ISSN: 0974-5823 Vol. 7 No. 4 April, 2022

International Journal of Mechanical Engineering

THE DIFFERENT METHODS OF USING ORGANIC SOLVENTS FOR DIRECT SYNTHESIS OF HYDROGEN PEROXIDE

S. HEMALAKSHMI[1], A. ILAKIYA[1], A. ABIYA[1] and S. RAMESH[1*]

Department of Chemistry, Theivanai Ammal College for Women (A), Villupuram, Tamil Nadu, India

Abstract

In this paper the direct synthesis of hydrogen peroxide (H_2O_2) from hydrogen and oxygen using gold palladium supported catalysis is investigated. The direct route represents a greener and suitable alternative to the current industrial manufacturing process. The main objectives of this study was to achieve the industrial requirements of H_2O_2 yields and selectivity, which would make the direct process industrially viable. In order to reach the required target, two innovative approaches for the direct synthesis of H_2O_2 were examined. Today catalysis is better defined as the acceleration of a chemical reaction due to the presence of a catalyst. A catalyst work by providing an alternative reaction mechanism comprising a different transition state characterized by a lower activation energy (E_a). Consequently, more molecules possesses sufficient energy to reach the transition state and overcome the energy activation barrier, allowing them to react and be transformed into products. this process can be described by the Boltzmann distribution equation.

INTRODUCTION:

Hydrogen peroxide is a clear, colourless liquid which is completely miscible with water. It is the simplest peroxide containing a single oxygen-oxygen bond. It has a skewed structure with a dihedral angle of 111.5o in the gas phase, which minimizes repulsion between the lone pairs and O-H bond pairs. In the liquid and solid state the angle is affected by hydrogen bonding.

Hydrogen peroxide in the gas phase highlighting the skewed angle and bond lengths. Compared to water, the energy content of hydrogen peroxide is much higher, seen from the heats of formations for water and H_2O_2.

1) H_2 + ½ O_2 H_2O ?H = -286 kJmol-1

2) H_2 + O_2 H_2O_2 ?H = -188 kJmol-1

The decomposition of hydrogen peroxide produces water, gaseous oxygen and heat (100.4 kJ mol-1). The rate of decomposition can be controlled by the temperature and concentration of the peroxide, as well as on the presence of impurities and stabilisers. Since the activation energy for the cleavage of the oxygen-oxygen bond is rather low (?H = -71 kJ mol-1), traces of many substances can start the reaction, including most of the transition metals and their compounds, as well as certain organic compounds. Although H_2O_2 will oxidize some reactions unaided, for faster reactions the addition of an activating agent, such as Fentons reagent, is required.

Hydrogen peroxide is a strong, versatile oxidant, which can oxidise a broad variety of inorganic and organic substrates in liquid phase reactions. It is effective over the whole pH range, with high oxidation potential,

Acidic – H_2O_2 + 2H+ + 2e2H_2O (E0 = 1.763 eV at pH 0)

Alkaline - H_2O_2 + 2OHH_2O + 2O_2 + 2e- (E0 = 0.878 eV at pH 14)

H_2O_2 possesses both nucleophillic and electrophillic properties. In alkaline solution H_2O_2 dissociates forming a perhydroxyl anion, HO- , which is a powerful nucleophile reacting readily with a number of compounds including aldehydes and electron deficient olefins. In a highly acidic medium H_2O_2 can be protonated, forming $H_3O_2{}^+$, which is crucial to its use in wastewater treatment where it has the ability to reduce chlorine and hypochlorite. This electorphillic form can also be utilised for phenol hydroxylation.

Green Chemistry:

Green chemistry, also known as sustainable chemistry, is the design, manufacture and application of chemical products that reduce or eliminate the use or generation of substances that are hazardous to human health and the environment. It is a science-based non-regulatory, economically driven approach toward sustainable development that has grown substantially since the concept fully emerged in the 1990’s. Today, the following 12 Principles of Green Chemistry developed by Paul Anastas and John, C., Warner, 4 are used as a guideline and criteria by chemical scientists.

1. **Prevention** – It is better to prevent waste than to treat or clean up waste after it has been created.
2. **Atom Economy** – Synthetic methods should be designed to maximise the incorporation of all materials used in the process into the final product.

3. **Less Hazardous Chemical Synthesis** – Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

4. **Designing Safer Chemicals** – Chemical products should be designed to affect their desired function while minimising their toxicity.

5. **Safer Solvents and Auxiliaries** – The use of auxiliary substances (e.g. solvents, separation agents, etc) should be made unnecessary wherever possible and innocuous when used.

6. **Design for Energy Efficiency** – Energy requirements of chemical processes should be recognised for their environmental and economic impacts and should be minimised. If possible, synthetic methods should be conducted at ambient temperature and pressure.

7. **Use of Renewable Feedstock's** – A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.

8. **Reduce Derivatives** – Unnecessary derivatisation (use of blocking groups, protection /de-protection, temporary modification of physical/chemical processes) should minimised or avoided if possible, because such steps require additional reagents and can generate waste.

9. **Catalysis** – Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

10. **Design and Degradation** – Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.

11. **Real – Time anyalysis for Pollution Prevention**– Analytical methodologies need to be further developed to allow for real-time, in process monitoring and control prior to the formation of hazardous substances.

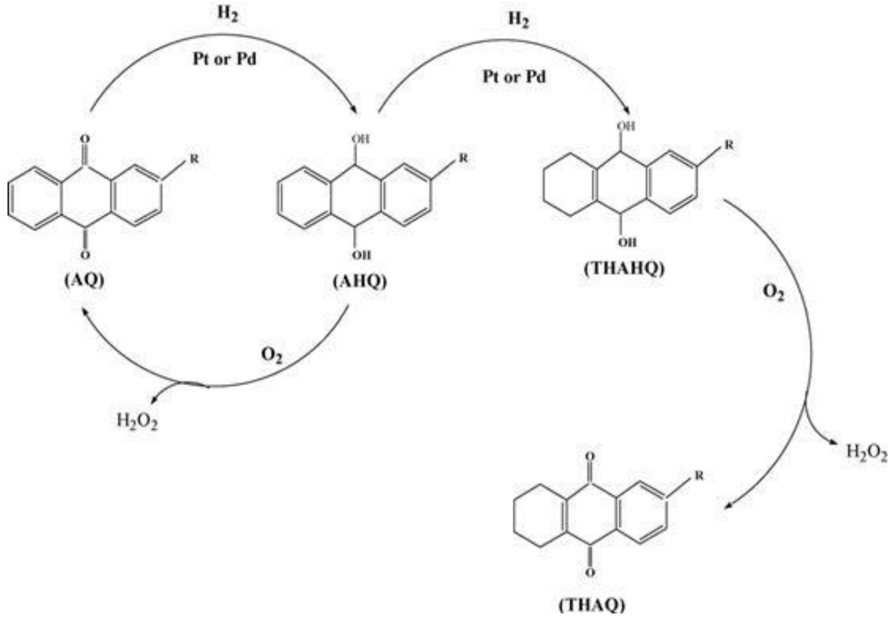
12. **Inherently Safer Chemistry for Accident Prevention** – Substances and the form of a substance used in a chemical process should be chosen to minimise the potential for chemical accidents, including releases, explosions and fires.

MATERIAL AND METHOD

In a rapidly expanding market the annual world production of hydrogen peroxide, currently c.a. 2.2 million metric tons growing at roughly 10 % per annum, however, it is forecast to reach 4.67 million metric tons by 2017, mainly due to its demand in large scale chemical synthesis.

H_2O_2 was first obtained on an industrial scale via a wet chemical process by treating barium peroxide with nitric acid. However, the high production costs limited H_2O_2 application. This was followed by large-scale production of hydrogen peroxide by electrolysis which can be traced back to Meidinger in 1895. This proved to be an economically viable process for the production of highly concentrated solutions of hydrogen peroxide of high purity and stability however, on-site electrochemical production of H_2O_2 for industrial applications requires a production method with higher reaction rates, higher efficiency and lower costs.

Currently, the anthraquinone oxidation (AO) process accounts for >95% hydrogen peroxide production worldwide. This industrial process was first developed by Hans – Joachim Riedl and Georg Pfliederer, in 1939, with the first production plant being introduced by IG Farben-industrie in Germany in the 1940's. Since then significant improvements have been made in each of the four major steps: hydrogenation, oxidation, hydrogen peroxide extraction and treatment of the working solution. This has made the process more efficient and able to gain very high yields of peroxide per cycle at concentrations as high as 70 wt%.



Firstly the working solution, 2-alkylanthraquinone (AQ) (usually 2-ethyl, 2-tert-buyl or 2- amylanthraquinone) in an appropriate solvent/s, is hydrogenated over a nickel or palladium based catalyst, to the corresponding anthraquinol or anthrahydroquinone (AHQ). The AHQ undergoes further hydrogenation to yield the corresponding tetrahydroanthrahydroquinone (THAHQ), Figure. This process is carried out under relatively mild conditions, normally temperatures of 40-50 ºC and a hydrogen partial pressure of up to 4 bar are utilised. This step has two serious drawbacks: excessive hydrogenation and rapid deactivation.

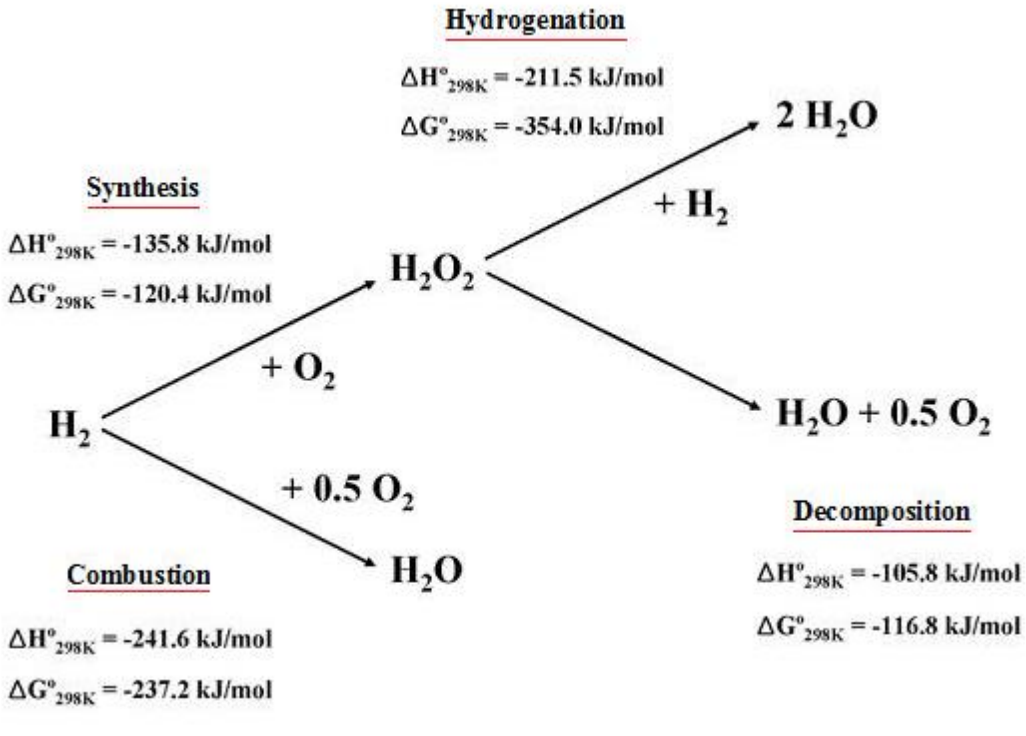
The solution containing the AHQ and THAHQ is separated from the hydrogenation catalyst and oxidised, usually by air, to regenerate the corresponding AQ and tetrahydroanthraquinone (THAQ) and equimolecular amounts of hydrogen peroxide. The oxidation is carried out non-catalytically by bubbling air through the solution at 30-60ºC and near atmospheric pressure. The reaction occurs by means of a well-documented free-radical mechanism.

Emerging alternatives

Direct synthesis of hydrogen peroxide using Pd catalysts

Until very recently predominately supported Pd catalysts have been used in the direct synthesis of H_2O_2. Since the first patent by Henkel and Weber in 1914, which utilised a Pd catalyst, it has been known that Pd is effective, for the liquid-phase hydrogenation of O2 by H_2 to form H_2O_2.

However, two major drawbacks have prevented the process from an industrial application being accomplished. Firstly, due to safety issues H_2/O_2 mixtures need to be outside the flammability limits (5-95 v/v% for H2 in O_2), H_2 concentrations less than 5 vol% H_2 are typically used. Secondly, Pd catalysts that are shown to be active for the direct H_2O_2 synthesis pathway are also active for the unwanted side reaction shown in Figure.



All these reactions are thermodynamically favourable and highly exothermic, however, H_2O_2 is an intermediate and selectivity towards H_2O_2 is severely limited by the consecutive decomposition and hydrogenation of H2O2. This is borne out by the heat contents (H) and the free energy values (G) shown in Figure. Factors that can influence the rate of H_2O_2 decomposition/hydrogenation are listed below.

- Catalyst design - hydrophobicity of catalyst etc
- Reaction conditions - H2/O2 ratio in feed, reaction time, catalyst amount, etc
- Reaction medium
- Presence of acids (i.e. H+ ions)
- Presence of halide ions in reaction medium and/or catalyst
- Oxidation state of Pd in catalyst
- Presence of a second metal in Pd catalyst

Electrolysis / Fuel Cells

A promising alternative is the production of hydrogen peroxide with inexpensive fuel cells, which unlike electrolytic devices do not require electrical energy. The electrochemical reduction of O2 in acidic and alkaline media proceeds through two pathways which are mainly determined by the electrocatalyst and electrode potential: four electron reduction of O_2 into H_2O and two-electron reduction into H_2O_2.

O_2 + 4H+ + 4e- $2H_2O$

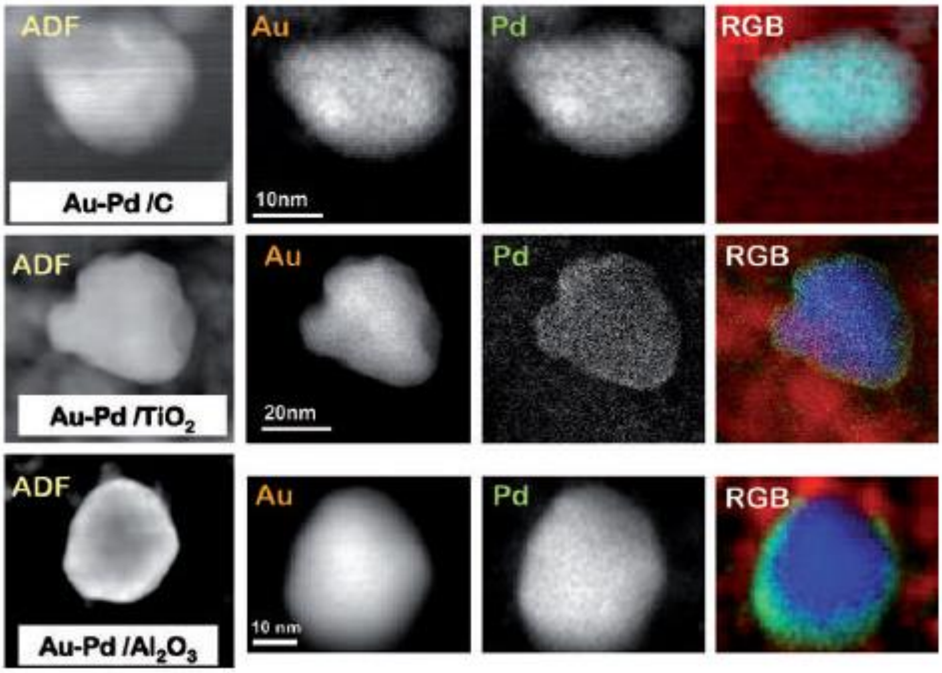
O_2 + $2H_2O$ + 2e- H_2O_2 + 2OH

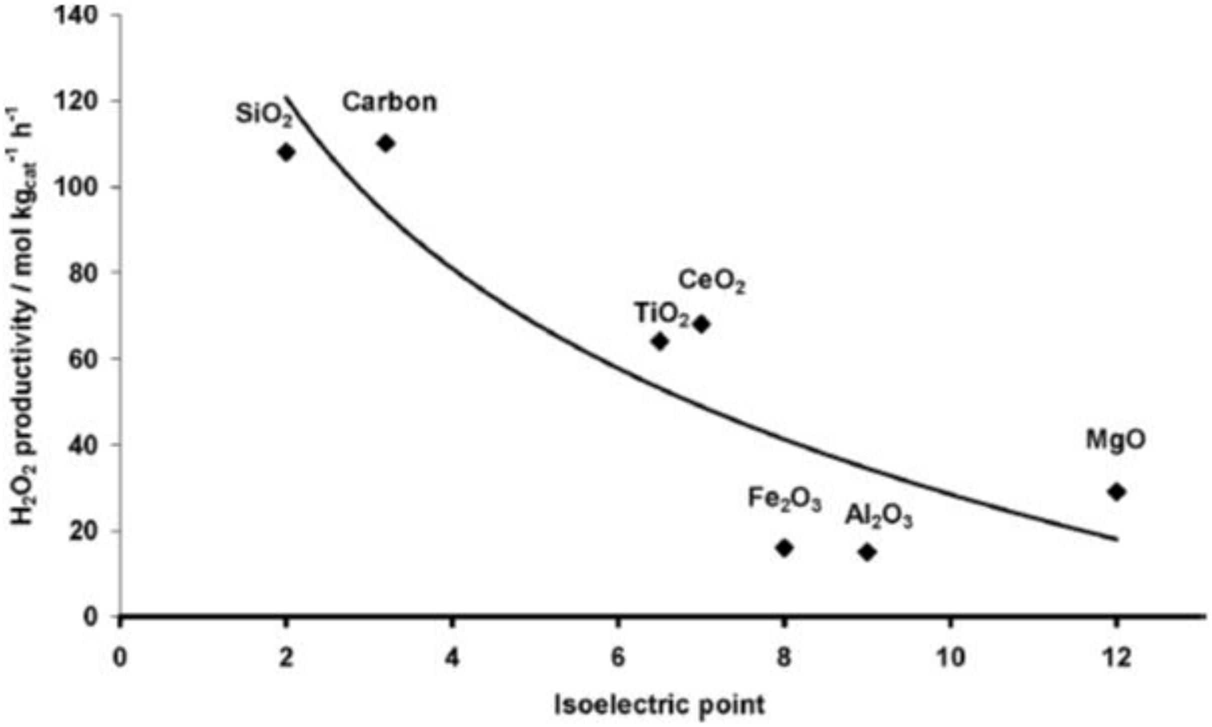
The most promising results have been obtained by Yamanaka who have reported the H_2O_2 could be synthesised with selectivity of 93 % using a fuel-cell system. In this fuelcell system, Pt and carbon were used for H_2 activation and H_2O_2 synthesis and a cation membrane (viz. Nafion) was used for preventing the diffusion of H_2O_2.

Direct Synthesis of Hydrogen Peroxide Using Au-Pd Catalysts (Cardiff)

Hutchings discovered Au/Al_2O_3 was active for the liquid-phase direct synthesis of hydrogen peroxide. Its activity was relatively low compared to the monometallic Pd analogue. However, the most important discovery was the improved activity and selectivity of Au-Pd catalysts, prepared by the impregnation of Al2O3 with Au and Pd simultaneously, compared to Pd/Al_2O_3. Initial investigations used supercritical CO_2 (sc-CO_2) as the olvent. However, in subsequent experiments, due to high H_2O_2 decomposition rates in the sc-CO_2 reactions, a methanol-water solvent was utilised without the addition of promoters. The reactions were performed in a three-phase system (catalyst-solid, solvent-liquid, and reagents-gas) in a sealed stainless steel autoclave. The effect of reaction conditions on the direct H_2O_2 synthesis, have previously been studied. The total reaction pressure and the methanol-water solvent composition had profound effects on the rate of H_2O_2 synthesis, as both parameters affected the amount of H_2 available, in the solvent, for the reaction to take place. However, as expected, the reaction temperature, the H_2/O_2 molar ratio and the reaction time also had significant effects. By fine tuning of the parameters very high reaction rates for the synthesis of H_2O_2 were achieved with Au-Pd alloy catalysts.

Interestingly, Au-Pd/TiO_2 catalysts effective for low-temperature CO oxidation prepared by deposition precipitation (DP) were inactive for the direct H_2O_2 synthesis, whereas impregnation materials showed the opposite trend. It was concluded that this activity was due to the particle size distribution and the nano-particle morpholo gy. DP produced Au particles of the correct size (< 5 nm) to be active for CO oxidation and relatively large Au nano-crystals (ca. 25 nm), present on the impregnation Au/TiO, are active for selective hydrogenation of O_2 to H_2O_2.

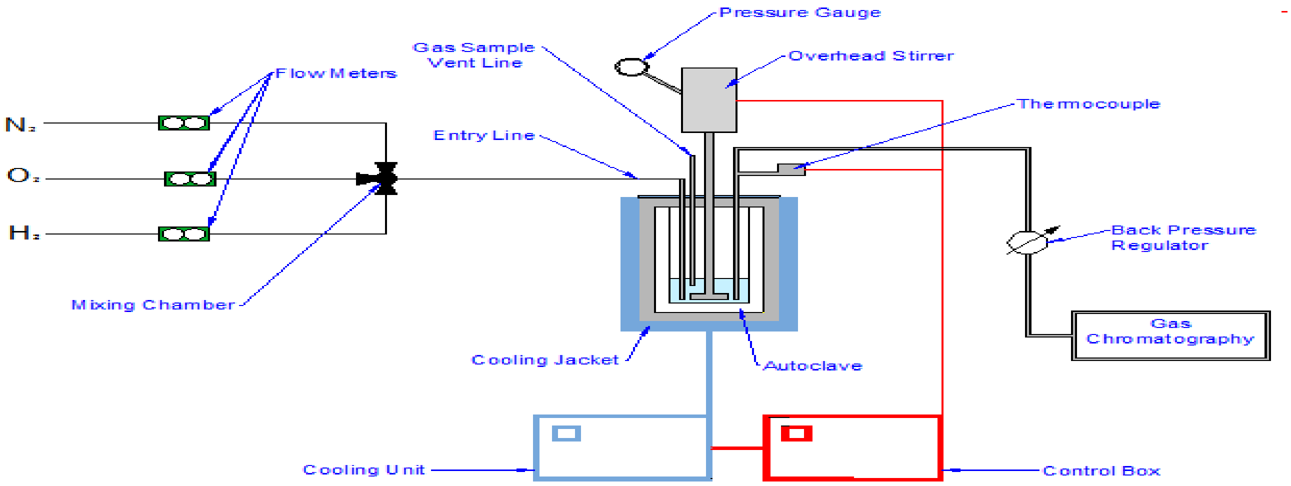




Direct Synthesis of Hydrogen Peroxide - Batch reactor:

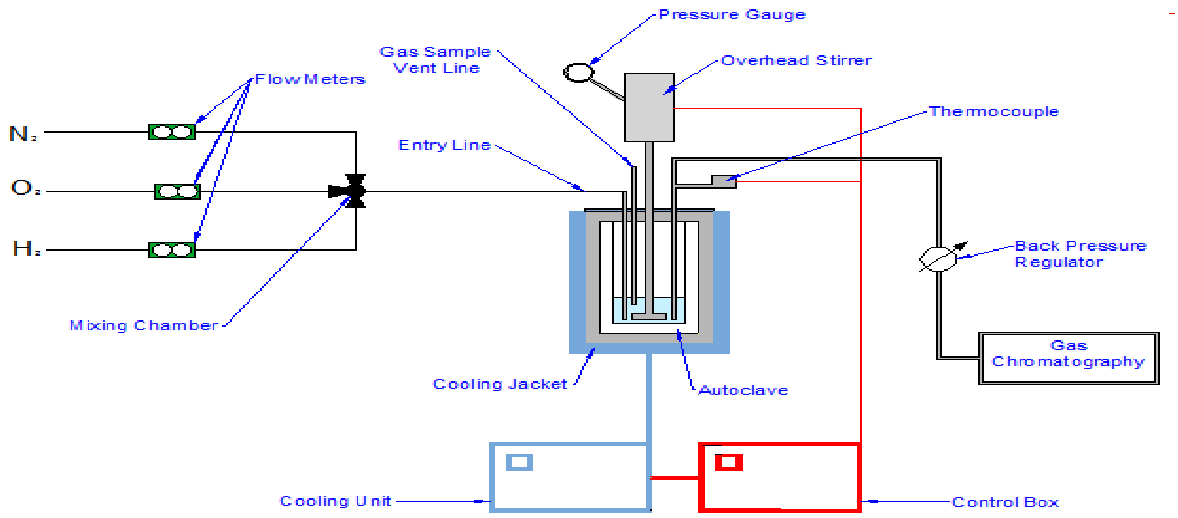
Catalytic tests were performed using a Parr Instruments stainless steel autoclave with a nominal volume of 100 ml and a maximum working pressure of 2000 psi. However, for convenience a Teflon liner was used reducing the volume to ca.75 ml.

The autoclave was equipped with an overhead mechanical stirrer (0-2000 rpm) and provision for measurement of temperature and pressure. The desired temperature was maintained with a cooling jacket. Two pre-mixed gas cylinders (5 %H2 / CO_2 and 25 %O_2 / CO_2 supplied by BOC) were connected.



Direct Synthesis of Hydrogen Peroxide - Semi-Continuous Flow Reactor:

catalytic tests under a continuous flow of gas were performed inside a modified batch reactor, with a nominal volume of 100 ml and a maximum working pressure of 2000 psi. Three flow meters with the possibility to regulate the rate of gas flow were installed. A mixing chamber with an internal volume of 150µm was positioned in order to make a homogenous combination of the three gases. At the exit of the reactor a back pressure regulator was installed; it controlled the inlet pressure by balancing an adjustable spring force against the inlet gas flow, making it possible to work with a fixed pressure inside the autoclave. Finally a gas chromatographer (GC-14 B SHIMADZU) was installed on line to measure the concentration of gases coming out of the reactor.



Application of Hydrogen Peroxide:

H_2O_2 decomposes to give only water and oxygen as the only reaction products, making it an environmentally safe oxidising agent for many large-scale applications, such as pulp and paper bleaching, textile applications, detergent applications, wastewater treatment, and chemical oxidation processes,

One of the most important applications is currently its use in pulp and paper bleaching, as well as for treatment of wastewaters and a variety of industrial wastes. It has advantages over traditional chlorine and chlorine-containing bleaches and oxidants, such as sodium hypochlorite and sodium hydrochlorite, in that it is suitable for continuous processing, has no severe toxicity or effluent problems and is noncorrosive. The formation of the perhydroxyl anion, a nucleophile intermediate, is important for bleaching as it's responsible for the oxidation of chromophores in lignin through the cleavage of side chains.

Hydrogen peroxide is also used as a source of hydroxyl radicals which is the second most powerful oxidant after fluorine. They occur from single electron transfer reactions in the presence of an initiator, such as metals, enzymes (catalase) or heat. Generally, radicals produce more negative effects (delignification) than positive effects in the bleaching process, however, are useful for more complex advanced oxidation processes.

For processes in the fine chemical industry, operated using molecular oxygen, the presence of di-radical triplet states can potentially initiate homogeneous, non-catalysed background reactions in addition to the target reaction. Hence significant demand exists for green, atom efficient, singlet-state oxygen donors, such as hydrogen peroxide. H2O2 can be employed either directly or following transformation into a peroxocarboxylic acid, leading to an economically viable synthesis route for the manufacture of many organic and inorganic chemicals.

The potential of including hydrogen peroxide in large volume chemical synthesizes has been recognized following the commercialisation of the integrated HPPO (hydrogen peroxidepropylene oxide) process, in which the hydrogen peroxide required for the epoxidation is produced on site. BASF and Dow Chemical opened a joint-venture pilot plant in Antwerp in 2008 with a yearly capacity of producing about 2x105 metric tons. In Japan, an increase in the consumption of hydrogen peroxide has stemmed from the commercialisation of Sumitomo's route to caprolactam.

Result and Discussion

In order to stabilise a Au-Pd/AwC catalyst prepared using impregnation, calcination in static air at 400°C for 3h is required. Calcination at 400°C is also critical to the catalysts activity towards the hydrogenation pathway being switched off under the reaction conditions utilised. These are two key traits a catalyst material would require for the direct H_2O_2 synthesis to become viable at an industrial level.

However, explaining why these activity traits are only observed for the material calcined at 400°C proves difficult. Below is a summary of the trends observed in surface composition and activity towards H_2O_2 synthesis, with increasing calcination temperature:

- H_2O_2 synthesis activity decreases
- H_2O_2 hydrogenation activity decrease, with hydrogenation switching off at 400 °C
- Catalyst stability increases, with stability being achieved at 400 °C
- Chloride concentration decreases and we observe more ionic, negatively charged Cl^{x-} species
- Pd/Au ratio increases for temperatures up to 300 °C then stabilises at a value of around 4.2

- Improved overall metal dispersion

The detailed XPS and STEM measurements highlighted a number of trends in the surface composition, with increasing calcination temperature, which could be responsible for the catalytic activity observed ind ividually or simultaneously. This makes it difficult to identify the crucial feature/s required to switch off H_2O_2 hydrogenation.

The characterisation, by XRD and STEM , of the carbon supported material showed that carbidic species are present in the bulk and on the surface of the catalyst. This hasn't been observed previously for comparable impregnation catalysts, and the comparable selectivities to benzaldehyde of the physical grinding and impregnation derived catalysts suggest the carbidic species do not have an obvious effect on catalyst performance. However, when producing catalysts on a larger scale or lower metal content this may become an important issue. The presence of interstitial carbon has not been reported previously for carbon supported catalysts prepared by impregnation, so it is believed that the carbon exists as a result of acetate decomposition in an inert atmosphere. This carbon could be removed by calcination in oxygen; however the oxidation state will change and at high temperature the particles may sinter causing deactivation. Krishnankutty. proposed a model, in which a Pd/C catalyst could contain a mixture of particles, type A-D, with various extents of carbon coverage; each type could affect the catalyst performance differently. The aim and objectives of this research and the topic of this thesis are set out in chapter one. The anthraquinone auto-oxidation (AO) process currently used for the production of hydrogen peroxide suffers from requiring large amounts of energy and a continuous refill of the organic solvents due to unwanted side reactions, which makes it only economically viable on a large scale. Solvay have outlined that if certain requirements are met (H_2 selectivity > 90 %; $[H_2O_2]$ > 8 wt %) the direct process would be able to challenge the AO process and allow H_2O_2 to be produced on site where required. As discussed in chapter one, many important developments in the research of the direct H_2O_2 synthesis, since the first patent in 1914, have already been achieved by research groups worldwide.

In this paper a number of aspects of the direct synthesis of H_2O_2 were studied, by looking at the design of the catalyst and varying reaction conditions together with the reactor. Conclusions have been recorded at the end of each chapter. It can be seen that the percentage of hydrogen peroxide produced has varied dependent on the conditions. However, although the requirements outlined by Solvay have not been achieved, the advantage of direct H_2O_2 synthesis to industry, the economy and the environment is so important that further study of variations in heterogeneous catalysis is necessary.

Specific lines of research were undertaken in an attempt to establish the active site responsible for the synthesis, hydrogenation and decomposition of H_2O_2 and to produce higher H_2O_2 concentrations. The most important results achieved within this thesis are highlighted.

Acknowledgement

The authors of this paper are thankful to the Department of Chemistry, Theivanai Ammal College for Women (A), Tamil Nadu, India, for their invaluable support and for providing all the research facilities. The authors are also thankful to the financial support from TNSCST project, Chennai for helping and providing fund facilities for this research work.

Reference

1.T. A. Paul, G. H. Lauren and C. W. Tracy, in Green Chemical Syntheses and Processes, American Chemical Society, Editon edn., 2000, vol. 767, pp. 1-6.

2. P. T. Anastas and J. C. Warner, Green Chemistry: Theory and Practice, Oxford University Press, New York, 1998.

3.S. Hermans, R. Raja, J. M. Thomas, B. F. G. Johnson, G. Sankar and D. Gleeson, Angewandte Chemie International Edition, 2001, 40, 1211-1215.

4.J. K. Edwards, B. Solsona, E. N. N, A. F. Carley, A. A. Herzing, C. J. Kiely and G. J. Hutchings, Science, 2009, 323, 1037-1041.

5. . E. Cao, M. Sankar, E. Nowicka, Q. He, M. Morad, P. J. Miedziak, S. H. Taylor, D. W. Knight, D. Bethell, C. J. Kiely, A. Gavriilidis and G. J. Hutchings, Catalysis Today

6. G. A. Somorjai and Y. Li, Introduction To Surface Chemistry And Catalysis, Second Edition.,John Wiley & Sons, New Jersey, 2010.

7. R. Noyori, Chemical Communications, 2005, 1807-1811

8. P. Landon, P. J. Collier, A. F. Carley, D. Chadwick, A. J. Papworth, A. Burrows, C. J. Kiely and G. J. Hutchings, Physical Chemistry Chemical Physics, 2003, 5, 1917-1923.

9. V. R. Choudhary, Y. V. Ingole, C. Samanta and P. Jana, Industrial & Engineering Chemistry Research, 2007, 46, 8566-8573

10. P. Landon, P. J. Collier, A. F. Carley, D. Chadwick, A. J. Papworth, A. Burrows, C. J. Kiely and G. J. Hutchings, Physical Chemistry Chemical Physics, 2003, 5, 1917-1923.

11. M. P. Kapoor, Y. Ichihashi, T. Nakamori and Y. Matsumura, Journal of Molecular Catalysis A: Chemical, 2004, 213, 251-255.

12. E. N. Ntainjua, M. Piccinini, J. C. Pritchard, J. K. Edwards, A. F. Carley, C. J. Kiely and G. J.Hutchings, Catalysis Today, 2011, 178, 47-50.
13. P. Biasi, N. Gemo, J. R. Hernández Carucci, K. Eränen, P. Canu and T. O. Salmi, Industrial & Engineering Chemistry Research, 2012, 51, 8903-8912.
14. M. Piccinini, E. Ntainjua N, J. K. Edwards, A. F. Carley, J. A. Moulijn and G. J. Hutchings, Physical Chemistry Chemical Physics, 2010, 12, 2488-2492.
15. Y. Voloshin, J. Manganaro and A. Lawal, Industrial & Engineering Chemistry Research, 2008, 47, 8119-8125.