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PHILOSOPHICAL TRANSACTIONS A

Direct synthesis of hydrogen peroxide in water at ambient temperature

David A. Crole, Simon J. Freakley, Jennifer K. Edwards and Graham J. Hutchings*

Cardiff Catalysis Institute and School of Chemistry, Main Building, Park Place, Cardiff, CF10 3AT, UK

Summary

The direct synthesis of hydrogen peroxide from hydrogen and oxygen has been studied using an Au-Pd/TiO$_2$ catalyst. The aim of this work is to understand the balance of synthesis and sequential degradation reactions using an aqueous, stabiliser-free solvent at ambient temperature. The effects of the reaction conditions on the productivity of hydrogen peroxide formation and the undesirable hydrogenation and decomposition reactions are investigated. Reaction temperature, solvent composition and reaction time have been studied and indicate that when using water as the solvent the hydrogen peroxide decomposition reaction is the predominant degradation pathway, which provides new challenges for catalyst design which has previously focused on minimising the subsequent hydrogenation reaction. This is of importance for the application of this catalytic approach for water purification.

Introduction

Hydrogen peroxide (H$_2$O$_2$) is a significant commodity chemical with an annual usage now exceeding 3 million tonnes per annum and increasing[1]. H$_2$O$_2$ is used in a number of selective oxidation processes, such as the synthesis of propene oxide from propene and H$_2$O$_2$[2], and also non-synthetic applications which make use of its oxidative properties such as cleaning and bleaching. The existing indirect anthraquinone process for producing H$_2$O$_2$ is highly optimised to give high H$_2$ selectivity towards H$_2$O$_2$, however, it only proves to be economically viable when operated at a large scale, typically 10^5 tons/annum, and hence production currently has to be centralised. Due to this, H$_2$O$_2$ is transported to the point of use in a high concentration aqueous solution with added stabilisers, necessitating dilution and potentially removal of stabilisers for it to be effective for many uses, particularly bleaching applications when it is used in very dilute form (3-8 vol%)[3].

The ability to produce H$_2$O$_2$ at a desired concentration at the point of use could prove to be a green and economical process. This could potentially be achieved via the direct synthesis of H$_2$O$_2$ from oxygen and hydrogen to localise the supply of H$_2$O$_2$. Whilst a conceptual simple reaction unfortunately the formation of water is thermodynamically preferred and so the design of the catalyst for the synthesis reaction is of prime importance. Monometallic Pd catalysts have been extensively studied for this reaction[3-5], however, these catalysts can hydrogenate H$_2$O$_2$ if no acid or halide stabilisers are present. Hutchings and co-workers found that Au–Pd catalysts are selective and productive, even in the absence of promoters such as acid and halides[6].

Various solvents, generally consisting of water and/or alcohols, in combination with acid and/or halide promoters, have been used for the heterogeneously catalysed direct synthesis of H_2O_2. We have extensively reported experiments using a methanol and water mixture in an approximate 2:1 ratio, generally in the absence of acid or halides([1], [6], [7]). Lunsford and co-workers utilised a water or ethanol solvent with the addition of chloride, bromide, hydrochloric acid and sulphuric acid promoters([8-11]). Choudhary and co-workers utilise an acidic aqueous medium (sulphuric or phosphoric acid), in most cases with one or more halide promoter([12-21]). Park and co-workers use a solution of methanol with dissolved NaBr([22-32]). Biasi and co-workers generally use methanol in the absence of promoters([33-39]), but have also used acidified, bromide-promoted aqueous solutions([40]). There are, however, limited studies on the aqueous direct synthesis of H_2O_2 in the absence of promoters.

If the generation of H_2O_2 in aqueous solution without additives becomes viable, it would negate the necessity for the extraction of synthesised H_2O_2 from the anthraquinone process solvents. Furthermore, the removal of stabilisers (as with anthraquinone process produced H_2O_2) or promoters (as may be necessary for H_2O_2 produced by acid or halide promoted direct synthesis) would not be required. The ability to efficiently generate H_2O_2 in a water stream also presents opportunities for water cleaning technologies to be developed. It is this latter application for which there is considerable current interest as H_2O_2 could then have the potential to replace chlorine as a disinfectant for water which would only be possible if stabiliser-free H_2O_2 can be produced in water.

In this work, we examine the effect on the productivity and hydrogenation/decomposition rates of a 2.5% Au 2.5% Pd / TiO_2 catalyst when reaction conditions are moved towards the use of water as a solvent and room temperature reactions. These conditions present a more environmentally friendly and economical reaction compared to previously used conditions([6]) as there are no energy demands for heating or cooling and the H_2O_2 requires no further extraction/purification. Using this study to help understand the effect of changing reaction parameters on all processes associated with the direct synthesis of H_2O_2 and identify challenges therein will allow for rational design of catalysts for optimal function in an aqueous / ambient temperature reaction condition.

Experimental

Catalyst preparation

The 2.5 wt% Au-2.5 wt% Pd/TiO_2 catalyst was prepared by wet impregnation of TiO_2 (Degussa, Aeroxide P25). A solution of $HAuCl_4 \cdot 3H_2O$ (1.25 ml, 10g Au/ml, Johnson Matthey), solid $PdCl_2$ (0.0208 g, Johnson Matthey) and de-ionised water (1 ml) were combined and stirred at 80 °C until the $PdCl_2$ was completely dissolved. At this point TiO_2 (0.475 g) was added and the mixture continuously stirred and heated until a thick paste was formed. The paste was dried in an oven (110 °C, 16 h), ground to a fine powder and calcined under static air (400 °C, 3 h, 20 °C min^{-1}).

H_2O_2 synthesis, decomposition and hydrogenation

H_2O_2 synthesis, hydrogenation and decomposition experiments were evaluated using a Parr Instruments stainless steel autoclave with a volume of either 100 ml or 50 ml and a maximum working pressure of 14 MPa. To evaluate H_2O_2 synthesis the following reaction conditions were used. The autoclave was charged with catalyst (0.010 g) and solvent (8.5 g HPLC grade H_2O and/or HPLC grade methanol, Fischer Scientific) and sealed. The autoclave was then purged three times with 5% H_2/CO_2 before filling with 5% H_2/CO_2 to a pressure of 2.9 MPa (420 psi) followed by the addition of a further 1.1MPa (160 psi) 25% O_2/CO_2 (both BOC speciality gasses). The reaction mixture was stirred at 1200 rpm at systematically varied reaction times and temperatures. H_2O_2 yield was determined by titrating aliquots of the filtered post-reaction solution with acidified $Ce(SO_4)_2$ solution (c.a. 0.01 M, Sigma Aldrich) in the presence of Ferroin indicator (c.a. 0.1 ml, Sigma Aldrich).

H_2O_2 hydrogenation and decomposition experiments were carried out with a similar procedure to that of H_2O_2 synthesis experiments but only 420 psi (2.9 MPa) 5% H_2/CO_2 or 420 psi (2.9 MPa) 25% O_2/CO_2 were added to the reactor, respectively. Furthermore, a reaction solvent containing 4 wt% H_2O_2, prepared by the addition of H_2O_2 solution (50 wt%, 0.68 g, Sigma Aldrich) to H_2O (7.82 g), was used. The concentration of H_2O_2 in the reaction solution was accurately

determined before and after the reaction by titrating aliquots of the reaction solution with acidified $Ce(SO_4)_2$ in the presence of Ferroin indicator. When a hydrogenation experiment is performed, the measured degree of H_2O_2 degradation represents the sum of both hydrogenation and decomposition processes; thus net hydrogenation can be determined by subtracting the measured decomposition value from the measured total hydrogenation/degradation value, assuming that the reactions happen independently of each other. Aside from the noted differences, reaction parameters are identical to those used for synthesis reactions.

Results and Discussion

In our previous studies on the direct synthesis of H_2O_2,([4](#), [6](#), [41](#)) reaction conditions have been standardised to allow differences in H_2O_2 yield to solely reflect differences in catalyst performance. The reaction parameters in these experiments were a 2.9 g H_2O/5.6 g methanol solvent mixture, temperature of 2 °C and a reaction duration of 30 min (gas compositions and pressures identical to those reported in the experimental procedure).([6](#)) In this work, conditions for the direct synthesis of H_2O_2 are investigated at a range of temperatures and solvent compositions with the aim of understanding how the reaction system affects the balance of H_2O_2 synthesis versus the sequential degradation pathways.

Time on line studies were carried out in the previously utilised H_2O/methanol solvent mixture in addition to H_2O and methanol solvents. Productivity values are reported in figure 1a and show that in each system the productivity is highest at short reaction times as expected when the H_2 concentration will be highest and also the rates of H_2O_2 degradation will be minimal due to the low concentrations of H_2O_2 in the reaction mixtures. Comparing the solvent compositions it is clear to see that the productivity is highest when methanol is used and lowest when H_2O is used across the reaction times investigated. Using Henry's law to compare the solubility of hydrogen in the three solvent compositions shows that hydrogen solubility is around an order of magnitude higher in methanol compared to H_2O, with Henry's constant (H^{cp}) values at 20°C of 9.34×10^{-3} mol atm^{-1} L^{-1} and 8.04×10^{-4} mol atm^{-1} L^{-1} respectively. The amount in ppm of H_2O_2 present in each reaction is shown in figure 1b. We observed that almost all of the H_2O_2 synthesised in the methanol solvent is produced in the first 5 min, whereas in H_2O the maximum H_2O_2 concentration is only attained after 40 min reaction. These observations indicate that the performance of the catalyst in the different solvent compositions is likely to be governed by gas solubility and mass transport effects. The effect of gas solubility can also control the balance of the synthesis / hydrogenation / decomposition pathways in the direct synthesis process shown in scheme 1.

The hydrogenation and decomposition reactions of the different solvent compositions were also studied in an analogous manner using the same catalyst. For the decomposition reaction, figure 2a, it was observed that the relationship between the amounts of H_2O_2 decomposed and time is close to linear for all solvent compositions. It was observed that the least decomposition occurs in the methanol solvent, followed by the H_2O/methanol solvent and the greatest decomposition occurring in the H_2O solvent. These reactions were conducted without the presence of H_2 in the autoclave which indicates the low decomposition rate observed in the methanol solvent is not a result of competitive hydrogenation reactions and in fact H_2O_2 is stabilised in the methanol solvent with respect to the water solvent.

For sequential hydrogenation, figure 2b, we see an inverse of the trend seen for decomposition, with the lowest extent of hydrogenation with respect to time in a H_2O solvent where H_2 solubility will be limited compared to alcohol containing solvent compositions. Methanol and H_2O/methanol solvents appear to have very similar initial rates of hydrogenation, indicating that the addition of 66% methanol to H_2O reduces the mass transport limitations and the catalyst is likely operating in the kinetic regime. The plots for hydrogenation activity tend to plateau at long reaction times; this indicates that after an extended reaction the extent of hydrogenation becomes limited by the availability of hydrogen in solution. These observations indicate that when changing the reaction conditions for the direct synthesis, additional considerations need to be made in terms of catalyst design. If direct synthesis of H_2O_2 is to be successfully achieved in water as solvent, supressing the decomposition reaction becomes an important factor in catalyst design, not only the suppression of the sequential hydrogenation, as has been the focus of all previous research.

Figure 3 shows an extended study of the solvent effects on the three competing reactions. We observe a maximum measured productivity of H_2O_2 during a 30 min reaction in the 34% H_2O solvent, this is the solvent ratio which has previously been found to be optimal for the Au-Pd / TiO_2 catalyst when tested at 2 °C. Increasing the methanol content of the solvent past this point has little effect on the observed productivity, however it increases the rate of H_2O_2 hydrogenation due to the increased H_2 solubility. The observation that the net H_2O_2 produced remains somewhat constant suggests the fact that the synthesis reaction also increases in proportion to the increased H_2 solubility. These results again highlight the need to design catalysts with reaction conditions in mind. In H_2O rich solvent compositions where H_2 availability is low compared to methanol rich solvent compositions, the hydrogenation and decomposition reactions occur with similar rate (600 mol kg$_{cat}^{-}$

^{1} h^{-1} net hydrogenation vs 450 mol kg$_{cat}^{-1}$ h^{-1} decomposition in an aqueous system) so catalyst design should focus on minimising both reactions equally. In methanol rich solvent compositions the synthesis activity is increased due to the higher H$_2$ availability but as a consequence so is the H$_2$O$_2$ hydrogenation reaction. At this condition the rates of hydrogenation are much higher than the rates of decomposition (790 mol kg$_{cat}^{-1}$ h^{-1} net hydrogenation vs 110 mol kg$_{cat}^{-1}$ h^{-1} decomposition in a methanol system) suggesting that when working at conditions with high hydrogen availability, de-convoluting the selective and unselective hydrogen activation is most important.

H$_2$O$_2$ synthesis productivity and the activity of the two degradation processes, decomposition and hydrogenation, at increasing temperatures are shown in figure 4. Net H$_2$O$_2$ productivity was found to decrease significantly with increasing temperature; this is tied to the fact that we see an increase in both degradation processes with increasing temperature. At a temperature of 50 °C we observe for the first time the decomposition rate to be higher than the hydrogenation rate which could be a result of increased thermal decomposition rates of H$_2$O$_2$.

Conclusions

Changing the reaction conditions for the direct synthesis of H$_2$O$_2$ from the 'standard' conditions using methanol/water at 2 °C to 'aqueous / ambient' conditions we observe a marked decrease in H$_2$O$_2$ yield. This is due in part to increased H$_2$O$_2$ degradation that occurs with both an increase in reaction temperature and an increased amount of H$_2$O in the solvent. The decreased yield is also due to a reduced rate of H$_2$O$_2$ synthesis due the reduced H$_2$ solubility that again occurs with both an increase in temperature and an increased amount of H$_2$O in the solvent. The concomitant positive effect of reduced H$_2$ solubility in the 'aqueous / ambient' conditions is that the hydrogenation of H$_2$O$_2$ is relatively less of a concern than under 'standard' conditions. This means that catalysts that are highly active but somewhat unselective due to over hydrogenation under 'standard' conditions may prove productive under the 'aqueous / ambient' conditions that will be required in water purification applications. It is therefore clear that an improved catalyst design is required to synthesise hydrogen peroxide from H$_2$ and O$_2$ in water as solvent at ambient temperature. The main concern to be addressed is the catalyst activity as the catalyst needs to operate with much lower levels of dissolved H$_2$. To achieve this we consider that catalysts with smaller active nanoparticles could provide the improvement required. In addition, changes in the catalyst formulation should be explored using compositions in which gold, which is not particularly active for the direct synthesis of hydrogen peroxide, is substituted for other components such as tin oxide. (42)

Additional Information

Data Accessibility

Readers can contact opendata@cardiff.ac.uk

Competing Interests

The authors have no competing financial interests.

Authors' Contributions

David A. Crole, Simon J. Freakley, Jennifer K. Edwards and Graham J. Hutchings each provided substantial contributions to conception and design, or acquisition of data, or analysis and interpretation of data, drafting the article or revising it critically for important intellectual content and final approval of the version to be published. The research was directed by Graham J. Hutchings.

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Figure and table captions

Figure 1 – Time on line H_2O_2 productivity (a) and yield (b) in water, 34% water / 66% methanol and methanol solvent systems.
■ – Methanol, ● – 34% Water / 66% Methanol, ▲ - Water.
Conditions: Reaction time as indicated, 8.5g solvent, 100 ml autoclave, ambient temperature (20-25°C), 1200rpm, 10mg catalyst, 420 psi H_2/CO_2 + 160 psi $O_2/CO2$.

Figure 2 – Time on line H_2O_2 decomposition (a) and net hydrogenation (b) in water, 34% water / 66% methanol and methanol solvent systems.

■ – Methanol, ● – 34% Water / 66% Methanol, ▲ - Water.

Conditions: Reaction time as indicated, 8.5g solvent, 100 ml autoclave, ambient temperature (20-25°C), 1200rpm, 10mg catalyst, 420 psi H_2/CO_2 (a) or 420 psi O_2/CO_2 (b).

Figure 3 – H_2O_2 productivity, decomposition and net hydrogenation as a function of solvent composition.

■ – Productivity, ● – Net Hydrogenation, ▲ - Decomposition.

Conditions: 30 min reaction time, 8.5g solvent as indicated, 50 ml autoclave, 20°C, 1200rpm, 10mg catalyst, 420 psi H_2/CO_2 + 160 psi O_2/CO_2 (productivity), 420 psi H_2/CO_2 (hydrogenation) or 420 psi O_2/CO_2 (decomposition).

Figure 4 – H_2O_2 productivity, decomposition and net hydrogenation in water as a function of temperature in aqueous solvent.

■ – Productivity, ● – Net Hydrogenation, ▲ - Decomposition.

Conditions: 30 min reaction time, 8.5g H_2O solvent, 50 ml autoclave, temperature as indicated, 1200rpm, 10mg catalyst, 420 psi H_2/CO_2 + 160 psi O_2/CO_2 (productivity), 420 psi H_2/CO_2 (hydrogenation) or 420 psi O_2/CO_2 (decomposition).

Scheme 1

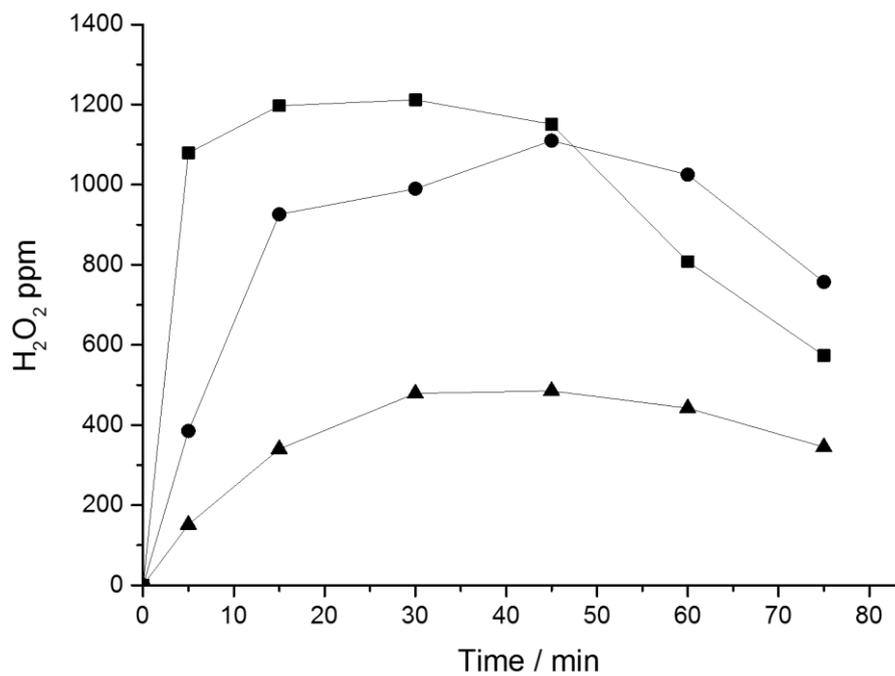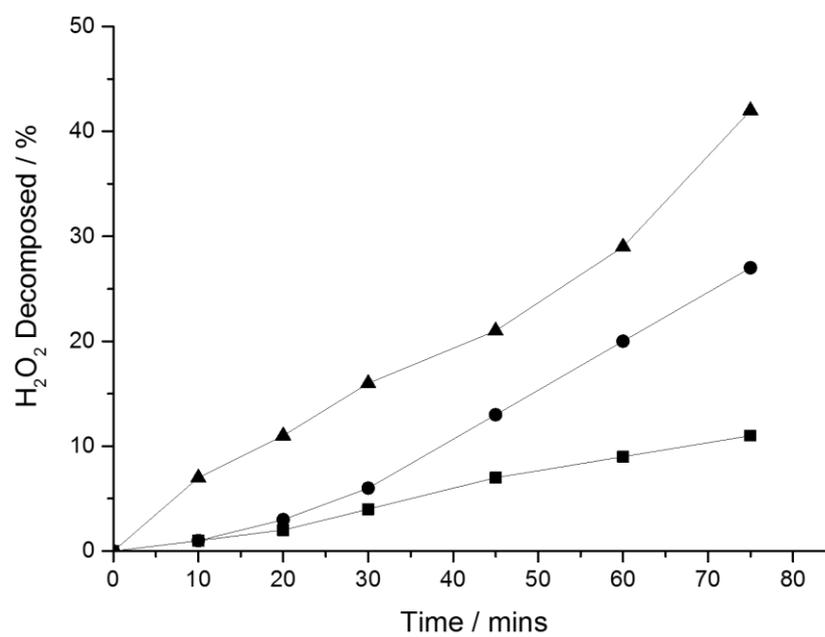Reaction scheme for the direct synthesis of hydrogen peroxide.

Figures

Figure 1

a)
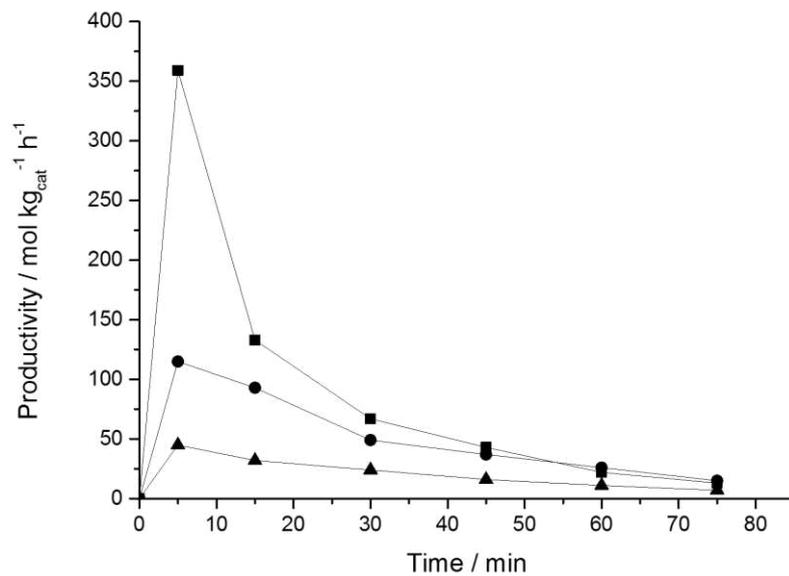
b)

Figure 2

a)

b)
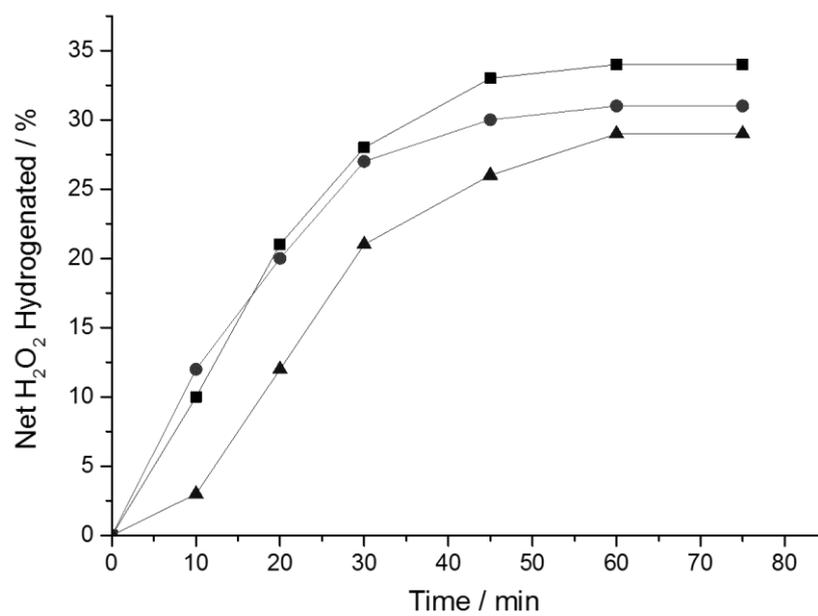
Figure 3

Figure 4

Scheme 1

$$H_2 + O_2 \longrightarrow H_2O_2 \xrightarrow{\ H_2\ } 2\,H_2O$$

$$H_2O + 0.5\,O_2$$