^+ and Rb^+ into the structure of the heteropolyacid, while other studies have investigated palladium exchanged heteropolyaicds immobilized onto mesoporous silica for the synthesis of H_2O_2.[157, 158] Interestingly these catalysts have been shown to outperform the analogous catalysts utilising a more conventional, less acidic, support under reaction conditions likely to be more favored by industry; (i.e. ambient temperature and a water only solvent) likely due to the increased selectivity imparted by the acidity of the support.[145]

Mesoporous silicas such as MCM-41[138, 158] and SBA-15[159-161] have seen growing interest as supports for the direct synthesis of H_2O_2 due to their high surface area, which allows for a high dispersion of active sites, and an ordered channel struture which can alleviate issues associated with mass transfer. In addition the large pore size of mesoporous silicas allows for the majority of active metal to be accomodated within the mesoporous framework. This aids in preventing agglomeration of metal nanoparticles during the course of the reaction and balances the need for high nanoparticle dispersion, resulting in high activity, and minimal O_2 dissociaiton which is necessary for high catalytic selectivity.[159] Both Park et al.[162] and Rodríguez-Gómez et al.[119] have investigated the functionalisation of SBA-15 through the grafting of organic functional groups, with the introduction of amine groups in particular resulting in a significant enhancement in catalytic selectivtiy through the suppression of H_2O_2 decomposition.

Application of H_2O_2 as an in situ oxidant.

Propylene oxidation to propylene oxide.
The selective oxidation of propylene to propylene oxide yields one of the major starting materials in industrial chemistry, with propylene oxide finding application in the production of surfactants, polyurethane and resins. Until recently propylene oxide has been manufactured on an industrial scale through the use of chlorohydrin or hydroperoxides.[14] The first process reacts propene with Cl_2 to produce chlorohydrin, which is dehydrochlorinated using an aqueous alkali solution, producing an equimolar quantity of aqueous alkali metal chloride along with the required product, which incurs significant removal and treatment costs. The use of

hydroperoxides is more environmentally friendly than the use of chlorohydrin but is greatly dependent on the market value of the co-product obtained alongside propylene oxide (styrene or tert-butanol).[163] In recent years a new alternative, the HPPO process, utilising H_2O_2 as an oxidant, has offered significant environmental and economic advantages over the alternative processes. An appealing alternative to the HPPO process involves the in situ production of H_2O_2, either in the liquid or vapour phase, over supported precious metals, notably Pd, Au, and Pt, or combinations thereof. A range of supports have been explored within the literature including; TS-1,[164-169] Ti-MCM-41[170-172] and oxides[173-175] where H_2O_2 is activated at mild temperatures by isolated Ti(IV) sites present within the support structure. However, catalytic selectivity towards propylene oxide is still a concern with the use of promoters common place. In particular Uphade et al. have reported the use of CsCl as a promoter for Au / Ti-MCM-41 catalysts, leading to an enhancement in Au particle size, with a resulting 5 % increase in selectivity towards propene oxide.[170] While Chen and Beckman have reported it is possible to achieve a four-fold increase in selectivity towards propylene oxide over a low loaded PdPt / TS-1 catalyst, through the use of ammonium acetate. They report that even at low concentrations ammonium acetate is able to supress unwanted side reactions, including the acid catalysed hydrolysis of propylene oxide to propylene glycol. The focus of future research must now be placed on achieving high selectivity towards propylene oxide in the absence of promoters.

The Fenton process.
The Fenton process, the catalytic formation of hydroxyl and hydroperoxy radicals by the disproportionation of hydrogen peroxide, can be considered one of the most efficient means for the degradation of organic pollutants in wastewater streams at low to moderate concentrations.[176-178] Numerous studies have investigated the efficacy of H_2O_2 generated in situ over Pd-Fe based catalysts utilising a range of hydrogen sources such as formic acid, hydroxylamine and hydrazine.[179-183] Indeed Underhill et al.[184] have recently reported that superior rates of phenol conversion can be achieved from H_2O_2 generated in situ from molecular H_2 and O_2, compared to preformed

H_2O_2, with this superiority ascribed to the absence of stabilising compounds, such as phosphoric acid and acetanilide, found in commercial H_2O_2.[42]

Methane valorisation to methanol.
The selective oxidation of methane, a major component of natural gas, to methanol is an attractive means to produce a versatile chemical feedstock. However, the direct catalytic upgrading of methane is yet to be achieved under environmentally friendly conditions on a scale that is industrially viable. Methane conversion to methanol on an industrial scale currently utilises harsh conditions, with temperatures exceeding 800 ^{0}C, to produce synthesis gas which can then be converted into methanol. This approach although highly selective is associated with high energy and capital demands. As such significant economic and environmental advantages may be reached through the selective oxidation of methane at milder reaction conditions. Initial work focussed on the use of supported Pt catalysts but required the use of concentrated H_2SO_4 as the oxidant.[185] However a significant breakthrough occurred with the use of environmentally benign oxidants such as H_2O_2.[186, 187] The application of in situ generated H_2O_2 overcomes the significant drawbacks associated with the anthraquinone process, the means by which H_2O_2 is generated on an industrial scale and Lin et al.[188] were amongst the first to investigate the in situ generation of H_2O_2 for the oxidation of methane, starting from O$_2$, CO in a trifluoroacetic acid / H_2O solvent system in the presence of Pd-based catalyst. Building on this work numerous studies have since investigated the conversion of methane to more versatile chemical feedstocks based on the O_2/CO/H_2O system,[189, 190] as well as the synthesis of H_2O_2 directly from H_2 and O_2, avoiding the initial water gas shift reaction to produce H_2 in situ.[191, 192] Recently Rahim et al. have demonstrated that significant improvements in selectivity towards methanol can be achieved through the use of H_2O_2 generated in situ when compared to the use of pre-formed H_2O_2, under comparatively mild reaction conditions.[193]

Despite demonstration of the feasibility of the selective oxidation of short chain alkanes via H_2O_2 generated in situ further work is required for this approach to be considered industrially viable, with low productivities and a need for a reduction in the formation of the products of over oxidation, namely CO_2, significant challenges for future research.

Cyclohexane oxidation and the production of KA oil.
Cyclohexanone and cyclohexanol are important chemical feedstocks for the production of ε-caprolactam and adipic acid, key intermediates for the production of Nylon-6 and Nylon-6,6. In addition, cyclohexanol and cyclohexanone are also used as stabilising agents and homogenizers for synthetic detergents and soaps. The production of cyclohexanone and cyclohexanol (KA oil) on an industrial scale currently relies on the un-catalysed oxidation of cyclohexane with air at elevated temperatures.[194-198] To limit over oxidation to unwanted by-products conversion is limited to below 10 % and additional steps are implemented to improve cyclohexanone : cyclohexanol ratio.[199]

Numerous studies have investigated the use of H_2O_2 as a replacement oxidant for molecular O_2. Due to its greater reactivity H_2O_2 allows for significantly lower temperatures to be utilised, with the current auto-oxidation process requiring temperatures in excess of 140 ^{0}C.[200] A range of supports have been explored including vanadium phosphorous oxide, which demonstrated near complete conversions of the substrate, however the catalyst displayed poor selectivity towards KA oil due to a high formation of cyclohexyl peroxide.[201] Spinace et al. was amongst the first to investigate the activity of TS-1 for the oxidation of cyclohexanone.[202] However, further work by the same group reported the ability of TS-1 to catalyse the further oxidation of cyclohexanol to unwanted by-products, which can lead to the deactivation of the catalyst through the blocking of the TS-1 pore system.[200] Expanding on this initial work Shi et al. developed a titanium silicate with a hollow structure (HTS) and enhanced Lewis acidity that offered higher activity towards KA oil compared to that observed for TS-1 alone.[203] Rezaei et al. have reported a reusable KIT-6 supported vanadium pyrophosphate catalyst for cyclohexane at low temperatures.[204] However the reported selectivity is still not sufficient for industrial application, even at low conversion rates.

The in situ generation of H_2O_2 for the oxidation of cyclohexanone has recently been studied by Kuznetsova and co-workers utilising Pt based catalysts. It is reported that the addition of small quantities of ionic

liquids containing Br- and HSO_4^- anions are able to stabilise the peroxide-intermediates, resulting in an enhanced yields of KA oil. [205, 206] A further study by Li et al. revealed the catalytic activity of zeolite-Y supported AuPd catalysts for the oxidation of cyclohexane, with only cyclohexanol observed as the desired product, however this is likely due to the relatively short reaction times investigated.

Conclusion and Future Perspectives.

The direct synthesis of H_2O_2 from H_2 and O_2 offers potential significant environmental and economic benefits over the current means of H_2O_2 production, i.e. the anthraquinone process. However, despite extensive research for over 100 years the direct synthesis of H_2O_2 from H_2 and O_2 is still not industrially viable, although research into this challenging reaction has gained momentum in the past decade.

Although Pd based catalysts have received the greatest attention perhaps one of the biggest breakthroughs in the field came from the finding that incorporating Au into supported Pd catalysts can dramatically enhance catalytic selectivity, without the need for acid or halide additives. Further investigations have since shown that the incorporation of several other secondary metals, including Pt and Ni into supported Pd catalysts can greatly enhance catalytic selectivity and activity. While the use of high surface and acidic supports have been shown to inhibit the agglomeration of metal nanoparticles and enhance H_2O_2 selectivity, respectively.

Numerous computational studies have led to a greater understanding of the active sites responsible for the direct synthesis of H_2O_2, its degradation and the competitive formation of H_2O as well as aiding experimentalists in the design of new catalysts. However, further study is required to improve catalyst activity for use in a semi-continuous / continuous regime, where contact time between H_2, O_2 and the catalyst is significantly shorter than that utilised in batch reactors. This is likely to be required if the direct synthesis route is to be utilised on an industrial scale. In addition further research is required to gain a better understanding of catalyst lifetime and how catalytic structure and morphology changes on-stream.

Selective oxidation using H_2O_2 generated in situ from H_2 and O_2 offers an attractive alternative to current processes, removing the need for the storage of large quantities of H_2O_2 on site prior to use as well as allowing for the use of milder reaction conditions, in particular high temperatures associated with auto-oxidation reactions, with obvious environmental and economic benefits. Furthermore the lack of stabilising agents, such as acids can promote catalyst and reactor lifetime, which are concerns that arise when pre-formed H_2O_2 is utilised. Often oxidative catalytic systems have utilised a two-step process; the production of H_2O_2, usually over noble metals, followed by its activation and use in the oxidation of the target substrate. This has often required the diffusion of H_2O_2 from catalytic species responsible for its generation to a secondary, sometimes homogeneous component, with the Fenton reaction a well-studied example. However, often reaction conditions utilised are unfavourable towards H_2O_2, resulting in the conversion of H_2O_2 to H_2O. To mitigate this, future catalytic development should, where feasible, centre on single active sites responsible for both H_2O_2 production and activation. Where consolidation into one active site is not possible, research should focus on means to avoid diffusion limitations and the resulting degradation of H_2O_2. The higher activity observed for H_2O_2 generated in situ compared for both the selective oxidation of methane as well as the degradation of waste stream contaminants is particularly exciting and highlights the potential benefits that can be unlocked through the production of an in situ oxidant.

In conclusion the growing global demand for commodity and fine chemicals, coupled with the environmental need to replace chloride-based bleaching agents particularly in the treatment of waste streams, will lead to an increasing need for H_2O_2 over the coming decades.

It is suggested that as it has been demonstrated that H_2O_2 can be synthesised with 100 % selectivity based on H_2 focus should now be placed on increasing catalytic activity towards H_2O_2 production. At present the highest concentration of H_2O_2 reported is approximately 1 wt.%[80] however, to be competitive with current means of H_2O_2 production significantly greater concentrations are required. It is hoped that with

growing interest from the scientific community and increased collaboration between theoreticians, experimentalists and chemical engineers this target will soon be met by a commercialised direct synthesis process.

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