The direct synthesis of hydrogen peroxide over Au-Pd supported nanoparticles under ambient conditions.

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Abstract.

The direct synthesis of hydrogen peroxide (H_2O_2) from molecular H_2 and O_2 over Au-Pd / TiO_2 catalysts prepared using a modified impregnation methodology is studied. Initially we investigated the role of Au: Pd ratio on the catalytic activity towards H_2O_2 formation and its subsequent degradation under conditions that have previously been found to be optimal for the formation of H_2O_2 using high pressure reactants and low temperatures. Subsequently, we have conducted a detailed study of H_2O_2 synthesis under ambient conditions which are both more challenging for achieving high yields of H_2O_2 and are more likely to be used for future industrial applications.

Introduction.

Hydrogen peroxide (H_2O_2) is a highly versatile, environmentally friendly oxidant, with the only by-product of its application being water. The primary application of H_2O_2 is found in the paper and textile industries,[1, 2] where it is used as a bleaching agent and in the production of bulk chemicals, with typical applications found in the integrated hydrogen peroxide to propylene oxide (HPPO) process,[3, 4] the ammoximation of cyclohexanone to the corresponding oxime, a key intermediate in the production of Nylon-6[5-7], and the production of KA oil, a mix of cyclohexanone and cyclohexanol, from cyclohexane.[8, 9] Furthermore, H_2O_2 is finding increasing application in water treatment, superseding chlorine containing oxidants, primarily due to increasing environmental protection legislation.[10, 11] The ability of H_2O_2 to destroy chemicals found in waste streams such as thiocyanate, nitrate and hypochlorite is well known.[12, 13] In recent years increasing focus has been placed on the treatment of organic pollutants from wastewater streams with numerous studies reporting the efficacy of H_2O_2 used in conjunction with Fenton's reagent,[14-18] with the photo-Fenton process, in particular, representing an interesting alternative approach.[19-21]

Annual global production of H_2O_2 is growing at a rate of approximately 4 % year on year with demand forecast to exceed 5 million tons per annum by 2020.[22] Currently, production of H_2O_2 on an industrial scale is dominated by the well-established anthraquinone oxidation (AO), also known as in-direct process, which accounts for more than 95 % of the global H_2O_2 production. Although the AO process is highly efficient, there are some concerns regarding its carbon efficiency, with the unselective hydrogenation of the anthraquinone H_2-carrier molecule requiring its continual replacement.

The direct synthesis of H_2O_2 from molecular H_2 and O_2 represents an attractive alternative to the AO process, offering a more atomically efficient route to H_2O_2 and allowing for the potential production of H_2O_2 at the point of final use. Although supported Pd catalyst are highly active towards the direct synthesis of H_2O_2, they often display poor selectivity, with high rates of H_2O_2 degradation, through hydrogenation and decomposition pathways. To inhibit these sequential, undesirable, reactions, halide and acidic stabilisers are often utilised,[23-26] which lead to additional costs associated with reactor corrosion and the removal of these stabilising agents downstream. However, it has been well reported that through combining Au with Pd it is possible to significantly enhance catalytic activity and selectivity towards H_2O_2 in the absence of strong acid and halide stabilising agents.[27, 28] The synergistic enhancement achieved through the addition of Au to Pd, although still not fully understood, has been well reported in the literature [29-31] since it was first observed by Landon et al.[32] There is wide debate over the cause of this synergistic enhancement, with electronic, structural and isolation effects, or a combination of these, all potential causes for the enhanced selectivity of Au-Pd catalysts. It

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is likely that in many cases the observed synergy is a combination of these factors. To date these supported AuPd catalysts have most often been studied using low reaction temperatures with high pressure gases and a water/alcohol co-solvent mixture. Typically CO_2 has been the diluent of choice to ensure mixtures of H_2 and O_2 do not enter the explosive region, with the explosive region of H_2/O_2 mixtures known to be much narrower when using CO_2 as a diluent compared to other inert gases. Furthermore the use of CO_2 provides the additional benefit of increasing H_2O_2 stability through the formation of carbonic acid in-situ. However, the use of other diluent gases, such as argon and nitrogen, are also common, with nitrogen in particular often used due to lower associated costs. [12] Although these conditions are ideal for the direct synthesis of H_2O_2 they are likely to be undesirable on an industrial scale due to the associated increased financial costs. As such, we have investigated the effect of key reaction parameters on catalytic activity and selectivity towards H_2O_2 over a series of 1 %AuPd/TiO$_2$ catalysts, prepared via a modified impregnation methodology, starting with those conditions previously optimised and moving towards those more likely to be more suitable for future industrial application. Sankar et al.[33] have previously extensively studied a modified impregnation methodology for the preparation of AuPd/TiO$_2$ catalysts demonstrating an enhanced catalytic performance in the direct synthesis of H_2O_2, with H_2O_2 synthesis rates found to be four times greater than an analogous catalyst prepared by a conventional impregnation methodology. This enhancement has been ascribed to a significant decrease in mean particle size and improved Au dispersion and formation of AuPd alloyed nanoparticles. With such excellent rates of H_2O_2 synthesis compared to conventional impregnation analogues we believe they are an appropriate choice for further study.

Experimental.

Catalyst Preparation.

1 %Au, Pd and Au-Pd/TiO$_2$ catalysts have been prepared (on a weight basis) by a modified impregnation procedure, based on methodology previously reported in the literature[33] and have been shown to result in enhanced dispersion of Au in particular when compared to conventional impregnation procedures. The procedure to produce 0.5%Au–0.5%Pd/TiO$_2$ (2 g) is outlined below, with a similar methodology utilised for mono- and bi-metallic catalysts, of varying Au: Pd ratio.

Aqueous acidified PdCl$_2$ solution (1.667 mL, 0.58 M HCl, 6 mg mL^{-1}, Sigma Aldrich) and aqueous HAuCl$_4$.3H$_2$O solution (0.8263 mL, 12.25 mg mL^{-1}, Strem Chemicals) were mixed in a 50 mL round bottom flask and heated to 60 °C with stirring (1000 rpm) in an thermostatically controlled oil bath, with total volume fixed to 16 mL using H$_2$O (HPLC grade). Upon reaching

65 $^{\circ}$C, TiO$_2$ (1.98 g, Degussa, P25) was added over the course of 5 minutes with constant stirring. The resulting slurry was stirred at 60 $^{\circ}$C for a further 15 min, following this the temperature was raised to 95 $^{\circ}$C for 16 h to allow for complete evaporation of water. The resulting solid was ground prior to heat treatment in a reductive atmosphere (flowing 5 % H$_2$ / Ar, 400 °C, 4h, 10 °C min^{-1}).

Direct synthesis of H$_2$O$_2$.

Hydrogen peroxide synthesis was evaluated using a Parr Instruments stainless steel autoclave with a nominal volume of 100 mL, equipped with a PTFE liner so that total volume is reduced to 66 mL, and a maximum working pressure of 14 MPa. To test each catalyst for H$_2$O$_2$ synthesis, the autoclave liner was charged with catalyst (0.01 g) and solvent (5.6 g methanol and 2.9 g H$_2$O). The charged autoclave was then purged three times with 5% H$_2$ / CO$_2$ (0.7 MPa) before filling with 5% H$_2$ / CO$_2$ to a pressure of 2.9 MPa, followed by the addition of 25 % O$_2$ / CO$_2$ (1.1 MPa). Pressure of 5% H$_2$ / CO$_2$ and 25 % O$_2$ / CO$_2$ are given as gauge pressures. The reaction was conducted at a temperature of 2 °C, for 0.5 h with stirring (1200 rpm). The above reaction parameters are based on optimum conditions we have previously used for the synthesis of H$_2$O$_2$.[34] H$_2$O$_2$ productivity was determined by titrating aliquots of the final solution after reaction with acidified Ce(SO$_4$)$_2$ (0.0085 M) in the presence of ferroin indicator. Catalyst productivities are reported as mol$_{H2O2}$kg$_{cat}^{-1}$h^{-1}.

Catalyst activity towards H$_2$O$_2$ synthesis was also evaluated under conditions considered more unfavourable towards H$_2$O$_2$ formation. These conditions were identical to those outlined above but using water as reaction medium, N$_2$ as diluent for H$_2$ (5% H$_2$/N$_2$) and O$_2$ (25% O$_2$/N$_2$) and a reaction temperature of 25 ^{0} C. Reactor temperature was controlled using a HAAKE K50 bath/circulator using an appropriate coolant.

Catalytic conversion of H$_2$ and selectivity towards H$_2$O$_2$ were determined using a Varian 3800 GC fitted with TCD and equipped with a Porapak Q column.

H$_2$ conversion (Equation 1) and H$_2$O$_2$ selectivity (Equation 2) are defined as follows:

$$\mathrm{H_2 Conversion\ (\%)} = \frac{\mathrm{mmol}_{H2\,(t(0))} - \mathrm{mmol}_{H2\,(t(1))}}{\mathrm{mmol}_{H2\,(t(0))}} \times 100\ (eq\ 1\ )$$

$$\mathrm{H_2O_2\ Selectivity\ (\%)} = \frac{\mathrm{H_2O_2 detected\ (mmol)}}{\mathrm{H_2\ consumed\ (mmol)}} \times 100\ (eq\ 2)$$

Total autoclave capacity was determined via water displacement to allow for accurate determination of H_2 conversion and H_2O_2 selectivity. When equipped with PTFE liner (reducing nominal volume to 66 mL) the total volume of an unfilled autoclave was determined to be 93 mL, which includes all available gaseous space within the autoclave.

Degradation of H_2O_2.

Catalytic activity towards H_2O_2 degradation was determined in a similar manner to the direct synthesis activity of a catalyst. The autoclave liner was charged with methanol (5.6 g), H_2O_2 (50 wt. % 0.69 g), HPLC standard H_2O (2.21 g) and catalyst (0.01 g), with the solvent composition equivalent to a 4 wt. % H_2O_2 solution. From the solution 2 aliquots of 0.05 g were removed and titrated with acidified $Ce(SO_4)_2$ solution using ferroin as an indicator to determine an accurate concentration of H_2O_2 at the start of the reaction. The autoclave was pressurised with 2.9 MPa 5 % H_2 / CO_2 (gauge pressure). The reaction was conducted at a temperature of 2 °C, for 0.5 h with stirring (1200 rpm). After the reaction was complete the catalyst was removed from the reaction mixture and two aliquots of 0.05 g were titrated against the acidified $Ce(SO_4)_2$ solution using ferroin as an indicator. The degradation activity is reported as $mol_{H2O2}kg_{cat}^{-1}h^{-1}$.

Catalyst activity towards H_2O_2 degradation was also evaluated under reaction conditions considered more unfavourable towards H_2O_2 formation. These conditions were identical to those outlined above but using only water as reaction medium, N_2 as diluent for H_2 (5 % H_2/N_2) and a reaction temperature of 25 ^{0} C.

Catalyst Characterisation.

X-ray photoelectron spectroscopy (XPS) analyses were made on a Kratos Axis Ultra DLD spectrometer. Samples were mounted using double-sided adhesive tape and binding energies were referenced to the C (1s) binding energy of adventitious carbon contamination that was taken to be 284.7 eV. Monochromatic AlK_α radiation was used for all measurements; an analyser pass energy of 160 eV was used for survey scans while 40 eV was employed for detailed regional scans. The intensities of the Au (4f) and Pd (3d) features were used to derive the Au : Pd and Pd(II) : Pd(0) surface ratios.

The bulk structure of the catalysts was determined by powder X-ray diffraction using a (θ-θ) PANalytical X'pert Pro powder diffractometer using a Cu K_α radiation source, operating at 40 KeV and 40mA. Standard analysis was carried out using a 40 min run with a back filled sample, between 2θ values of 10 – 80°. Phase identification was carried out using the International Centre for Diffraction Data (ICDD).

Transmission electron microscopy (TEM) was performed on a JEOL JEM-2100 operating at 200 kV. Samples were prepared by dispersion in ethanol by sonication and deposited on 300 mesh copper grids coated with holey carbon film. Energy dispersive X-ray analysis (EDX) was performed using an Oxford Instruments X-Max^N 80 detector and the data analysed using the Aztec software.
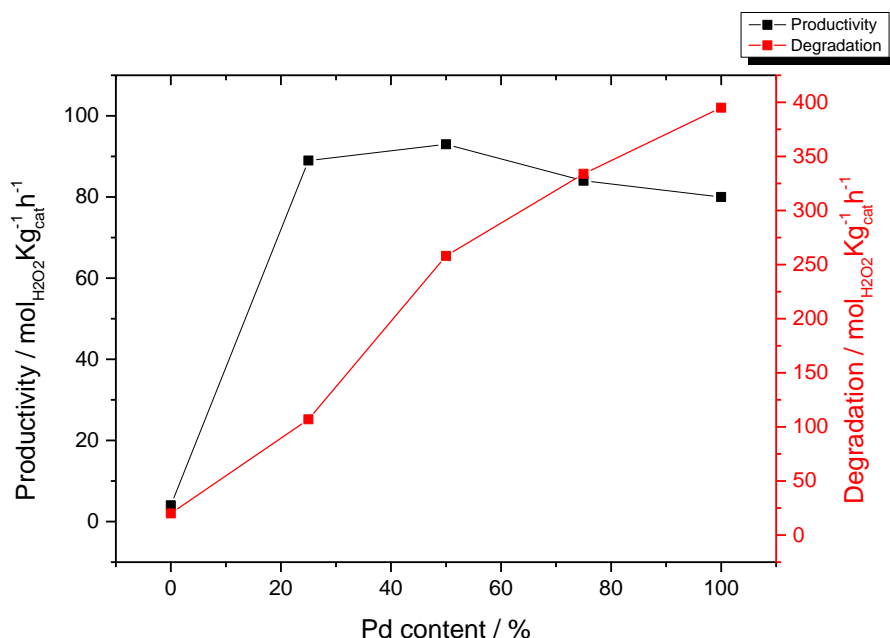
Total metal loading and metal leaching from catalyst supported was quantified using microwave plasma - atomic emission spectroscopy (MP-AES). Fresh catalysts were digested (25 mg catalyst, 2.5 ml aqua-regia, 24 h) prior to analysis using an Agilent 4100 MP-AES, while post reaction solutions were also analysed after filtration of the solid material. Metal concentrations were determined by response at two characteristic emissions wavelengths for Au (242.8 nm, 267.6 nm) and Pd (340.5 nm, 363.5 nm) and the resultant concentrations averaged. The concentration response of Au and Pd were calibrated using commercial reference standards (Agilent), in all cases $r^2 > 0.999$.

Results and Discussion.

Our initial studies, under conditions previously optimised for H_2O_2 synthesis,[35] investigated the effect of Au: Pd ratio (comparison of theoretical and actual metal loadings see in Table S.1) on catalytic activity towards both the synthesis of H_2O_2 and its subsequent degradation over catalysts prepared using a modified impregnation methodology (Figure 1). We observe that an enhancement in catalytic activity can be achieved through the combination of Au and Pd with H_2O_2 synthesis rates of the 0.75 %Au-0.25 %Pd / TiO_2 catalyst (89 $mol_{H2O2}Kg_{cat}^{-1}h^{-1}$) greater than that of either monometallic 1 %Au/TiO_2 (4 $mol_{H2O2}Kg_{cat}^{-1}h^{-1}$) or 1 %Pd/$TiO_2$ (80 $mol_{H2O2}Kg_{cat}^{-1}h^{-1}$) catalysts. These findings are consistent with our previous investigations into the effect of Au: Pd ratio over catalysts produced via sol-immobilisation, suggesting that the synergistic effect between Au and Pd is independent of preparation method.[36] Further addition of Pd yields minimal variation in the rates of H_2O_2 synthesis relative to that of the 0.75 %Au-0.25 %Pd / TiO_2 catalyst but rates of H_2O_2 degradation increases significantly, with H_2O_2 degradation activity of the 0.25 %Au-0.75 %Pd / TiO_2 catalyst in excess of ten times that observed for the 0.75 %Au-0.25 %Pd / TiO_2catalyst.

Previous work by Edwards et al. has shown that for catalysts prepared by a conventional wet-impregnation methodology, H_2O_2 synthesis rates are greatest when prepared with a Au :Pd ratio of 1 : 1 by weight, with either Pd-rich or lean compositions resulting in significantly decreased H_2O_2 yields.[34] In comparison, the catalysts prepared by modified impregnation as shown in Figure 1 exhibit minimal variation in H_2O_2 synthesis activity between a Pd content of 25 and 75 % of total metal loading, suggesting that the relationship between catalyst composition and activity is sensitive to catalyst preparation parameters.

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Figure 1. Catalytic activity of 1%AuPd/TiO_2 towards H_2O_2 synthesis and its subsequent degradation as a function of Pd content at 2 °C.
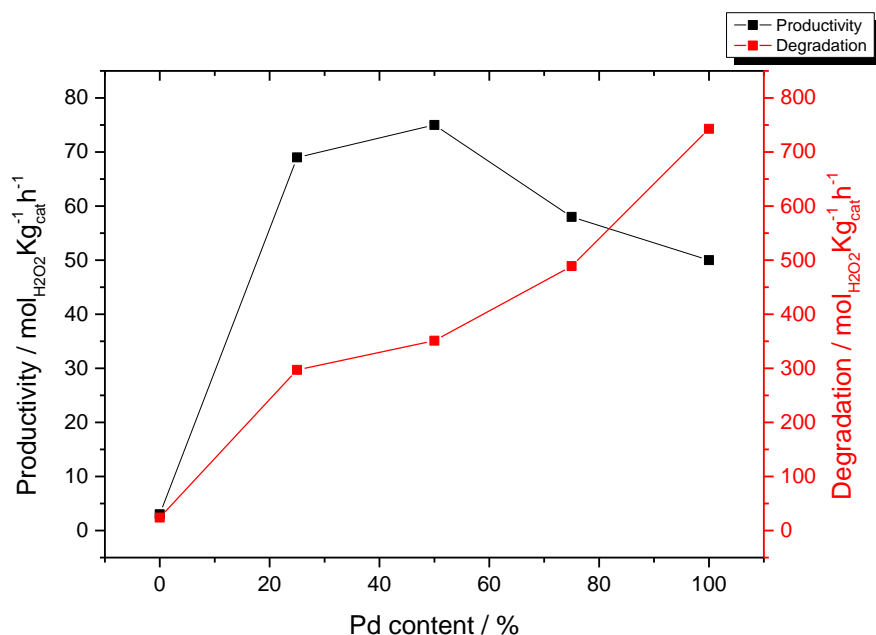
The majority of research into AuPd supported catalysts for the direct synthesis of H_2O_2 has focussed on the use of sub-ambient temperatures, known to both promote H_2O_2 stability through inhibition of the undesirable decomposition pathway.[35] However, the costs associated with the use of sub-ambient temperatures are likely to prohibit its application in the direct synthesis of H_2O_2 on an industrial scale. As such, we next chose to investigate the effect of the Au: Pd ratio on catalytic activity towards H_2O_2 synthesis and subsequent degradation at a temperature of 25 °C (Figure 2). As expected, given the low stability of H_2O_2 even at mild temperatures, rates of H_2O_2 degradation increase significantly for all catalysts, with the exception of the 1%Au/TiO_2 catalyst which was observed to offer rates of H_2O_2 synthesis (3 $mol_{H2O2}kg_{cat}^{-1}h^{-1}$) and degradation (24 $mol_{H2O2}kg_{cat}^{-1}h^{-1}$) near identical to that observed at sub-ambient temperatures. Again, as under our standard reaction conditions, rates of H_2O_2 degradation correlate well with Pd content, with degradation rates of 1 %Pd / TiO_2 (743 $mol_{H2O2}kg_{cat}^{-1}h^{-1}$) over twice that of the 0.75 %Au-0.25 %Pd / TiO_2 catalyst (297 $mol_{H2O2}kg_{cat}^{-1}h^{-1}$). Interestingly H_2O_2 synthesis rates of 0.75 %Au-0.25 %Pd / TiO_2 (69 $mol_{H2O2}kg_{cat}^{-1}h^{-1}$) and 0.5 %Au-0.5 %Pd / TiO_2 (75 $mol_{H2O2}kg_{cat}^{-1}h^{-1}$) bimetallic catalysts are similar to those observed

under sub-ambient reaction temperatures, despite the significant increase in H_2O_2 degradation rates, indicating that these catalysts are tolerant to the use of ambient reaction temperature. The observation that rates of H_2O_2 synthesis are maintained to a greater extent over Au-rich catalysts highlights the key role Au plays in achieving high catalytic performance.

Figure 2. Catalytic activity of 1%AuPd/TiO_2 towards H_2O_2 synthesis and its subsequent degradation as a function of Pd content at 25 °C, in a water/methanol reaction medium.
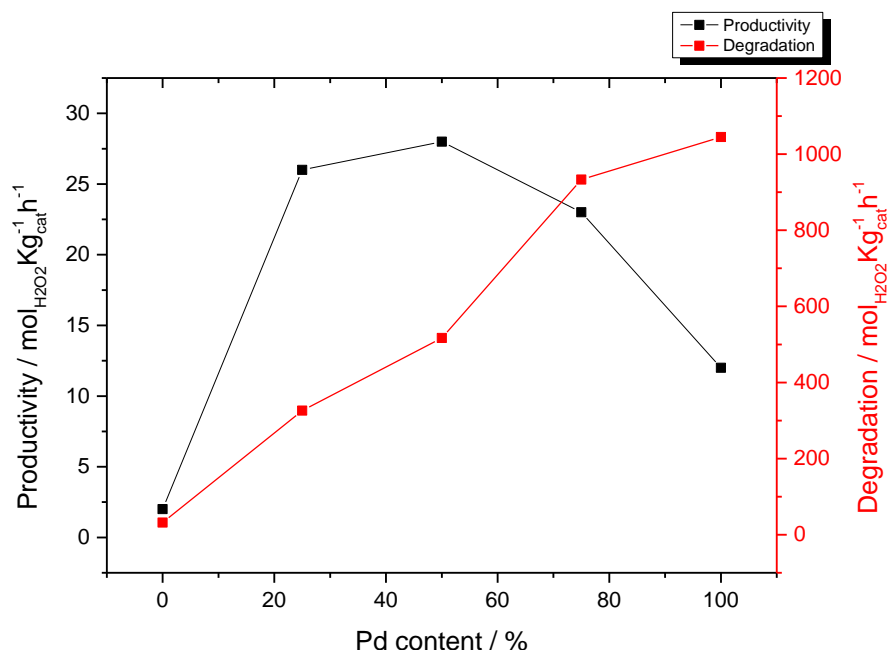

H_2O_2 direct synthesis reaction conditions: Catalyst (0.01g), H_2O (2.9g), MeOH (5.6g), 5% H_2 / CO_2 (420 psi), 25% O_2 / CO_2 (160 psi), 0.5 h, 25 °C 1200 rpm.
H_2O_2 degradation reaction conditions: Catalyst (0.01g), H_2O_2 (50 wt.% 0.68 g) H_2O (2.22g), MeOH (5.6g), 5% H_2 / CO_2 (420 psi), 0.5 h, 25 °C 1200 rpm.

A number of different solvents have been studied for the direct synthesis of H_2O_2, including water,[37] ethanol[38, 39] and methanol.[40] Water is most often utilised due to its non-toxic, non-flammable nature, with the low solubility of reaction gases in water often overcome through the use of an alcohol co-solvent, resulting in improved mass transfer of reactants and in turn increased rates of H_2O_2 production.[39, 41] With Paunovic et al. providing a comprehensive study on the choice of co-solvent.[42] In particular, methanol has been widely studied as a co-solvent, due to increased reactant solubility but also as it results in the suppression of H_2O_2 decomposition.[35] Furthermore, the key role of the solvent has been recently elucidated by Wilson and Flaherty, with the presence of protic solvents, such as water and methanol shown to be key to H_2O_2 production.[43] Whilst the use of alcohol/water solvent mixtures has been shown to lead to increased H_2O_2 synthesis rates and indeed may be appropriate for a number of industrially relevant applications, most industrial applications require H_2O_2 solutions diluted in water. In particular, the use of H_2O_2 as a bleaching agent for pulp and textiles favours the use of H_2O_2 diluted in water, in part due to the additional costs

associated with the separation of methanol from the product streams. Therefore, we have investigated the effect of carrying out H_2O_2 synthesis and degradation reactions in H_2O-only at a temperature of 25 °C (Figure 3). As reported previously the 1 %Au/TiO_2 catalyst was observed to offer H_2O_2 synthesis and degradation activities almost identical to those observed under our standard reaction conditions, which are more conducive to H_2O_2 production. Despite the relative invariance of the 1 %Au/TiO_2 catalyst towards changes in reaction conditions, the H_2O_2 synthesis productivity of the monometallic catalyst is an order of magnitude lower than the bimetallic Au-Pd catalysts, highlighting the benefit combining Au with Pd. For all other catalysts, H_2O_2 synthesis rates were significantly lower under these conditions compared to those observed using a H_2O/methanol solvent system at the same reaction temperature and this can be attributed to a combination of decreased solubility of H_2 in water and the ability of methanol to enhance H_2O_2 stability. Interestingly, under these conditions H_2O_2 degradation rates of the 0.75 %Au-0.25 %Pd / TiO_2 catalyst (326 $mol_{H2O2}kg_{cat}^{-1}h^{-1}$) are comparable to that observed in the presence of a water/methanol solvent (297 $mol_{H2O2}kg_{cat}^{-1}h^{-1}$) again clearly highlighting the importance of Au in maintaining catalytic selectivity towards H_2O_2. It should be noted that under these reaction conditions all Pd containing catalysts offer H_2O_2 synthesis rates significantly greater than that previously reported for the nitric acid washed 2.5%Au-2.5%Pd / C catalyst (4 $mol_{H2O2}kg_{cat}^{-1}h^{-1}$)[37] which we have observed to be completely selective towards H_2O_2 under our standard reaction conditions.[44] Indeed, the H_2O_2 synthesis activity of the 0.5%Au-0.5 %Pd/TiO_2 catalyst (28 $mol_{H2O2}kg_{cat}^{-1}h^{-1}$) is seven times that of the nitric acid washed 2.5%Au-2.5%Pd/C catalyst, despite a much lower metal loading.

Figure 3. Catalytic activity of 1%AuPd/TiO$_2$ towards H$_2$O$_2$ synthesis and its subsequent degradation as a function of Pd content, at 25 °C in a water only reaction medium.

Such unfavourable reactions conditions have been previously explored by Crole et al., who report that a 2.5%Au-2.5%Pd/TiO$_2$ catalyst prepared by conventional impregnation exhibited a H$_2$O$_2$ synthesis activity of 24 mol$_{H2O2}$kg$_{cat}^{-1}$h^{-1}.[45] The analogous modified impregnation prepared catalyst with equal amount of Au and Pd (on a weight basis) presented in this work show comparable H$_2$O$_2$ synthesis activity (28 mol$_{H2O2}$kg$_{cat}^{-1}$h^{-1}) despite containing significantly less metal, and as a result, are considerably more active on a per metal basis.

The wide range over which H$_2$/O$_2$ gas mixture is explosive (5-95 v/v% for H$_2$ in O$_2$) necessitate the use of 'inert' diluent gases to operate below the lower explosive limit. Often CO$_2$ has been chosen as a diluent for H$_2$/O$_2$ gas mixtures due in part to the acidification effect of CO$_2$ on the reaction solvent, forming carbonic acid in-situ. It is well known that H$_2$O$_2$ stability is improved through the use of acidic conditions, through inhibition of the H$_2$O$_2$ decomposition pathway.[46, 47] Furthermore, the presence of CO$_2$ has been shown to lead to an increase in H$_2$ solubility in a range of organic solvents including methanol.[48] However, a similar enhancement is not observed in water only systems.[49] The increased costs associated with using CO$_2$ as a gaseous diluent is, however, likely to preclude its application on an industrial scale. We therefore investigated the effect of replacing the CO$_2$ with a less expensive diluent, N$_2$, for the direct synthesis of H$_2$O$_2$ and its subsequent degradation (Figure 4). As expected, catalytic selectivity towards H$_2$O$_2$ decreases, while the degradation rates greatly increase. In

particular, the degradation activity of the 0.5%Au-0.5%Pd/TiO_2 catalyst (1019 $mol_{H2O2}kg_{cat}^{-1}h^{-1}$) doubled with the use of N_2 in comparison to that observed in the presence of CO_2 (517 $mol_{H2O2}kg_{cat}^{-1}h^{-1}$), which was accompanied by a corresponding decrease in H_2O_2 synthesis rates (13 $mol_{H2O2}kg_{cat}^{-1}h^{-1}$). As for the other reaction conditions presented in this work the presence of high Au content to maintain catalytic performance under such unfavourable conditions, with the 0.75%Au-0.25%Pd/TiO_2 catalyst observed to offer the greatest rates of H_2O_2 synthesis (16 $mol_{H2O2}kg_{cat}^{-1}h^{-1}$) when using H_2O as the solvent and N_2 as reaction gas diluent.

Figure 4. Catalytic activity of 1%AuPd/TiO_2 towards H_2O_2 synthesis and its subsequent degradation as a function of Au:Pd ratio, at 20 ^{0} C, water only reaction medium and N_2 as reaction gas diluent.

H_2O_2 direct synthesis reaction conditions: Catalyst (0.01g), H_2O (8.5g), 5% H_2 / N_2 (420 psi), 25% O_2 / N_2 (160 psi), 0.5 h, 25 ^{O}C 1200 rpm.
H_2O_2 degradation reaction conditions: Catalyst (0.01g), H_2O_2 (50 wt.% 0.68 g) H_2O (7.82g), 5% H_2 / N_2 (420 psi), 0.5 h, 25 ^{O}C 1200 rpm.

Comparison of catalytic selectivity towards H_2O_2 and H_2 conversion for the 0.5%Au-0.5%Pd/TiO_2 catalyst during the H_2O_2 synthesis reactions, reveals how the choice of conditions, namely solvent, temperature and gas diluent can influence the catalytic performance (Table 1).

Perhaps most interesting is the significant increase in H_2 conversion observed with the increase in reaction temperature, with this increasing from 40 % under sub-ambient a reaction temperature of 2 °C to 56% for the analogous reaction carried out at 25 $^\circ$C. This can be related to the increased solubility of H_2 in methanol with increasing temperature. The significant decrease in selectivity towards H_2O_2 upon increasing reaction temperature, from 44 % at a

reaction temperature of 2 °C to 14 % at 25 °C is attributed to the increased rate of H_2O_2 degradation as well as the low stability of H_2O_2.

Furthermore, the role of the gaseous diluent is clearly highlighted, with catalytic selectivity towards H_2O_2 and H_2O_2 concentration decreasing significantly with the replacement of the gaseous diluent from CO_2 (8 %, 0.06 wt.% H_2O_2) to N_2 (3 %, 0.02 wt.% H_2O_2), although the rate of H_2 conversion remains similar. It should be noted that, even under ideal reaction conditions, H_2O_2 concentrations are significantly lower than those typically produced via the current industrial means of production. This highly efficient process is able to produce H_2O_2 concentrations of approximately 0.6-1.8 wt.%,[50] which is then raised through numerous distillation steps to exceed 70 wt.% prior to shipping. However, typical applications utilise much lower final concentrations of H_2O_2, requiring dilution by the end user prior to use.
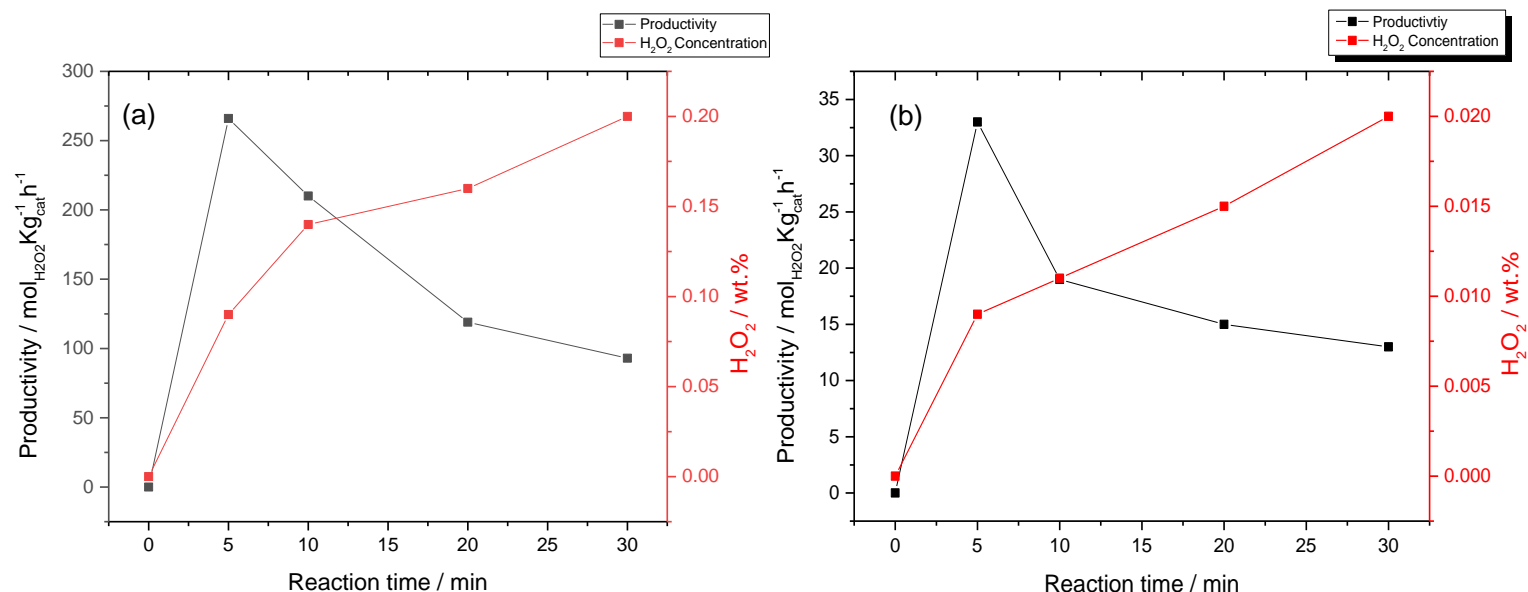
Table. 1. The role of reaction conditions on H_2 conversion and H_2O_2 selectivity over 0.5%Au-0.5%Pd / TiO_2.

Reaction Conditions (temp / solvent / gas diluent)	H_2 Conversion / %	H_2O_2 Selectivity / %	Productivity / $mol_{H2O2}kg_{cat}^{-1}h^{-1}$	H_2O_2 concentration / wt.%
2^0 C, H_2O/MeOH, CO_2	40	44	93	0.20
25^0 C, H_2O/MeOH, CO_2	56	14	75	0.15
25^0 C, H_2O, CO_2	29	8	28	0.06
25^0 C, H_2O, N_2	22	3	13	0.02

H_2O_2 direct synthesis reaction conditions: Catalyst (0.01g), solvent (8.5g), 5% H_2 / (N_2 / CO_2) (420 psi), 25% O_2 / (N_2 / CO_2) (160 psi), 0.5 h, 2-25 °C 1200 rpm.

Further comparison of catalytic activity of the 0.5%Au-0.5%Pd/TiO_2 catalyst towards H_2O_2 formation under ideal (2°C, H_2O/MeOH, CO_2) and non-ideal (25°C, H_2O, N_2) conditions can be seen in Figure 5. It is possible to observe that under both sets of reaction conditions H_2O_2 yield tends away from a linear relationship with reaction time, with this in part due to the activity of the catalyst towards H_2O_2 degradation, in particular under non-ideal reaction conditions. It is noteworthy that under both sets of reaction conditions H_2O_2 concentration continues to increase throughout the course of the reaction time studied. However, H_2O_2 concentrations produced using our optimised conditions (0.02 wt. %) are an order of magnitude greater than that observed when using non-ideal conditions (0.002 wt.%) clearly demonstrating the key role reaction conditions play in determining catalytic activity.

Figure 5. Reaction time profile for 0.5%Au-0.5%Pd/TiO_2 under (a) conditions optimised for H_2O_2 formation and (b) those more likely to be industrially applicable.
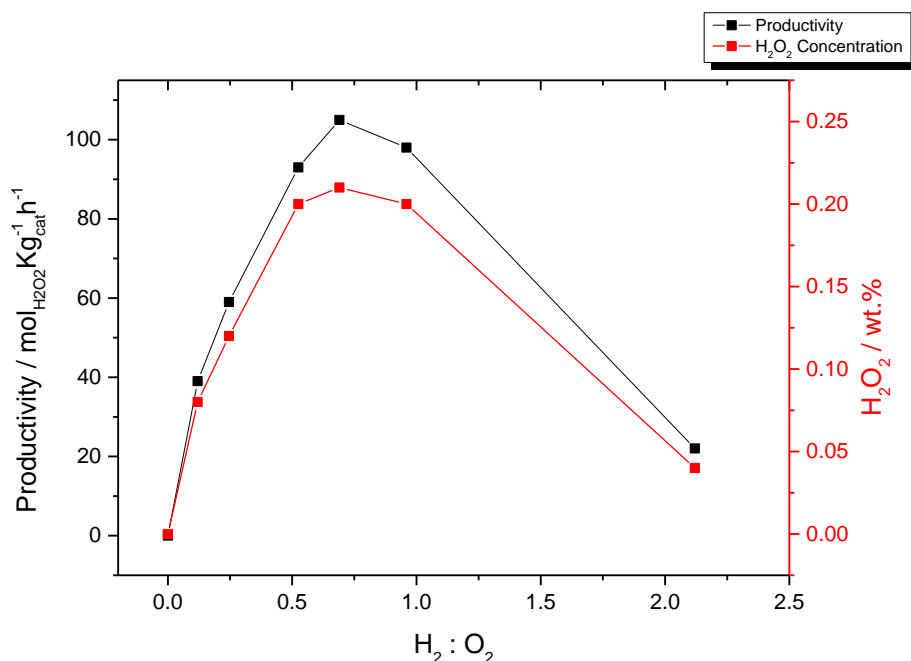

[a]**H_2O_2 direct synthesis reaction conditions**: Catalyst (0.01g), H_2O (2.9g), MeOH (5.6g), 5% H_2 / CO_2 (420 psi), 25% O_2 / CO_2 (160 psi), 0.5 h, 2 ^{O}C 1200 rpm.
[b]**H_2O_2 direct synthesis reaction conditions**: Catalyst (0.01g), H_2O (8.5g), 5% H_2 / N_2 (420 psi), 25% O_2 / N_2 (160 psi), 0.5 h, 25 ^{O}C 1200 rpm.

These observations, when coupled with the variation in H_2 conversion between reaction conditions optimised for H_2O_2 synthesis and those more likely to be adopted on an industrial scale (Table 1) suggest that catalytic performance is likely governed by gas solubility. In order to establish the extent that H_2 availability dictates H_2O_2 formation rate we varied H_2: O_2 ratio while maintaining total pressure, under conditions previously optimised for H_2O_2 synthesis (Figure 6). As expected we observe a clear variation in H_2O_2 synthesis activity, with the optimal H_2:O_2 ratio found to be 0.69 resulting in a marginal increase in catalytic activity (105 $mol_{H2O2}kg_{cat}^{-1}h^{-1}$) over that observed under our standard reaction conditions where H_2: O_2 is equal to 0.52 (93 $mol_{H2O2}kg_{cat}^{-1}h^{-1}$). As H_2: O_2 ratios diverge significantly from a value of 0.69 we observe a considerable decrease in H_2O_2 synthesis activity, with this attributed to a combination of limited reagent availability and an increase in H_2O_2 degradation, with the hydrogenation of H_2O_2 in particular likely responsible for H_2O_2 consumption at increased H_2: O_2 ratios. Finally it should be noted that there is little variation in CO_2 content regardless of H_2:O_2 ratio, with the formation of carbonic acid in-situ known to stabilise H_2O_2.[41] In fact the CO_2 content of the gas mixture varies by only approximately 12 % on moving from a H_2: O_2 ratio of 0.12 to 2.12. As such it is reasonable to assume that the significant loss in activity is not related to lower CO_2 content.

Figure 6. The effect of H_2: O_2 ratio on H_2O_2 concentration over 0.5%Au-0.5%Pd/TiO_2 under optimal reaction conditions.

H_2O_2 direct synthesis reaction conditions: Catalyst (0.01g), H_2O (2.9g), MeOH (5.6g), 5% H_2 / CO_2 (420 psi), 25% O_2 / CO_2 (160 psi), 0.5 h, 2 ^{O}C 1200 rpm.

Catalyst Characterisation.

In order to determine if a change in mean nanoparticle size or metal dispersion can account for the difference in catalytic selectivity towards H_2O_2, we investigated the bi- and mono-metallic AuPd catalysts by both XRD (Figure S.1) and TEM (Table 2, Figure S.2). Analysis by XRD reveals that upon impregnation of Au and Pd and after exposure to a reductive heat treatment at 400 ^{0} C no reflections associated with Au or Pd could be observed, indicating the highly dispersed nature of metal nanoparticles. The high metal dispersion is further corroborated by TEM analysis which shows a relatively tight particle size distribution, which is often difficult to achieve for AuPd catalysts prepared by conventional wet impregnation methods.[51] However, the presence of some larger nanoparticles (>10 nm) is observed, with these likely to be Au dominant in composition, as previously reported in the literature.[51-53]

It is observed that upon addition of Pd, mean particle size decreases significantly from 8.4 nm for the 1%Au / TiO_2 catalyst to 2.8 nm for the 0.5%Au-0.5%Pd/TiO_2 catalyst, which is in agreement with our previous studies.[33]. The bimetallic catalysts of varying metal composition show similar activity towards the direct synthesis of H_2O_2 under all conditions investigated despite exhibiting a discrepancy in mean particle size, which suggests that particle size alone is not responsible for the activity of the catalysts. Previous investigations

by Tian et al.[54] revealed that the catalytic performance of mono-metallic Pd catalysts remains unchanged when particle size is increased beyond 2.5 nm, which is also in agreement with our findings.[55] It should be noted that although the presence of Pd in the 1%Pd/TiO$_2$ catalyst has been established by EDX analysis (Figure S.3) we are unable to determine mean nanoparticle size via TEM, due to issues associated with resolution limits. As previously reported by Sankar et al.[33], analysis by EDX reveals the highly dispersed nature of Pd on the support and as such we ascribe the inability to observe Pd via TEM to be a result of small nanoparticle size, rather than the poor dispersion of Pd.

Table 2. Particle Size of 1%AuPd/TiO$_2$ catalysts as determined by TEM.

Catalyst	Mean Particle Size / nm (Standard Deviation)
1%Au / TiO$_2$	8.4 (3.0)
0.75%Au-0.25%Pd/TiO$_2$	4.8 (5.2)
0.5%Au-0.5%Pd/TiO$_2$	2.8 (0.7)
0.25%Au-0.75%Pd/TiO$_2$	4.9 (1.4)
1%Pd / TiO$_2$	n.d

All catalysts exposed to a reductive heat treatment (4 h, 400 ^{0} C, 10 ^{0} Cmin^{-1}, 5%H$_2$/Ar).
n.d: unable to determine.

It is well known that it is possible to tailor catalytic activity and selectivity through modification of Pd^{2+} : Pd^0, with metallic Pd widely reported to be more active towards H$_2$O$_2$ synthesis than PdO.[56, 57] Indeed, there is growing support within the literature that Pd^0 is the true active site for H$_2$O$_2$ synthesis.[52, 58] XPS analysis (Table 3) reveals that there is minimal change in Pd^{2+} : Pd^0 ratio upon the incorporation of Au into a 1 %Pd / TiO$_2$ catalyst, which correlates well with H$_2$O$_2$ synthesis rates. Although it should be noted that it was not possible to determine Pd^{2+}:Pd^0 ratio for the 0.75 %Au-0.25 %Pd/TiO$_2$ catalyst due to the low Pd content.

It is possible to correlate the maintenance of H$_2$O$_2$ synthesis rates of the bi-metallic AuPd catalysts with catalytic activity towards H$_2$O$_2$ degradation, which decreases significantly upon Au introduction. It is this enhancement in selectivity which is believed to be responsible for the minimal change in H$_2$O$_2$ synthesis rates observed over the supported AuPd catalysts regardless of Pd content. The ability of Au to enhance catalytic performance through incorporation into supported Pd catalysts is well known. Wilson et al. have recently observed that the greater catalytic performance of Au-rich, bi-metallic AuPd catalysts is as a result of significant electronic changes made to Pd by Au, with the activation enthalpies for both H$_2$O$_2$ formation and the hydrogenation of H$_2$O$_2$ to H$_2$O increasing with Au content.[59] While it is also possible that with increasing Au content there is an inhibition in the formation of contiguous Pd ensembles which have previously been attributed to lead to increased cleavage of the O-O bond present in both H$_2$O$_2$ and O$_2$, leading to the formation of H$_2$O and a loss of catalytic selectivity.[60] It is likely that both electronic and geometric modifications contribute

to the enhancement in catalytic performance observed with the addition of Au to a supported Pd catalyst.

Table 3. Elemental Surface Composition of 1%AuPd/TiO$_2$ catalysts as determined by XPS analysis.

Catalyst	Au: Pd	Pd $^{2+}$: Pd^0
1%Au / TiO$_2$	-	-
0.75%Au-0.25%Pd/TiO$_2$	0.71	n.d.
0.5%Au-0.5%Pd/TiO$_2$	0.32	0.29
0.25%Au-0.75%Pd/TiO$_2$	0.15	0.30
1%Pd / TiO$_2$	-	0.29

All catalysts exposed to a reductive heat treatment (4 h, 400 ^{0} C, 10 ^{0} Cmin^{-1}, 5%H$_2$/Ar).
n.d: unable to determine

Analysis of Au and Pd leaching after H$_2$O$_2$ synthesis via ICP (Table S. 2) reveals that under our standard reaction conditions and those considered to be the least conducive to H$_2$O$_2$ stability (water only solvent, 25 °C and N$_2$ diluent) leaching of Au and Pd is minimal. We observe no Au leaching under either set of reaction conditions, while leaching of Pd is minimal (0.2 %) and only observed under reaction conditions that are less favourable to H$_2$O$_2$ stability. The high stability of supported AuPd catalysts for the direct synthesis of H$_2$O$_2$ have been well reported in the literature when prepared by a conventional wet impregnation methodology [34, 55] and we can now report a similar high stability of catalysts produced via a modified impregnation procedure.

Conclusion.

In conclusion we have investigated the effect of key reaction conditions on the catalytic activity towards the direct synthesis and subsequent degradation of H$_2$O$_2$, over a series of stable 1%AuPd/TiO$_2$ catalysts prepared by a modified impregnation procedure, in a batch reactor. We highlight that the presence of Au is key in maintaining catalytic performance under conditions that are considered less conducive to H$_2$O$_2$ formation but more likely to be favoured on an industrial scale. However, selectivity is still a major concern and although we recognise the ability to better discern differences in catalytic performance under more realistic industrial conditions it is clear that further efforts on catalyst design are now required.

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