ENVIRON-FRIENDLY PRODUCTION OF HYDROGEN PEROXIDE FROM DIRECT CATALYTIC LIQUID PHASE OXIDATION OF HYDROGEN OR HYDROGEN-CONTAINING COMPOUNDS

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CERTIFICATE

This is to certify that the work incorporated in the thesis, **“Environ-Friendly Production of Hydrogen Peroxide from Direct Catalytic Liquid Phase Oxidation of Hydrogen or Hydrogen-Containing Compounds”** submitted by **Mr. Prabhas Jana,** for the Degree of **Doctor of Philosophy,** was carried out by the candidate under my supervision in the Chemical Engineering & Process Development Division, National Chemical Laboratory, Pune – 411 008, India. Such material as has been obtained from other sources has been duly acknowledged in the thesis.

Dr. V. R. Choudhary

(Research Supervisor)

DECLARATION

I hereby declare that the thesis **“Environ-Friendly Production of Hydrogen Peroxide from Direct Catalytic Liquid Phase Oxidation of Hydrogen or Hydrogen-Containing Compounds”** submitted for the degree of Doctor of Philosophy to the University of Pune has not been submitted by me for a degree to any other University.

Prabhas Jana

Dedicated
to
My Father

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Summary and Conclusions

Summary and Conclusions

"Green Chemistry" is a central issue, in both academia and industry, with regard to chemical synthesis in the 21st century. Without this approach, industrial chemistry is not sustainable. Thus, the development of environmentally benign and clean synthetic technology is a goal of research and industry. Oxidation is a core technology in the industry and there is a need to use environ-friendly oxidants in various oxidation processes. Hydrogen peroxide is an environ-friendly strong oxidizing agent. Hence, its demand for domestic/industrial wastewater treatment, water disinfections, catalytic oxidation processes and other industrial applications has been increasing day-by-day. In recent years hydrogen peroxide has become more and more popular as an environmentally benign reagent, mainly because it produces water as the only by-product. Hence, the global demand of hydrogen peroxide is growing rapidly as environmental pressure for the replacement of undesirable oxidants (such as organic hydroperoxides, $KMnO_4$, $K_2Cr_2O_7$, K_2CrO_4, etc.) and bleaching agents (e.g. oxychlorides) in commercial oxidation or bleaching processes.

Currently, most hydrogen peroxide is produced by the sequential oxidation and reduction of anthraquinone. The process is only economically viable on a relatively large scale and this necessitates the transportation and storage of concentrated solution of hydrogen peroxide, which is hazardous. In view of this, most hydrogen peroxide is used for cleaning or in the paper and textile industries and only a small fraction is used for the manufacture of chemicals and in wastewater treatments.

The H_2-to-H_2O_2 oxidation ($H_2 + O_2 \rightarrow H_2O_2$) is covered in a number of patents throughout the world. However, as yet this process is not commercialized; it is considered as a "dream process". Apart from its hazardous nature, the main problem associated with this process is the low H_2O_2 selectivity (or high selectivity for the water formation). This is because of the undesirable thermodynamically highly favoured non-selective water forming reactions, such as the parallel H_2-to-water oxidation ($H_2 + 0.5\ O_2 \rightarrow H_2O$) and consecutive H_2O_2 decomposition ($H_2O_2 \rightarrow H_2O + 0.5\ O_2$) and/or hydrogenation ($H_2O_2 + H_2 \rightarrow 2\ H_2O$), occurring simultaneously with the desirable H_2-to-H_2O_2 oxidation over the same catalyst.

Also, because of the increasing environmental concerns, the use of H_2O_2 in a number of organic oxidation processes (e.g. epoxidation of olefins, hydroxylation of aromatics/olefins, oxidation of benzylic $–CH_2OH$ to $–CHO$ or $–COOH$, etc.) for the synthesis of fine/specialty chemicals is increasing widespread and growing day-by-day. Hence, the use of *in situ* generated H_2O_2 for the organic oxidation reactions is not only of scientific interest but also of great practical importance. However, the progress made in this hot topic is rather slow mostly because of the requirement of an efficient method for the *in situ* H_2O_2 generation in an environmentally friendly manner, particularly at mild conditions for avoiding or minimizing the mismatch between the optimal condition required for the *in situ* H_2O_2 generation and the consecutive step of consumption of the generated H_2O_2 in the oxidation of organic substrates. It is, therefore, interesting to develop an environmentally cleaner method for the *in situ* H_2O_2 generation, eliminating the catalyst/by-product separation and corrosion problems.

The work for the Ph.D thesis was undertaken as a part of the comprehensive R & D programme in our laboratory (NCL, Pune) for developing a highly active and selective catalyst for the direct oxidation of hydrogen to hydrogen peroxide by thoroughly investigating the factors affecting both the hydrogen conversion activity and hydrogen peroxide selectivity of supported palladium catalyst (including the H_2O_2 decomposition/hydrogenation activity of the catalyst) and also for developing a non-hazardous, greener method having high potential for the *in situ* H_2O_2 generation, required for organic oxidation reactions both in aqueous and/or non-aqueous medium, using easily separable and reusable solid catalysts form the hydrogen-containing compounds (viz. hydrazine and its salts or hydroxyl amine and its salt)

The thesis has been divided into eight chapters, as follows.

Chapter 1 Introduction - Objectives and Scope

In this chapter, a general introduction including background and literature survey, covering

- properties and applications of hydrogen peroxide,
- various methods of preparation of H_2O_2 other than the direct oxidation route,
- direct oxidation of hydrogen to hydrogen peroxide, and
- hydrogen peroxide destruction (by decomposition and hydrogenation reactions) over supported metal catalysts,

and also the objectives/scope of the Ph.D work have been presented.

Chapter 2 Experimental

In this chapter, the experimental procedures for

- the preparation and/or modification of various supported Pd catalysts and supported nano-gold catalysts,
- the characterization of the catalysts by different surface and bulk analytical tools (viz. XRD, XPS, SEM, TEM, ICP), and
- the catalytic reactions [direct oxidation of H_2 by O_2 to H_2O_2, decomposition of H_2O_2 and hydrogenation of H_2O_2 and the reduction of O_2 by hydrogen-containing compounds (viz. hydrazine hydrate and its salt, and hydroxylamine and its salt)]

have been described.

Chapter 3 Direct Oxidation of H_2 to H_2O_2 over Supported Pd Catalysts: Influence of Support, Calcination Temperature, Oxidation State of Pd, Loading of Pd and Halide Promoter Present in the Reaction Medium

Effects of the catalyst reduction (by hydrazine), calcination temperature (400 º - 800 ºC), support (viz. Al_2O_3, SiO_2, CeO_2, ZrO_2, Hβ or HM) and Pd loading on the performance of supported PdO (2.5 wt%) catalyst in the H_2-to-H_2O_2 oxidation (with H_2:O_2 = 1:1) in an aqueous acidic (0.1 M H_3PO_4) medium under ambient conditions have been investigated. All the supported PdO catalysts showed lower H_2 conversion activity but higher H_2O_2 selectivity, as compared to their reduced counter parts. The catalyst performance for the net H_2O_2 formation is strongly influenced by both the support and calcination temperature of the supported PdO catalysts. The catalysts calcined at 400 ºC showed better performance. Among the catalysts, PdO/Al_2O_3 catalyst (calcined at 400 ºC) showed the best performance (17.0 % H_2O_2 yield) in the H_2-to-H_2O_2 oxidation. However, the effect of calcination temperature varied depending upon the Pd loading. For the Pd loading of 0.2 wt%, the H_2O_2 formation (or H_2O_2 yield) decreased with increasing the catalyst calcination temperature. This trend is gradually changed with increasing the Pd loading. At the Pd loading of 5 or 10 wt%, the trend is totally reversed; the H_2O_2 formation increased markedly with increasing the calcination temperature. The influence of the calcination temperature of PdO/Al_2O_3 catalyst on its H_2O_2 decomposition and hydrogenation activities has also been investigated. Both the H_2O_2 decomposition and hydrogenation activities increased with increasing the calcination temperature.

Chapter 4 Direct Oxidation of H_2 to H_2O_2 and Decomposition/hydrogenation of H_2O_2 over Commercial Pd/C and Pd/Al_2O_3 Catalysts in Aqueous Acidic Medium Containing Bromide Promoter: Influence of Pretreatment Condition on Pd Particle Size and Catalytic Performance of the Catalyst

Influence of thermal pretreatments (under N_2, air or H_2 gas atmosphere at 500 ºC or 700 ºC) to Pd/Al_2O_3 (or Carbon) catalyst on its Pd particle size and also on its performance in the H_2-to-H_2O_2 oxidation and H_2O_2 destruction (by decomposition and/or hydrogenation) reactions in aqueous acidic (0.1 M H_3PO_4) medium containing Br promoter have been investigated. The thermal pretreatment in N_2 or H_2 at 500 ºC or 700 ºC of Pd/Al_2O_3 caused an appreciable increase in its net H_2O_2 formation activity and Pd particle size; the highest H_2O_2 yield was found when the catalyst was pretreated at 700 ºC (in H_2). However, the pretreatment at 700 ºC in H_2 to Pd/C resulted in an appreciable decrease in its catalytic activity and H_2O_2 yield due to the increase in its Pd particle size. The pretreatment at 500 ºC in air to Pd/Al_2O_3 (followed by its reduction by hydrazine), however, caused a large decrease in both the Pd particle size and the H_2O_2 formation activity of the catalyst. Thus, the influence of thermal pretreatment under different conditions to supported Pd catalysts on their catalytic performance in the H_2-to-H_2O_2 oxidation cannot be generalized; it depends strongly upon the catalyst support – Pd cluster interactions in the presence of Br promoter.

Chapter 5 Synergetic Effect of Two Halogen Promoters Present in the Reaction Medium or in the Catalyst on the H_2O_2 Formation and Destruction over Pd/C (or Al_2O_3) Catalyst

A strong synergetic effect of two different halide anions (viz. F^- and I^-, Cl^- and I^-, Cl^- and Br^-, and F^- and Br^-) at optimum concentration in the catalyst or in an acidic reaction medium has been observed in the H_2-to-H_2O_2 oxidation over Pd/C, Pd/Al_2O_3, and halogenated Pd/Al_2O_3 catalysts. The synergetic effect promotes the net H_2O_2 formation by inhibiting the H_2O_2 decomposition and hydrogenation reactions. The effect is most pronounced for the combination of fluoride (or chloride) and iodide anions. Influence of the addition of F (0 – 1.1 mmol/g) in the pre-brominated Pd/Al_2O_3 (Br loading = 0.13 mmol/g) and also that of Br (0 – 1.3 mmol/g) in the pre-fluorinated Pd/Al_2O_3 (F loading = 0.53 mmol/g) on the net H_2O_2

formation in the H_2-to-H_2O_2 oxidation (with H_2/O_2 mole ratio of 1.0) over the halogenated catalysts have been investigated. In both the cases, the highest synergetic effect (resulting in the highest net H_2O_2 formation) produced by the addition of other halogen is observed at its optimum concentration (viz. 0.13 mmol Br/g in the fluorinated Pd/Al_2O_3 and 0.13 mmol F/g in the pre-brominated Pd/Al_2O_3). The beneficial synergetic effect of the two halogens is also found to be strongly influenced by the way of incorporation of the two halogens in the catalyst. The fluorination (at optimum concentration of 0.13 mmol F/g) of the pre-brominated (0.13 mmol Br/g) Pd/Al_2O_3 led to the best catalyst for the H_2-to-H_2O_2 oxidation with 100 % H_2 conversion and 78 % H_2O_2 yield/selectivity.

Chapter 6 H_2-to-H_2O_2 Oxidation over Highly Active/selective Bromine and Fluorine Promoted Pd/Al_2O_3 Catalyst: Influence of Halogen Promoter Concentration and Process Parameter

Influence of the O_2/H_2 mole ratio in the gaseous feed and also that of other reaction conditions [viz. concentration of H_3PO_4 (0 – 5 mol/dm^3), temperature (0º – 50 ºC), gas (H_2 and O_2) space velocity (5.8 – 23.4 h^{-1}) and reaction time 90 – 8 h)] on the H_2O_2 formation in the H_2-to-H_2O_2 oxidation over the Br(1 wt%)-F(1 wt%)-Pd(5 wt%)/Al_2O_3 catalyst in aqueous acidic medium have been thoroughly investigated. The influence of the O_2/H_2 ratio, reaction temperature and acid concentration on the destruction of H_2O_2 by its decomposition and/or hydrogenation reactions over the catalyst in the acidic reaction medium has also been studied. The net H_2O_2 formation (H_2O_2 yield) over the catalyst is passed through a maximum with increasing the acid concentration (at 0.1 – 0.3 M H_3PO_4) in the reaction medium, reaction temperature (at 27 ºC) and O_2/H_2 ratio (at O_2/H_2 = 1.0). However, it decreased largely with increasing the gas space velocity and reaction period. The H_2O_2 decomposition and hydrogenation activities of the catalyst increased appreciably with increasing the reaction temperature and decreased with increasing the acid concentration. The H_2O_2 destruction during the H_2-to-H_2O_2 oxidation is increased with increasing the concentration of H_2 relative to that O_2 due to the increased H_2O_2 hydrogenation rate over the catalyst. The net rate of H_2O_2 formation in the H_2-to-H_2O_2 oxidation decreased sharply with increasing the amount of H_2O_2 added to the reaction mixture at the reaction start; the presence of H_2O_2 has a detrimental effect on the net formation of H_2O_2.

Chapter 7 Factors Strongly Influencing H_2O_2 Decomposition and/or Hydrogenation over Pd/Al_2O_3 Catalyst in the Presence of H_2

Hydrogen peroxide destruction by its decomposition and/or hydrogenation to water in the presence of H_2 over Pd(5 wt%)/Al_2O_3 catalyst in an aqueous reaction medium, similar to that used in the H_2-to-H_2O_2 oxidation, has been thoroughly investigated at different reaction conditions. The H_2O_2 destruction is strongly influenced by the oxidation state of Pd in the catalyst and also by the presence of different halide anions (viz. F^-, Cl^-, Br^- and I^-) in the acidic aqueous medium or in the catalyst, depending upon the concentration of halide anions. The cations associated with halide anions have, however, a little or no influence on the H_2O_2 destruction. The chloride or bromide anions drastically inhibit the rapid H_2O_2 decomposition, but promote the H_2O_2 hydrogenation, which is much slower than the H_2O_2 decomposition. The H_2O_2 destruction reactions are strongly influenced by the halide anion and acid concentrations. The presence of acid (protons) plays a very important role in drastically reducing the H_2O_2 destruction, particularly in the presence of chloride anions. Both in the presence and absence of Cl^- or Br^- anions, the H_2O_2 destruction activity of the catalyst is markedly reduced because of the oxidation of Pd but it is drastically increased due to the presence of H_2. A plausible reaction mechanism for the rapid H_2O_2 decomposition and slower H_2O_2 hydrogenation reactions, prevailing under the different reaction conditions, has also been discussed.

Chapter 8 Hydrogen Peroxide from Reduction of O_2 with Hydrogen Containing Compounds (viz. Hydrazine, Hydroxylamine or Their Salts) over Supported Pd or Nano-Gold Catalysts in Aqueous or Non-Aqueous Medium

The formation of H_2O_2 by the reduction of O_2 with hydrazine or their salt over the brominated Pd(5 w%)/Al_2O_3 catalyst and the decomposition of N_2H_4 (from $N_2H_4.H_2SO_4$) and its reaction with H_2O_2 under similar reaction conditions (in the absence of O_2) have been studied. H_2O_2, which is an intermediate product of the O_2 reduction, is involved in further consecutive reactions. It can be converted to water via its decomposition and/or reaction with the unconverted N_2H_4. Both the consecutive reactions are drastically retarded in the presence of protons and Br promoter.

In situ H_2O_2 generation in high yields from the reduction of O_2 by hydroxylammonium salt or hydroxylamine with the formation of environmentally benign by-products (viz. N_2 and water) in aqueous (viz. water) or non-aqueous (viz. methanol or ethanol) medium in the absence of acid and/or halide promoter, even at ambient conditions, using a heterogeneous nano-gold (viz. nano-size Au particles) and Pd/Al_2O_3 catalysts have been investigeted. The reduction of O_2 by hydroxylammonium salt to H_2O_2, however, requires preneutralization of the salt by alkali; in the absence of the neutralization, only water is formed in the reaction. Influence of the concentration of bromide (KBr) promoter, reaction period, temperature, catalyst loading and initial concentration of hydroxylammonium sulfate on the formation of H_2O_2 in O_2 reduction by hydroxylamine over Pd(1 wt%)/Al_2O_3 catalyst in a neutral aqueous medium at close to the ambient conditions has been investigated. Effect of pH and temperature on the destruction of H_2O_2 and its reaction with hydroxylamine, occurring in the consecutive reactions, over the catalyst in the presence or absence of bromide promoter and the destruction of hydroxylamine in absence of O_2 have also been studied. The H_2O_2 destruction increases markedly with increasing the pH of medium and reaction temperature but it is found to decrease in the presence of hydroxylamine. For the highest net H_2O_2 formation, not only the optimum pH (7.0) of reaction medium but also the optimum other reaction conditions (viz. bromide promoter concentration, reaction period, temperature or catalyst loading) are necessary. The reaction path and mechanism for the generation of H_2O_2 have also been suggested.

Chapter 1

Introduction – Literature Survey, Objectives and Scope

Chapter 1

Introduction – Literature Survey, Objectives and Scope

1.1. A Short Introduction to Catalysis

Catalysts have been used by mankind for over 2000 years [1]. The first observed uses of catalysis were in the making of wine, cheese and bread. However, it wasn't until 1835 that Berzelius began to tie together observations of earlier chemists by suggesting that small amounts of a foreign source could greatly affect the course of chemical reactions. This mysterious force attributed to the substances was called catalytic. He derived it from the Greek words *kata*, which stands for down, and *lusein*, which means to split or break. Later, in 1895, Willium Ostwald was the first to write down a definition of a catalyst: "A catalyst is a substance that changes the rate of a chemical reaction without itself appearing in the products" [2]. It is important to note that a catalyst does not influence the thermodynamic equilibrium of reactants and products. Therefore, the current definition is slightly better, though close to Ostwald's description: "A catalyst is a substance that increases the rate of approach to thermodynamic equilibrium of a chemical reaction without being substantially consumed" [2].

Today, almost 70 % of all chemicals that are produced have been in contact with a catalyst somewhere in their synthesis process. This number stresses the importance of the role of catalysis in the chemical industry. Without a catalyst, processes are less clean and sometimes impossible to perform. In principle, catalysis can be used to abate environmental pollution in two ways: a) by the improvement or cleaning up of the well established process or b) by the replacement of the existing process in such a way that the substituted process will be more efficient and/or cleaner than the earlier one. The subject of this thesis is closely related with the second category i.e. replacement of the established process with a highly efficient and/or cleaner process.

1.2. Background of the Work

"Green Chemistry" is a central issue, in both academia and industry, with regard to chemical synthesis in the 21st century. Without this approach, industrial chemistry is not sustainable. Thus, the development of environmentally benign and clean synthetic technology is a goal of research and industry. Oxidation is a core technology in the industry that can be used either to functionalise molecules using selective or partial oxidation or to remove pollutants using non-selective or total oxidation. Therefore, there is a need to use environ-friendly oxidants in various oxidation processes. Molecular oxygen is the preferred oxidant, but to date, although well explored in the bulk and petrochemical industries, remarkably few processes are operating using O_2 as the oxidant. One problem is that dioxygen has a triplet ground state, whereas the organic substrates typically have singlet ground states; consequently, activation of the substrate is required, and often the temperatures required to achieve this are excessive for the reactions of interest. Form the green chemistry perspective [3,4], hydrogen peroxide is the next most preferred oxidant, because water is the byproduct after oxygen donation. In recent years hydrogen peroxide has become more and more popular as an environmentally benign reagent, mainly because it produces water as the only by-product. In view of this, there is significant interest in using hydrogen peroxide as an oxygen source, which has brought renewed efforts in both the synthesis and use of hydrogen peroxide. Hence, the global demand of hydrogen peroxide is growing rapidly as environmental pressure for the replacement of undesirable bleaching agents (e.g. oxychlorides) in textile and pulp/paper industries, for wastewater treatment and water disinfections [5-9], etching and purification of electronic materials, metallurgic processes and, also for catalytic oxidation processes in the synthesis of fine and bulk chemicals [8-28]. The cosmetic and pharmaceutical industry also uses the disinfecting properties of H_2O_2.

Thenard discovered H_2O_2 in 1818 [29], since then to the beginning of the 20th century, solutions containing about 3% of H_2O_2 were obtained by the hydrolysis of barium peroxide with sulfuric acid. Since then, a number of alternative processes based on electrochemical (viz. electrolysis of sulfuric acid and cathodic reduction of dioxygen [30-33]) and chemical (viz. autoxidation of hydroquinone compounds [34-36], isopropanol oxidation [37, 38], etc) processes have been worked out for the manufacture of H_2O_2. Synthesis of H_2O_2 from carbon monoxide, water and oxygen catalyzed by gallium phosphine complexes [39] and also by the palladium complexes [40-43] have been reported. Bianchi et al have reported that the palladium complexes containing bidentate nitrogen ligands can efficiently catalyze the reaction with productivity comparable to that of the current commercial process [43]. However, the process is still not suitable for practical application. Synthesis of H_2O_2 employing fuel cell system has been reported earlier [44,45]. More recently, direct and continuous production of H_2O_2 with 93% selectivity employing fuel cell has been reported [46]. However, most of the H_2O_2 is produced mainly by the sequential hydrogenation and oxidation of an alkyl anthraquinone, which involves indirect oxidation of hydrogen [34]. There are several problems associated with the anthraquinone process, including the cost of the complex quinone solvent system and the requirement for periodic replacement of anthraquinone due to hydrogenation. This process is only effective on a large scale (> 20000 tpa) and consequently this necessitates the transportation and storage of concentrated solutions of hydrogen peroxide when required for use in the fine chemicals industry, because only relatively small amounts are required at any one time. Hence, there is a significant mismatch between the current scales of production and usage. The development of a new, highly efficient, and smaller-scale manufacturing process for H_2O_2 is, therefore, of significant commercial interest

The liquid phases direct oxidation of H_2 by O_2 to H_2O_2 is an attractive alternative to the presently practiced anthraquinone process. In the H_2-to-H_2O_2 oxidation, the only undesired product formed is water; hence the process is environment friendly. Also since the process is based on direct oxidation of H_2, it is expected to be more economical than the anthraquinone process. Efforts are, therefore, being made to produce H_2O_2 by more economical and environmentally clean process based on the direct oxidation of H_2 to H_2O_2 using Pd-based catalysts. The process is covered in several patents but yet this process is not commercialized; it is considered as a *dream process*. Apart from its hazardous nature, the main problem associated with this process is the low H_2O_2 selectivity (or high selectivity for the water formation). This is because of the undesirable thermodynamically highly favoured non-selective water forming reactions, such as the parallel H_2-to-water oxidation ($H_2 + 0.5\ O_2 \rightarrow H_2O$) and consecutive H_2O_2 decomposition ($H_2O_2 \rightarrow H_2O + 0.5\ O_2$) and/or hydrogenation ($H_2O_2 + H_2 \rightarrow 2\ H_2O$), occurring simultaneously with the desirable H_2-to-H_2O_2 oxidation over the same catalyst. Therefore, there is an urgent need for developing a highly active and selective catalyst for the direct oxidation of hydrogen to hydrogen peroxide by thoroughly investigating the factors affecting both the hydrogen conversion activity and hydrogen peroxide selectivity of supported palladium catalyst (including the H_2O_2 decomposition/hydrogenation activity of the catalyst).

Since, the transport, storage and handling of H_2O_2 is quite hazardous, the use of *in situ* generated H_2O_2, as soon as it is produced, in the organic oxidations will have not only of scientific interest but also of great practical importance. However, the progress made in this topic is rather slow mostly because of an efficient method for the *in situ* H_2O_2 generation in an environmentally friendly manner, particularly at mild conditions for avoiding or minimizing the mismatch between the optimal condition required for the *in situ* H_2O_2 generation and the consecutive step of consumption of the generated H_2O_2 in the oxidation of organic substrates. It is, therefore, interesting to develop a new environmentally cleaner method for the *in situ* H_2O_2 generation, eliminating the catalyst/by-product separation and corrosion problems.

Conventionally, H_2O_2 can be generated *in situ* by the oxidation of hydroanthraquinone [34]. However, the use of this method for the *in situ* H_2O_2 generation is limited because of the use of a complex quinone solvent system and also due to the difficulties in separation of the solvent, unconverted hydroquinone and product of the reaction (anthraquinone) from the product(s) of organic oxidations. Direct oxidation of H_2 to H_2O_2 is a clean but highly hazardous process and hence its use for the *in situ* H_2O_2 generation is very dangerous. Hence, there is an urgent need for developing a new non-hazardous route for *in situ* generation of H_2O_2 in the synthesis of fine/bulk chemicals in organic oxidation reactions. Efforts are, therefore, being made to investigated a more environ-friendly/greener method for the *in situ* H_2O_2 generation in high yields from the reduction of O_2 by hydrogen containing compounds with the formation of environmentally benign by-products (viz. N_2 and water) in aqueous or non-aqueous medium in the absence of acid and/or halide promoter, even at ambient conditions, using heterogeneous catalysts.

1.3. About Hydrogen Peroxide

Hydrogen peroxide should really be called hydrogen dioxide. Its chemical formula is H_2O_2. It contains one more atom of oxygen than water (H_2O). By now every one is aware of the ozone layer that surrounds the earth. Ozone consists of three atoms of oxygen (O_3). This protective layer of ozone is created when ultraviolet-light from the sun splits an atmospheric oxygen molecule (O_2) into two single unstable oxygen atoms. These single molecules combine with others to form ozone. Ozone isn't very stable; in fact, it will quickly give up that extra atom of oxygen to falling rainwater to form hydrogen peroxide. Thus, nature produces its own hydrogen peroxide.

It is found in rain and snow; in fresh fruit and vegetables; and in colostrums, the first milk that a mother produces, where it provides a defense against infection until the baby's own immune system develops and is able to produce its own hydrogen peroxide. Hydrogen peroxide is produced during normal aerobic cell metabolism in both plant and animal cells [47] (Figure 1.1) and its formation involves a number of enzymatic reactions especially with superoxide dismutase enzyme (SOD). During mitochondrial respiration, O_2 acts as a terminal acceptor of electrons with 4-electron reduction yielding H_2O. However, there is a finite probability of 1-electron reduction of O_2 to O_2^- followed by rapid dismute to H_2O_2 [48]. This reaction can occur spontaneously or is catalyzed by SOD.

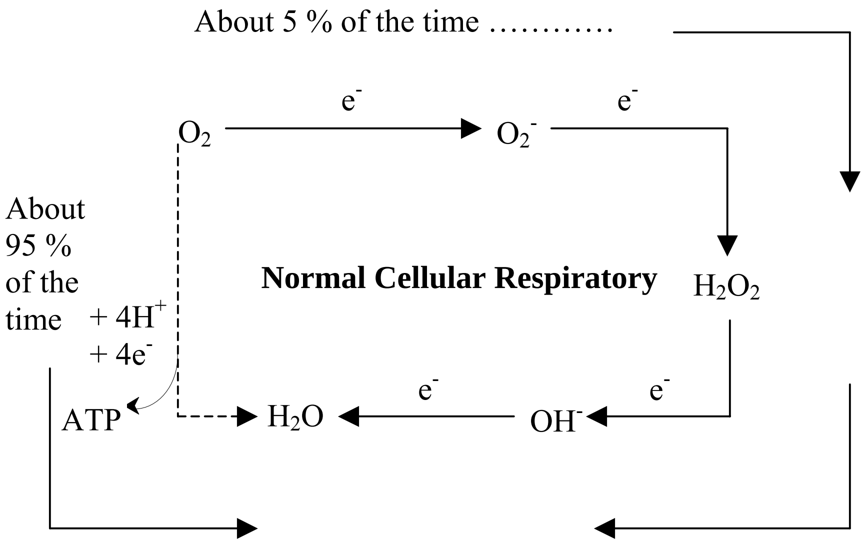


Figure 1.1: Schematic of the normal cellular respiratory process.

1.3.1. Description of H_2O_2

Hydrogen peroxide is a two-electron reduction of dioxygen molecule [49]:

$$O_2 + 2e^- + 2H^+ \rightarrow H_2O_2$$

The diatomic O_2 molecule in a ground state is a free radical that has two unpaired electrons in π*2p antibonding orbital. The addition of two electros to O_2 will give peroxide ion (O_2^{2-}), which is not a radical as shown in Figure 1.2. In ground state O_2 atoms are bonded by two covalent bonds, but in O_2^{2-} by one bond only. Therefore, the oxygen-oxygen bond in O_2^{2-} ion is much weaker as compared to O_2 in the ground state.

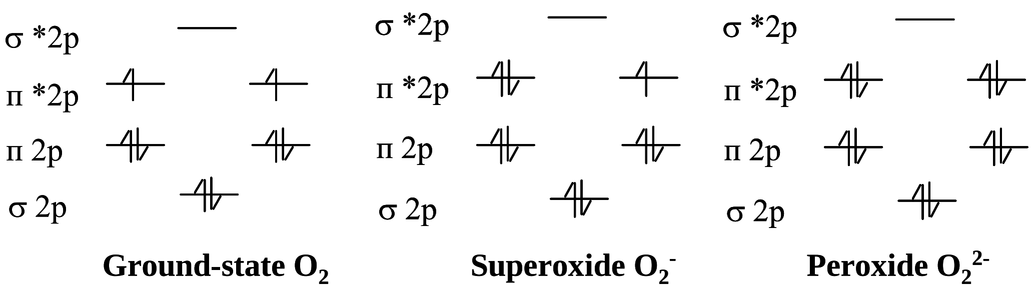


Figure 1.2: Electronic configuration of the diatomic oxygen molecule.

1.3.2. H_2O_2 Structure

Hydrogen peroxide is a polar molecule having dipole moment of 2.26×10^{-18} esu. This polarity indicates a linear or trans-planner configuration of H_2O_2 (Figure 1.3) [49].

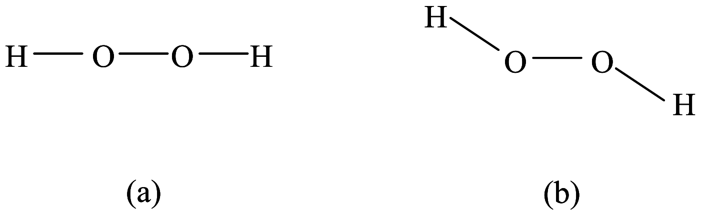
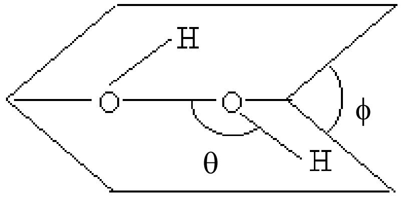


Figure 1.3: a) Linear b) and trans-planar configuration of H_2O_2.

However, three dimensional skew chain structure is preferred (Figure 1.4) [49]. The 2p electrons of the oxygen atom are the main contributor to the chemical bonds in H_2O_2. One of the 2p electrons of each oxygen atom forms the oxygen-oxygen σ bond and another will combine with the 1s of the hydrogen to form another σ bond. This leaves the third p orbital occupied by a lone pair of electron in each oxygen atom. As a result, it prefers the skew chain like structure due to the electrostatic repulsion of the lone pair of electron on each oxygen atom. Hydrogen peroxide belongs to **C_{2h}** point group.



Bond length, O — O	0.1453 ± 0.0007 nm
Bond length, O — H	0.0998 ± 0.0005 nm
Bond angle (θ),	102.7 ± 0.3º
Azimuthal angle (ϕ)	90.2 ± 0.6º

Figure 1.4: Skew chain structure of H_2O_2 molecule.

1.4. Properties of Hydrogen Peroxide

1.4.1. Physical Properties

Hydrogen peroxide is clear, colorless and nonflammable liquid having water like

Table 1.1: Physical properties of hydrogen peroxide

Property	Unit	Value	
		H_2O_2	H_2O
mp	ºC	-0.43	0
bp (101.3 kPa)	ºC	150.2	100
Heat of melting	$J\ g^{-1}$	368	334
Heat of vaporization (at 25 ºC)	$J\ g^{-1}\ K^{-1}$	1519	2443
Specific heat	$J\ g^{-1}\ K^{-1}$		
Liquid (25 ºC)		2.629	4.182
Gas (25 ºC)		1.352	1.865
Relative density	$g\ cm^{-3}$		
at 0 ºC		1.470	1.000
at 25 ºC		1.443	0.997
Viscosity	mpa.s		
at 0 ºC		1.819	1.792
at 20 ºC		1.249	1.002
Critical temperature	ºC	457	374.2
Critical pressure	MPa	20.99	21.44
Refractive index	n_D^{20}	1.408	1.333

appearance, but it has a characteristic pungent odor. It is miscible with water in all proportions and also soluble in variety of organic solvents such as in alcohols, acids, ethers and aromatic compounds. Table 1.1 summarizes the physical properties of H_2O_2 comparing with H_2O [9].

1.4.2. Chemical Properties

1.4.2.1. Dissociation: Hydrogen peroxide is weakly acidic in aqueous solution, with a dissociation constant of 1.78×10^{-12} (pk_a= 11.75) at 20 ºC. As a weak acid, hydrogen peroxide forms salts with various metals.

1.4.2.2. Decomposition: The pure hydrogen peroxide solution is stable with weak decomposition. The rate at which it decomposes depends on the temperature and concentration. The stability of hydrogen peroxide solution increases with increasing its concentration. The decomposition rate increases 2.2 – 2.3 times for each 10 ºC rise from ambient to 100 ºC [9].

$$H_2O_2\,(g) \rightarrow H_2O\,(g) + 0.5\,O_2\,(g) \qquad \Delta H = -\,105.8\ \text{KJ/mol.}$$

Other factors accelerating the decomposition of hydrogen peroxide are as follows:

pH	:	Decomposition accelerates in alkaline solution. The maximum stability of H_2O_2 is in between pH 3.5 - 4.5.
Impurities	:	Presence of heavy metals and their ions, especially iron, copper, manganese, nickel and chromium.
Active surfaces:		Metal surfaces such as Pt, Pd or Ag, MnO_2, Charcoal.
Radiation	:	Especially the radiation of short wave length.

1.4.2.3. Oxidation and Reduction: Hydrogen peroxide (H_2O_2) contains oxygen in an intermediate oxidation state between molecular oxygen (O_2) and water (H_2O). Therefore, it can behave both as an oxidizing and a reducing agent (Table 1.2).

Form Table 1.2, it can be concluded that systems with a redox potential (E_0) > + 1.80 V and with a redox potential (E_0) < - 0.66 V at pH 0 cannot be oxidized by H_2O_2 [9]. Similar conclusion can be drawn for systems at pH 14.

Table 1.2: Standard potential of H_2O_2 at different pH

(a) H_2O_2 as an oxidizing agent		(b) H_2O_2 as a reducing agent	
Redox Reacton	Standard potential E_0 (V)	Redox Reacton	Standard potential E_0 (V)
pH 0		pH 0	
$HOOH + 2\ H^+ + 2\ e^- \rightarrow 2\ HOH$	+ 1.80	$HOOH \rightarrow 2\ H^+ + O_2 + 2\ e^-$	- 0.66
pH 14		pH 14	
$HOOH + 2\ e^- \rightarrow 2\ OH^-$	+ 0.87	$HOOH + 2\ OH^- \rightarrow 2\ HOH + O_2 + 2\ e^-$	+ 0.08

1.4.2.4. Substitution: The hydrogen atom of H_2O_2 can be substituted by alkyl and acyl groups, leading to the formation of alkyl or acyl peroxides.

H — O — O — alkyl	alkyl hydroperoxides
Alkyl — O — O — alkyl	dialkyl peroxides
H — O — O — acyl	percarboxylic acid
Acyl — O — O — acyl	diacyl peroxides.

These compounds are commercially used as catalysts for polymerization and also as oxidizing agents for a number of specialized reactions [9]. Inorganic peroxides of calcium, magnesium and zinc can be prepared from their corresponding hydroxides and monoperoxysulfuric acid, which can be made from sulfuric trioxide, or sulfuric acid with H_2O_2.

1.4.2.5. Molecular Addition: H_2O_2 is weak acid, and it can form hydroperoxide or peroxide salts or derivatives of many salts. The best known example of this is sodium borate, which forms sodium perborate, $[Na_2B_2(O_2)_2(OH)_4].6H_2O$, used as a bleaching detergent in laundry industry. Reaction between H_2O_2 and urea produces carmamide peroxide, used for whitening teeth.

1.5. Uses of H_2O_2

1.5.1. Industrial Uses

1.5.1.1. Bleaching Agent: Environmental concerns have led the pulp and paper industry to turn to alkaline solutions of H_2O_2 as a replacement for chlorine and, in some cases, for hypochloride and chlorinedioxide in bleaching applications, as its great advantage is that the degradation product is water. In the pulp and paper industry, it is used to bleach sulfate and sulfate cellulose, wood pulp, and wastepaper, and to brighten wood veneers and wooden structures. It is widely used in the textile industry for bleaching cotton, linen, bast fibres, wool, silk, polyester fiber, and polyurethane fiber.

A massive amount of H_2O_2 is converted to sodium perborate, sodium percarbonate, metallic peroxies or percarboxylic acids, which are less harsh than chlorine based cleaning agents, are used as cleaning detergents for washing cloths and fabrics in laundry industry. It is used to remove the colour of oils and wax.

1.5.1.2. Environmental Applications: H_2O_2 is an ecologically desirable pollution-control agent because it yields only water or oxygen on decomposition. Thus, it's use increases day-by-day to convert domestic and industrial effluents to an environmentally compatible state. It is used to detoxify effluents containing formaldehyde, phenols, or cyanide (e.g. wastewater from mines and tempering works, galvanizer concentrate, photochemical effluents), and to deodorize sulfur-containing effluents. Smoke and exhaust gases containing sulfur dioxide can be completely detoxified with H_2O_2.

1.5.1.3. Chemical Synthesis: H_2O_2 is very important in organic chemistry for epoxidation and hydroxylation (manufacturing of plasticizers and stabilizers for the plastic industry), oxidation (manufacturing of amine oxides as washing-up liquids), oxohalogenation , and initiation of polymerization. Interest in H_2O_2 as an active chemical ingredient for preparing other large-volume chemicals is growing day by day.

1.5.1.4. Other Uses: Sulfuric acid solutions of H_2O_2 are used for the pickling and chemical polishing of copper, brass, and other copper alloys, as well as for etching and cleaning printed circuit boards. Highly purified H_2O_2 is used in the manufacture of silicon semiconductor chips to clean silicon disks and to remove photoresist layers. It is also used for *in situ* leaching in underground uranium mining. It is a highly efficient disinfectant especially for packaging materials and is also used as a propellant in space technology.

1.5.2. Domestic Uses

H_2O_2 is not only used in industry, it enters to our house also. Household H_2O_2 solutions are commonly found in concentrations of 3-5 % solution. It is commonly used (typically around 5 %) by beauticians for coloring hair. In lower concentration (3 %), it is used medically for cleaning wounds and removing dead tissue. 3 % H_2O_2 solution can be used to remove bloodstains from carpets and clothing. Some gardeners have also professed the value of H_2O_2 in their watering solutions. They claim that its spontaneous decomposition releases oxygen to plant that can enhance root development and also help to treat root rot, which is cellular root death due to lack of oxygen. Table 1.3 summarizes the various applications of H_2O_2 as per grade.

Table 1.3: Applications of hydrogen peroxide as per grade

Sr.No	% H_2O_2/Grade	Applications
1.	3 %/ Drug grade	Used as antimicrobial agent for treating wounds and sanitizing agent.
2.	6 %/ Practical grade	Used by beauticians for coloring hair.
3.	30 %/ Reagent grade	Used for manufacture of high-value fine chemicals, pharmaceuticals or agrochemicals and, also used in medical research.
4.	30-32 %/ Electronic grade	Used for washing transistor and integrated chips.
5.	35 %/ Technical grade	Used for municipal or industrial wastewater treatments/disinfections, bleaching pulp/paper also for cosmetic and laundry applications.
6.	50 %/Food grade	Used in food products like cheese, eggs, whey products. Also used to spray inside of foil-lined containers for food storage that is known as the aseptic packaging system.
7.	90 %	Used by the military as a source of oxygen. Also used as a propulsion source in rocket fuel.

1.6. Manufacturing Methods of H_2O_2

The industrial production of H_2O_2 passed through three phases, starting with wet chemical processes, followed by electrochemical processes, and then by organic auto oxidation processes [9]. Almost all hydrogen peroxide is now produced by organic auto oxidation processes, primarily the anthraquinone process. The processes are discussed below.

1.6.1. Wet Chemical Processes

In 1818, L. J. Thenard [29] obtained H_2O_2 for the first time by reacting barium peroxide with nitric acid. This process was improved by using hydrochloride acid to release H_2O_2. The water-soluble barium chloride, which is formed simultaneously, was precipitated with sulfuric acid.

$$BaO_2 + 2\ HCl \rightarrow BaCl_2 + H_2O_2$$

$$BaCl_2 + H_2SO_4 \rightarrow BaSO_4\downarrow + 2\ HCl$$

$$BaO_2 + H_2SO_4 \rightarrow BaSO_4\downarrow + H_2O_2$$

With this reaction, Thenard established the foundation for the commercial manufacture of aqueous H_2O_2 solutions based on wet chemical processes, which began around 1880.

Drawbacks: The 3 % aqueous H_2O_2 solutions manufactured by barium peroxide process had only a limited market because of their high production cost, low H_2O_2 content, and unsatisfactory stability due to impurities.

1.6.2. Electrochemical Processes

In 1853, Medinger discovered the formation of H_2O_2 during electrolysis of aqueous sulfuric acid [30]. In 1878, Berthelot showed that peroxodisulfuric acid is formed during this electrolysis and then hydrolyzed by water to give sulfuric acid and H_2O_2 via peroxomonosulfuric acid [31].

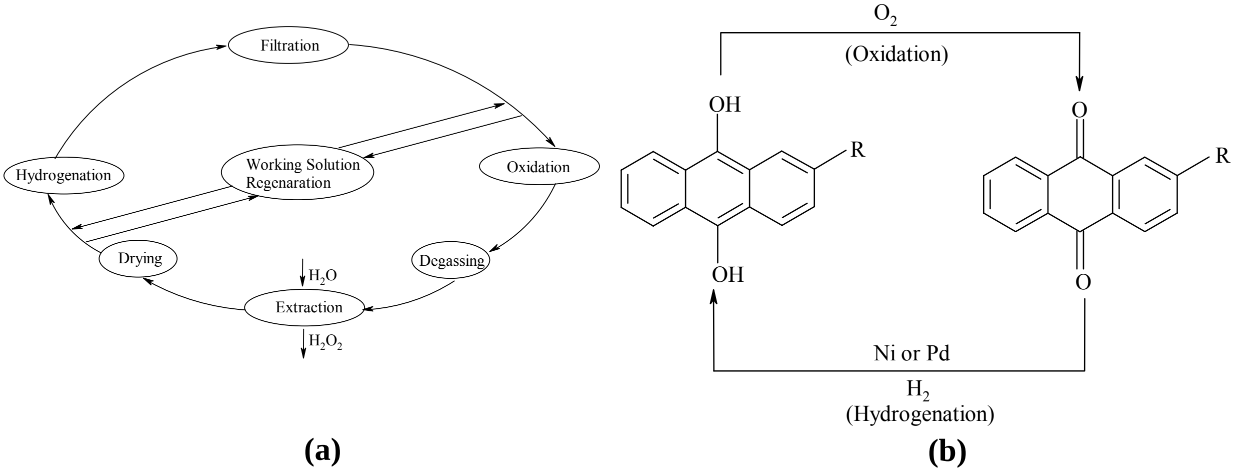
$$\begin{aligned} 2\ H_2SO_4 &\rightarrow H_2S_2O_8 + H_2 \\ H_2S_2O_8 + H_2O &\rightarrow H_2SO_5 + H_2SO_4 \\ H_2SO_5 + H_2O &\rightarrow H_2SO_4 + H_2O_2 \\ 2\ H_2O &\rightarrow H_2O_2 + H_2 \end{aligned}$$

There are several electrochemical processes. In these processes, an ammonium sulfate solution was electrolyzed instead of free sulfuric acid, and the resulting ammonium peroxodisulfate (Degussa – Weissenstein and Riedel – Loewenstein process) or potassium peroxodisulfate made from it (Munich and Pietzsch – Adolph process) was hydrolysed.

Drawbacks: All these processes have a very high-energy consumption and an unsatisfactory yield.

1.6.3. Organic Auto Oxidation Processes

1.6.3.1. Anthraquinone Process (AQ Process): In 1901, Manchot discovered that hydroquinones (or hydrazobenzenes) react quantitatively with oxygen to form quinines and H_2O_2 [35]. The azobenzene process showed two major technical drawbacks; hydrogenation of azobenzene was performed with sodium amalgam whereas oxidation of hydrozobenzene produced satisfactorily only in alkaline solution. Pfleiderer and Riedel overcome these problems by using alkylated anthraquinones, instead of azobenzene. The process is known as the Riedel – Pfleidereer process, was developed in Germany by BASF during World War-II (1935 – 1945) [34,36].



(a) **(b)**

Figure 1.5: (a) Flow diagram and (b) the two key step of the AQ process.

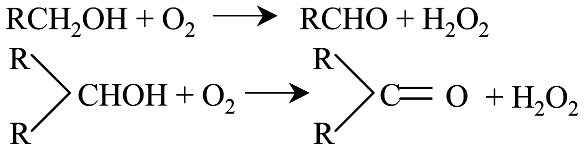
In this process (Figure 1.5), a 2-alkyl anthraquinone is dissolved in a mixture of an aromatic and a long chain alcohol (a mixture often called the “working solution”) and then hydrogenated over a palladium catalyst in a three-phase reactor. The resulting anthrahydroquinone is oxidized by air in a subsequent reactor (non-catalytic two phase reaction), producing H_2O_2 and regenerating the anthraquinone. The H_2O_2 is stripped from the organic working solution into water in a counter-current column, producing a solution that contains usually 30 % by weight H_2O_2. The aqueous H_2O_2 is then distilled to remove impurities and also to raise the concentration to as high as 70 %.

Drawbacks: The AQ process has supplanted all of its competitors because it generates H_2O_2 continuously at mild temperatures (40 – 60 ºC) while preventing contact between H_2 and O_2 during production. The AQ process, however, suffers from several inefficiencies as follows:

i) Use of costly complex solvent system to keep both the reactant and product in the solution,
ii) Loss of quinone due to non-selective hydrogenation,
iii) Elaborate treatments to remove degradation products and organic maters,
iv) Deactivation of hydrogenation catalyst, and
v) Involvement of several hazardous steps.

The production cost of H_2O_2 is, therefore, high for this process. The process is cost-effective only on a large-scale operation (> 20,000 tonnes per annum). The transportation of H_2O_2 from the point of manufacture to the point of use is therefore, becomes costly for this large-scale industrial process.

1.6.3.2. Shell Process (2-propanol Process): In 1945 Harris discovered that primary and secondary alcohols react with oxygen to form H_2O_2 and an aldehyde or ketone respectively [37].



$$RCH_2OH + O_2 \longrightarrow RCHO + H_2O_2$$

$$R_2CHOH + O_2 \longrightarrow R_2C{=}O + H_2O_2$$

A process for the production of H_2O_2 and acetone by atmospheric oxidation of 2-propanol was first suggested by Rust [38]. The aldehydes formed in the reaction with primary alcohols are oxidized easily, only the oxidation of secondary alcohols, specially 2-propanol, has industrial importance.

Drawbacks: Several side reactions take place. To reduce the formation of byproducts, particularly acetic acid that affects the quality of H_2O_2, the oxidation is carried out in several consecutive steps at decreasing temperature.

1.7. Literature Survey on Direct Oxidation of H_2 to H_2O_2 by O_2 (A Dream Process)

Currently, most of the H_2O_2 is produced by the sequential oxidation and reduction of anthraquinone [34,36]. Although used on a multi-million tonne scale annually, there are drawbacks to the anthraquinone process (which involves ***the indirect oxidation of H_2 to H_2O_2***), such as the use of expensive quinone solvent system and the requirement of periodic replacement of anthraquinone due to hydrogenation. In addition, the process is only economically viable on a relatively large scale and this necessitates the transportation and storage of concentrated solution of H_2O_2, which is hazardous. In view of this, most of the H_2O_2 is used for cleaning or in the paper and textile industries and only a small fraction is used for the manufacture of fine chemicals and in wastewater treatments. To use H_2O_2 for wastewater treatments and synthesis of fine and bulk chemicals, its production cost must be lowered appreciably. For this H_2-to-H_2O_2 oxidation should be the appropriate alternative of the anthraquinone process, because direct oxidation of H_2 to H_2O_2 is more atom economical.

The identification of a direct route for the synthesis of H_2O_2 from the reaction of H_2 and O_2 would be highly beneficial. For example, there will be the possibility of small-scale distributed synthesis. At present, no commercial process exists, but there has been significant interest in this reaction in industrial laboratories. Apart from its hazardous nature, the main problem associated with the H_2-to-H2O2 oxidation process is the low H_2O_2 selectivity (or high selectivity for the water formation). This is because of the undesirable thermodynamically highly favoured non-selective water forming reactions, such as the parallel H_2-to-water oxidation ($H_2 + 0.5\ O_2 \rightarrow H_2O$) and consecutive H_2O_2 decomposition ($H_2O_2 \rightarrow H_2O + 0.5\ O_2$) and/or hydrogenation ($H_2O_2 + H_2 \rightarrow 2\ H_2O$), occurring simultaneously with the desirable H_2-to-H_2O_2 oxidation over the same catalyst. Because of these serious problems with this process, the direct oxidation of hydrogen-to-hydrogen peroxide is often considered as a ***Dream Reaction***. If this process is developed and commercialized successfully, it would be a major breakthrough in the oxidation process technology. The literature reports on this novel approach of H_2O_2 production are presented in Tables 1.4 - 1.7.

Henkel et al first patented this process in 1914 [50]. Since then a number of patents on this process have been issued. However, the modern era of research into the direct reaction began in 1976 with a patent granted to the Tokuyama Soda Co. of Japan (DE 2528604 B2). A silica supported Pd catalyst was used in a 0.3 M mixed HCl + H_2SO_4 in a batch reactor at 20 atm (P_{H2} = 5.8 atm; P_{O2} = 14.2 atm) and 30 ºC. The reaction produced a 6.6mol% solution of aqueous H_2O_2 after 20 hours. The metal catalyzed direct oxidation of H_2 to H_2O_2 is covered in several patents [51−124], which have been summarized in Tables 1.6-1.8.

Homogeneous alternative of the heterogeneous process, with the reaction medium comprising an immisible mixture of water and organic solvent e.g. fluorocarbon, chlorobenzene, xylene etc, in which an organometallic pd-complexes were dissolved, for the production of H_2O_2 has been reported [51-53]. Another homogeneous process for the synthesis of H_2O_2, employing an iridium complex as the catalyst in presence of a quinone has also been reported [54].

Most of the efforts have been made to produce H_2O_2 by the direct oxidation of H_2 by O_2 using supported Pd-based catalysts. Pospelova et al [125-127] published a series of three papers in 1961 on the direct oxidation of H_2 to H_2O_2. They discussed that a necessary condition for the production of considerable amounts of H_2O_2 by the catalytic action of palladium (which is responsible for H_2O_2 formation) from H_2/O_2 gas mixture in the liquid medium is the protection of H_2O_2 from catalytic decomposition. The role of acid in the synthesis of H_2O_2 from H_2/O_2 gas mixture consists in preventing the decomposition of H_2O_2. They noted that H_2O_2 yield reaches to a maximum value with short contact time and when the catalyst was poisoned (by HCN or HCl) to prevent decomposition of H_2O_2. They noted a strong effect of H_2/O_2 ratio on the overall reaction rate and the yield of H_2O_2 in the H_2-to-H_2O_2 oxidation in aqueous acidic reaction medium.

Fu et al [128] reported that the active catalysts for H_2O_2 synthesis include platinum group metals attached to hydrophobic carbon, supported on a mixture of hydrophobic and hydrophilic materials. Only palladium catalysts supported on a hydrophobic component were found to be selective towards H_2O_2 formation. The Pd supported on hydrophobic fluorinated carbon catalyst showed maximum H_2O_2 selectivity (8.7 %) at 25 ºC and 0.65 Mpa pressure. They concluded that the decisive factor in the synthesis of H_2O_2 is the hydrophobicity of the catalyst; the Pd metal size or its area is found to be less important.

Sellers and co-workers [129] concluded based on their theoretical work, using the bond order conservation-Morse potential (BOC-MP) model, that the formation of H_2O_2 by direct oxidation of H_2 by O_2 is more favorable on Au and Ag than Pt and Pd. They have discussed that depending on the experimental conditions; the reaction of H_2 and O_2 on noble metals may proceed along a H_2O_2 channel or a H_2O channel where OOH radicals and OH radicals, respectively, play a fundamental role. They have also concluded that promoter will play an important role for the production of H_2O_2.

Thompson and co workers [130] employed supported Pd-Pt on porous zirconium phosphate viologen phosphonate material for the synthesis of H_2O_2 from H_2 and O_2. They observed at O_2/H_2 ratio of 1.0, the highest H_2O_2 concentration was obtained. In another work, Thompson and co-workers [131] used a combination of an organic catalyst (viologen) for the activation of O_2 and Pd metal for the activation of H_2 for the direct synthesis of H_2O_2, using methanol in conjugation with H_2SO_4 as the reaction medium. They concluded that H_2 splits into protons and electrons by the noble metal, with the electrons being transferred to the viologen group. The reduced viologen then reacts with O_2 to give the product, H_2O_2.

Park et al [132] reported the generation of H_2O_2 from H_2 and O_2 over Pd containing zeolite beta catalysts adsorbed with organic compounds such as 1,4-benzoquinone, hydroquinone, azobenzene and hydrazobenzene. They suggested that hydroquinone acts as a strong hydrogen transfer agent to promote the production of H_2O_2 from H_2 and O_2 in cooperation with a Pd catalyst.

Choudhary et al [133] reported non-hazardous direct oxidation of H_2 to H_2O_2 using novel composite Pd-membrane catalyst. Almost 100% H_2 conversion with high H_2O_2 selectivity (70 %) was obtained with the membrane catalyst.

Beckman et al [134] reported the generation of H_2O_2 from H_2 and O_2 using CO_2 as the solvent and a CO_2-soluble Pd catalyst.

Choudhary and co-workers reported the direct synthesis of H_2O_2 from the mixed feed of H_2 and O_2 (maintaining H_2 concentration in O_2 below the explosion limit) over the Pd-containing fluorinated or sulfated alumina, zirconia, ceria, yittria, gallia [135] and also the oxidized and reduced Pd-containing zeolite catalysts [136] at room temperature and atomospheric pressure. They observed modification of the supports (Al_2O_3 or ZrO_2) by fluorination or sulfatation prior to Pd loading on them causes a drastic increase in the H_2O_2 selectivity in the H_2-to-H_2O_2 oxidation. They observed that the H_2O_2 selectivity in the H_2 oxidation over the catalyst depends largely on the acidity of the reaction medium. The activation of supported Pd catalysts due to their surface/subsurface oxidation by their various oxidative pretreatments leading to the drastic increase in the H_2O_2 selectivity has also been reported by Choudhary et al [137].

Lunsford et al [138,139] also reported the synthesis of H_2O_2 from H_2 and O_2 over the colloidal Pd catalysts in liquid reaction medium. They have concluded that the rate of H_2O_2

formation in the reaction is proportional to the amount of Pd colloid rather than the total amount of Pd in the system. From the $^{18}O_2$ isotopic study they have shown that oxygen remains in the diatomic form during the production of H_2O_2 in the H_2-to-H_2O oxidation.

Hutchings et al [140] reported direct formation of H_2O_2 from H_2/O_2 mixture over a gold catalyst using methanol and supercritical CO_2 as the reaction medium; good H_2O_2 selectivity in the reaction was obtained only after the addition of Pd to the gold catalysts. In another work [141], they reported the H_2O_2 formation over the Pd/sulfonated carbon catalyst in a mixture of methanol and water as the reaction medium. They noted that the use of low temperature and short reaction time are the key factors for achieving high H_2O_2 selectivity in the reaction. The addition of HBr in the reaction medium promotes the H_2O_2 selectivity in the direct oxidation of H_2 to H_2O_2. They have concluded that, at higher temperatures, H_2 combustion to water becomes more important leading to the decrease of the H_2O_2 selectivity.

Haruta and co-workers reported the direct synthesis of H_2O_2 from H_2 and O_2 over highly dispersed Au catalysts [142]. They have identified that the gold nanoparticles are only active for the production of H_2O_2 from H_2 and O_2.

Burch et al [143] reported that the use of low metal loading, an organic co-solvent (e.g. ethanol or acetonitrile) and reduced Pd as the catalytic metal all lead to good activity and selectivity in the direct oxidation of H_2 to H_2O_2.

Yamanaka et al reported the production of H_2O_2 using fuel cell system [44]. Recently in another publication, they have reported the direct and continuous production of H_2O_2 with 93% selectivity using a modified fuel cell system [46]. They employed a three-phase boundary (gaseous O_2, aqueous electrolyte and solid cathode) system for improving the H_2O_2 concentration. A porous cation membrane in the cathode compartment, which prevents diffusion of H_2O_2 from the cathode to the anode side, was employed. A 7 wt% H_2O_2 was produced continuously at a rate of 8.3 $L.h^{-1}.m^{-2}$. They concluded that, to produce a concentrated H_2O_2 solution, concentration of O_2 at the cathode should be increased.

Lunsford [144] provided a brief review on the H_2-to-H_2O_2 oxidation.

Fierro and co-workers [145] reported the direct synthesis of H_2O_2 with Pd–loaded sulfonic acid polystyrene resin in a methanol : water (96:4) mixture in presence of HBr in the reaction medium. Fairly high H_2O_2 concentration with H_2 conversion > 90% was obtained in the process. They have concluded that the high performance of the catalyst is due to the presence of a larger fraction of Pd^{II} ions interacting with the $–SO_3H$ groups of the resin.

Lunsford and co-workers [146] studied the mechanism of H_2O_2 and H_2O formation in the Pd catalyzed reaction between H_2 and O_2 in an aqueous medium. They concluded that H_2O is formed both by a parallel reaction between H_2 and O_2 and by a secondary reduction of H_2O_2 by H_2. The parallel reaction is inhibited by the presence of bromine. They suggested that the presence of bromide ions increases the selectivity of H_2O_2 in the reaction, possibly by blocking sites in the catalyst for O_2 dissociation. H_2O_2 is stable in the presence of O_2 but is reduced by H_2 to H_2O.

Choudhary et. al [147] reported that the incorporation of bromide ions, particularly at optimum concentration, in the supported Pd catalysts by their bromination causes a drastic improvement in their performance (both the H_2O_2 selectivity and yield) in the direct oxidation of H_2 to H_2O_2.

Lunsford et. at. [148] reported that ethanol is superior to water as the liquid phase for the direct formation H_2O_2 from H_2 and O_2 over a Pd/SiO_2 catalyst. They found that in ethanol, the active Pd component remains on the SiO_2 surface but in water it first becomes colloidal and then converted to relatively large particles of palladium black. In another similar work [149], they also suggested that the H_2SO_4/ethanol phase is active and selective for the direct formation of H_2O_2; because in the presence of O_2, active ions are formed from ethanol and these ions block the Pd ensembles.

Guo et. al. [150] have reported the direct and continuous synthesis of concentrated H_2O_2 via the gas-phase reaction of H_2/O_2 non-equilibrium plasma under ambient conditions.

Ishihara et. al. [151] studied that Au supported on SiO_2 exhibits high activity to H_2O_2 formation by direct oxidation of H_2 by O_2. They concluded that the high H_2O_2 formation rate is due to the low activity of the SiO_2 supported catalyst for H_2O_2 decomposition. They have also reported that a small amount of Pd is also effective for increasing the H_2O_2 formation rate.

Strukul et. al. [152] have used tubular catalytic membranes (Pd membrane) for the synthesis of H_2O_2 under mild conditions. They observed that the catalytic activity depends on the oxidation state of surface Pd atoms (a pre-oxidation step is necessary) and the temperature (temperature as low as 2-5 ºC favor H_2O_2 synthesis over decomposition).

Hutchings et. al. [153] studied in details the direct synthesis of H_2O_2 from H_2 and O_2 using TiO_2-supported Au, Pd and Au-Pd catalyts. They found that the Au-Pd/TiO_2 materials calcined at 400 ºC are highly active and selective for H_2O_2 synthesis (114 $mol_{H2O2}.h^{-1}.kg_{cat}^{-1}$ and 93 % H_2O_2 selectivity).

Choudhary et. al. [154] have studied in details the influence of the presence of protons (mineral acid) and different halide anions (F^-, Cl^-, Br^- or I^-) in the aqueous reaction medium on the H_2O_2 formation in the direct oxidation of H_2 to H_2O_2 over different supported Pd catalysts. They reported that among the halide anions, only the chloride and bromide anions (particularly for the Pd/C and metal oxide supported Pd, respectively) act as catalyst promoter for drastically enhancing the H_2O_2 selectivity or H_2O_2 yield, however, for their promoting action, the presence of protons is a must. They have also reported that the cations associated with the halide anions are found to play only a little or no role in controlling the conversion or selectivity in H_2-to-H_2O_2 oxidation and H_2O_2 destruction reactions. In another work, Choudhary et. al. [155] have investigated the influence of oxidation state, support and precious metal additives (Au, Pt, Rh and Ru) on the direct H_2O_2 synthesis over Pd-based catalysts. They concluded that the Pd oxidation state is found to be more important for determining the H_2O_2 yields than particle size and surface area of the catalyst. They have also observed that the H_2O_2 yield in the H_2-to-H_2O_2 oxidation passes through a maximum with increasing the Au, Pt concentration, whereas addition of Rh and Ru is found to be detrimental.

Strukul et. al. [156] observed that the use of Pd/Pt bimetallic catalysts in the direct synthesis of hydrogen peroxide shows higher H_2O_2 yield and selectivity with respect to the monometallic Pd catalyst. For example, when a catalyst comprises of Pd/Pt ratio of 18 was used, three times increase in H_2O_2 selectivity was observed. In another work, Strukul et. al. [157] studied the direct synthesis of H_2O_2 using palladium-based catalysts supported on anion-doped zirconia. They found that the 2.5 % Pd loaded on anion-doped zirconia samples show good catalytic activity, selectivity, mechanical stability, and reusability. Methanol was reported to be the best solvent for the direct oxidation process.

Recently, Hutchings et. al. [158, 159] reported the direct synthesis of H_2O_2 from H_2 and O_2 using zeolite-supported Au catalysts and Al_2O_3 supported Au-Pd catalysts. They studied the effect of calcination temperature of these catalysts and found that for uncalcined catalysts high rates of H_2O_2 formation is observed, but these catalysts are unstable and loose Au during use.

They suggested that catalysts calcined at 400 ºC are more stable and can be reused without loss of gold.

Very recently, Lunsford et. al. [160] studied that chloride ions, even in small amount, have a strong positive effect on the net formation of H_2O_2, because they inhibits the combustion of H_2 and limits the reduction and decomposition of H_2O_2. They concluded that the fundamental roles of Cl^- ions appears to be the inhibition of O-O bond breaking during the adsorption of O_2 and H_2O_2 and to inhibit the dissolution pf palladium in the reaction medium.

The large numbers of publications on the H_2-to-H_2O_2 oxidation in the open literature indicate the importance of the process. To make this process commercially feasible, it is necessary to develop a highly active, selective and reusable solid catalyst for the direct oxidation of H_2 to H_2O_2. This objective could be accomplished by thoroughly investigating the factors influencing the activity and H_2O_2 selectivity of different supported palladium catalysts in the direct H_2-to-H_2O_2 oxidation process and thereby developing a commercially acceptable catalyst and catalytic process for the direct H_2 to H_2O_2 oxidation.

1.8. Literature Survey on H_2O_2 Decomposition/Hydrogenation

H_2O_2 is an unstable intermediate product in the H_2-to-H_2O_2 oxidation process. This is because of the thermodynamically highly favoured H_2O_2 decomposition ($H_2O_2 \rightarrow H_2O + 0.5\ O_2$) and/or hydrogenation ($H_2O_2 + H_2 \rightarrow 2\ H_2O$) reactions, occurring after the formation of H_2O_2. Because of this, the study of H_2O_2 decomposition/hydrogenation has great practical and scientific importance to achieve the higher H_2O_2 yield in the H_2-to-H_2O_2 oxidation process.

The pure H_2O_2 is stable with weak decomposition. However, when it comes in contact with heavy metals or various organic compounds, or mixes with impurities, it produce O_2 and decomposition heat. The decomposition of H_2O_2 is influenced by several factors viz. catalytic amount of cations (e.g. elements of univalance or more such as Fe, Cu, Ni, Pb and Mn), active surfaces (especially rough surfaces), pH, and, also by radiation especially the rays of short wavelength. Apart from the H_2-to-H_2O_2 oxidation study, both homogeneous and heterogeneous catalyzed decomposition of H_2O_2 have been widely investigated in several papers [161-199] in the open literature.

In a few papers, heterogeneous Pd catalyzed H_2O_2 decomposition has been studied in the context of metal catalyzed direct oxidation of H_2 to H_2O_2. Pospelova et al [125,127] noted the inhibition of decomposition of H_2O_2 by hydrogen ions, which indicates that the catalytic activity in the heterogeneous decomposition is mainly due to HO_2^-, formed as a result of the dissociation, $H_2O_2 \Leftrightarrow HO_2^- + H^+$. The author concluded that in acid solution, H_2O_2 (which itself is an acid) forms a double layer at the boundary of the micro-crystals of Pd and the solution with an external coating of H^+ ions. In this layer, the dissociation of H_2O_2 is suppressed and the penetration of HO_2^- ions to the surface of the Pd is hindered. Fu et al [128] reported that Pd deposited on the hydrophilic supports is very efficient for H_2O_2 decomposition. They observed that if Pd is present on the hydrophobic support and then mixed with a small amount of palladium-free hydrophilic component, H_2O_2 is bound to decompose slowly. They also reported an increase in the amount of silica in Pd/carbon leads to rise in the rate of H_2O_2 decomposition.

Choudhary and co-workers [133,135-137,147,154,155,200] also studied the heterogeneous H_2O_2 decomposition over supported Pd catalysts in the context of direct oxidation of H_2 to H_2O_2. They observed the hydrophobic polymer membrane provides a barrier for returning the H_2O_2 back to the catalyst surface, once it is formed and adsorbed by the aqueous liquid medium which causes a large increase in the H_2O_2 selectivity in the H_2-to-H_2O_2 oxidation process [133]. They have shown that a total or subsurface oxidation of Pd to PdO by its oxidative pretreatment results in a drastic reduction of the H_2O_2 decomposition activity of the supported Pd catalysts [135-137,155]. They observed that when acidic medium is used in place of pure water as the reaction medium, catalytic H_2O_2 decomposition activity of the supported Pd catalysts is reduced appreciably. This shows the important role of H^+ for inhibiting the H_2O_2 decomposition. Influence of acid concentration on the kinetics of H_2O_2 decomposition over Pd/C catalyst has been thoroughly investigated [200]. They have also investigated that the H_2O_2 decomposition reaction over reduced Pd catalyst in an aqueous reaction medium is strongly influenced by the type of halide anions and their concentration in the reaction medium [154] or in the catalyst [147]. The H_2O_2 decomposition is decreased drastically due to the addition of Cl^-, Br^-, or I^- in the order of $I^- > Br^- > Cl^-$, but is increased due to the addition of F^-.

Ishihara et. al. [151] observed that the addition of small amount of Pd to Au/SiO_2 catalyst was effective for increasing H_2O_2 formation rate due to the improved H_2 activation capability. However, H_2O_2 formation rate decreased at the excess amount of Pd addition by the improved H_2O_2 decomposition activity of the catalyst. They also concluded that under the condition of non-halogen compound added, decomposition of H_2O_2 easily proceeds and so synthesis of H_2O_2 with high yield is rather difficult.

Very recently, Lunsford et. al. [160] studied the role of Cl^- ions on the decomposition of H_2O_2; they limit the decomposition of H_2O_2. They concluded that the fundamental role of Cl^- appears to be the inhibition of O-O bond breaking during the adsorption of H_2O_2 on the catalyst surface. Authors expected that this is due to the blocking of Pd ensembles on the surface or by electronic effects.

A little information is available on the hydrogenation of H_2O_2 over Pd catalyst [141,155,173]. A detailed study on H_2O_2 hydrogenation in the H_2-to-H_2O_2 oxidation process has been studied by Choudhary and co-workers [154]. They observed that in the presence of H_2, the H_2O_2 conversion over the Pd catalysts in the acidic medium occurs by the simultaneous H_2O_2 decomposition and hydrogenation reactions, depending upon the halide anions in the medium. In absence of any halide or in presence of fluoride anions, the H_2O_2 conversion is mainly due to a fast H_2O_2 decomposition. Whereas, in the presence of chloride or bromide anions, it is mainly by the H_2O_2 hydrogenation, which is much slower. In the halide promoted H_2-to-H_2O_2 oxidation reaction, the H_2O_2 hydrogenation rather than H_2O_2 decomposition plays dominating role in controlling H_2O_2 formation; under similar conditions, the H_2O_2 hydrogenation is much faster than the H_2O_2 decomposition.

Therefore, it is practically very important to investigate in details the kinetics of H_2O_2 decomposition/hydrogenation over Pd catalysts and also to know the factors (such as, presence of different halide anions and associated cations with or without acid, concentration of Cl^- and Br^- anions, different mineral acids, etc) affecting the rate of H_2O_2 decomposition/hydrogenation over the catalyst in an aqueous medium.

1.9. Literature Survey on O_2-to-H_2O_2 Reduction by Hydroxylamine, Hydrazine or Their Salts for the *in situ* Generation of H_2O_2

At present, the *in situ* H_2O_2 generation, required for organic oxidation reactions, is done by two methods – a) by indirect oxidation of H_2 employing anthraquinone carrier [201] and b) by the direct oxidation of H_2 by O_2 [202-205]. Conventionally, H_2O_2 can be generated *in situ* by the oxidation of hydroanthraquinone (hydroanthraquinone + $O_2 \rightarrow$ anthraquinone + H_2O_2). However, the use of this method for the *in situ* H_2O_2 generation is limited because of the use of a complex solvent system and also due to the difficulties in separation of the solvent, unconverted hydroquinone and product of the reaction (anthraquinone) from the product(s) of organic oxidations. Direct oxidation of H_2 to H_2O_2 is a clean but highly hazardous process and hence its use for the *in situ* H_2O_2 generation is very dangerous. The progress made in this topic is rather slow, mostly because of an efficient method for the *in situ* H_2O_2 generation in an environmentally friendly manner, particularly at mild conditions for avoiding or minimizing the mismatch between the optimal condition required for the *in situ* H_2O_2 generation and the consecutive step of consumption of the generated H_2O_2 in the oxidation of organic substrates. It is, therefore, interesting to develop a new environmentally cleaner method for the *in situ* H_2O_2 generation, eliminating the catalyst/by-product separation and corrosion problems.

Sheriff et. al. [206-209] used Mn (II or III) complexes (as homogeneous catalyst) for the reduction of O_2 (at 3 bar) by hydroxylamine to H_2O_2 in an aqueous medium under near ambient conditions. They concluded that the characteristic of this system is to produce high concentration of H_2O_2 probably due to the absence of free metal ions in the system to catalyze the decomposition of H_2O_2. However, the Mn-complexes, used as homogeneous catalysts in this process, are difficult to separate from the reaction mixture.

Recently Choudhary et. al. [210,211] suggested a new method based on selective reduction of O_2 by hydrazine or its salts, using easily separable and reusable supported Pd catalyst in aqueous medium (at ambient conditions), for *in situ* H_2O_2 generation. They concluded that the presence of both acid (protons) and bromide anions are essential for the selective reduction of O_2 by hydrazine to H_2O_2 and in their absence, the reaction leads only to the formation of water. However mineral acid and bromide promoters used in this method is expected to create corrosion problems for commonly used stainless-steel reactors in the organic oxidations.

Therefore, there is a practical need to investigate a more environ-friendly/greener method for the *in situ* H_2O_2 generation from the reduction of O_2 by hydrogen containing compounds with the formation of environmentally benign by-products (viz. N_2 and water) in the absence of acid and/or halide promoter in the reaction medium, even at ambient conditions, using a heterogeneous (easily separable and reusable) catalyst.

Table 1.4 ***Summary of work on the synthesis of H_2O_2 from mixed H_2 and O_2 feed using homogeneous catalysts (Patent survey)***

Patent No	Investigator (year)	Reaction medium/ promoter	Catalyst	Result /remark, if any	Ref
I	**II**	**III**	**IV**	**V**	**VI**
US 4,128,627	Paul N. Dyer and F. Moseley (1978)	A mixture of water and organic solvents viz. xylene, dichlorobenzene, chlorobenzene, etc	Pd-complexes, L_2MX_2 (where, L=ligand containing group 5b element (e.g. P), M = group 8 metal (preferably Pd) and X = halogen	1.73 wt% H_2O_2 was produced after 4 h.	**51**
US 4,336,240	F. Moseley et al (1982)	Mixture of water and an organic solvent (fluorocarbon).	Organometallic Pd- catalysts viz. bis (tri (pentafluorophenyl) phosphine) palladium dichloride, bis (tricyclohexylphosphine) palladium dichloride	With the 1,2 dichlorobenzene as a reaction medium 1.5 wt% H_2O_2 was obtained after 5h.	**52**
US 4,347,231	Michaelson et al (1982)	Two phase homogeneous catalysis system comprising an inert solvent e.g. toluene and aqueous solution and quinone e.g. benzoquinone, p-methoxy phenol promoter.	Iridium complex viz. chlorocarbonyl-bis-(triethylphosphine) iridium, cholorocarbonyl-bis-(tricyclohexyl phosphine) iridium etc.	In presence of a quinone promoter there was significant formation of H_2O_2 from H_2 and O_2 but in absence of any quinone promoter no H_2O_2 was formed.	**53**
US 4,347,232	Michaelson et al (1982)	An inert organic solvent viz. toluene, chlorobenzene xylene, dichlorobenzene etc	Pd(0) complexes of dibenzylidene acetone.	0.61 wt% H_2O_2 was obtained from the equal volume of H_2 and O_2 gas mixture at 150 psig and 25 ºC after 2 h.	**54**

Table 1.5: ***Summary of work on the synthesis of H_2O_2 from mixed H_2 and O_2 feed using heterogeneous catalysts (Patent survey)***

Patent No	Investigators (year)	Reaction medium/ promoter	Catalyst	Result /remark, if any	Ref
I	**II**	**III**	**IV**	**V**	**VI**
US 2,015,040	Apietz (1935)	Water vapour	Silent electric discharge	10% H_2O_2 was produced in aqueous solution. Energy required to produce 1.0 kg of H_2O_2 was 40kwh.	**55**
GB 1056126	G. W. Hopper (1967)	Aqueous acidic + organic	Pd/Silica gel	50% H_2O_2 yield relative to H_2 was obtained.	**56**
DE 2528601B2	Y.Izumi (1976)	0.3 M mixed solution of HCl + H_2SO_4	Pd/Silica	6.6 mol% aqueous solution of H_2O_2 was produced at 20 atm (P_{H2} = 5.8 atm; P_{O2} = 14.2 atm) and 30 ºC after 20 hours.	**57**
US 4,007,256	Kim et al (1977)	Water + nitrogen compound + a strong acid	Pd supported catalyst	An oxidation of organic compound in the reaction medium was carried out by the insitu generated H_2O_2 in the reaction medium.	**58**
US 4,009,252	Y.Izumi (1977)	Aqueous and/or mixture of organic and acidic aqueous	Pd/C pretreated with aldehyde or ketone and a dilute solution of HCl	2.46 M H_2O_2 was produced in a mixture consisting of 75% acetone and 25% 0.1 N H_2SO_4 over the aldehyde and HCl pretreated catalyst.	**59**
US 4,279,883	Izumi et al (1981)	Acidic aqueous	Platinum group metal supported catalysts	7.2 wt% H_2O_2 was obtained in the deionized water after 200 h at 5 ºC over the Pd/hydrous silicic acid catalyst.	**60**
US 4,335,092	Dalton, Jr. et al. (1982)	Mixture of alcohol, acid and formaldehyde	Supported Pd catalysts	The catalyst was produced 364 moles of H_2O_2/mole of Pd after 3h where the deactivation of the catalyst was completed.	**61**
US 4,336,238	Dalton, Jr. et al (1982)	Aqueous acidic	Pd/Carbon	A higher yield of H_2O_2 was obtained by continuously removing the acidic aqueous liquid from the reaction vessel where Pd salt was produced by solubilization of the Pd catalyst.	**62**

Table 1.5: ***(continued)……….***

I	II	III	IV	V	VI
US 4,336,239	Dalton, Jr. et al (1982)	An acidic medium containing an oxygenated or nitrogenous organic compound	Supported Group VIII noble metal catalyst.	40 % H_2O_2 selectivity at H_2O_2 formation rate of 1.2 moles H_2O_2/gm Pd/h was obtained in a solvent consisting of 80% acetone and 20% aqueous acidic mixture of 0.1 N H_2SO_4 and 0.01 N HCl.	**63**
US 4,379,778	Dalton, Jr. et al (1983)	An aqueous liquid, containing an acid and a non-acidic oxygen-containing organic compound	Pd/Carbon (pretreated with an aldehyde or ketone)	Pretreatment of the catalyst with aldehyde or ketone affects both the H_2O_2 decomposition and H_2O_2 yield in the process.	**64**
US 4,389,390	Dalton, Jr. et al. (1983)	Acidic aqueous	Pd/Carbon	77% H_2O_2 selectivity was obtained at a H_2O_2 formation rate of 0.83mole H_2O_2/gm Pd/hr at 7 ºC and 100 psig.	**65**
EP 0132294A1	L.W.Gosseer (1985)	0.1M HCl	Pd/Carbon	15 mol% H_2O_2 was obtained after 4 h at 100 atm pressure ((P_{H2} = 35 atm; P_{O2} = 70 atm).	**66**
US 4,661,337	Brill et al (1987)	Aqueous acidic	Supported noble metal catalyst	19.5 wt% H_2O_2 was obtained in 0.1 M HCl after 4h reaction over Pd (5%) /activated carbon catalyst.	**67**
US 4,681,751	L.W.Gosseer (1987)	Aqueous acidic (HCl) medium containing Cl^-/Br^- ions	Pd/Carbon	18.8 wt% H_2O_2 was obtained after 68 h at 400 psig pressure.	**68**
US 4,772,458	L.W.Gosseer et al (1988)	Aqueous medium containing H^+ and Br^- ions	Pd and Pt or combination of Pd-Pt supported carbon, silica, alumina	Presence of bromide ion in the reaction medium improves H_2O_2 yield and selectivity in the process.	**69**
US 4,832,938	L.W.Gosseer (1989)	Aqueous medium / Cl^- and/ or Br^- ions	Pd-Pt supported carbon, silica, alumina	18.4 wt% H_2O_2 at 63% H_2O_2 selectivity was obtained using Pd/alumina catalyst at 425 psig and 14ºC.	**70**
US 4,889,705	L. W. Gosser et al (1989)	Mixture of aqueous and organic (less than 2 wt%) and H^+ and Br^- ions.	Pt-Pd supported on carbon, silica and alumina.	Maximum H_2O_2 selectivity was obtained at a concentration of 0.1 M H^+ and Br^- in the reaction medium maximum.	**71**

Table 1.5: ***(continued)……….***

I	II	III	IV	V	VI
EP 0498166A1	Hiramatsu et al (1991)	Pt group supported metal catalysts with adsorbed halogenated organic compounds	Aqueous and/or acidic aqueous	0.73 wt% H_2O_2 at 70% H_2O_2 selectivity was obtained in an aqueous medium containing 70 ppm of aminotri (methylenephosphonic acid) over bromomethyldimethylsilane treated Pd (5%)/Alumina catalyst.	**72**
US 4,996,039	Pralus et al (1991)	Aqueous	Metal catalyst comprising platinum or palladium.	5.1 mg H_2O_2 was produced from 4.5 vol% H_2 in the gaseous mixture of (H_2 + O_2 + N_2) in 0.01 N HCl over 5% Pd/ carbon catalyst after 20 min.	**73**
US 5,082,647	Chuang et al (1992)	Acidic aqueous	VIII group metal on hydrophobic support.	0.23 wt% H_2O_2 was obtained after 5h.	**74**
US 5,132,099	Hiramatsu et al (1992)	Aqueous	Platinum group metal catalyst supported on a halogenated resin	The use of Pd/ halogenated material (halogenated resin) minimizes the corrosion of the reaction vessel and the catalyst dissolution in the reaction medium.	**75**
US 5,135,731	L.W.Gosseer and M. A. Paoli (1992)	Aqueous acidic containing halide and a phosphate compound	Pd and/or Pt supported on alumina, carbon, silica, and ion exchange resins.	Presence of multifunctional phosphonate and/or phosphate compound in the catalyst enhances H_2O_2 selectivity.	**76**
US 5,169,618	Maraschino et al (1992)	Aqueous	Pd/Carbon	71% H_2O_2 selectivity was obtained using a fixed bed continuous system and it was claimed that the H_2O_2 production cost by direct oxidation route should match with the anthraquinone process.	**77**
US 5,194,242	Paoli et al (1993)	Acidic aqueous	Group VIII metal catalysts	The H_2O_2 synthesis was carried out in an aqueous reaction medium in a pipeline reactor under plug-flow condition to establish a reaction zone for the reaction between H_2 and O_2.	**78**
US 5,236,692	Nagashima et al (1993)	Aqueous medium containing halogen promoters and H_2O_2 stabilizer	Platinum group metal catalyst supported on a solid acid carrier or a solid super acid carrier	Acid based corrosion of the reactor material and/or dissolution of the support material and the active component of the catalyst were avoided by employing superacidic material as the catalyst support.	**79**

Table 1.5: ***(continued)……….***

I	II	III	IV	V	VI
US 5,338,531	Chuang et al (1994)	Acidic aqueous	Group VIII metal supported on partially hydrophobic and partially hydrophilic support.	Improvement of both the H_2O_2 selectivity and catalyst stability were achieved by adding sodium and chloride ions in the reaction medium.	**80**
EP 6621235 A1	Tomita et al (1994)	Aqueous	Sn modified Pt group metal supported catalysts	0.38 wt% H_2O_2 was obtained at 48% H_2 selectivity over 0.5 wt% Pd on Tin (IV) oxide after 1h.	**81**
US 5,399,334	Kawakami et al (1995)	Water + organic	Hydrophilic Pt group metal catalysts	0.62 wt% H_2O_2 was obtained after 30 min at 36% H_2O_2 selectivity on 1%Pd/HP20 (styrene-divinylbenzene copolymer) catalyst	**82**
US 5,447,706	Van Weynbergh et al (1995)	Aqueous	Supported Pd or Pd associated with at least one more noble metal.	4.5 wt% H_2O_2 at 85% H_2O_2 selectivity was obtained over 2% Pd/BaSO4 catalysts at 25ºC after 8h.	**83**
US 5,480,629	Thompson et al (1996)	Organic	Composite catalyst containing of arsenic, phosphorous, zirconium, palladium and or platinum	A higher yield of H_2O_2 was obtained by increasing the reactor vessel volume and pressure of the system.	**84**
US 5,500,202	German et al (1996)	Aqueous and/or acidic aqueous	VIII group metal supported catalysts	The synthesis of H_2O_2 was carried out in a trickle bed reactor.	**85**
US 5,505,921	Luckoff et al (1996)	Mixture of acidic aqueous and organic solvent and containing Br^- anions	Supported bimetallic (e.g. Pd/gold, Pd/Ir, Pd/Rh) catalysts	55% H_2O_2 selectivity was obtained over the bimetallic Pd-Au (Pd/Au = 1) catalyst at a H_2O_2 formation rate of 0.306 mole H_2O_2 /gPd//h.	**86**
US 5,641,467	Huckins et al (1997)	Acidic aqueous	Group VIII metal supported catalysts	For preventing an explosive reaction between the H_2 and O_2, they were injected in dispersed minute bubbles into a rapidly flowing liquid medium	**87**
US 5,846,898	Chuang et al (1998)	Acidic aqueous	Pd on fluorinated carbon	A higher H_2O_2 selectivity was obtained by addition of sodium chloride into the reaction medium over Pd (on fluorinated carbon support) catalyst.	**88**

Table 1.5: ***(continued)……….***

I	II	III	IV	V	VI
US 5,925,588	Chuang et al (1999)	Acidic aqueous	Fluorinated carbon	Presence of chloride ions in the reaction medium increases the H_2O_2 selectivity in the H_2-to-H_2O_2 oxidation.	**89**
US 5,961,948	Wanngard et al (1999)	Aqueous + NaBr	VIII metals and gold supported on porous silica, alumina, carbon etc.	73% H_2O_2 selectivity was obtained using 3 vol% H_2 in the gas mixture (at 97 bar) in H_2SO_4 medium containing NaBr.	**90**
US 5,965,101	Goto et al (1999)	Methanol	Halide (chloride or bromide of Pt or Pd on titanosilicate.	0.06 wt% H_2O_2 was obtained after 2h reaction at rate of 0.04 mmol H_2O_2/mg of $PdBr_2$ /titanosilicate.	**91**
US 5,972,305	Park et al (1999)	Aqueous	Pd or Pt supported zeolite (encapsulated with organic compounds) catalysts.	Direct synthesis of H_2O_2 in aqueous solution was carried out in the presence of a compound (viz. alkyl anthraquinone or anthraquinone encapsulated zeolite) that can transfer H_2.	**92**
US 5,976,486	Thompson et al (1999)	Mixture of alcohol, aketone, water and a mineral acid.	The catalyst (inert particles of 1-100 microns) was coated with three to ten layers of a Zr or Hf-complex.	The complex composite catalyst employed in the H_2O_2 synthesis was prepared in such a way that the layers of complex in the catalyst allow only hydrogen to diffuse through it and contact the Group VIII metal.	**93**
US 6,042,804	Huckins et al (2000)	Acidic aqueous	Group VIII metal supported catalysts.	The H_2O_2 synthesis was performed by injecting dispersed minute bubbles H_2 and O_2 surrounded by the liquid medium of sufficient volume for preventing an explosive reaction between the H_2 and O_2.	**94**
US 6,168,775	Zhou et al (2001)	Aqueous	Supported noble metal (Pd and combination of Pd-Pt, Pd-Au, Pd-Os, Pd-Ru etc) phase controlled catalyst	8 wt% H_2O_2 was produced after 24 h.	**95**
US 6,210,651	Nystrom et al (2001)	Acidic aqueous	Group VIII metal supported catalysts.	The catalyst was comprises of a solid catalytically active material partially covered with a layer of a stationary phase of solid or liquid different from the catalytically active material such as silaneoxanes, silanes, ethers, esters, alcohols, acids and halides.	**96**

Table 1.5: *(continued)……….*

I	II	III	IV	V	VI
US 6,284,213	Paparatto et al (2001)	Water + alcohol.	Supported group VIII metal (e.g. Pd, Pt, Rh, Ru and Ir) on sulfonated carbon catalyst.	6.22 wt% H_2O_2 was obtained at 88% H_2 conversion and 86% H_2O_2 selectivity after 60 h.	**97**
US 6,346,228	Choudhary et al (2002)	Aqueous	Pd catalysts modified with the deposition of a hydrophobic polymer membrane	Coating of the hydrophobic layer on the supported Pd catalyst drastically reduces the H_2O_2 decomposition of the Pd catalyst and increases the H_2O_2 selectivity in the H_2-to-H_2O_2 oxidation.	**98**
US 6,375,920	Fischer et al (2002)	Aqueous, alcoholic or aqueous/alcoholic	Pd supported catalysts	5.6 wt% H_2O_2 was obtained at 43 % H_2 conversion and 70% H_2O_2 selectivity.	**99**
US 6,387,346	Bertsch-Frank et al (2002)	Mineral acid containing halide ions	Pd and the mixture of group VIII and group I metal supported catalysts (produced by spray pyrolysis or flame pyrolysis)	Addition of one or two metal from Group VIII and Group I of the Periodic Table to the Pd catalyst increases the H_2O_2 yield in the H_2 to H_2O_2 oxidation.	**100**
US 6,468,496	Jones et. al.				**101**
US 6,534,440	Choudhary et al (2003)	Aqueous	Pd/C, Pd/alumina, Pd/ceria, Pd/zirconia, Pd/gallia etc	The yield and selectivity of H_2O_2 in the H_2-to-H_2O_2 oxidation are drastically increased due to the oxidative pretreatment to the Pd catalysts.	**102**
US 6,576,214	Zhou et al (2003)	A mixture of solvent having one organic compound	Noble metal phase controlled catalyst	0.3 wt % H_2O_2 was obtained at a yield of 65 g/g Pd/h after 2h at 11.8% H_2 conversion.	**103**
US 6,630,118	Paparatto et al (2003)	Mixture of water and alcohol containing halide and acid promoters	Supported Bimetallic catalysts	4.5 wt% H_2O_2 was obtained at 86% selectivity after 50 h.	**104**
US 6,649,140	Paparatto et al (2003)	Alcohol and /or alcohol water mixture	Noble metal supported catalysts	1.8 wt% H_2O_2 was obtained at 61% molar selectivity after 30h in water medium.	**105**

Table 1.5: ***(continued)……….***

I	II	III	IV	V	VI
US 6,656,446	Backman et al (2003)	Carbon dioxide (preferably liquid or supercritical carbon dioxide)	CO_2 -philic catalyst of group 8, 9 or 10 metal (preferably Pd metal).	CO_2-philic catalyst being soluble or miscible in CO_2 and being suitable to catalyze the reaction of H_2 and O_2 to produce $H_2O_{2+.}$	**106**
US 6,685,818	Lehmann et al (2004)	Aqueous	Electrochemical process	With increasing the thickness of the membrane layer in MEU in the fuel cell, H_2O_2 concentration in the solution increases.	**107**
US 6,712,949	Gopal et al (2004)	Aqueous solution of mineral acid or acid salt (preferable pH = 0 – 6)	Redox catalyst (quinone compounds or polymer) used in electrochemical process	Redox catalyst is capable of reacting with O_2 in a reduced state to form H_2O_2 at current efficiencies of at least 35%, and is also capable of reduction electrochemically when in an oxidized state.	**108**
US 6,752,978	Huckins et al (2004)	Aqueous or acidic solution	Pt,or Pd or both on Al_2O_3, SiO_2 or C	H_2 and O_2 are separately injected into a liquid filled reactor to form a plurality of discrete individual bubbles in a continuous rapidly flowing liquid stream.	**109**
US 6,764,671	Hass et al (2004)	Organic solvent (preferably methanol is used)	80 wt% Pd and 0-20 wt% Pt, and 0-20 wt% Au and/or 0-5 wt% Ag in alloyed or non-alloyed form	In a trickle bed procedure with a cross-section loading of 0.3 m/h to 2 m/h, 4-10 wt% methanolic H_2O_2 is formed with high purity.	**110**
US 6,767,447	Uno et al (2004)	Aqueous solution	Electrochemical process	Feed water containing at least one salt (univalent metal ion) dissolved in a low concentration to produce hydrogen peroxide.	**111**
US 6,872,377	Fischer et al (2005)	A liquid stream comprising H_2O and/or a C_1-C_4-alkanol is passed through the reaction space	Stationary catalyst of Pd or (Pd+Pt) on Al_2O_3, SiO_2, C etc.	The apparent flow direction of the gas stream and the liquid stream are not parallel to one another. The process allows high gas throughputs with a small pressure drop.	**112**

Table 1.5: ***(continued)……….***

I	II	III	IV	V	VI
US 6,919,065	Zhou et al (2005)	H_2 in O_2 feed stream is used	Noble metal phase controlled catalyst; polymer is used for the desired phase of the noble metal atom on the support.	3.0 vol% H_2 in O_2 is used for advantageously producing H_2O_2 product at a selectivity exceeding 95% for a duration period of at least about 50 hours	**113**
US 7,005,528	Hass et al (2006)	Organic solvent (preferably methanol is used)	80 wt% Pd and 0-20 wt% Pt, and 0-20 wt% Au and/or 0-5 wt% Ag in alloyed or non-alloyed form		**114**
US 7,029,647	Tonkovich et al (2006)	Process feed stream and the staged addition feed stream are mixed in the microchannel reactor	catalyst comprise a metal from Group VIII or an oxide, or a mixture of two or more	Transferring heat from the process microchannel to a heat exchanger; and removing the product from the process microchannel.	**115**
US 7,048,905	Paparatto et al (2006)	Alcohol and /or alcohol water mixture with a acid or halogenated promoter	Catalyst based on Pd or Pt	It is possible to produce H_2O_2 (15 to 60 wt%), under safety conditions and with a molar selectivity towards H_2O_2 generally higher than 65%.	**116**
US 7,060,244	Devic (2006)	Aqueous acid medium, Br promoter and at least a surfactant as a surface active agent	Supported Bimetallic catalyst, Pd as major material and Pt as minor material	Fluorinated surface-active agents are very particularly suitable because of the high chemical stability and the high hydrophobicity of the fluorocarbon chain.	**117**
US 7,067,103	Rueter (2006)	Fixed bed/ebullated bed type or the slurry/fluidized bed type reactor	Preferably supported noble metal catalyst particles	Preferred ratio of O_2 to H_2 is 1:1 for production of H_2O_2 with high selectivity and excess O_2 recycle requirements are minimized.	**118**

Table 1.6: ***Summary of work on the synthesis of H_2O_2 from separated H_2 and O_2 feed (membrane process)***

Patent No	Investigators (year)	Reaction medium/ promoter	Catalyst	Result /remark, if any	Ref
US 4,393,038	Sun et al (1983)	Aqueous acidic medium containing phosphate stabilizer.	Gold plated Pd membrane	H_2O_2 yield obtained was 1.44% of the H_2 consumption rate in an acidic reaction medium over the $SnCl_4$ treated Pd membrane catalyst.	**119**
US 5,104,635	T. Kanada et al (1990)	Aqueous	Pt metal containing microporous membrane formed of a hydrophobic polymer.	The non-hazardous H_2O_2 synthesis was performed using a permselective membrane, which allows easy dissolution of O_2 and H_2 separately into the liquid medium maintaining high partial pressure of H_2 without exceedingly increasing the total pressure of the reaction system.	**120**
US 5,512,263	McIntyre et al (1996)	Gas phase	Composite membrane with multiphase conductivity path.	0.05 % H_2O_2 was obtained after 4.25 h.	**121**
US 5,800,796	Webb et al (1998)	Aqueous	The composite membrane comprising the substrate of both oxidizing and reducing agent	The synthesis of H_2O_2 from H_2 and O_2 gas mixture, without the direct reaction between H_2 and O_2 in the reaction medium was carried out by using a composite membrane.	**122**
US 6,432,376	Choudhary et al (2002)	Aqueous and/or acidic aqueous	Hydrophobic composite Pd-membrane catalyst	The potentially explosive reaction between H_2 and O_2 gas mixtures was eliminated by employing a membrane catalyst.	**123**
US 6,448,199	Choudhary et al (2002)	Aqueous and/or acidic aqueous	Hydrophobic composite Pd-membrane catalyst	Hydrophobic polymer membrane on the catalyst avoid direct contact between aqueous reaction medium containing H_2O_2 and catalytically active surface of membrane catalyst The H_2O_2 production selectivity was therefore drastically improved by reducing decomposition activity of the membrane catalyst.	**124**

Table 1.7: ***Summary of work on the direct synthesis of H_2O_2 from H_2 and O_2***

(W = catalyst weight, F = gaseous flow rate, T = temperature and P = Pressure)

Catalyst	Reaction medium/ promoter	Reaction condition	Result / Remarks, if any	Investigator (s) (Year)	Ref
I	II	III	IV	V	VI
Supported Pd catalysts	Aqueous acidic	Shpital'skii's dynamic apparatus was used at 300-400 vibrations per minute.	The optimum composition of the gas mixture in the synthesis of H_2O_2 is stiochiometric (H_2:O_2 = 1) and the yield of H_2O_2 increases with decrease of temperature.	Pospelova et al (1961)	**125**
Supported Pd catalysts	Aqueous acidic	,,	Pd doublet (Pd_2) is responsible for the synthesis of H_2O_2 in the reaction between from H_2 and O_2.	Pospelova et al (1961)	**126**
Supported Pd catalysts	Aqueous acidic	,,	Presence of acid in the reaction medium decreases catalytic decomposition of H_2O_2. HCN slows down both the synthesis and decomposition of H_2O_2.	Pospelova et al (1961)	**127**
Pd supported on hydrophobic and hydrophilic material	10% H_2SO_4	W = 1g, gaseous feed = 4.4 vol% H_2 in O_2, F = 250 ml/min, T = -10ºC to 25ºC, P = 5 to 23 atm.	The ratio of hydrophobic to hydrophilic catalyst properties is important to in determining the H_2O_2 yield. The maximum H_2O_2 selectivity obtained was 8.7 %.	Fu et al (1992)	**128**
Supported metallic catalysts	–	–	From the theoretical calculation it was proposed that Au and Ag will produce more H_2O_2 than that of Pd or Pt, but practically it is observed that only Pd catalyze the reaction.	Olivera et al (1994)	**129**
Porous metal phosphonate compound	0.1 N HCl	W = 25 mg, room temperature and atmospheric pressure.	The H_2O_2 formation depends upon the ratio of H_2 and O_2 in the gaseous feed and at O_2/H_2 = 1 the maximum H_2O_2 was obtained.	Thompson et al (1996)	**130**
Pd-Pt/TS-1	Methanol + water	T = 10 ºC P = [H_2 (7 bar), O_2 (10 bar) and N_2 (15 bar)]	The in situ generated H_2O_2 from O_2 and H_2 was employed for the epoxidation of propylene to propylene oxide.	Holderich et al (1999)	**131**
Palladium supported on hafnium phosphate viologen phosphonate	Methanol + H_2SO_4	Room temperature and atmospheric pressure	The electrons (from the splitting of H_2) are transferred to the viologen group and the reduced viologen reacts with O_2 producing H_2O_2.	Krishnan et al (2000)	**132**

Table 1.7: ***(continued)……….***

I	II	III	IV	V	VI
Organic compound adsorbed zeolite beta-supported Pd catalysts	0.01 N HCl	W = 0.1g, H_2:O_2= 1, room temperature and atmospheric pressure	Hydroquinone acts as a strong hydrogen transfer agent to promote the production of H_2O_2 from H_2 and O_2 in cooperation with a Pd catalyst.	S.-E. Park et al (2000)	**133**
Hydrophobic composite Pd membrane catalyst	0.02 M H_2SO_4	H_2 and O_2 separated by the membrane catalyst, T = 29 ºC and P = 1 atm.	100% H_2 conversion was achieved and the direct contact between H_2 and O_2 in the liquid was avoided with the membrane catalyst	Choudhary et al (2001)	**134**
CO_2 soluble Pd(II) or Pd (0) catalyst	super critical CO_2	W = 0.02 g, T = 25 ºC, P = 2500 psi	CO_2 was used as the reaction medium to overcome the transport limitations of the reactants in the process.	Hanchu et al (2001)	**135**
Pd-containing fluorinated or sulfated supports	Pure water and 0.02 M H_2SO_4	W = 0.5g, Gaseous feed = 1.7 vol% H_2 in O_2, F = 11.5 ml/min, P = 1 atm, T = 22 ºC.	A strong influence of catalyst reduction, fluorination or sulfonation of the catalyst support and protons in the medium on both the H_2O_2 destruction and H_2 oxidation was observed.	Choudhary et al (2002)	**136**
Pd containing zeolite catalysts	Pure water and 0.02 M H_2SO_4	W = 0.5g, gaseous feed = 1.7 vol% H_2 in O_2, T = 22ºC, P = 1 atm.	Fluorination of the support and oxidation of Pd to PdO lead to the enhancement of H_2O_2 yield in the H_2 to H_2O_2 oxidation.	Choudhary et al (2002)	**137**
Pd/Al_2O_3, Pd/ Ga_2O_3, Pd/ CeO_2, Pd/carbon, Pd/ ThO_2	0.02 M H_2SO_4	W = 0.5g, feed = 2.8 vol% H_2 in O_2, F = 11.5 ml/min, T = 22 ºC, P = 1 atm.	The presence of bulk or sub-surface PdO makes the supported Pd catalysts selective or active in the H_2-to-H_2O_2 oxidation.	Choudhary et al (2002)	**138**
Colloidal Palladium (introduced either via $PdCl_2$ or via Pd/SiO_2)	Aqueous acidic (acidified with HCl)	O_2/H_2 = 2, F = 30 ml/min, T = 25 ºC, P = 760 Torr.	Colloidal Pd is highly active in producing H_2O_2 in the reaction between H_2 and O_2 in the acidic aqueous medium.	Lunsford et al (2002)	**139**
Colloidal Palladium (introduced either via $PdCl_2$ or via Pd/SiO_2)	Aqueous acidic (acidified with HCl)	O_2/H_2 = 2, F = 30 ml/min, T = 25 ºC, P = 760 Torr.	The rate of H_2O_2 formation is proportional to the amount of colloidal Pd rather than the total amount of Pd in the system.	Lunsford et al (2003)	**140**
Supported bimetallic Pd-Au catalysts	supercritical CO_2	T = 2 ºC, P = 3.7 Mpa and O_2/H_2 mol ratio = 0.9-1.3.	The rate of H_2O_2 synthesis is markedly increased if Au-Pd alloy nanoparticles are generated by the addition of Pd in the Au catalyst.	Hutchings et al (2002)	**141**

Table 1.7: *(continued)………*

I	II	III	IV	V	VI
Pd/sulfonated carbon and bimetallic Pd-Au catalysts	Methanol/water mixture, supercritical CO_2	W = 0.05g, $H_2:O_2$ = 1:2, T = 2 ºC, P = 3.7 – 14 Mpa.	The addition of Pd to the Au catalyst and low temperature and short reaction time are beneficial to increase in the H_2O_2 yield/selectivity.	Landon et al (2003)	**142**
Supported nano gold catalysts	Water (P^H of which adjusted by adding HCl or NaOH)	$O_2:H_2$ = 3:7 (molar ratio), SV = 8000 mL/g-cat.h^{-1}), T= 278 - 298 K, P = 0.0 – 1.0 Mpa.	The size of Au particles on the support is the determining factor for the production of H_2O_2.	Okumura et al (2003)	**143**
Pd/TiO_2, Pd/WO_3, Pd/Al_2O_3, $Pd/F/Al_2O_3$	1.6 M H_3PO_4 / NaBr	W = 0.06g, 2.3% H_2 in 75%O_2 + 22.7% N_2, T = 25 ºC, P = 3.4 Mpa.	The low metal loading, an organic co-solvent and reduced Pd are the important factors that lead to the good activity and selectivity.	Burch et al (2003)	**144**
Al_2O_3 and ZrO_2 supported PdO catalysts	Acetone, methanol or water that contains 0.03 M different acids	O_2/H_2 = 2, F = 30 ml/min, T = 25 ºC, P = 760 Torr.	A number of fundamental issues have been discussed along with the active state of Pd, state of O_2 during reaction, etc.	Lunsford (2003)	**145**
Pd loaded sulfonic acid polystyrene resin	Methanol: water (96:4) + 12 ppm HBr	W = 0.8 g, $H_2:O_2:N_2$ = 2:48:50, F = 2500 ml/min, T = 40 ºC, P = 10 Mpa.	The high performance of the resin catalyst is due to the presence of a larger fraction of Pd^{II} ions interacting with the $–SO_3H$ groups of the resin.	Fierro et al (2004)	**146**
Colloidal palladium (added to the system Pd supported on microspheoidal silica)	0.1 N HCl + 0.01 M Br^-	T = 10 ºC, P = 1 atm, $O_2:H_2$ = 4	2 wt% H_2O_2 was obtained with selectivity, based on H_2 reacted, in excess of 90%. The parallel water formation reaction is inhibited by the presence of bromine.	Lunsford et al (2004)	**147**
Brominated Pd/Al_2O_3, Pd/ZrO_2, Pd/SiO_2, Pd/H-β or Pd/Ga_2O_3	0.03 M H3PO4 + 1 wt% Br (incorporated in the catalyst)	W = 0.5 g, feed = 4.6% H_2 in O_2, F = 15.5 ml/min, T = 27 ºC, P = 1 atm.	The incorporation of bromide ions in the supported Pd catalyst causes a drastic improvement in H_2O_2 selectivity and yield.	Choudhary et al (2004)	**148**
Pd/SiO2	0.17 N HCl (ethanol or water medium)	T = 10 ºC, P = 1 atm, $O_2:H_2$ = 4	Ethanol is superior to water as the liquid phase for the direct formation of H_2O_2 from H_2 and O_2 over a Pd catalyst.	Lunsford et al (2005)	**149**

Table 1.7: *(continued)……….*

I	II	III	IV	V	VI
Dielectric barrier discharge method used	Aqueous solution of 1.4 wt% NaCl	Feed = < 6% H_2 in O_2, F = 10 lt.h^{-1}, T = 25 ºC, P = 1 atm, voltage = 12.8kV, frequency = 12 kHz.	Under ambient conditions, H_2O_2 was obtained with 32.5% yield and 56.3% selectivity via the gas-phase reaction of H_2/O_2 non-equilibrium plasma.	Guo et al (2005)	**150**
Au/SiO_2 or $Au-Pd/SiO_2$	De-ionized water (pH 6)	W = 1 g, $H_2/(H_2+O_2)$ = 0.15, $(H_2+O_2):N_2$ = 4:1, T = 10 ºC	Au/SiO_2 and more preferably $Au-pd/SiO_2$ exhibit the high activity to H_2O_2 formation without addition of a halogen compound.	Ishihara et al (2005)	**151**
Pd on tubular catalytic membranes (TCM's)	0.03 M H_2SO_4 + 6 ppm NaBr	H_2 was fed at 2-3 bar, O_2-saturated acidic solution was circulated at 25 ml/min and 1 bar. T = 5 – 25 ºC.	TCM's are able to catalyze H_2O_2 synthesis at mild conditions with a fair productivity. A smooth metallic surface is necessary to improve the catalytic activity.	Strukul et al (2005)	**152**
Pd/SiO_2	Ethanol or water acidified with either H_2SO_4 or HCl	W = 0.05 g, $O_2:H_2$ = 4:1, F = 50 ml/min, T = 10 ºC, P = 1 atm.	H_2SO_4/ethanol system is the most favorable for peroxide formation than the H_2SO_4/water system.	Lunsford et al (2005)	**153**
TiO_2 supported Au-Pd catalysts	5.6 g MeOH and 2.9 g H_2O	W = 0.01 g, O_2/H_2 = 2:1, T = 2 ºC, P = 3.7 Mpa	The calcined $Au-Pd/TiO_2$ catalyst showed the highest activity for the synthesis of H_2O_2 (93 % selectivity) from the oxidation of H_2.	Hutchings et al (2005)	**154**
Pd/C, Pd/Al_2O_3, Pd/Ga_2O_3, Pd/SiO_2, Pd/ZrO_2, Pd/CeO_2	0.05 M H_2SO_4 or 0.03 M H_3PO_4, 0.9 or 2.7 M halide concentration.	W = 0.5 g, feed = 4.6 mol% H_2 in O_2, F = 15.5 ml/min, T = 27 ºC, P = 1 atm.	The promoting action of the halides is attributed mainly to the large decrease in the H_2O_2 decomposition and hydrogenation activities of the catalyst.	Choudhary et al (2006)	**155**
Pd-based catalysts	0.03 M H_3PO_4, 0.9 or 2.7 M halide concentration.	W = 0.5 g, feed = 4.6 mol% H_2 in O_2, F = 15.5 ml/min, T = 27 ºC, P = 1 atm.		Choudhary et. al. (2006)	**156**
Pd and/or Pt on tubular catalytic membranes (TCM's)	0.03 M H_2SO_4 + 6 ppm NaBr	H_2 was fed at 2-3 bar, O_2-saturated acidic solution was circulated at 25 ml/min and 1 bar. T = 5 – 25 ºC.	Pd/Pt bimetallic samples showed the hugher productivity and selectivity with an optimum molar ratio of 18.	Strukul et al (2006)	**157**

Table 1.7: *(continued)……….*

I	II	III	IV	V	VI
Pd supported on SO_4^{2-}, Cl^-, F^- and Br^- -doped ZrO_2	0.03 M H_2SO_4 aqueous, ethanolic, methanolic solution	W = 0.135 g, H2:O2:N2 = 10:10:80, F = 50 ml/min, T = 20 ºC, P = 1 atm.	The best results was obsedved in methanol, using higher O_2/H_2 ratio and sulfate doped ZrO2 catalyst.	Strukul et al (2006)	**158**
Zeolite supported Au catalysts	5.6 g MeOH and 2.9 g H_2O	W = 0.01 g, O_2/H_2 = 2:1, T = 20 ºC, P = 3.7 Mpa	Zeolite supported Au catalysts showed better activity than the other alumina or silica supported Au catalysts and the activity is related to the alumina content of the catalyst.	Hutchings et al (2006)	**159**
Alumina supported Au, Pd, and Au-Pd metal catalysts	5.6 g MeOH and 2.9 g H_2O	W = 0.05 g, O_2/H_2 = 2:1, T = 2 ºC, P = 3.7 Mpa	The addition of Pd to the Au catalyst increases the rate of H_2O_2 synthesis as well as concentration of H_2O_2 formed.	Hutchings et al (2006)	**160**
Pd/SiO_2	Ethanol or water acidified with either H_2SO_4 or HCl	W = 0.05 g, $O_2:H_2$ = 4:1, F = 50 ml/min, T = 10 ºC, P = 1 atm.	The positive effect of Cl^- on the surface Pd appears to result from the inhibition of O-O bond breaking in both the O_2 and H_2O_2.	Lunsford et al (2006)	**161**

Table 1.8: ***Summary of work done on the O_2-to-H_2O_2 reduction by hydroxylamine or hydrazine***

Catalyst	Reaction medium/ promoter	Reaction condition	Result / Remarks, if any	Investigator (s) (Year)	Ref
Mn (II) -catecholate complexes	100 cm^3 deionised water	Trion = $6x10^{-4}$ mol/dm^3, NH_2OH used = 0.5 mol/dm^3, pH = 8.0, F_{O2} = 0.7 dm^3/min, T = 25±0.5ºC	Mn(II) catecholate complexes uniquely and efficiently catalyze the production of H_2O_2 from hydroxylamine or hydrazine at pH 8.0.	Sheriff (1992)	**206**
Mn^{2+} -exchanged montmorillonite clay	100 cm^3 deionised water	Trion = $6x10^{-4}$ mol/dm^3, NH_2OH used = 0.5 or 1.0 mol/dm^3, pH = 8.0, T = 25±0.5ºC	Concentration of H_2O_2 > 0.40 mol/dm^3 in 50 min and turnover numbers $[H_2O_2]/[Mn^{2+}]$ > 10^5 were obtained.	Sheriff et. al. (1997)	**207**
Mn (III) -catecholate complexes	100 cm^3 deionised water	Trion = $6x10^{-4}$ mol/dm^3, NH_2OH used = 0.5 mol/dm^3, pH = 8.0, F_{O2} = 0.7 dm^3/min, T = 25±0.5ºC	The enzyme-like characteristic of this catecholate system has unique ability to activate O_2 for reduction to H_2O_2.	Sheriff et. al. (2003)	**208**
Mn (III) or Mn (IV) -catecholate complexes	100 cm^3 deionised water	Trion = $6x10^{-4}$ mol/dm^3, NH_2OH used = 0.5 mol/dm^3, pH = 8.0, F_{O2} = 0.7 dm^3/min, T = 25±0.5ºC	Neither labile coordination sites nor the oxidation state of the Mn are important to the catalytic system for the production of H_2O_2.	Sheriff et. al. (2004)	**209**
Boron containing Pd -catalysts	0.03 M H_3PO_4, 0.9 M halide concentration.	W = 0.5 g, F_{O2} = 1.5 ml/h, T = 27 ºC, P = 1 atm.	The presence of boron in the catalyst, the prereduction of the catalyst by hydrazine and also the presence of H^+ and Br^- anions in the reaction medium is must for H_2O_2 formation.	Choudhary et. al. (2005)	**210**
Pd/Al_2O_3, Pd/Ga_2O_3, Pd/C	0.1 M H_3PO_4, 0.9 M halide concentration.	W = 0.1 g, Hydrazine = 46 mmol/dm^3, F_{O2} = 10 ml/min, T = 27 ºC, P = 1 atm.	The reduction of O_2 by hydrazine (or its salt) leads to H_2O_2 formation with high yields only in the presence of Br^- anions and protons (mineral acid).	Choudhary et. al. (2005)	**211**

1.10. Objectives and Scope

The proposed work for the Ph.D thesis was undertaken as a part of the comprehensive R & D programme in our laboratory (NCL, Pune) for developing a highly active and selective catalyst for the direct oxidation of hydrogen to hydrogen peroxide by thoroughly investigating the factors affecting the hydrogen conversion activity and hydrogen peroxide selectivity of supported palladium catalysts in the H_2-to-H_2O_2 oxidation and also to explore new catalytic methods for the *in situ* generation of hydrogen peroxide (required for organic oxidations) with the following objectives.

1) To study the influence of catalyst support (Al_2O_3, SiO_2, Ga_2O_3, CeO_2, ZrO_2, H-β or HM), catalyst calcinations temperature (400 – 900 ºC), and oxidation state of Pd, loading of Pd and halide promoter in acidic reaction medium on the H_2-to-H_2O_2 oxidation (with H_2/O_2 feed ratio = 1.0) and H_2O_2 decomposition reactions over supported Pd catalysts under ambient conditions.
2) To study the influence of catalyst pretreatment under different temperatures (400 – 900 ºC) and gas atmosphere (O_2, N_2 or H_2) on the Pd particle size and catalyst performance in the H_2-to-H_2O_2 oxidation and H_2O_2 destruction (by H_2O_2 decomposition and/or hydrogenation) over commercial Pd/C and Pd/Al_2O_3 catalysts.
3) To investigate the synergetic effect of two halogen promoters present in acidic reaction medium or in catalyst on the net H_2O_2 formation (in H_2-to-H_2O_2 oxidation) and H_2O_2 destruction reactions over Pd/C and Pd/Al_2O_3 catalysts for developing highly active/selective catalyst for the H_2-to-H_2O_2 oxidation.
4) To study in details the influence of various process conditions (viz. H_2/O_2 ratio in feed, gas flow rate, initial concentration of H_2O_2, concentration of acid in the reaction medium, temperature, reaction time, etc) on the net H_2O_2 formation in the H_2-to-H_2O_2 oxidation and also on the H_2O_2 destruction over highly active/selective F-Br-promoted Pd/Al_2O_3 catalyst in acidic reaction medium.
5) To study in details the factors strongly influencing the H_2O_2 decomposition and/or hydrogenation (in aqueous medium) over Pd/Al_2O_3 catalyst in the presence of H_2.
6) To carry out detailed investigation on the *in situ* generation of H_2O_2 (required for the organic oxidations) by the O_2-to-H_2O_2 reduction by hydrazine, hydroxylamine or their

salts, using a reusable heterogeneous catalysts (viz. supported Pd or Au catalysts) and also o study the factors affecting the H_2O_2 generation.

1.11. References

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Chapter 2

Experimental Section

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2.1. Gases and Chemicals Used

The following gases and chemicals have been used

Helium	– High purity IOLAR-II Grade (99.9%) obtained from Indian Oxygen Ltd., Mumbai
Hydrogen	– IOLAR-II Grade obtained from Indian Oxygen Ltd., Mumbai
Nitrogen	– IOLAR-II Grade obtained from Indian Oxygen Ltd., Mumbai
Oxygen	– IOLAR-II Grade obtained from Indian Oxygen Ltd., Mumbai
Zero air	– IOLAR-II Grade obtained from Indian Oxygen Ltd., Mumbai
Palladium acetate	– 99.9% Lancaster, UK
Chloroauric acid	– Thomas Baker, Mumbai
Magnesium (II) Oxide	– Loba Chemie Lab. Pvt. Ltd., Mumbai
Calcium (II) Oxide	– Loba Chemie Lab. Pvt. Ltd., Mumbai
Lanthanum (IV) Oxide	– 99.9% Aldrich, USA
Yetarbium (IV) Oxide	– 99.9% Aldrich, USA
Gadolinium (IV) Oxide	– 99.9% Aldrich, USA
Terbium (IV) Oxide	– 99.9% Aldrich, USA
Gallium (III) Oxide	– 99.9% Aldrich, USA
Cerium (IV) Oxide	– 99.9% Aldrich, USA
Silica gel, B type	– Fuji division Ltd.
Zirconyl nitrate	– Loba Chemie Lab. Pvt. Ltd., Mumbai
Sulfuric acid	– (98%) Merck (India) Pvt. Ltd., Mumbai
Hydrochloric acid	– (32%) Merck (India) Pvt. Ltd., Mumbai
Phosphoric acid	– (AR) Merck (India) Pvt. Ltd., Mumbai
Acetonitrile	– Qualigens Fine Chemicals, Galxo (India) Ltd
Ammonium fluoride	– (Extra pure) Loba Chemie Lab. Pvt. Ltd., Mumbai
Ammonium chloride	– (Extra pure) Loba Chemie Lab. Pvt. Ltd., Mumbai
Ammonium bromide	– (99.9%) E. Merck (India) Ltd, Mumbai

Ammonium iodide	– (99.9%) E. Merck (India) Ltd, Mumbai
Sodium thiosulphate	– (AR Grade) s. d. Fine Chemicals, Mumbai
Starch powder	– (AR Grade) s. d. Fine Chemicals, Mumbai
Potassium dichromate	– (99%) E. Merck (India) Ltd, Mumbai
Potassium fluoride	– s. d. Fine Chemicals, Mumbai
Potassium chloride	– Qualigens Fine Chemicals, Galxo (India) Ltd
Potassium bromide	– s. d. Fine Chemicals, Mumbai
Sodium bromide	– Sisco Research Laboratory Pvt. Ltd, Mumbai
Potassium iodide	– E. Merck (India) Ltd, Mumbai
Hydrogen peroxide (30% w/w)	– E. Merck (India) Ltd, Mumbai
Dimethyl glyoxime	– (AR Grade) s. d. Fine Chemicals, Mumbai
Hydrazine hydrate	– (99% LR) s. d. Fine Chemicals, Mumbai
Hydrazine sulphate	– (LR) s. d. Fine Chemicals, Mumbai
Chloroform	– s. d. Fine Chemicals, Mumbai
Hydroxylamine	– Alfa-Aesar, USA
Hydroxylammonium sulphate	– Loba Chemie Lab. Pvt. Ltd., Mumbai
Hydroxylammonium chloride	– s. d. Fine Chemicals, Mumbai
Potassium bromate	– s. d. Fine Chemicals, Mumbai
Pyrogallic acid	– Johnson Chemicals, USA

2.2. Catalysts and Catalyst Preparation

2.2.1. Commercial Catalyst Used

The Pd(5 wt%)/C and Pd(1 wt%)/Al_2O_3 catalysts in their reduced form were obtained from Lancaster, UK. The Pd(5 wt%)/Al_2O_3 catalyst in their reduced form was obtained from Lancaster, UK and Alfa-Asear Lancaster, UK. All the catalysts were in fine powder form.

2.2.2. Preparation of Supported Pd (Oxidized and Reduced) Catalysts

The Al_2O_3 (prepared from bohemite by its calcination at 500 ºC for 2h) ZrO_2, CeO_2, SiO_2 (prepared from B-type silica gel, by calcining at 500 ºC for 3h), H-β (Si/Al = 27 and crystal size = 1.0 μm) and HM supported oxidized Pd (2.5 wt%) catalysts were prepared by impregnating the respective support with palladium acetate from its acetonitrile solution by the incipient wetness impregnation technique. After impregnation, the wet catalyst mass was dried at 100 ºC for 2h and then calcined under static air in a muffle furnace at 400 ºC for 2h.

The supported reduced Pd catalyst was prepared from the respective oxidized Pd catalyst by reducing it with an ammoniacal hydrazine solution at room temperature (27 ºC) for 2h followed by washing, filtration and drying at 100 ºC.

2.2.3. Modification of the Commercial Pd (5%)/Al_2O_3 (Lancaster) Catalyst by Its Halogenation

The halogenation of commercially available reduced Pd (5 wt%)/Al_2O_3 catalyst was done by impregnating the catalyst by respective ammonium halide from aqueous solution, using the incipient wetness technique. After the impregnation, the wet catalyst mass was dried at 100 ºC for 4h and then calcined at 400 ºC for 2h in presence of flowing N_2.

2.2.4. Preparation of Supported Nano-gold Catalyst by Homogeneous Deposition Precipitation (HDP) Method

All the supported nano-gold catalysts were prepared by the HDP method using the procedure reported earlier by Zanella et. al. [1] and Choudhary et. al. [2]. Schematic presentation of the HDP method is given in Figure 2.1.

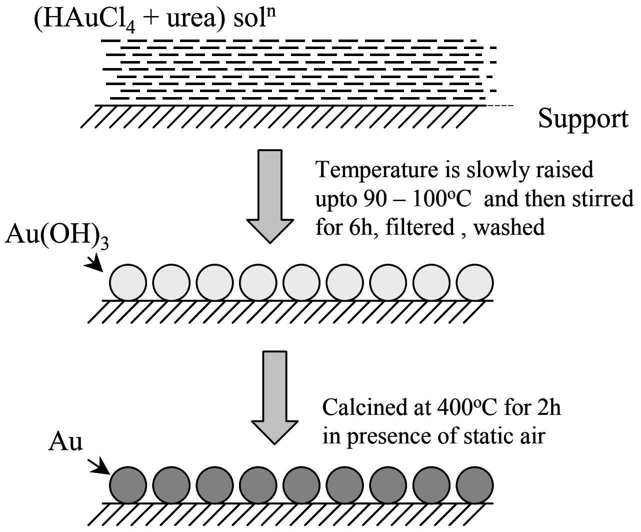


Figure 2.1: Schematic diagram of homogeneous deposition precipitation (HDP) method.

In a typical procedure, a known amount of an aqueous $HAuCl_4.3H_2O$ solution was added to 300 ml of distilled water. Known quantity of urea (normally 50 times more than that required for hydrolysis of gold chloride) was then added to the solution. To this clear solution a metal oxide support was immersed. The temperature of the resulting slurry was increased gradually to 98 ± 2 ºC and the temperature as well as pH was continuously monitored using pH electrode fitted with temperature controller assembly of Global Electronics Ltd., Chennai, India. The temperature was maintained for 6h. The pH of the reaction mixture (initially 2.0 to 2.5 at room temperature) gradually increased with increase in temperature and the final pH of the slurry was 7.5 ± 0.5, depending upon the support used. The solid mass was filtered, washed with distilled water, dried and finally calcined at 400 ºC for 2h in presence of static air.

2.3. Physicochemical Characterization of Catalysts

The catalysts were characterized by various techniques, which provide important information about different physicochemical features of the catalyst, as follows:

2.3.1. Spectroscopic Techniques

2.3.1.1. Powder X-ray diffraction (XRD): The structure of a crystal can be determined using the technique of X-ray diffraction (XRD). X-rays have wavelength in the Å range, are sufficiently energetic to penetrate solids and are well suited to probe their internal structure. It is used to identify the bulk phases, degree of crystallinity, unit cell parameters and to estimate particle size. The X-ray diffraction patterns are obtained by measurement of the angle at which an X-ray beam is diffracted by the sample. To observe a diffraction signal, the diffracted light must interfere constructively. For this, the crystal plane must be oriented with respect to the incident rays, so that the path difference is equal to integrated multiple of the wavelength of X-ray radiation, this is called as Bragg's equation [3].

$$n\lambda = 2d_{hkl} \sin\theta$$

where n = an integer known as the order of reflection, λ = wavelength of X-rays, d_{hkl}= the distance between the two hkl planes (h, k and l represent the Miller indices of the respective planes) and 2θ = the angle of diffraction.

XRD analysis: The Pd and Au phases with their oxidation state in the supported catalysts were determined by X-ray powder diffraction method using a Holland Phillips, PW/1730 X-ray generator with a CuKα radiation (λ = 1.5406 Å, 40 kV, 25 mA). The identification of phase is based on the comparison of the set of reflections of the sample with that of pure reference phases distributed by International Center for Diffraction Data (ICDD). The average particle size of the Pd and Au particle was estimated using the Debye-Scherrer equation:

$$D = \frac{k\,\lambda}{\beta\cos\theta}$$

where D = thickness of the crystal, k is a constant, λ = wavelength of X-rays, β = full width at half maximum at Bragg's angle 2θ [4].

2.3.1.2. X-ray photoelectron spectroscopy (XPS): XPS is based on the photoelectric effect. When an X-ray photon of energy hν is incident on a solid mater, the kinetic energy (E_k) and the binding energy (E_b) of the ejected photoelectrons can be related as follows: $E_k = h\nu - E_b$. In XPS one measures the intensity of photoelectrons N(E) as a function of their kinetic energy E_k. Because a set of binding energies is characteristic for an element, XPS can be used to analyze the composition of samples. Binding energies are not only element specific but contain chemical information as well: the energy levels of core electrons depend on the chemical state of the atom [5,6]. Photoelectron peaks are labeled according to the quantum numbers of the level from which the electron originate.

XPS analysis: Surface chemical analysis of the catalyst was done by the X-ray photoelectron spectroscopy (XPS) using a VG-scientific ESCA-3 MK II electron spectrometer (C1s with binding energy = 285.0 eV was taken as an internal standard). All the measurements were done on as received powder samples using MgKα X-ray at room temperature. The errors in all binding energy (BE) values were within ± 0.2 eV.

2.3.1.3. Inductive coupled plasma – atomic emission spectroscopy (ICP-AES): Inductive Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES) is one of several techniques available in analytical atomic spectroscopy [7]. The basic aim of analytical atomic spectroscopy is to identify elements and quantify their concentration in various media. The procedure consists of three general steps: atom formation, excitation and emission. Before excitation, an element that is bound in a specific matrix must be separated from that matrix, so that their atomic emission spectrum is free from interferences. ICP-AES utilizes a plasma (a plasma is an electrically neutral, highly ionized gas that consists of ions, electrons and atoms) as the atomization and excitation source. Once the electron is in the excited state, the atom emits light, which is characteristic of that particular element.

ICP-AES analysis: The gold content in the materials was determined by ICP-AES using a Perkin Elmer Analyzer. The samples for ICP analysis were prepared by dissolving 0.05 g of sample in a 5 ml of aqua regia. The solution was left for 30 min to dissolve all solids and thereafter filtered. Distilled water was used to wash the filter assembly and glassware in order to remove all gold from the glassware and then filtrate was diluted to 25 ml with distilled water.

2.3.2. Microscopic Techniques

Electron microscopes are instruments, which uses beam of highly energetic electrons to create magnified images of tiny crystals or particles. An electron gun emits a beam of high energy electron that travels through a series of magnetic lences, which focus the electron to a very fine spot or sample. Interactions occur inside the irradiated sample. The electrons emitted from each point of the sample form the final image. The striking electrons may remain unscattered and transmitted through the specimen (TEM) [8] or may be elastically scattered (without loss of energy) or may be inelastically scattered (SEM) [9] producing low energy secondary electrons.

2.3.2.1. Scanning Electron Microscope (SEM): SEM is used particularly to examine the topology and morphology of the sample. It is used for thick specimen. The incoming beam of electrons interacts with sample inelastically and causes ionization of the electron in the sample atom. These ionized electrons are termed as ‘secondary electrons’. The detector detects either secondary electrons or back-scattered electrons as a function of the position of the primary beam. The secondary electrons have low energies (10-20 eV) and originate from the surface region of the sample whereas back-scattered electrons come from deeper and carry information on the composition of the sample, because heavy elements are more efficient scatterers and appear brighter in the image.

SEM Analysis: The SEM micrographs of the sample were obtained in a Leica Steroscan 40 instrument.

2.3.2.2. Transmission Electron Microscope (TEM): TEM uses thin specimens in which the unscattered transmitted electrons provide the image. TEM provides information about the size, shape and arrangement of particles in specimen. In TEM, a high intensity primary electron beam passes through a condenser to produce parallel rays, which impinge on the sample. As the attenuation of the beam depends on the density and the thickness, the transmitted electrons form a two-dimensional projection of the sample mass, which is subsequently magnified by the electron optics to produce a so-called bright field image.

TEM Analysis: TEM images were recorded using a JEOL JEM-1200EX transmission electron microscope operating at 100 kV. The sample was prepared from an acetone suspension of solid sample by placing a drop of the sample solution on a carbon coated copper grid.

2.3.3. Surface Area Measurements by Nitrogen (N_2) Adsorption (Single Point Method)

The determination of surface area is most commonly performed by measuring the amount of gas adsorbed (typically nitrogen) at cryogenic temperatures (liquid nitrogen) at a given pressure, the BET equation is employed to compute the number of adsorbed gas molecules that would be required to form a nano-layer on the surface. With knowledge of the cross-sectional area of the gas molecules adsorbed, the surface area can be easily calculated.

Surface area analysis: The surface area of the catalysts was determined using a Monosorb Surface Area Analyzer (Quantachroma Corp., USA) based on dynamic adsoption/desorption of N_2. Before carrying out surface area measurement experiments, the catalyst (0.5 - 0.1 g) was pretreated *in situ* in the sample cell at 300 ºC for 1h in flow of a mixture of He and N_2 (30 mol% N_2) to remove the traces of moisture or any other gases. The sample was then cooled by using liquid nitrogen and the adsorption/desorption count of N_2 was determined. The analyzer was calibrated by injecting a known amount of air.

The surface area was calculated from the observed desorption counts instead of the adsorption ones, as follows:

$$S\ (m^2.g^{-1}) = \frac{\text{Desorption counts x 2.84}}{\text{wt. of catalyst x counts of 1 ml of air}}$$

(2.84 m^2 area = 1 ml N_2 or air, counts are expressed in terms of surface area, m^2).

2.4.Chemical Analysis

2.4.1. Quantitative Analysis of H_2O_2 by Iodometric Titration Method

H_2O_2 reacts with iodide in presence of acid solution in accordance with the equation:

$$\overbrace{H_2O_2 + 2\,H^+ + 2\,\underbrace{I^- = I_2}_{-\,2e} + 2\,H_2O}^{+\,2e}$$

The reaction rate is comparatively slow, but increases with increasing acid concentration. Generally, 2 N H_2SO_4 solution is used for the reaction. The liberated iodine is titrated with thiosulfate solution, incorporating a starch indicator [10].

$$\overbrace{I_2 + 2\,\underbrace{S_2O_3^{2-} = S_4O_6^{2-}}_{-\,2e} + 2\,I^-}^{+\,2e}$$

Thus- 2 $S_2O_3^{2-} \equiv H_2O_2$

$\therefore$ 1 ml 1 N $Na_2S_2O_3 \equiv 0.01701$ g of H_2O_2.

Procedure: 20 ml reaction mixture was added gradually to a solution of pure potassium iodide in 10 ml of 2 N sulfuric acid contained in a stoppered conical flask. The mixture was allowed to stand for 15 minutes and then 100 ml of distilled water was added to the mixture with washing the wall of the conical flask. The liberated iodide was titrated with standard 0.1 N thiosulfate solution with the addition of 2 ml of starch solution when the color of the iodine solution was nearly discharge. The end point was from blue to colourless solution. A blank run was also carried out at the same time. To get the accurate reading of thiosulfate, the value of blank run was subtracted from the value of the reaction mixture. The formation of H_2O_2 in the reaction mixture was then calculated by using the above equation.

2.4.2. Detection of Pd Leaching

Pd leaching (if any) from the Pd catalyst in the reaction medium, after the reaction, was detected by adding an aqueous ethanolic dimethyl glyoxime (1%) solution to a 5 ml of filtrate reaction mixture [10]. The solution was then allowed to stand for long period. The observed yellow orange precipitate of palladium dimethylglyoximate indicates the presence of palladium (in trace amounts) in the reaction mixture.

2.4.3. Analysis of Hydrazine

Hydrazine reacts with potassium iodate under usual Andrews conditions as follows [10]:

+ 4e

$$IO_3^- + N_2H_4 + 2\,H^+ + Cl^- = ICl + N_2 + 3\,H_2O$$

- 4e

Thus- $KIO_3 \equiv N_2H_4$

$\therefore$ 1 ml 0.025 M $KIO_3 \equiv 0.0008013$ g of N_2H_4

Procedure: 5 ml of reaction mixture was added to a mixture of 30 ml of concentrated hydrochloric acid, 20 ml of water and 5 ml of chloroform. The mixture was then titrated with standard 0.025 M KIO_3 solution slowly from the burette, with shaking of the stoppered conical flask bewteen the additions, until the organic layer was just decolorised. The hydrazine remained in the solution was calculated by using the above equation.

2.4.4. Analysis of Hydroxylamine

Hydroxylamine reacts with potassium bromate in the presence of acid as follows [10]:

$$+\,6e$$

$$NH_2OH + BrO_3^- = NO_3^- + Br^- + H^+ + H_2O$$

$$-\,6e$$

Thus- $KBrO_3 \equiv NH_2OH$

$\therefore$ 1 ml 1 N $KBrO_3 \equiv 0.005505$ g of NH_2OH

Procedure: 5 ml of reaction mixture was added to a solution of 25ml of M/60 $KBrO_3$ and 50 ml 4 N H_2SO_4. When the colour of the solution became just yellow, 2 g of pure potassium iodide was added to the mixture. The liberated iodine was titrated with standard thiosulfate solution similar to that in the hydrogen peroxide analysis.

2.5. Catalytic Reactions

2.5.1. Direct Oxidation of H_2 to H_2O_2 over Supported Pd Catalysts

The schematic diagram of the experimental setup used for the catalytic oxidation of H_2 to H_2O_2 is given in Figure 2.2. The direct oxidation of H_2 by O_2 to H_2O_2 over supported catalysts was carried out at atmospheric pressure (95 kPa) in a magnetically stirred jacketed glass reactor (capacity 100 cm^3) containing 0.1 g of catalyst in the fine powder form and an aqueous acidic solution (50 cm^3) as a reaction medium. A H_2/O_2 gas mixture in the 1:1 ratio was bubbled (using a fine glass tip) continuously through the reaction medium containing the catalyst under vigorous stirring speed at a constant temperature. The temperature of the reaction was controlled by passing water continuously through the jacketed reactor from the thermostatic water bath. The output gases were collected at atmospheric pressure using a constant pressure gas collector as shown in Figure 2.2. The yield of H_2O_2 was calculated by using this equation:

$$H_2O_2 \text{ yield } (\%) = \frac{H_2O_2 \text{ formed (mmols)}}{H_2 \text{ input (mmols)}} \times 100$$

The H_2O_2 selectivity was calculated by using the graphical method as follows.

Although, a number of reactions occure simultaneously in the H_2-to-H_2O_2 oxidation:

$$H_2\,(g) + O_2\,(g) \rightarrow H_2O_2\,(l) \quad \ldots\ldots\ldots\ldots\ldots \quad 2.1$$

$$H_2\,(g) + 0.5\,O_2\,(g) \rightarrow H_2O\,(l) \quad \ldots\ldots\ldots\ldots\ldots \quad 2.2$$

$$H_2O_2 \rightarrow H_2O\,(l) + 0.5\,O_2 \quad \ldots\ldots\ldots\ldots\ldots \quad 2.3$$

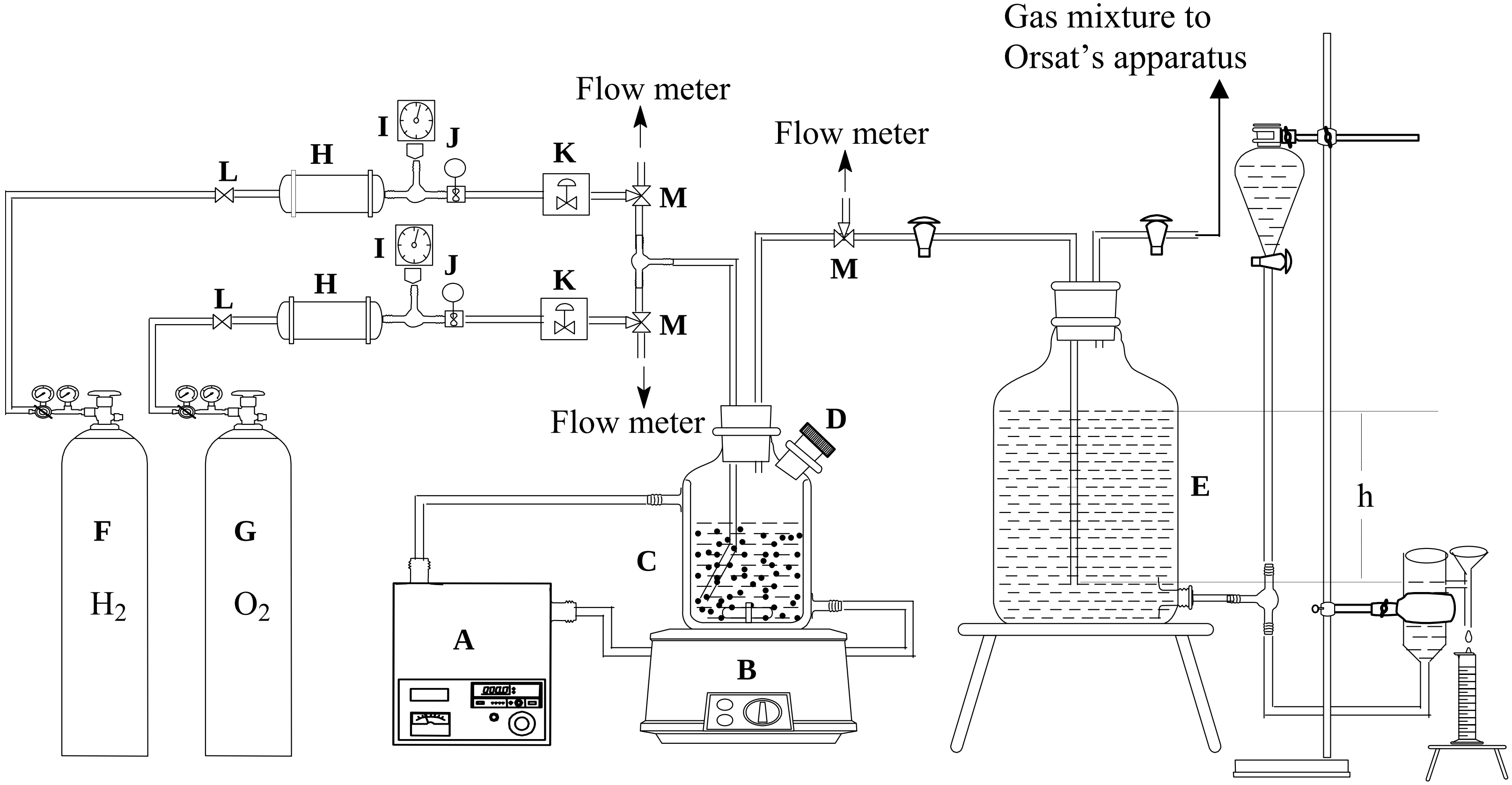
$$H_2O_2 + H_2 \rightarrow 2\,H_2O\,(l) \quad \ldots\ldots\ldots\ldots\ldots \quad 2.4$$

the last two reactions, when subtracted from each other lead to reaction 2.2. Hence, the consumption of H_2 and O_2 essentially follows the stoichiometry of reactions 2.1 and 2.1. Therefore, it is possible to estimate the H_2O_2 selectivity with the value of H_2O_2 yield, amounts (moles) of H_2 and O_2 in feed and the total amount (moles) of gas (H_2 + O_2) collected after the reaction. If the total amount of H_2 and O_2 fed to the reactor are x and y (moles), reaspectively, and the H_2O_2 formed in the reaction is z (moles), then according to the reactions 2.1 and 2.2, the amount of H_2 and O_2 consumed in the reaction would be $[1 + (100 - S)/S]z$ in each at different H_2O_2 selectivities [where S = H_2O_2 selectivity (%)]. Therefore, the total amount of gas collected (C, moles), after the reaction would be –

$$\begin{aligned} C &= \{x - [1 + (100 - S)/S]z\} + \{y - [1 + (100 - S)/S]z\} \\ &= x + y - 2\,[1 + (100 - S)/S]z \\ &= x + y - bz \quad \text{where, } b = 2\,[1 + (100 - S)/S] \text{, depends upon the } H_2O_2 \text{ selectivity.} \end{aligned}$$

Therefore, the total amount of gas collected (moles) after the reaction, at different H_2O_2 selectivities would be as follows.

Selectivity of H_2O_2, S (%)	Total gas collected, C (moles)	b
100	$x + y - 2\,z$	2
75	$x + y - 2.5\,z$	2.5
50	$x + y - 3.5\,z$	3.5
25	$x + y - 6.5\,z$	6.5
20	$x + y - 8.0\,z$	8.0
10	$x + y - 15.5\,z$	15.5
5	$x + y - 75.5\,z$	75.5
1	$x + y - 150.5\,z$	150.5



A = Cryostat for water circulation; B = Magnetic stirrer; C = Glass reactor; D = Injection port; E = Constant pressure gas collector; F = Hydrogen gas cylinder; G = Oxygen gas cylinder; H = 1000 cc bomb; I = Pressure gauge; J = Pressure controller; K = Differential flow controller (DFC); L = Two way valve; M = Three way valve.

Figure 2.2: Experimental set up for liquid phase direct oxidation of H_2 to H_2O_2.

The plotting of H_2O_2 selectivity (%) vs. b value will give a graph shown in Figure 2.3.

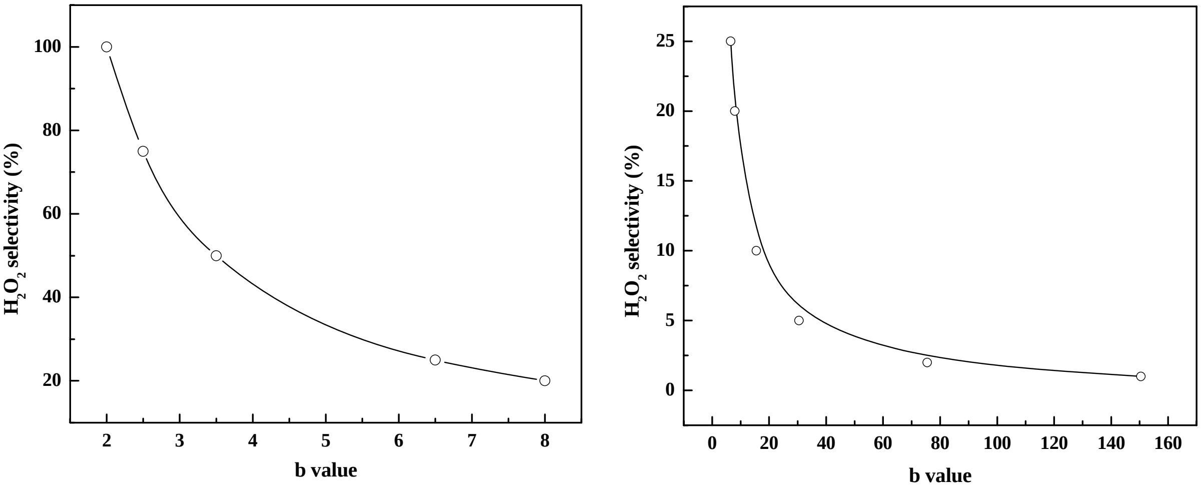


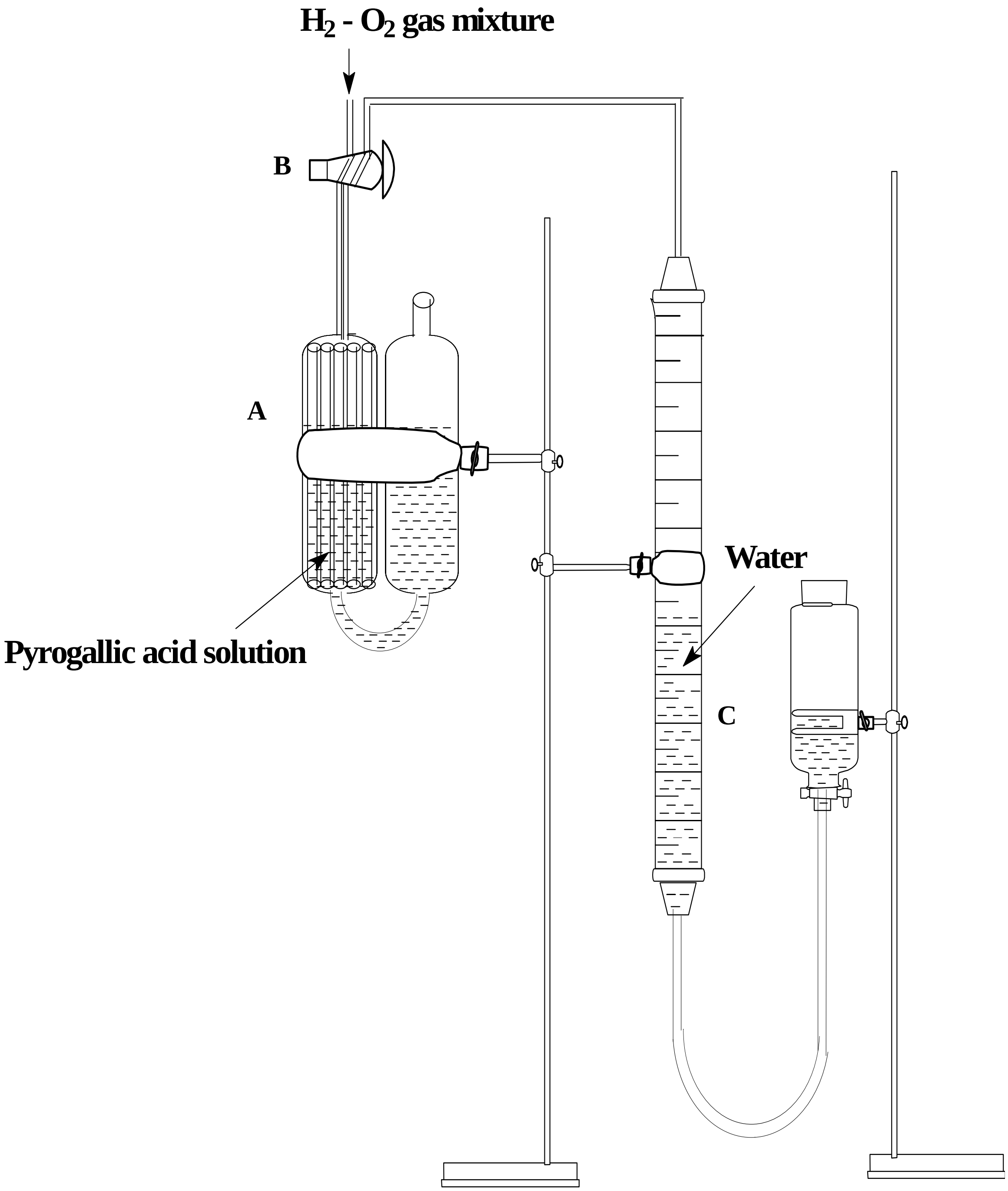
Figure 2.3: Plot of H_2O_2 selectivity vs. b value.

Now, in our experiments, the C, x, y and z values can be measured. By using these values, the b value can be calculated and from the b value, the corresponding H_2O_2 selectivity can be estimated from the graph. In this way, the H_2O_2 selectivity was estimated from the measured quantities of C, x, y and z in the direct oxidation of H_2 to H_2O_2 experiments.

The H_2 conversion was estimated from the H_2O_2 yield and selectivity, as follows.

$$\text{Conversion of } H_2\ (\%) = \frac{\text{Yield of } H_2O_2\ (\%)}{\text{Selectivity of } H_2O_2\ (\%)} \times 100$$

Alternatively, H_2 conversion was also determined by measuring the amount of unconverted H_2, by analyzing the H_2 remained in the gas collected, using an Orsat apparatus (Figure 2.4), in which pyrogallic acid solution was used for chemically absorbing O_2 from the gas mixture (H_2 and O_2). Then, the H_2O_2 selectivity was calculated from the H_2O_2 yield and H_2 conversion, as follows.



A = Absorption U-tube, B = two way stopcock, C = graduated burette

Figure 2.4: Orsat's apparatus for the measurement of O_2 in the H_2-O_2 gas mixture.

$$H_2O_2 \text{ Selectivity (\%)} = \frac{\text{Yield of } H_2O_2 \text{ (\%)}}{H_2 \text{ conversion (\%)}} \times 100$$

The results obtained from both the methods were found to be almost the same, within less than 5 % error.

2.5.2. Catalytic Decomposition of H_2O_2 over Supported Pd Catalysts

The catalytic decomposition of H_2O_2 over the supported Pd catalysts was carried out in a magnetically stirred jacketed glass reactor (capacity: 100 cm^3, Figure 2.4) containing 0.1 g catalyst and 50cm^3 of an aqueous reaction medium, with or without containing acid and/or halide anions, by injecting through the rubber septum a 1.0 ml of 30% H_2O_2 solution in the reactor under vigorous stirring. The gas (O_2) liberated in the decomposition of H_2O_2 ($H_2O_2 \rightarrow H_2O + 0.5\ O_2$) at a constant atmospheric pressure was measured as a function of time, using a constant pressure gas collector [12] as shown in Figure 2.5.

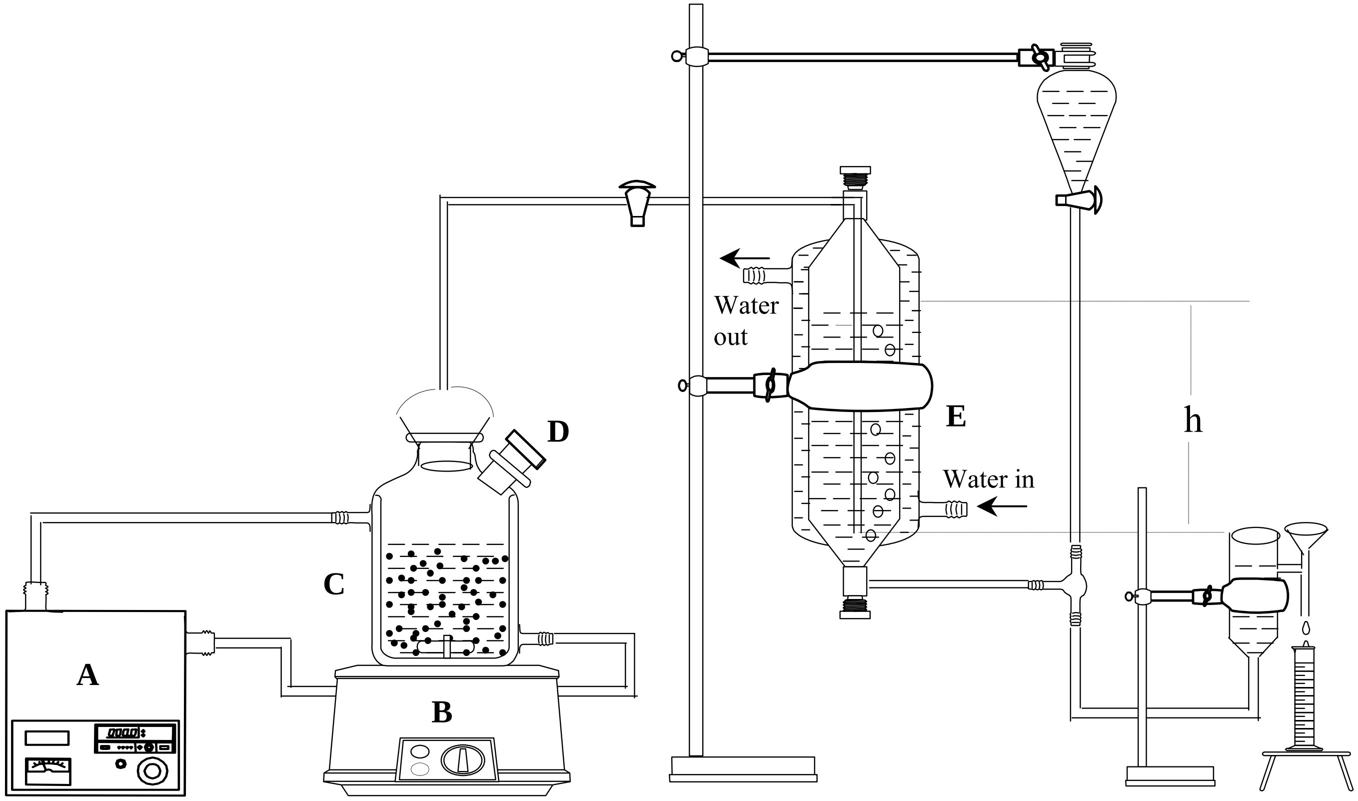
The percent H_2O_2 decomposition data was estimated as follows:

H_2O_2 decomposition (%) = $[V_t/V_T] \times 100$ (where, V_t = volume of O_2 evolved in time t and V_T = volume of O_2 evolved in the complete decomposition of H_2O_2 in the reactor). The H_2O_2 decomposition activity of the supported catalysts was evaluated in terms of a pseudo first order rate constant (k_d) according to the first order rate expression: $\ln [V_T/(V_T - V_t)] = k_d\, t$. From the slope of the $\ln [V_T/(V_T - V_t)]$ vs. t plot; pseudo first order H_2O_2 decomposition rate constant (k_d) was evaluated.

The corrected volume of O_2 liberated in the decomposition of H_2O_2 ($H_2O_2 \rightarrow H_2O + 0.5\ O_2$ was calculated by the given formula:

$V_{\text{corrected (at NTP)}} = [V\text{- volume of } H_2O_2 \text{ solution injected}] \times [\{P - P_w - (h/13.6)\}/760] \times [273/T_w]$

Where, V is the volume of water displacement (cm^3), P is the atmospheric pressure (mm Hg), P_w is the vapor pressure of water at the respective temperature of the gas collector, h is the height of the water column and T_w is the temperature of the gas collector (in K).



A = Cryostat for water circulation; B = Magnetic stirrer; C = Glass reactor; D = Injection port; E = Constant pressure gas collector.

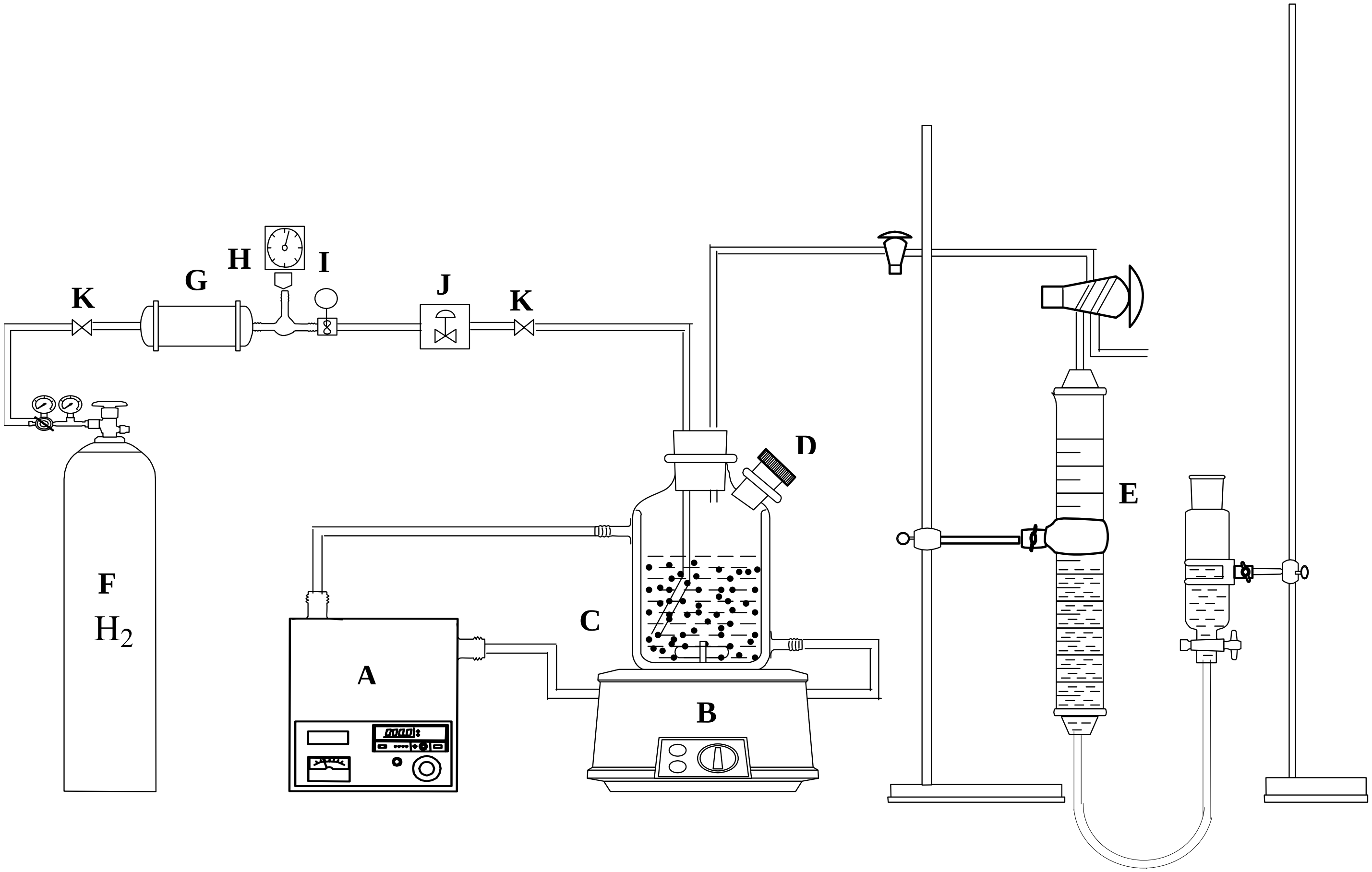
Figure 2.5: Experimental set up for catalytic decomposition of H_2O_2.

2.5.3. Hydrogenation of H_2O_2 over Supported Pd Catalysts

The catalytic conversion of H_2O_2 under static H_2 was carried out in a jacketed glass reactor (capacity: 100 cm^3) containing 0.1 g catalyst (in fine powder form) and 50 cm^3 of an aqueous acidic solution with or without containing halide anions, as follows: at first all the air in the reactor (containing the reaction medium, with or without promoters and catalyst) was thoroughly flushed by passing a stream of pure H_2 (30 cm^3/min) for a long period (1 h). After that the reactor was connected (using a two way stopcock as shown in Figure 2.6) to the gas burette filled with water. A measured volume of H_2 was placed in the gas burette by displacing water from it by H_2 and H_2 gas valve was closed. After that 1 ml of 30% H_2O_2 was injected into the reactor under vigorous stirring and the gas evolved in the H_2O_2 decomposition or consumed in the H_2O_2 hydrogenation was measured quantitatively at a constant (atmospheric) pressure, using the gas burette, as a function of time. The independent analysis of unconverted H_2O_2 (by iodometric titration) in the reaction medium by taking out the reaction mixture, as a function of time, was also undertaken for selected experiments for confirming the validity of the analysis and also when there was gas evolution due to initial fast H_2O_2 decomposition.

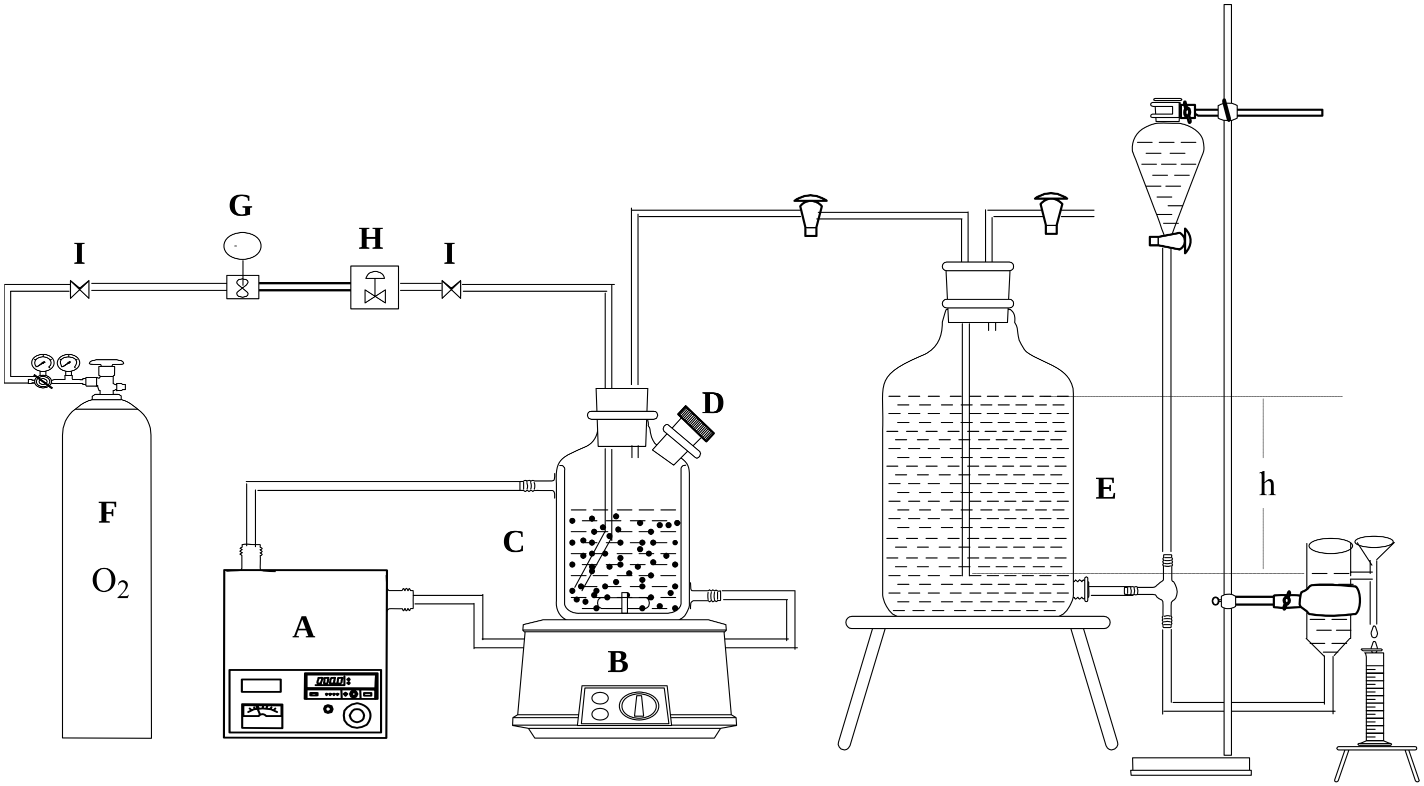
2.5.4. Reduction of Molecular O_2 to H_2O_2 by Hydrazine or Hydrazine sulfate over Supported Pd Catalysts

The schematic diagram of the experimental setup used for the catalytic reduction of O_2 to H_2O_2 by hydrazine from hydrazine salt is given in Figure 2.7. The catalytic reduction of O_2 by hydrazine or hydrazine salt to hydrogen peroxide over the supported Pd catalysts was carried out in a magnetically stirred jacketed glass reactor (capacity: 100 cm^3) containing 0.1 g catalyst in a fine powder form and an aqueous reaction medium (50 cm^3), with or without containing different halide anions and/or mineral acids, to which a known quantity of hydrazine hydrate or hydrazine salt was added. Pure O_2 (99.9%) was continuously bubbled through the reaction mixture under vigorous stirring at atmospheric pressure (95 kPa) and constant temperature. Passing continuously thermostatic water (maintained at a desired temperature) through the jacketed reactor, the temperature of the reaction was controlled. The H_2O_2 formed in the reaction mixture (after separating the catalyst from the reaction mixture by filtration) was determined by iodometric titration. The unconverted hydrazine (if any) was determined by potassium iodate titration. The conversion of hydrazine and H_2O_2 yield were obtained from the



A = Cryostat for water circulation; B = Magnetic stirrer; C = Glass reactor; D = Injection port; E = Gas burette; F = Hydrogen gas cylinder; G = 1000 cc bomb; H = Pressure gauge; I = Pressure controller; J = Differential flow controller (DFC); K = Two way valve.

Figure 2.6: Experimental set up for catalytic hydrogenation of H_2O_2 under static condition.



A = Cryostat for water circulation; B = Magnetic stirrer; C = Glass reactor; D = Injection port; E = Gas burette; F = Hydrogen gas cylinder; G = 1000 cc bomb; H = Pressure gauge; I = Pressure controller; J = Differential flow controller (DFC); K = Two way valve.

Figure 2.7: Experimental set up for catalytic reduction of O_2 to H_2O_2 by the hydrogen containing compounds.

initial (C_{N2H4} at t = 0) and final (C_{N2H4} at t = t) concentration of N_2H_4 in the reaction mixture.

$$\text{Conversion of } N_2H_4\ (\%) = \frac{(C_{N2H4} \text{ at } t = 0 - C_{N2H4} \text{ at } t = t)}{(C_{N2H4} \text{ at } t = 0)} \times 100$$

$$\text{Yield of } H_2O_2\ (\%) = \frac{\text{Moles of } H_2O_2 \text{ formed in the reaction medium}}{2 \times (\text{Moles of } N_2H_4 \text{ initially present in the reaction medium})} \times 100$$

The factor 2 was taken since one mole of N_2H_4 gives two moles of H_2O_2 (according to the reaction: $N_2H_4 + 2\ O_2 \rightarrow 2\ H_2O_2 + N_2$).

2.5.5. Reduction of Molecular O_2 to H_2O_2 by Hydroxylamine or Hydroxylammonium Salt over Supported Au and/or Pd Catalysts

The catalytic reduction of O_2 by hydroxylamine or hydroxylammonium salt to hydrogen peroxide over the supported Pd catalysts was carried out using the same magnetically stirred jacketed glass reactor (Figure 2.7) containing 0.1 g catalyst in a fine powder form and an aqueous or non-aqueous reaction medium (50 cm^3), with or without containing different halide anions, to which a known quantity of hydroxylamine or hydroxylammonium salt was added. Then, the pH of the solution was maintained to 7.0 by adding base or acid. A pure O_2 (99.9%) was continuously bubbled through the reaction mixture under vigorous stirring at atmospheric pressure (95 kPa) and constant temperature. Passing continuously thermostatic water maintained at a desired temperature through the jacketed reactor, the temperature of the reaction was controlled. The H_2O_2 formed in the reaction mixture (after separating the catalyst from the reaction mixture by filtration) was determined by iodometric titration. The unconverted hydrazine was determined by adding potassium bromate solution to the reaction mixture followed by iodometric titration. The conversion of hydroxylamine and H_2O_2 yield was obtained from the initial (C_{NH2OH} at t = 0) and final (C_{NH2OH} at t = t) concentration of NH_2OH in the reaction mixture, as follows.

$$\text{Conversion of } NH_2OH\ (\%) = \frac{(C_{NH2OH} \text{ at } t = 0 - C_{NH2OH} \text{ at } t = t)}{(C_{NH2OH} \text{ at } t = 0)} \times 100$$

The factor 2 was taken since two moles of NH_2OH give one mole of H_2O_2 (according to the reaction: $2\ NH_2OH + O_2 \rightarrow N_2 + 2\ H_2O + H_2O_2$).

$$\text{Yield of } H_2O_2\ (\%) = \frac{(\text{Moles of } H_2O_2 \text{ formed in the reaction medium}) \times 2}{(\text{Moles of } NH_2OH \text{ initially present in the reaction medium})} \times 100$$

2.6. References

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Chapter 3

Direct Oxidation of H_2 to H_2O_2 over Supported Pd Catalysts: Influence of Support, Calcination Temperature, Oxidation State of Pd, Loading of Pd and Halide Promoter Present in the Reaction Medium

Chapter 3

Direct Oxidation of H_2 to H_2O_2 over Supported Pd Catalysts: Influence of Support, Calcination Temperature, Oxidation State of Pd, Loading of Pd and Halide Promoter Present in the Reaction Medium

3.1. Background and Objective of the Present Work

The use of hydrogen peroxide as a bleach in the pulp and paper industry and as an oxidant in the wastewater treatments and for the epoxidation and other organic oxidation reactions has been increasing day-by-day. This has resulted in a renewed interest in the direct synthesis of H_2O_2 from H_2 and O_2 [1-22]. Olivera et. al. [23] predicted from their theoretical work that gold could be more active for the H_2O_2 synthesis by direct oxidation with O_2, as compared to other noble metals. However, it is reported in several studies [5,6,8,14,15,19,20] that supported gold catalyst is active for H_2O_2 formation only under particular reaction condition (viz. at high pressure). Whereas, palladium showed an appreciable H_2O_2 formation activity in the H_2-to-H_2O_2 oxidation under or close to the ambient reaction conditions [1-4,7,9-13,16-18,21,22]. It is also found that an addition of Pd to the gold catalyst is quite effective for increasing the H_2O_2 formation [14,21]. Therefore, palladium is unique in catalyzing the formation of H_2O_2 in the H_2-to-H_2O_2 oxidation.

In spite of the fact that the H_2-to-H_2O_2 oxidation process over Pd containing catalysts have been studied and patented extensively, it is not yet commercialized. However, recently Degussa [24] announced the start of a demonstration plat for the process. One of the main problems for practically exploiting this process is the following non-selective parallel and consecutive water forming reactions, occurring simultaneously with the H_2-to-H_2O_2 forming reaction in the process [16,25].

$H_2 + O_2 \rightarrow H_2O_2$ (H_2O_2 forming reaction) (3.1)

$H_2 + 0.5\ O_2 \rightarrow H_2O$ (parallel direct water forming reaction) (3.2)

$H_2O_2 \rightarrow H_2O + 0.5\ O_2$ (consecutive H_2O_2 decomposition reaction) (3.3)

$H_2O_2 + H_2 \rightarrow 2\ H_2O$ (consecutive H_2O_2 hydrogenation reaction) (3.4)

Hence, continuous effects are being made to increase both the H_2O_2 selectivity and yield (i.e. H_2O_2 formation activity) through the catalyst and/or process improvements and also by reducing the rate of the undesirable reactions (reactions 3.2 – 3.4) through some means.

Earlier we have studied the H_2-to-H_2O_2 oxidation over several supported Pd catalysts (viz. Pd/C, Pd/ZrO_2, Pd/Al_2O_3, Pd/SiO_2, Pd/Ga_2O_3, Pd/CeO_2, Pd/ThO_2, Pd/Hβ, etc.) with a gaseous feed consisting of 4 mol% of H_2 in O_2 under the ambient reaction conditions [2-4,16,18,21,22]. We observed that the H_2O_2 yield in H_2-to-H_2O_2 oxidation process is strongly influenced by the support used for the deposition of Pd [21]. We have also shown that the H_2O_2 selectivity/yield of supported Pd catalysts can be drastically increased with a large decrease in the H_2O_2 decomposition activity of the catalyst due to a partial (i.e. surface/sub-surface) or complete (i.e. bulk) oxidation of Pd from the catalysts [1-4]. The use of halogen anions (as catalyst promoter), particularly bromide or chloride anions in acidic reaction medium [8,10,16,17,22] or in a catalyst [11] has also been reported to drastically improve the H_2O_2 selectivity/yield for different supported Pd catalyst. Our recent studies [11,16,22] showed also a large decrease in the H_2O_2 destruction (by H_2O_2 decomposition and/or hydrogenation) activity of supported Pd catalysts due to addition of the halide promoters in the acidic reaction medium or directly in the catalyst. However, a little or no information is available on the effects of supports, Pd loading, calcination temperatures and halide promoters on the net formation activities of oxidized Pd catalysts (i.e. supported PdO catalysts).

The present study was undertaken with the objective of investigating the influence of catalyst parameters, such as different supported PdO catalysts, calcination temperature, Pd loading and reduction of PdO catalysts, in the oxidation of H_2 by O_2 to H_2O_2 (with a gaseous feed consisting of 50 mol% H_2 in O_2) in an aqueous acidic (0.1 M H_3PO_4) medium with or without containing different halide anions. The H_2O_2 decomposition and hydrogenation activities of the selected best supported PdO catalyst, calcined at different temperatures and with different Pd loadings, have also been determined under the conditions similar to that employed in the H_2-to-H_2O_2 oxidation.

3.2. Catalysts and Brief Experimental Procedures

The supported PdO (2.5 wt.% Pd) catalysts were prepared by impregnating the supports (viz. Al_2O_3, SiO_2, CeO_2, ZrO_2, Hβ and HM) with palladium acetate from its acetonitrile solution by the incipient wet impregnation technique, described in the section 2.2.2, followed by drying on a water bath and decomposing the catalyst mass at 400 ºC for 2 h in a flow of O_2-free nitrogen. For studying the influence of catalyst calcination temperature the supported PdO catalysts were further calcined under air in muffle furnace at different temperatures for 2h.

The PdO/Al_2O_3 catalysts with different Pd loadings (0.2 to 10 Wt%) were prepared by impregnating γ-Al_2O_3 (obtained from the calcination of bohemite at 400 ºC for 4 h in a muffle furnace), in a fine powdered form, with a desired amount of palladium acetate from its acetonitrile solution by the incipient impregnation technique, described in the section 2.2.2. The PdO/Al_2O_3 catalysts (with the different Pd loadings) were further calcined at different temperatures (600 º, 800 º and 900 ºC) in the muffle furnace (in air) for 2 h. Colour of the PdO/Al_2O_3 catalysts was light brown to dark brown, depending upon the Pd loading.

The supported Pd catalysts were prepared from the supported PdO catalysts by reducing them with an ammoniacal hydrazine solution at room temperature (25 °C) for 2h followed by washing, filtration and drying in vacuum oven.

The PdO/Al_2O_3 (Pd loading = 5 wt%) calcined at different temperatures were characterized by XRD using a Holland Philips, PW/1730 X-ray generator with CuK_α radiation ($\lambda = 1.5406$ Å).

The experimental procedure for the direct oxidation of H_2 to H_2O_2 by O_2 and destruction of H_2O_2 in absence H_2 (i.e. in presence of air) and presence of H_2 over the Pd catalysts have already been described in section 2.5.1, 2.5.2 and 2.5.3, respectively. All the reactions over the Pd catalysts were carried out at atmospheric pressure (95 kPa) in a jacketed magnetically stirred glass reactor (capacity 100 cm^3) containing 0.1 g catalyst in a fine power form and an aqueous acidic (0.1 M H_3PO_4) solution (50 cm^3) as a reaction medium with or without containing different halides in the reaction medium (1.0 $mmol/dm^3$). The direct catalytic H_2-to-H_2O_2 oxidation was carried out by continuously passing H_2 and O_2 through the medium at the following reaction conditions: H_2 flow rate = 180 cm^3/h, O_2 flow rate = 180 cm^3/h, temperature = 27 ºC and reaction period = 1.0 h. The H_2 conversion, H_2O_2 yield and H_2O_2 selectivity was calculated by using the equations given in the section 2.5.1.

The H_2O_2 decomposition and hydrogenation reactions over the PdO/Al_2O_3 catalysts were carried out in the same described above reactor in the presence of static air and H_2, respectively, by injecting 1.0 cm^3 of aqueous 30 wt% H_2O_2 solution through a rubber septum in the acidic reaction medium (50 cm^3) containing 0.1 g catalyst at 27 ºC and following the reactions as a function of time.

3.3. Effect of Mass Transfer on the Reaction Between H_2 and O_2

The rate of reaction between the H_2 and O_2 in liquid medium depends upon the mass transfer of the reactants to the catalyst sites [8]. It is, therefore, important that experiments to investigate the formation of H_2O_2 in the reaction between H_2 and O_2 should be carried out under conditions at which the mass transfer has only a little or no influence on the reaction rate. In our earlier work [18], the conversion of H_2 was studied with different agitation rates remaining all other variables constant (Figure 3.1).

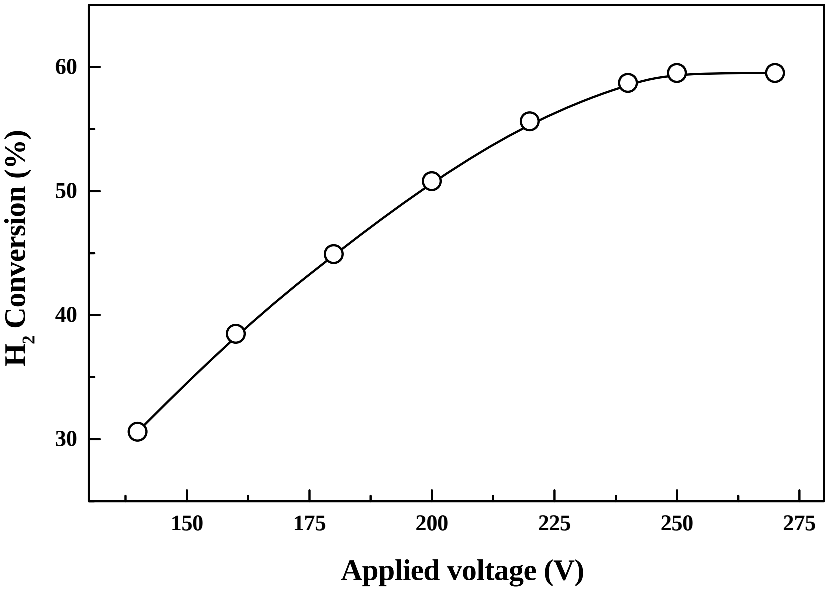

Figure 3.1: Effect of the stirring speed on the conversion of H_2 in the reaction between H_2 and O_2 over the reduced Pd/C catalyst in aqueous acidic (0.03 M H_3PO_4) reaction medium.

The stirring speed was adjusted by altering the applied voltage (V) to the magnetic stirrer. At the lower stirring speeds, the conversion of H_2 is dependent on the stirring speed.

However, above 230V there is no significant change in the H_2 conversion, indicating the absence of gas-liquid mass transfer effect on the reaction. For the subsequent experiments, the stirrer speed was set at 260 V.

3.4. H_2-to-H_2O_2 Oxidation over Different Supported Palladium Catalysts

3.4.1. Influence of the Catalyst Reduction

Results showing the comparison between the PdO and Pd catalysts (with Pd loading of 2.5 wt%), prepared by using different catalyst carriers (viz. Al_2O_3, SiO_2, CeO_2, ZrO_2, Hβ and HM), for their H_2 conversion and H_2O_2 formation activity in the H_2-to-H_2O_2 oxidation in an aqueous acidic (0.1 M H_3PO_4) reaction medium are presented in Tables 3.1.

Table 3.1: Comparison of the H_2 conversion and H_2O_2 formation activities of the supported catalysts (in oxidized and reduced forms) in the H_2-to-H_2O_2 oxidation [X_{H2} = conversion of H_2, Y_{H2O2} = yield of H_2O_2 and S_{H2O2} = selectivity of H_2O_2].

Catalyst	X_{H2} (%)	S_{H2O2} (%)	Y_{H2O2} (%)
Oxidized catalysts[a]			
PdO/Al_2O_3	68.0	24.5	17
PdO/SiO_2	28.1	31.0	8.7
PdO/ZrO_2	45.0	30.0	13.5
PdO/CeO_2	39.2	26.5	10.4
PdO/Hβ	69.3	20.5	14.2
PdO/HM	48.7	23.0	11.2
Reduced Catalysts[b]			
Pd/Al_2O_3	74.3	<1.0	<1.0
Pd/SiO_2	80.0	9.5	7.6
Pd/ZrO_2	73.1	13.0	9.5
Pd/CeO_2	84.4	13.5	11.4
Pd/Hβ	87.7	6.5	5.7

[a] Supported PdO catalysts (calcined at 400 ºC). [b] Prepared from the supported catalysts (calcined at 400 ºC) by their reduction with hydrazine.

The comparison of the results in Table 3.1 reveals that, after the reduction, the H_2 conversion activity of all the catalysts is increased appreciably but their H_2O_2 selectivity is largely reduced. The supported catalysts in their oxidized form showed much higher H_2O_2 selectivity than that showed by the reduced catalysts. Hence, further studies were carried out using the different oxidized catalysts (supported PdO catalysts) calcined at different temperatures, to know the influence of catalyst calcination temperature and catalyst support on the H_2O_2 formation.

3.4.2. Influence of the Catalyst Calcination Temperature

Results showing the influence of catalyst calcination temperature (400 º - 600 ºC) on the H_2 conversion activity and H_2O_2 selectivity/yield for the different supported PdO (2.5 wt% Pd) catalysts are presented in Figures 3.2 – 3.7.

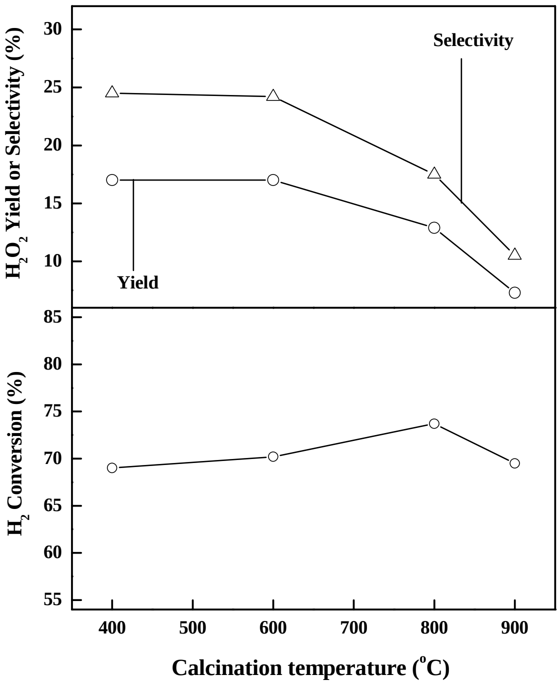

Figure 3.2: Effect of the catalyst calcination temperature on the performance of PdO/Al_2O_3 catalyst in the H_2-to-H_2O_2 oxidation (H_2:O_2 = 1:1) at 27 ºC.

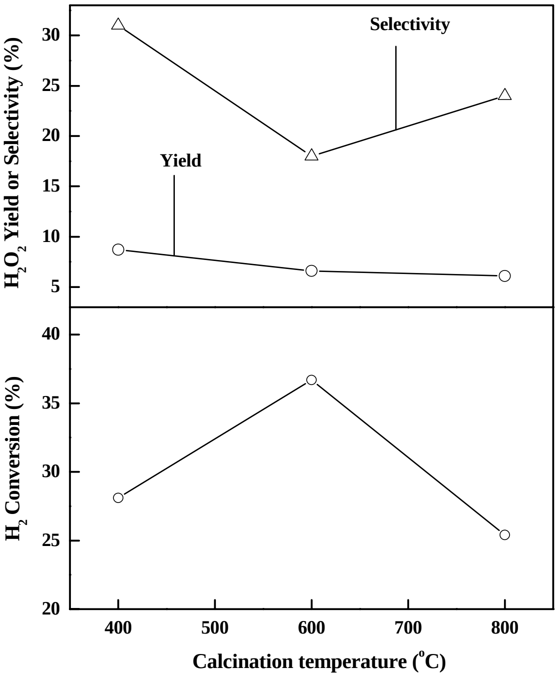

Figure 3.3: Effect of the catalyst calcination temperature on the performance of PdO/SiO_2 catalyst in the H_2-to-H_2O_2 oxidation (H_2:O_2 = 1:1) at 27 ºC.

When the catalyst calcination temperature is increased from 400 ° to 800 °C, following important observations can be made.

- For the PdO/Al_2O_3 (Figure 3.2), the H_2 conversion is increased but both the H_2O_2 selectivity and yield remained unaffected up to the calcination temperature (T_c) of 600 °C. However, above the T_c of 600 °C, there was a large decrease in both the H_2O_2 selectivity and yield; indicating a large decrease in the H_2O_2 formation activity at the higher calcination temperature (800 °C).
- For the PdO/SiO_2 and PdO/CeO_2 catalysts (Figures 3.3 and 3.4), the H_2 conversion passed through a maximum but the H_2O_2 selectivity passed through a minimum, both at the same calcination temperature (600 °C). The highest H_2O_2 yield for the PdO/SiO_2 and PdO/CeO_2 catalysts was observed at the T_c of 400° and 600 °C, respectively.

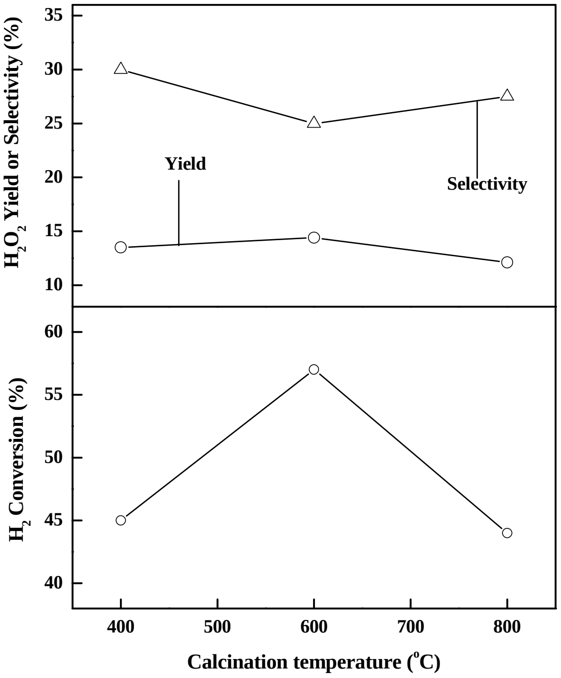

Figure 3.4: Effect of the catalyst calcination temperature on the performance of PdO/CeO_2 catalyst in the H_2-to-H_2O_2 oxidation ($H_2:O_2$ = 1:1) at 27 °C.

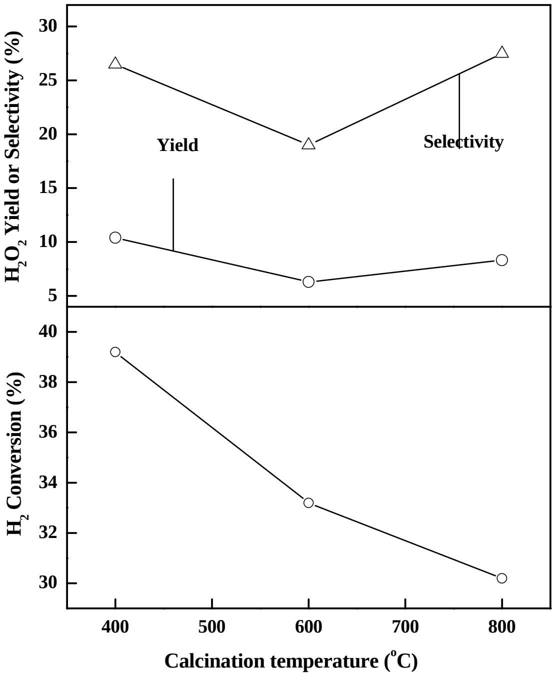

Figure 3.5: Effect of the catalyst calcination temperature on the performance of PdO/ZrO_2 catalyst in the H_2-to-H_2O_2 oxidation ($H_2:O_2$ = 1:1) at 27 °C.

- For the PdO/ZrO_2 and PdO/HM catalysts (Figures 3.5 and 3.7), the H_2 conversion decreased continuously but the H_2O_2 selectivity passed through a maximum (at T_c = 600 ºC). In both the cases, the highest H_2O_2 yield was observed at the T_c of 400 ºC.
- For the PdO/Hβ catalyst (Figure 3.6), the H_2 conversion passed through a maximum (at T_c = 600 ºC) but both the H_2O_2 selectivity and yield decreased continuously.

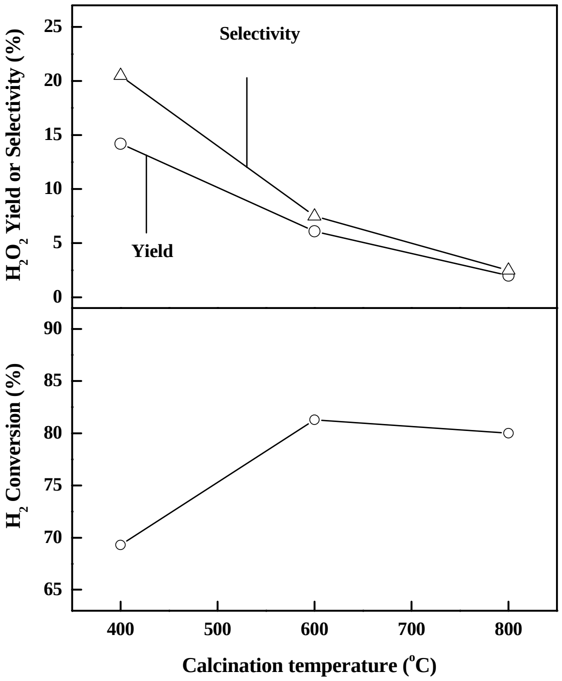

Figure 3.6: Effect of the catalyst calcination temperature on the performance of PdO/Hβ catalyst in the H_2-to-H_2O_2 oxidation (H_2:O_2 = 1:1) at 27 ºC.

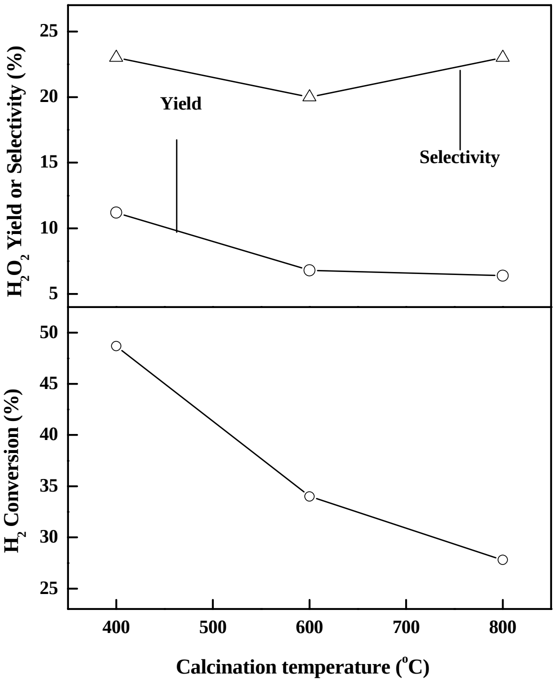

Figure 3.7: Effect of the catalyst calcination temperature on the performance of PdO/HM catalyst in the H_2-to-H_2O_2 oxidation (H_2:O_2 = 1:1) at 27 ºC.

These observations indicate a strong influence of the calcination temperature on the H_2O_2 formation activity of the different supported PdO catalysts, depending upon the support used in the catalysts. Neverthless, the best catalyst performance (i.e. highest H_2O_2 yield) was observed when the catalyst (except the PdO/CeO_2) was calcined at 400 ºC. The influence of catalyst calcination temperature may however change, if the Pd loading in the supported PdO catalysts is changed.

3.4.3. Influence of the Catalyst Support

Results in Figure 3.8 show a strong influence of the support used in the supported PdO catalyst on its H_2 conversion and H_2O_2 formation activities in the H_2-to-H_2O_2 oxidation.

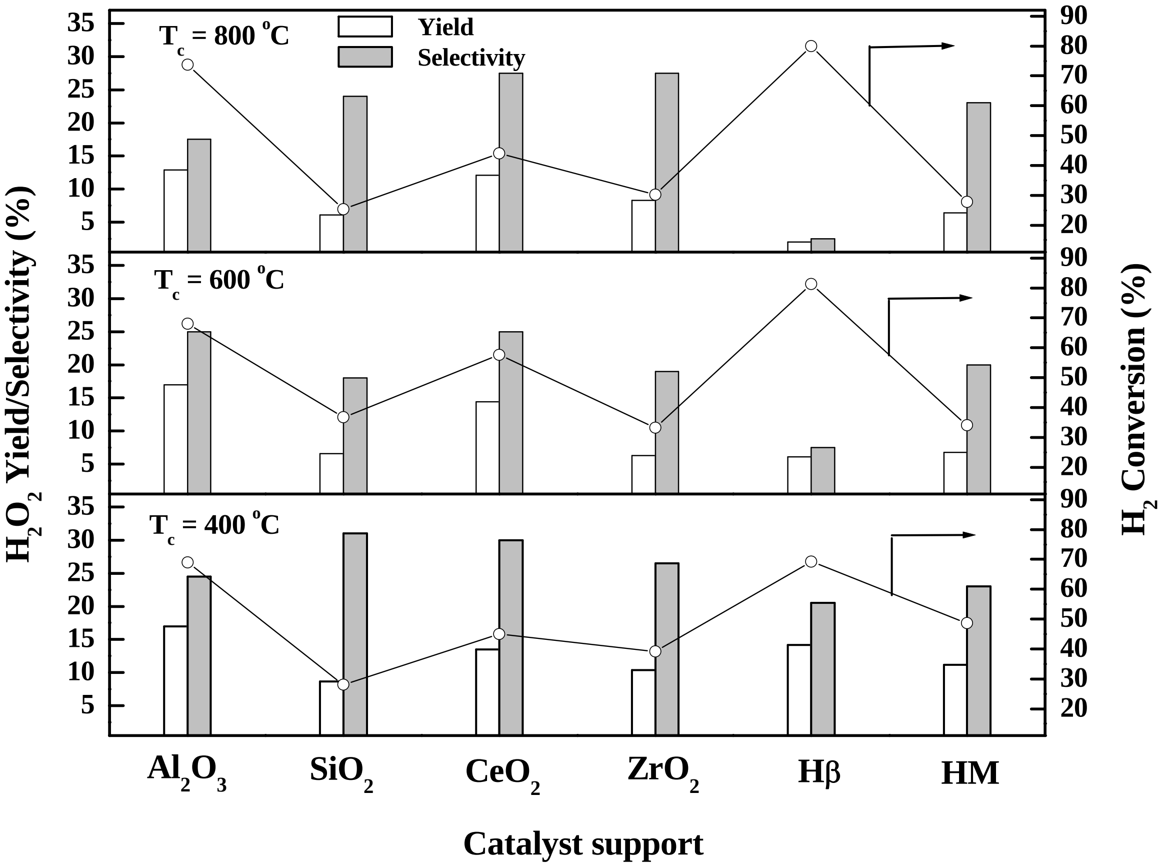

Figure 3.8: Effect of the support of the supported PdO catalysts calcined at three different temperatures on their performance in the H_2-to-H_2O_2 oxidation (H_2:O_2 = 1:1) at 27 ºC.

It may be noted that the influence of support depends strongly upon the catalyst calcination temperature. For the catalysts calcined at 400 ºC, the order of performance for the catalyst support is Al_2O_3 > Hβ > CeO_2 > HM ≥ ZrO_2 > SiO_2. For the catalysts calcined at 600 º and 800 º, the order is changed to Al_2O_3 ≥ CeO_2 > HM ≥ Hβ and ZrO_2, and Al_2O_3 and CeO_2 > ZrO_2 > HM > SiO_2 > Hβ, respectively. Neverthless, among the supports, the most preferred support for the supported PdO catalyst is Al_2O_3.

3.4.4. Influence of the Catalyst Calcination Temperature on H_2O_2 Decomposition and Hydrogenation Activities

Results showing the influence of the calcination temperature of the PdO (2.5 wt% Pd)/Al_2O_3 (which is the best selected catalyst among the different supported PdO catalyst for the H_2-to-H_2O_2 oxidation) on its H_2O_2 decomposition (in the absence of H_2) and hydrogenation activities in the acidic medium at 27 ºC are presented in Figures 3.9 and 3.10, respectively.

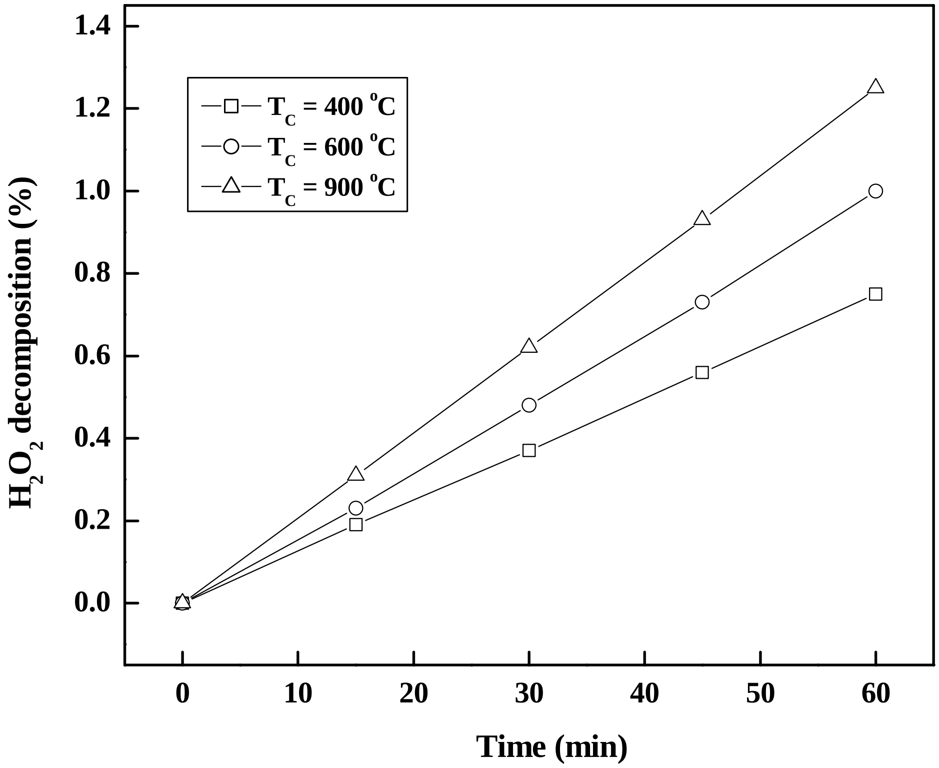

Figure 3.9: Effect of catalyst calcination temperature on the H_2O_2 decomposition activity of PdO (2.5 wt% Pd)/Al_2O_3 catalyst (at 27 ºC).

It is interesting to note from the results that both the H_2O_2 decomposition and hydrogenation rates are increased appreciably with increasing the catalyst calcination temperature. The observed smaller rates of hydrogenation in the initial short reaction periods (Figure 3.10) are expected because of the generation of Pd^o from PdO on the catalyst surface by the reduction by H_2 of the PdO during the initial reaction period.

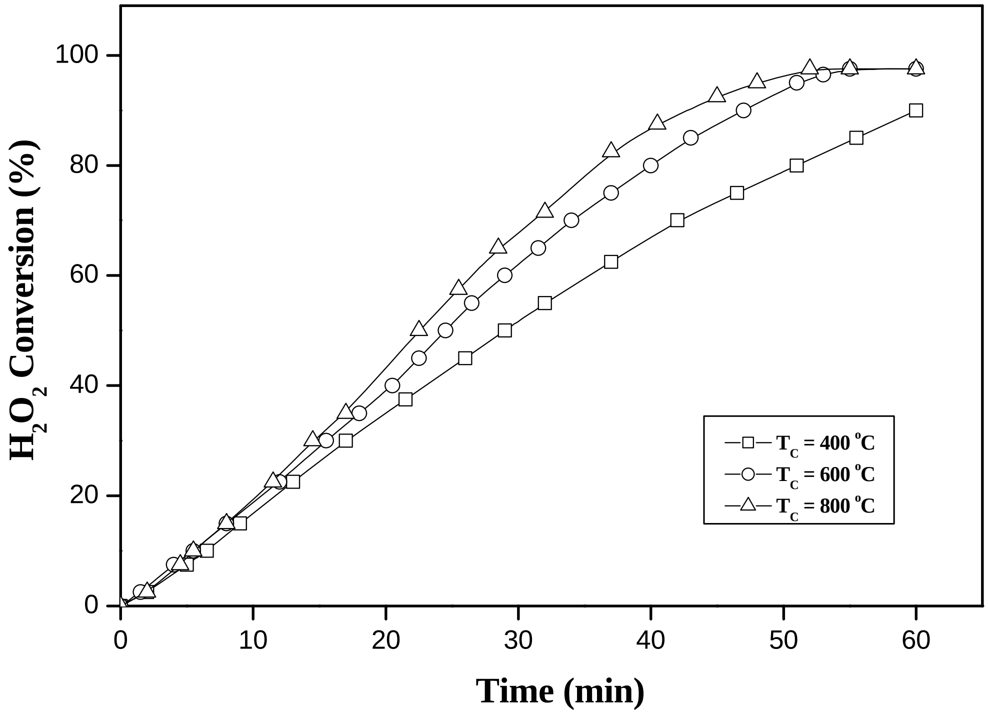

Figure 3.10: Effect of catalyst calcination temperature on the H_2O_2 hydrogenation activity of PdO (2.5 wt% Pd)/Al_2O_3 catalyst (at 27 ºC).

It may be noted that the increase in the H_2O_2 decomposition and hydrogenation activities of the catalyst (Figures 3.9 and 3.10) is consistent with the observed decrease in the H_2O_2 formation activity of the catalyst with increasing its calcination temperature (Figure 3.2).

3.5. H_2-to-H_2O_2 Oxidation over the Selected Best PdO/Al_2O_3 Catalyst

3.5.1. Influence of the Calcination Temperature

Results showing the influence of calcination temperature (300 º to 900 ºC) of the PdO/Al_2O_3 catalysts with different Pd loadings (0.2 to 10 wt%) on the H_2 conversion and H_2O_2 selectivity/yield in the H_2-to-H_2O_2 oxidation in an aqueous acidic (0.1 M H_3PO_4) medium (in the absence of any halide promoter) are presented in Figures 3.11 – 3.14. Whereas, Figure 3.15 shows the XRD spectra of the PdO(5 wt%)/Al_2O_3 catalyst calcined at different temperatures and periods. The effect of the catalyst calcination temperature on the H_2O_2 decomposition and hydrogenation activities of the PdO/Al_2O_3 catalyst with the Pd loading of 5 wt% is shown in Figures 3.16 and 3.17, respectively.

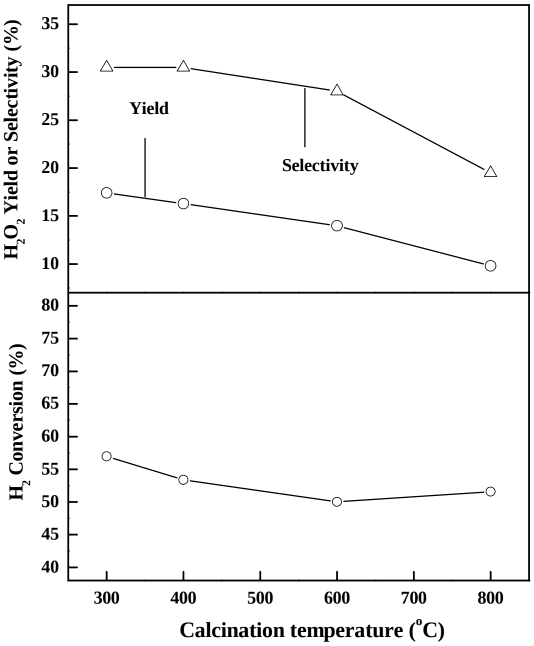

Figure 3.11: Influence of the calcination temperature of PdO(0.2 wt% Pd)/Al_2O_3 on the H_2-to-H_2O_2 oxidation (H_2:O_2 = 1:1) at 27 ºC.

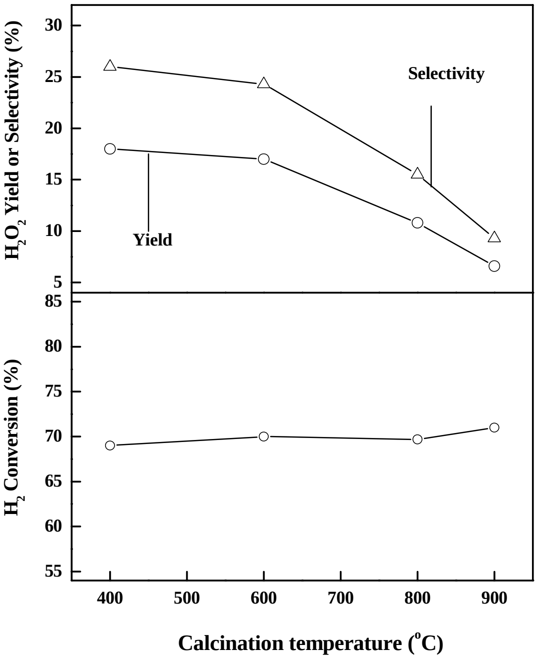

Figure 3.12: Influence of the calcination temperature of PdO(0.5 wt% Pd)/Al_2O_3 on the H_2-to-H_2O_2 oxidation (H_2:O_2 = 1:1) at 27 ºC.

The results in Figures 3.11 – 3.14 show that, for all the catalysts (Pd loading = 0.2 to 10 wt%), the influence of calcination temperature on the net H_2O_2 formation or on both the H_2O_2 selectivity and yield is much larger than that on the H_2 conversion; the change in the H_2 conversion activity of the catalysts with increasing their calcination temperature, even by 500 ºC, is quite small. It is, however, very interesting to note from the trends of the variation of the H_2O_2 formation with the calcination temperature for the catalysts (with the different Pd loadings) that the H_2O_2 formation trend is gradually changed and then reversed, depending upon the Pd loading in the catalyst. For the catalysts with the lower Pd loadings (≤ 2.5 wt% Pd), both the H_2O_2 selectivity and yield are decreased with increasing the calcination temperature. On the contrary, for the catalysts with the higher Pd loadings (5.0 and 10 wt%), both the H_2O_2 selectivity and yield are increased largely, indicating a large increase in the net H_2O_2 formation, with increasing the calcination temperature.

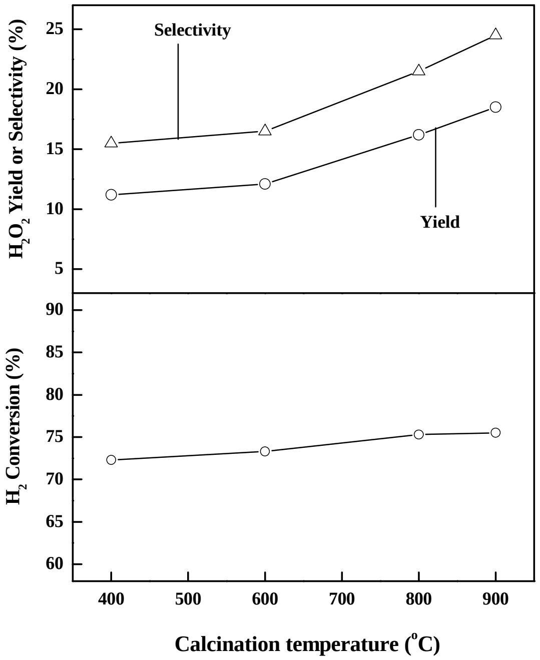

Figure 3.13: Influence of the calcination temperature of PdO(5.0 wt% Pd)/Al_2O_3 on the H_2-to-H_2O_2 oxidation (H_2:O_2 = 1:1) at 27 ºC.

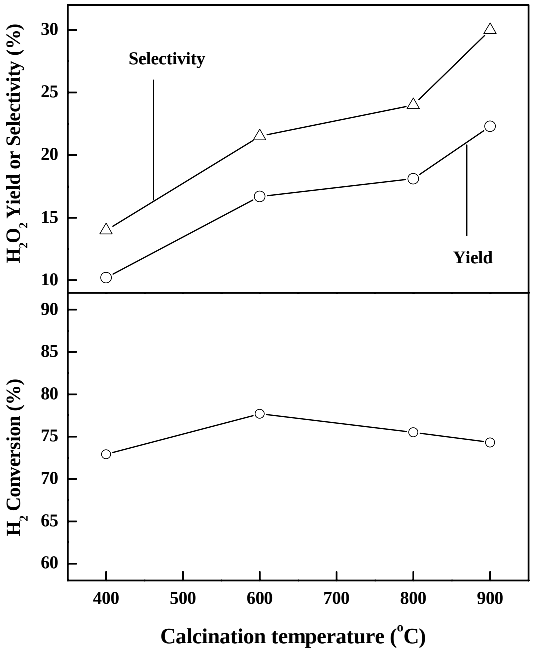

Figure 3.14: Influence of the calcination temperature of PdO(10 wt% Pd)/Al_2O_3 on the H_2-to-H_2O_2 oxidation (H_2:O_2 = 1:1) at 27 ºC.

At the calcination temperature of 400 ºC, the H_2O_2 formation over the PdO/Al_2O_3 with high Pd loading (5 or 100 wt%) is much lower than that over the PdO/Al_2O_3 with lower Pd loadings. However, when the period of calcination (at 400 ºC) of the catalyst with the high Pd loading (5 wt%) was increased from 2 to 16 h, its H_2O_2 formation activity increased very appreciably (H_2O_2 yield was increased from 4.7 % to 30.5 %), with only a small change in the H_2 conversion (74 ± 2 %). The observed calcination period effect suggest that the poor H_2O_2 formation activity of the catalyst with high Pd loading may be due to the incomplete decomposition of the palladium acetate (deposited in the Al_2O_3) to PdO during the catalyst calcination at 400 ºC for the shorter period (2 h) and/or because of the incomplete removal of the carbon formed in the decomposition. The calcination at the longer period (16 h at 400 ºC) also caused an appreciable crystal growth (from 10.7 nm to 12.5 nm) of the PdO on the catalyst, as seen from the narrowing of the XRD peak for PdO (2θ = 33.9º) [Figure 3.15].

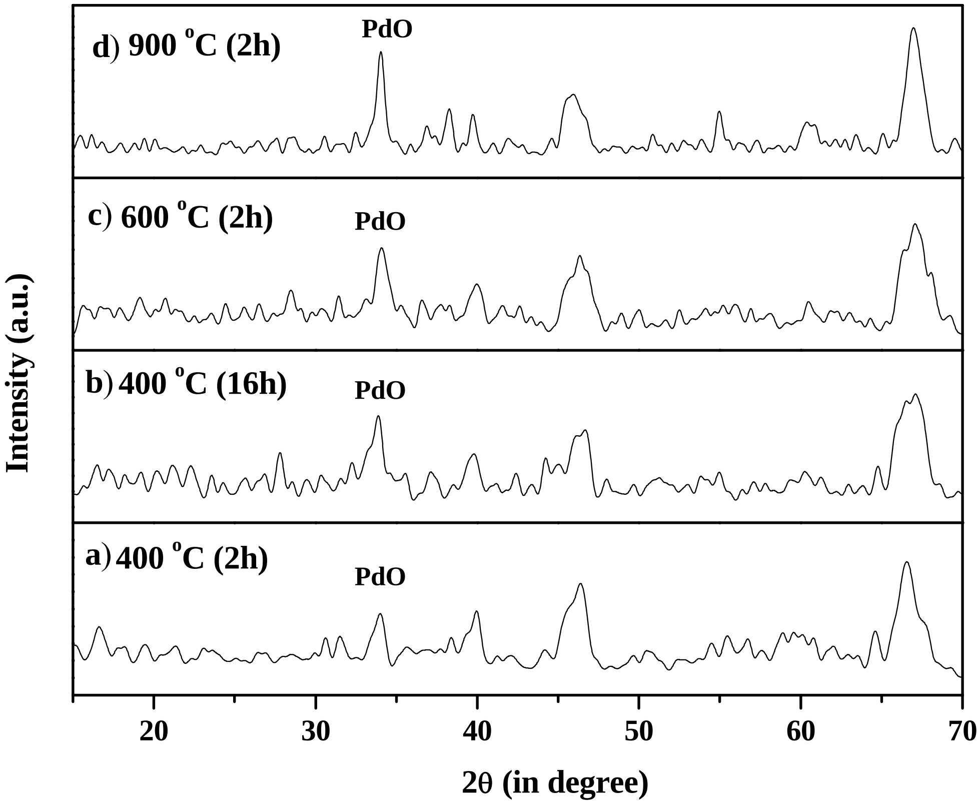

Figure 3.15: XRD spectra of the PdO(5 wt% Pd)/Al_2O_3 catalyst calcined at different temperatures / periods.

For the PdO (5 wt%)/Al_2O_3 catalyst, the PdO particle size was increased with increasing the catalyst calcination temperature, as seen from the narrowing of the XRD peak for PdO (at 2θ = 33.9º) (Figure 3.15). The crystal size of PdO at the calcination temperatures of 400 º, 600 º and 800 ºC has been estimated as 10.6, 13.2 and 17.0 nm, respectively. It is interesting to note that the catalyst sintering with an appreciable crystal growth of PdO caused a large improvement in the H_2O_2 formation activity of the catalysts with the high Pd loading. However, for the catalysts with lower Pd loadings (≤ 2.5 wt%), their sintering at the higher calcination temperatures is expected to cause the observed decrease in their H_2O_2 formation activity. Further detailed investigations are necessary to understand the above controversial results.

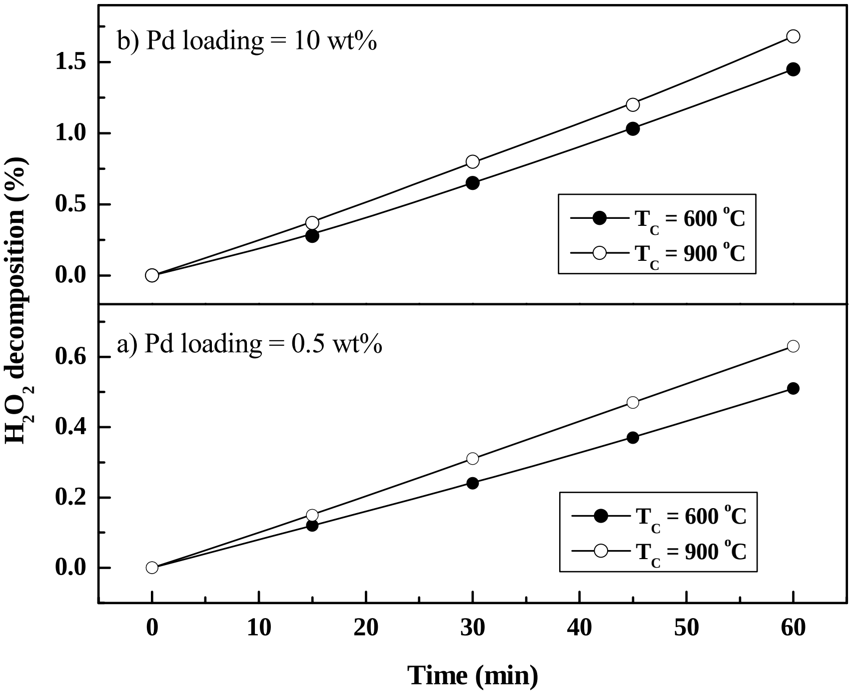

Figure 3.16: Influence of the calcination temperature (T_c) and Pd loading of the PdO/Al_2O_3 on its H_2O_2 decomposition activity in the acidic medium (at 27 °C).

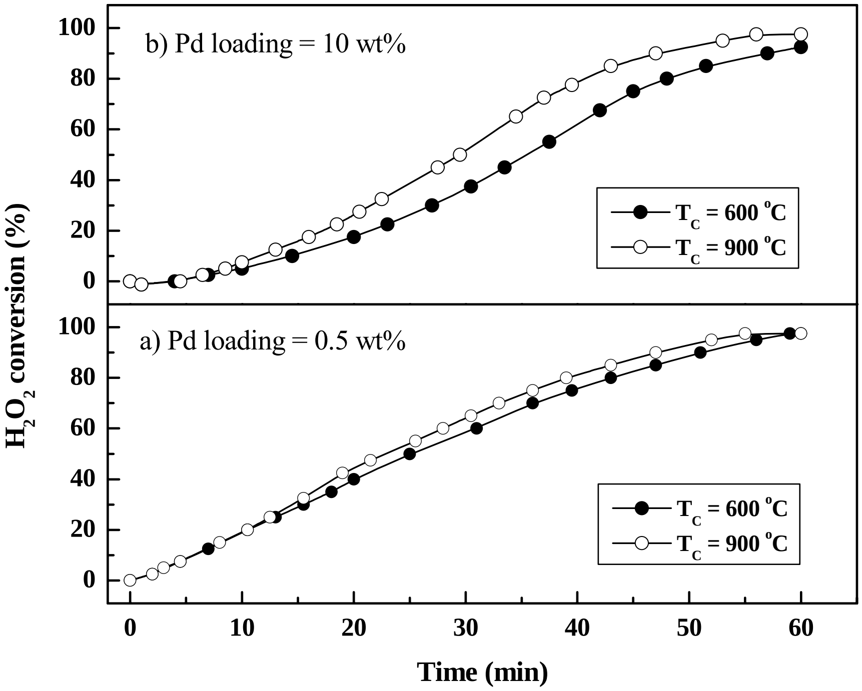

Figure 3.17: Influence of the calcination temperature (T_c) and Pd loading of the PdO/Al_2O_3 on its H_2O_2 hydrogenation activity in the acidic medium (at 27 °C).

It is also interesting to note that both H_2O_2 decomposition (Figure 3.16) and hydrogenation (Figure 3.17) rates are increased appreciably with increasing the calcination temperature of PdO/Al_2O_3 with two different Pd loadings (0.5 and 5.0 wt%). The short reaction induction period or slower rate of the H_2O_2 hydrogenation at the initial period (Figure 3.17) is expected because of the reduction by H_2 of the surface/subsurface PdO to Pd; the induction period is larger for the catalyst with the larger Pd loading.

3.5.2. Influence of the Pd Loading

The influence of Pd loading in the PdO catalyst calcined at three different temperatures (400 °, 600 ° and 800 °C) has been clearly brought out in Figure 3.18.

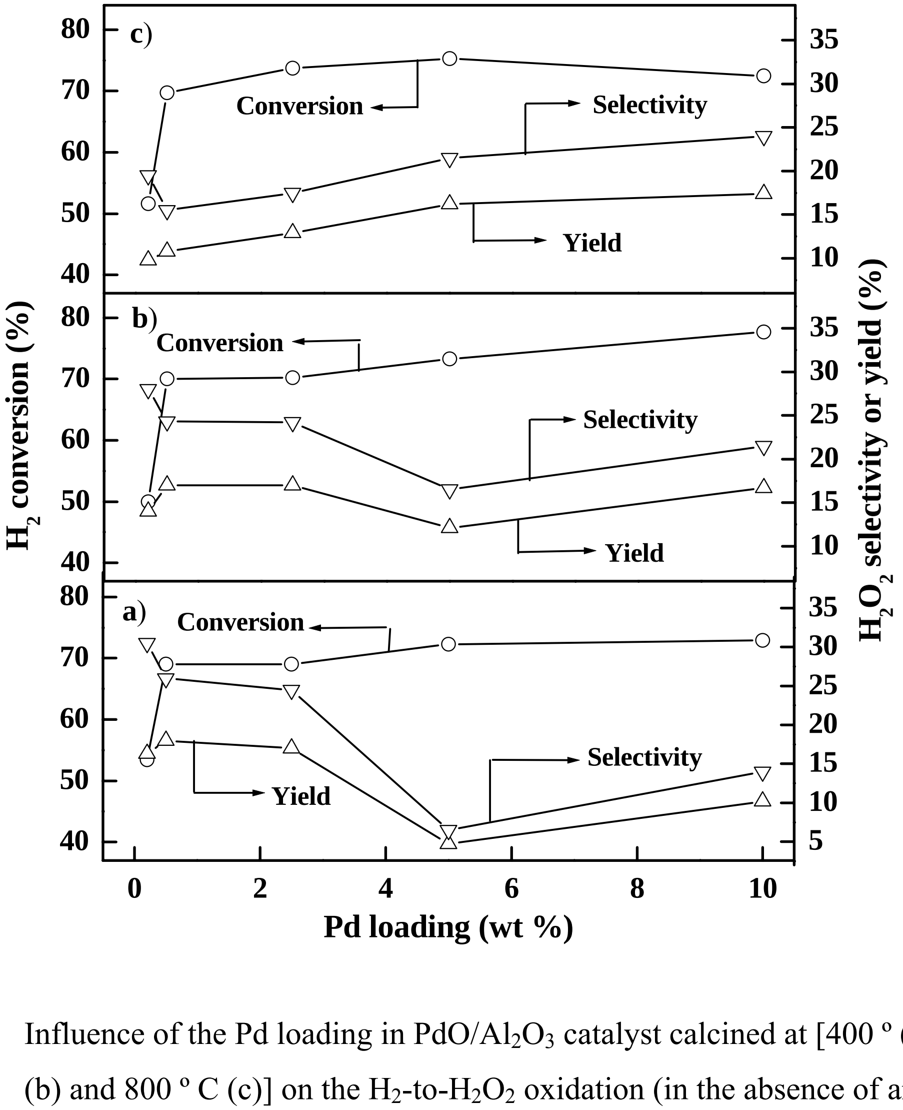

Figure 3.18: Influence of the Pd loading in PdO/Al_2O_3 catalyst calcined at [400 ° (a), 600 ° (b) and 800 ° C (c)] on the H_2-to-H_2O_2 oxidation (in the absence of any halide promoter) at 27 °C.

With increasing the Pd loading, the H_2 conversion and H_2O_2 selectivity/yield are changed as follow.

- For all the catalyst calcination temperatures, the H_2 conversion is increased sharply up to the Pd loading of 0.5 wt%; for the higher Pd loading, the increase is, however, much smaller and the increase of Pd loading from 5 to 10 wt% for the catalyst calcined at 800 ºC caused a small decrease in the H_2 conversion.
- The H_2O_2 selectivity is passed through a minimum, depending upon the catalyst calcinations temperature. At the calcination temperature of 400 º, 600 º and 800 ºC, the minimum is observed for the Pd loading of 5, 2.5 and 0.5 wt%, respectively. At the lower calcination temperatures (400 º and 600 ºC), the highest H_2O_2 selectivity is observed for the lowest Pd loading (0.2 wt%) but, at the higher calcination temperature (800 ºC), it is observed for the highest Pd loading (10 wt%).
- At the high calcination temperature (800 ºC), the H_2O_2 yield is increased with increasing the Pd loading. However, at the lower calcination temperature (400 ºC and 600 ºC), it is passed through maximum and minimum for the Pd loading of 0.5 and 5.0 wt%, respectively.

A comparison of the results (Figure 3.18) reveal that the trends for both the H_2O_2 selectivity and yield are also changed gradually with increasing the calcination temperature from 400 º to 800 ºC, indicating a strong dependence of the influence of Pd loading upon the catalyst calcination temperature. Thus, the effects of two individual catalyst – parameters (calcination temperatures and Pd loading) on the H_2O_2 formation are interrelated; the two are dependent on each other. Neverthless, the PdO (0.5 wt% Pd)/Al_2O_3 calcined at 400 ºC and PdO(5.0 wt%)/Al_2O_3 calcined at 900 ºC showed the best H_2O_2 formation performance.

3.5.3. Influence of the Catalyst Reduction

The results of the H_2O_2 formation over the PdO/Al_2O_3 catalysts with Pd loading of 0.5 and 5 wt% (calcined at 400 º and 900 ºC, respectively), before and after their reduction by hydrazine, in the acidic medium in both the absence and presence of different halide anions (1.0 mmol/dm^3) are presented in Table 3.2.

A comparison of the results showed that, in both the presence and absence of the halide anions, the catalyst reduction causes an increase in the H_2 conversion but a decrease in the

H_2O_2 selectivity. The H_2O_2 yield, except in the presence of Br^- anions for the catalyst with 5 wt% Pd, is also decreased due to the catalyst reduction.

Table 3.2: Results showing the influence of catalyst reduction (PdO → Pd) and different halides (1.0 mmol/dm^3) in the acidic medium on the H_2-to-H_2O_2 oxidation over PdO/Al_2O_3 catalysts.

Halide in medium	Before catalyst reduction				After catalyst reduction			
	X_{H2} (%)	S_{H2O2} (%)	Y_{H2O2} (%)	TOF[a] (h^{-1})	X_{H2} (%)	S_{H2O2} (%)	Y_{H2O2} (%)	TOF[a] (h^{-1})
A) Catalyst: PdO/Al_2O_3 (0.5 wt% Pd) calcined at 400 °C								
Nil	69	26	18	308	75	8	6	103
KF	69	28	19	325	76	14	8	137
KCl	66	34	22	376	73	29	21	359
KBr	46	42	19	325	42	38	16	274
KI	11	20	2	34	13	9	1	17
B) Catalyst: PdO/Al_2O_3 (5.0 wt% Pd) calcined at 900 °C								
Nil	76	25	19	33	80	2	2	3
KF	75	21	16	27	76	1	<1	1
KCl	71	31	22	38	77	19	14	24
KBr	66	44	29	50	81	40	32	55
KI	9	0.0	0.0	0.0	10	0.0	0.0	0.0

[a] Turned over frequency, defined as the rate of net H_2O_2 formed (moles) per mole of PdO or Pd (in the catalyst) per hour.

3.5.4. Influence of the Presence of Halide Anions

Earlier studies [16,22] showed strong influence of the presence of different halide anions (viz. F^-, Cl^-, Br^- or I^-) in the acidic reaction medium on the H_2O_2 formation in the H_2-to-H_2O_2 oxidation over different reduced Pd catalysts. The cations associated with the halide anions showed only a little or no influence on the H_2O_2 formation and destruction reactions

[16,22]. The results showing the influence of the addition of different halide anions (F^-, Cl^-, Br^- or I^-) in the acidic medium on the H_2 conversion and H_2O_2 selectivity/yield in the H_2-to-H_2O_2 oxidation over the two best selected PdO/Al_2O_3 catalysts, before and after their reduction, are presented in Table 3.2. The turned over frequency (TOF) values for the net H_2O_2 formation over the catalysts are also included in Table 3.2.

A comparison of the results for the oxidized and reduced catalysts provides the following important information about the influence of the different halide anions on the H_2O_2 formation.

The influence of a particular halide on the H_2O_2 formation depends upon both the oxidation state and loading of Pd in the catalyst. The presence of F^- anions caused a large decrease in the H_2O_2 formation over the reduced catalysts but it caused only a small change (a small increase) in the H_2O_2 formation over the oxidized catalysts; the influence of F^- anions on the H_2O_2 is stronger for the catalyst with a larger Pd loading (5 wt%). The catalyst (both reduced and oxidized forms) with a low Pd loading (0.5 wt%) showed best H_2 formation performance in the presence of chloride promoter but that with a high Pd loading (5 wt%) showed best performance in the presence of bromide promoter. The detrimental effect of the iodide added to the reaction medium on the H_2O_2 formation (which arises from the catalyst poisoning by the iodide anions) is more pronounced for the catalyst with the high Pd loading (5 wt%).

When the oxidized and reduced catalysts are compared for their TOF for the net H_2O_2 formation, the Pd or PdO (0.5 wt% Pd)/Al_2O_3 catalysts showed much higher H_2O_2 formation per mole of Pd or PdO (in the catalyst) per hour.

The dependence upon the two different catalysts of the influence of different halide anions may be attributed to a large difference in the particle size of PdO and Pd in the two catalysts, before and after their reduction, because of the large difference in their Pd loadings and also in their calcination temperatures; larger the Pd loading and higher the calcinations temperature, larger is the particle size of PdO or Pd in the catalyst.

3.6. Conclusions

From the present studies on the influence of different supports, calcination temperature, Pd loading, reduction and presence of different halides on the H_2O_2 formation in the H_2-to-

H_2O_2 oxidation over PdO/Al_2O_3 catalyst in an aqueous acidic (0.1 M H_3PO_4) medium, following important conclusions have been drawn.

1) After reduction (by hydrazine), the supported PdO (2.5 wt% of Pd) catalysts [prepared using different catalyst carriers (viz. Al_2O_3, SiO_2, CeO_2, ZrO_2, Hβ and HM)] showed higher H_2 conversion activity but much lower H_2O_2 selectivity.
2) The H_2 conversion and H_2O_2 formation (i.e. H_2O_2 yield) activities of the different supported PdO catalysts are strongly influenced by the catalyst calcination temperature, depending upon the catalyst support and/or by the catalyst – support interactions, depending upon the catalyst calcination temperature. Among the different catalyst carriers, Al_2O_3 is the most preferred catalyst carrier for supporting PdO; the PdO/Al_2O_3, particularly calcined at 400 ºC, showed the best performance (both the H_2O_2 selectivity and yield) in the H_2-to-H_2O_2 oxidation.
3) Both the H_2O_2 decomposition and hydrogenation activities of the PdO/Al_2O_3 catalyst are increased with increasing the catalyst calcination temperature. The increase in the H_2O_2 destruction activities is consistent with the observed decrease in the H_2O_2 formation activity of the catalyst with increasing its calcination temperature.
4) The H_2O_2 formation is also strongly influenced by the catalyst calcination temperature, depending strongly upon the Pd loading in the catalyst. The trends showing the variation of the H_2O_2 formation (i.e. both the H_2O_2 selectivity and yield) with the calcination temperature are changed gradually, and then reversed, with increasing the Pd loading.
5) The reduction of the PdO/Al_2O_3 catalysts causes an increase in the H_2 conversion but a decrease in the H_2O_2 selectivity, in both the absence and presence of different halide anions (F^-, Cl^-, Br^- or I^-) in the acidic reaction medium.
6) The influence of the different halide anions on the H_2O_2 formation depends strongly upon the oxidation state of Pd and also upon the Pd loading of the catalyst.

In summary, the influence of a particular catalyst parameter (viz. catalyst support, calcination temperature, Pd loading, reduction of PdO to Pd or halide catalyst promoter) on the H_2O_2 formation depends strongly upon the other catalyst parameters and hence it cannot be generalized.

3.7. References

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Chapter 4

Direct Oxidation of H_2 to H_2O_2 and Decomposition/Hydrogenation of H_2O_2 over Commercial Pd/C and Pd/Al_2O_3 Catalysts in Aqueous Acidic Medium Containing Bromide Promoter: Influence of Pretreatment Condition on Pd Particle Size and Catalytic Performance of the Catalyst

Chapter 4

Direct Oxidation of H_2 to H_2O_2 and Decomposition/Hydrogenation of H_2O_2 over Commercial Pd/C and Pd/Al_2O_3 Catalysts in Aqueous Acidic Medium Containing Bromide Promoter: Influence of Pretreatment Condition on Pd Particle Size and Catalytic Performance of the Catalyst

4.1. Background and Objective of the Present Work

Direct Pd-catalyzed oxidation of H_2 to H_2O_2 by O_2 is of great practical importance for replacing the presently practiced hydroquinone auto-oxidation process for the production of H_2O_2, an environ-friendly versatile oxidizing agent. The hydroquinone auto-oxidation process involves complicated indirect oxidation of H_2 to H_2O_2 and, moreover, it is economical only for the large scale production of H_2O_2 [1]. Since the last few years, the H_2-to-H_2O_2 oxidation has arose interest of a number of researchers, as can be seen from a large number of recent publications on this process [2-21]; the start of a demonstration plant for this process has also been announced recently by Degussa [22]. This process, however, has not yet been commercialized because of the problems related to the H_2O_2 selectivity/yield and safety.

The net H_2O_2 formation in the H_2-to-H_2O_2 oxidation is controlled by the following parallel and consecutive reactions [13,23].

$H_2 + O_2 \rightarrow H_2O_2$ (parallel H_2O_2 forming reaction) (4.1)
$H_2 + 0.5\ O_2 \rightarrow H_2O$ (parallel direct water forming reaction) (4.2)
$H_2O_2 \rightarrow H_2O + 0.5\ O_2$ (consecutive H_2O_2 decomposition reaction) (4.3)
$H_2O_2 + H_2 \rightarrow 2\ H_2O$ (consecutive H_2O_2 hydrogenation reaction) (4.4)

Our recent studies [13] showed that the H_2O_2 destruction by the consecutive water forming reactions (reactions 4.3 and 4.4) are strongly inhibited and, thereby, the net H_2O_2 formation (or H_2O_2 yield) over supported Pd catalysts is drastically increased due to the addition of Cl^- or Br^- anions in an aqueous acidic reaction medium. The use of chloride or bromide as the catalyst promoter in the H_2-to-H_2O_2 oxidation has also been reported in other recent studies

[8,9,14,19,20]. It is also interesting to know an influence of the particle size of Pd on the net H_2O_2 formation in the H_2-to-H_2O_2 oxidation process and also on the H_2O_2 destruction reactions under similar conditions. However, no detailed investigation on this has been reported so far.

The present study was undertaken with the objective of investigating the influence of different thermal pretreatments [under different gas (viz. inert, oxidizing or reducing) atmospheres and temperatures] to the Pd/Al_2O_3 and Pd/C catalysts, used in our earlier studies [13,20,21] on the net H_2O_2 formation in the H_2-to-H_2O_2 oxidation and also on the H_2O_2 decomposition/hydrogenation reactions, in an aqueous acidic medium containing Br promoter.

4.2. Catalysts and Brief Experimental Procedures

Pre-reduced Pd(5 wt%)/Al_2O_3 (Alfa-Aesar) and Pd(5 wt%)/C (Lancaster) catalysts, in their fine powdered form, were obtained from Lancaster, U.K. These catalysts were thermally pretreated in a quartz tubular reactor in a flow of gas (Viz. N_2, air or H_2) at 500 ºC or 700 ºC for 8 h. Before its use, the catalyst thermally pretreated in air was reduced by an ammoniacal hydrazine. The catalysts, with or without thermal treatment, were characterized by XRD [using a Holland Philips,PW/1730 X-ray generator with CuK_α radiation (λ = 1.5406 Å)] and by TEM [using a JEOL JEM-1200EX transmission electron microscope operating at 100 kV].

The detailed experimental procedures for the direct oxidation of H_2 to H_2O_2 by O_2 and destruction of H_2O_2 in absence H_2 (i.e. in presence of air) and presence of H_2 over the Pd catalysts have already been described in sections 2.5.1, 2.5.2 and 2.5.3. The H_2-to-H_2O_2 oxidation reaction over the catalysts was carried out in a magnetically stirred glass reactor (100 cm^3), using aqueous 0.1 M H_3PO_4 as the aqueous acidic reaction medium, under vigorous stirring at the following reaction conditions: amount of catalyst = 0.1 g, volume of reaction medium = 50 cm^3, concentration of KBr in the reaction medium = 1.0 mmol/dm^3, gaseous feed = a mixture of H_2 and O_2 (1:1) at a total gas flow rate of 6.0 cm^3/min, pressure = atmospheric (95 kPa), temperature = 27 ºC and reaction period = 1.0 h. The H_2O_2 formed was determined by the iodometric titration. The H_2 conversion, H_2O_2 yield and H_2O_2 selectivity was calculated by using the equations given in the section 2.5.1.

The H_2O_2 decomposition (in the absence of H_2) and hydrogenation (in the presence of H_2) reactions over the catalysts were carried out in the same reactor described above, in the presence of static air and static H_2, respectively, by injecting 1.0 cm^3 of aqueous 30 wt% H_2O_2

through a rubber septum in the acidic reaction medium (50 cm^3) containing KBr (1.0 $mmol/dm^3$) under vigorous stirring and following the reactions as a function of time.

4.3. Influence of Thermal Pretreatment to Pd/Al_2O_3 and Pd/C

The X-ray diffraction patterns for the Pd/Al_2O_3 and Pd/C catalysts, before and after their thermal pretreatments, are presented in Figures 4.1 and 4.2, respectively. The XRD of Pd/Al_2O_3 catalyst without pretreatment (Figure 4.1a) indicates that the catalyst contains very small size Pd particles (i.e. highly dispersed) on bohemite; the XRD peak for Pd (at 2θ = 40º) is very small. When the catalyst was heated at 500 ºC in air, the thermally treated catalyst (after reduction by hydrazine) showed a broad XRD peak for (at 2θ = 40º) on γ-alumina (Figure 4.1b). The thermally treated Pd/Al_2O_3 at 500 º or 700 ºC showed narrow XRD peak for Pd on γ-

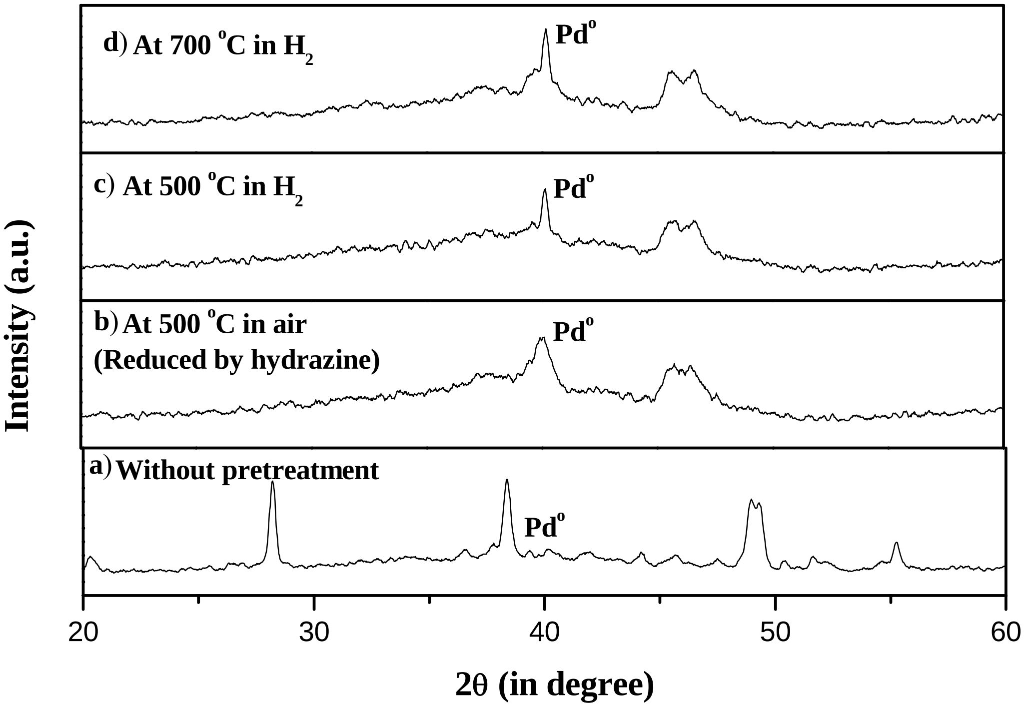

Figure 4.1: XRD of the Pd/Al_2O_3 catalyst thermally pretreated at different temperatures and gas atmospheres.

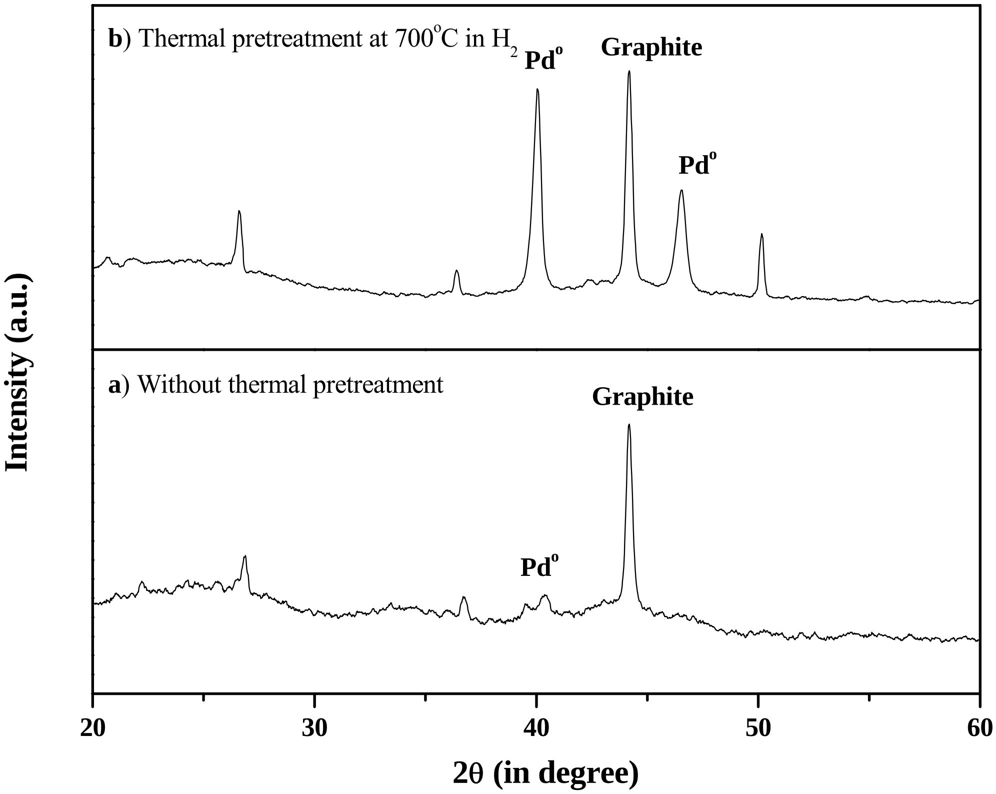

Figure 4.2: XRD of the Pd/C catalyst with or without thermal pretreatment at 700 °C in H_2.

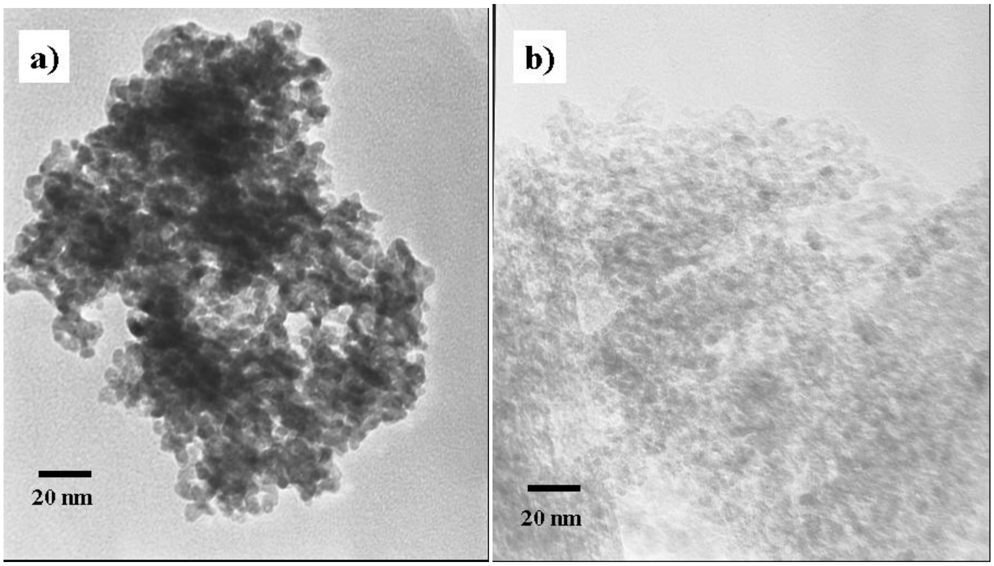

Figure 4.3: TEM photograph of a) Pd/Al_2O_3 (without pretreatment) and b) Pd/Al_2O_3 pretreated in air at 500 °C and reduced by ammoniacal hydrazine.

alumina (Figures 4.1c and 4.1d). The XRD of Pd/C (Figure 4.2a), without pretreatment, shows that the XRD peak for Pd is very small and broad, indicating the presence of very small particles of Pd in the catalyst. After the thermal treatment at 700 ºC in H_2, much larger and sharper XRD peaks for Pd (at 2θ = 40 º and 47º) due to the growth of Pd particles during the thermal treatment are observed (Figure 4.2b). The data of Pd particle size, determined from the XRD peak broadening, for both catalysts, before and after their thermal pretreatments, are included in Table 4.1.

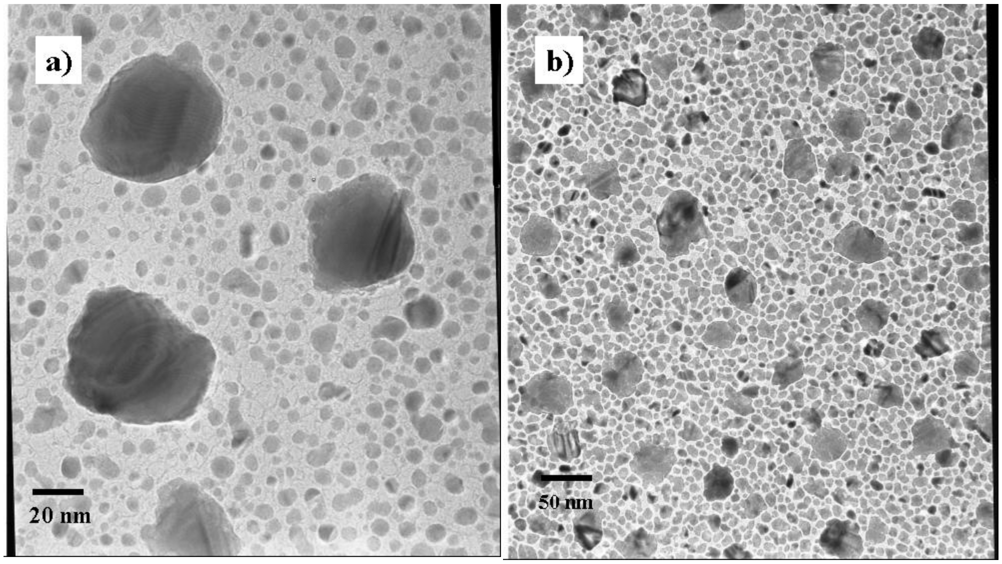

Figure 4.4: TEM photograph of the Pd/Al_2O_3 pretreated in N_2 at 500 ºC.

Results showing the influence of thermal pretreatment to Pd/Al_2O_3 catalyst under different conditions on the particle size and morphology of supported Pd are presented in Figures 4.3-4.5. Whereas, the TEM photographs of Pd/C catalyst, before and after its thermal pretreatment at 700 ºC in H_2, are shown in Figure 4.6.

The Pd/Al_2O_3 and Pd/C catalysts, before and after their thermal pretreatments under different gas atmospheres (N_2, air or H_2) and/or temperatures (500 ºC or 700 ºC), are compared in Table 4.1 for their performance in the H_2-to-H_2O_2 oxidation (with H_2/O_2 feed ratio of 1.0) in an acidic (0.1 M H_3PO_4) aqueous medium containing bromide anions (1.0 mmol/dm^3). The H_2O_2 destruction [by the H_2O_2 decomposition (reaction 4.3) and hydrogenation (reaction 4.4)] activity of both the catalysts, before and after their thermal pretreatment, was also determined at the conditions similar or close to that employed in the H_2-to-H_2O_2 oxidation. Results of the H_2O_2 decomposition (in air) and hydrogenation (in H_2) over the Pd/Al_2O_3 catalysts are presented in Figures 4.7 and 4.8 and that over the Pd/C catalysts are given in Figures 4.9 and 4.10. The initial rates of the H_2O_2 decomposition and hydrogenation reactions over the catalysts are included in Table 4.1.

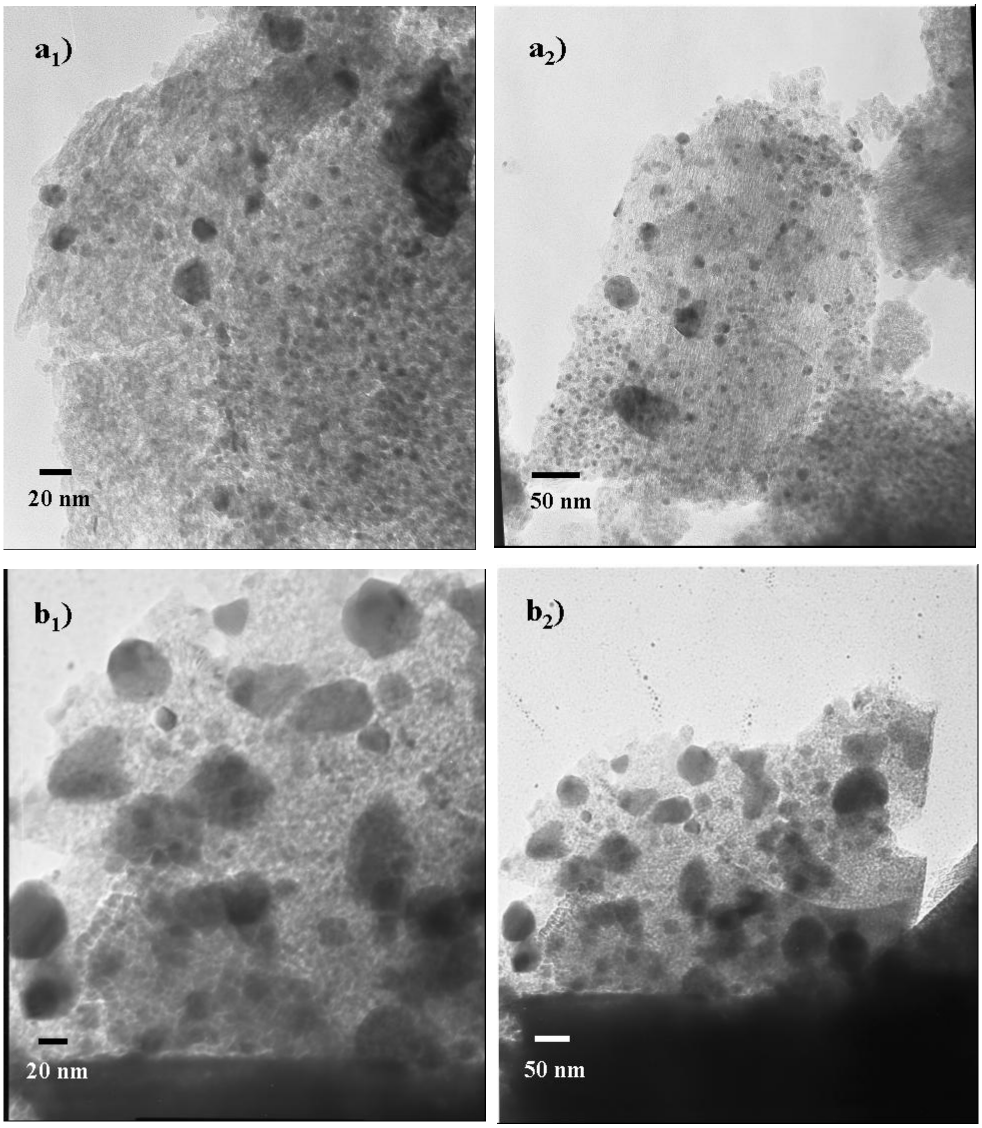

Figure 4.5: TEM photograph of the Pd/Al_2O_3 catalyst pretreated in H_2 at 500 ºC (a_1, a_2) and 700 ºC (b_1, b_2).

4.3.1. Influence on Pd Particle Size

A comparison of the TEM results for the thermally pretreated Pd/Al_2O_3 at 500 ºC under different gas atmospheres (Figures 4.3-4.5) shows that 1) the treatment under air causes redispersion of the Pd from the catalyst with a small decrease in the Pd particle size (Figure 4.3), and 2) after the treatment under N_2 or H_2, some of the Pd particle grew into much larger Pd particles, leading to a biomodal dispersion of the Pd particles (Figures 4.4 and 4.5). The inc-

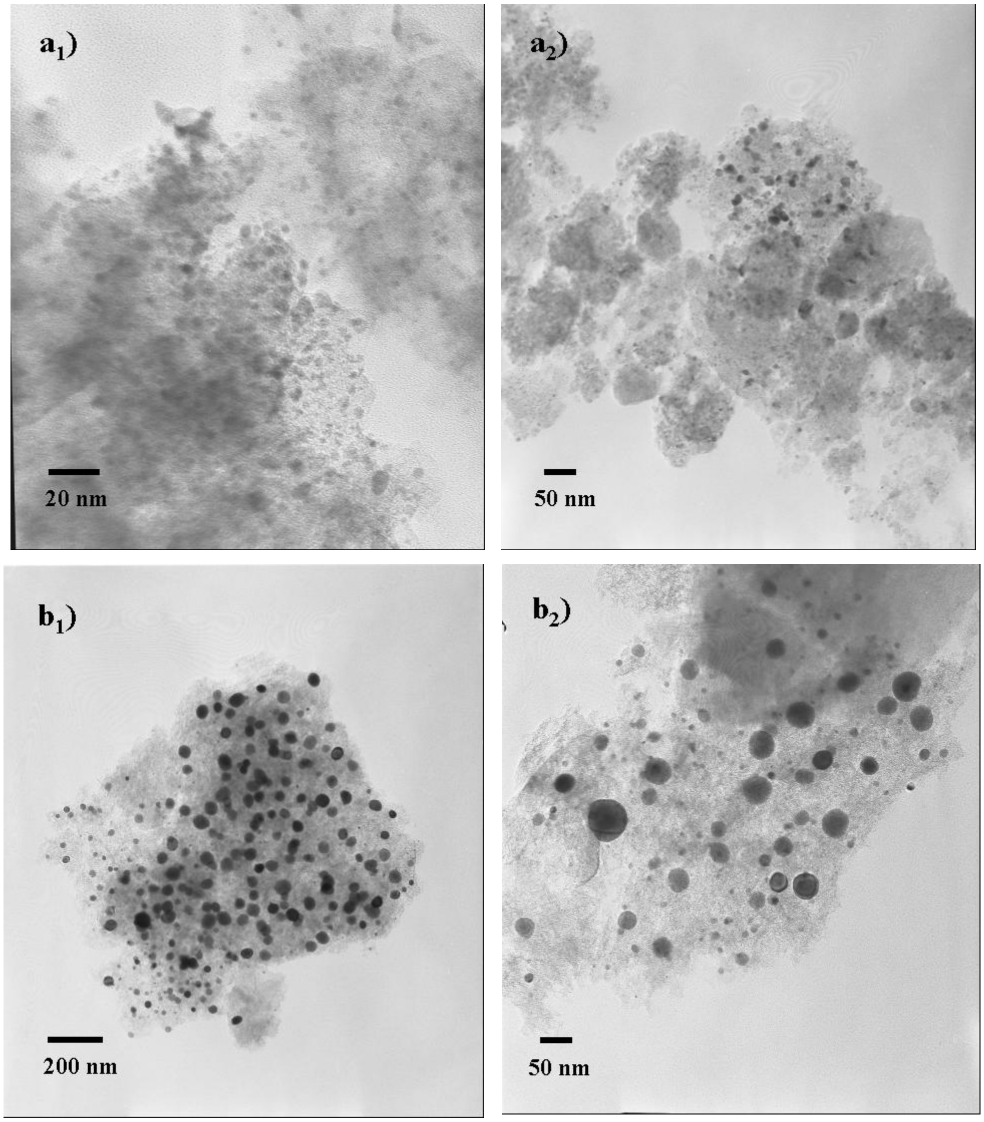

Figure 4.6: TEM photograph of a) Pd/C (without pretreatment) and b) Pd/C pretreated in H_2 at 700 ºC.

Table 4.1: Results of the direct oxidation of H_2 to H_2O_2 and H_2O_2 destruction reaction in presence of air and H_2 over the Pd/Al_2O_3 and Pd/C catalysts, thermally pretreated at different conditions, in an aqueous acidic (0.1 M H_3PO_4) reaction medium containing KBr (1.0 mmol/dm^3) [where X_{H2} = conversion of H_2, Y_{H2O2} = yield of H_2O_2 and S_{H2O2} = selectivity of H_2O_2].

Thermal pretreatment to catalyst		Particle size of Pd (nm)		H_2-to-H_2O_2 oxidation			Initial rate of H_2O_2 destruction (h^{-1})	
Gas atm.	Temp. (^{o})	TEM	XRD	X_{H2} (%)	Y_{H2O2} (%)	S_{H2O2} (%)	In air[a]	In H_2[b]
Catalyst: Pd/Al_2O_3								
Without pretreatment		8	--	89.8	44.0	49.0	0.10	1.4
N_2	500	8 & 25	--	82.7	45.5	55.0	0.04	1.5
Air	500[c]	7	10	78.3	27.8	35.5	0.05	2.1
H_2	500	9 & 17	--	97.4	51.6	53.0	0.03	1.9
H_2	700	20 & 30	28	95.5	53.5	56.0	0.02	1.6
Catalyst: Pd/Carbon								
Without pretreatment		7	8	100	36.8	36.8	0.24	2.7
H_2	700	20 & 40	29	81.6	29.8	36.5	0.20	2.1

[a and b] H_2O_2 destruction by its decomposition and hydrogenation, respectively. [c] After the thermal treatment, the catalyst was reduced by ammoniacal hydrazine.

rease in the treatment temperature from 500 ºC to 700 ºC under H_2 resulted in a further growth of both the small and large Pd particles (Figure 4.5). The TEM photographs (Figures 4.4 and

4.5) show that the Pd particles for all the thermally treated catalysts have irregular shape. The Pd particle size determined from the XRD peak broadening for Pd (at 2θ = 40º) for the different thermally treated Pd/Al_2O_3 catalysts is consistent with that observed from TEM of the catalysts (Table 4.1).

The TEM photographs of Pd/C catalyst with and without the thermal treatment (Figure 4.6) also show a large increase in the Pd particle size of the catalyst after its thermal treatment at 700 ºC (in H_2). The Pd particles have irregular shape. These observations are similar to that observed for the Pd/Al_2O_3 thermally treated in H_2 at 500 º or 700 ºC (Figures 4.3a and 4.5).

4.3.2. Influence on Catalytic Performance

From the results in Table 4.1 and Figures 4.7 and 4.8, following important observations can be made. The influence of thermal treatment to Pd/Al_2O_3 at the same temperature (500 ºC) on the net H_2O_2 formation (in the H_2-to-H_2O_2 oxidation) and H_2O_2 destruction activities of the catalyst depends strongly on the gas atmosphere (N_2, air or H_2) employed in the treatment, as follows.

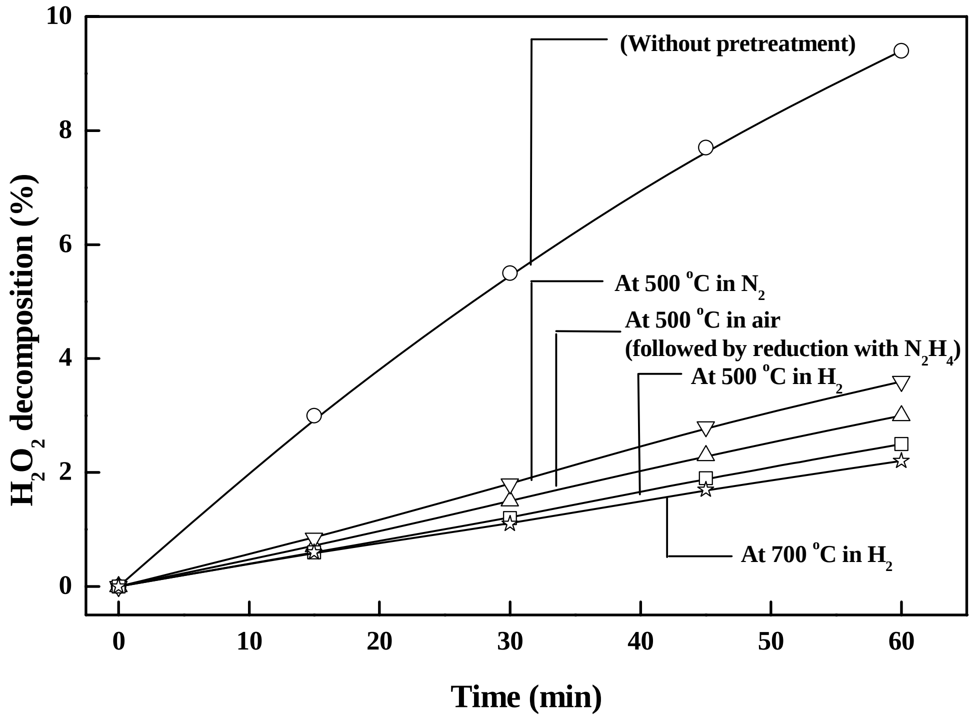

Figure 4.7: Effect of the different thermal pretreatments to Pd/Al_2O_3 catalyst on its H_2O_2 decomposition (in air) activity at 27 ºC.

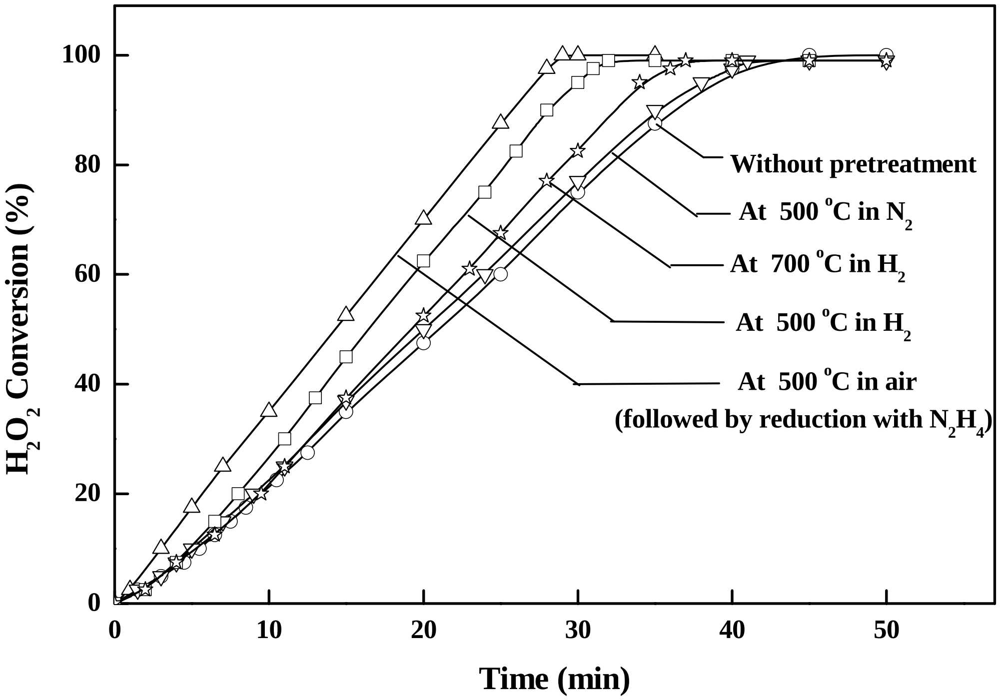

Figure 4.8: Effect of the different thermal pretreatments to the Pd/Al_2O_3 catalyst on its H_2O_2 hydrogenation activity at 27 °C.

- The treatment under N_2 caused a decrease in the H_2 conversion activity but an increase in the H_2O_2 selectivity/yield. It caused a large decrease in the H_2O_2 decomposition activity but a little or no change in the H_2O_2 hydrogenation activity.
- The treatment under air (followed by reduction with hydrazine) caused an appreciable decrease in both the H_2 conversion activity and H_2O_2 selectivity. It also caused a large decrease in the H_2O_2 decomposition activity but an appreciable increase in the H_2O_2 hydrogenation activity. Earlier studies on Au/Zeolite, and Au-Pd/Al_2O_3 (or TiO_2) catalysts [11,15,16] also showed that after calcinations at 400 °C (in air), the catalysts show less activity for the H_2O_2 formation.
- The treatment under H_2 caused an appreciable increase in both the H_2 conversion activity and H_2O_2 selectivity/yield. However, it resulted in a large decrease in the H_2O_2 decomposition activity but an increase in the H_2O_2 hydrogenation activity.
- Among the different gas atmosphere employed during the thermal pretreatment, the best catalyst performance for the H_2-to-H_2O_2 oxidation is observed when Pd/Al_2O_3 was

thermally pretreated in H_2 atmosphere. The thermal treatment in air resulted into the catalyst having poor activity and selectivity in the H_2-to-H_2O_2 oxidation.

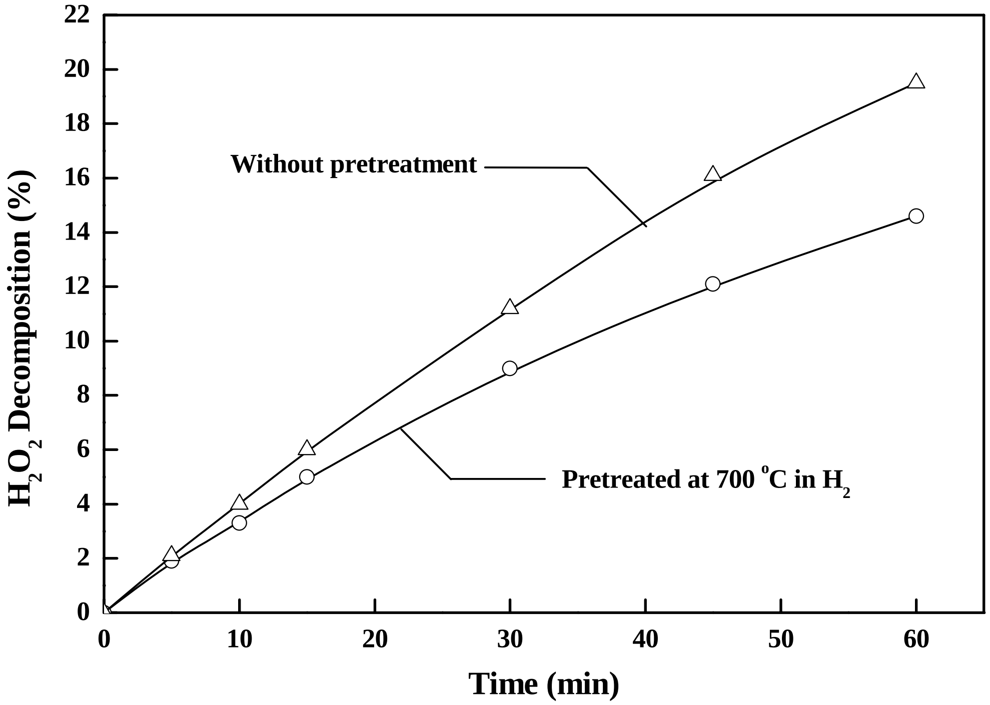

Figure 4.9: Effect of the thermal pretreatment at 700 ºC in H_2 to Pd/C catalyst on its H_2O_2 decomposition (in air) activity at 27 ºC.

A comparison of the results for the Pd/Al_2O_3 catalysts pretreated in H_2 at 500 º and 700 ºC (Table 4.1) reveals the following important information. With increasing the pretreatment temperature from 500 º to 700 ºC,

1) the Pd particle size of the catalyst increases markedly,
2) both the H_2O_2 selectivity and yield increase, but
3) the H_2O_2 decomposition and hydrogenation activities of the catalyst decrease.

It is interesting to note that the observed large growth of Pd particles (or the catalyst sintering) has caused only a very small decrease in the H_2 conversion activity, while increasing significantly both the H_2O_2 selectivity and yield. The observed increase in the H_2O_2 formation activity is consistent with the appreciable decrease in both the H_2O_2 decomposition and hydrogenation activities of the catalyst.

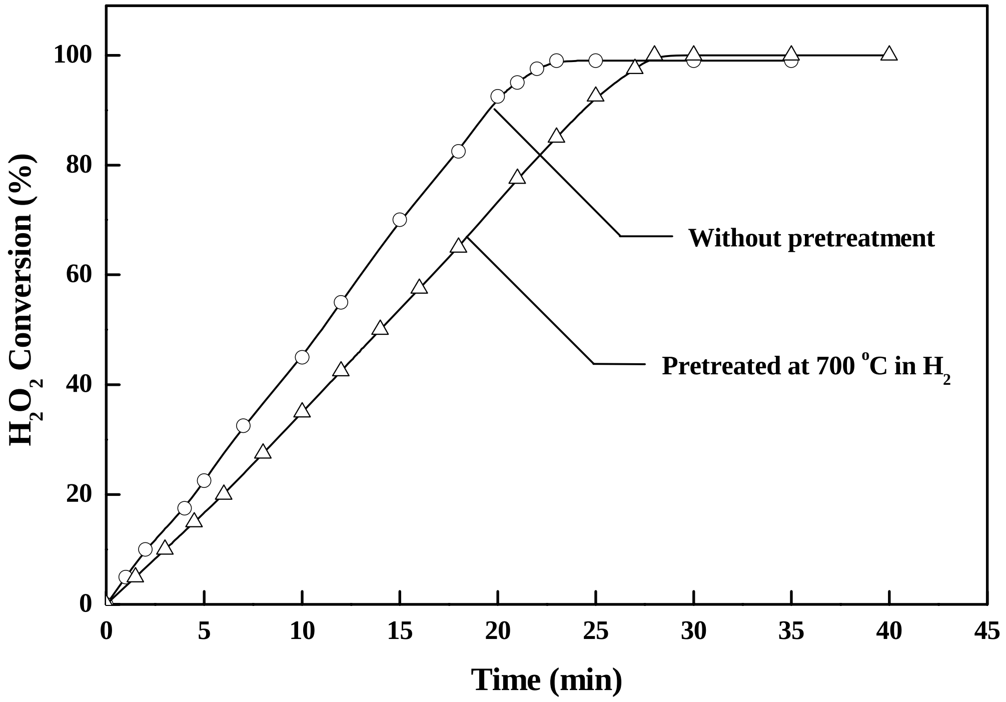

Figure 4.10: Effect of the thermal pretreatment at 700 ºC to the Pd/C catalyst on its H_2O_2 hydrogenation activity at 27 ºC.

The thermal treatment to Pd/C, however, caused a large decrease in the H_2 conversion activity of the catalyst without significantly affecting the H_2O_2 selectivity in the H_2-to-H_2O_2 oxidation; after the thermal treatment, the H_2O_2 yield is decreased appreciably (Table 4.1). The thermal treatment also resulted in a decrease in both the H_2O_2 decomposition (Figure 4.9) and hydrogenation (Figure 4.10) activities of the catalyst. These observations are different from that for the Pd/Al_2O_3 catalyst thermally pretreated under the similar conditions. For the Pd/Al_2O_3 catalyst, after its thermal treatment (at 700 ºC in H_2), both the H_2 conversion and H_2O_2 selectivity (and consequently the H_2O_2 yield) are increased appreciably and also both the H_2O_2 decomposition and hydrogenation activities of the catalyst are decreased (Table 4.1). This indicates that the influence of thermal treatment to supported Pd catalyst on its catalytic performance in the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition/hydrogenation reactions depends upon the catalyst support. The catalyst support – Pd cluster interactions in the presence of catalyst promoter (adsorbed Br^- anions [13]) seem to play an important role in deciding the catalytic performance of supported Pd catalysts in the H_2O_2 formation and destruction reactions.

The rate of H_2O_2 decomposition over the Pd/Al_2O_3 and Pd/C catalysts shows dependence upon the H_2O_2 concentration (Figures 4.7 and 4.9). In our earlier studies, the H_2O_2 decomposition over the Pd/C [24,25] and Pd/Al_2O_3 [13,25] catalysts was found to be first order with respect to H_2O_2. However, H_2O_2 conversion vs. reaction time plots for the H_2O_2 hydrogenation over the catalysts are linear (Figures 4.8 and 4.10) indicating that the hydrogenation reaction is zero order with respect to the H_2O_2 concentration.

A comparison of the H_2O_2 decomposition and hydrogenation rates (Table 4.1) shows that the H_2O_2 hydrogenation activity of all the Pd/Al_2O_3 and Pd/C catalysts is very much higher than their H_2O_2 decomposition activity. The destruction of H_2O_2 (after its formation by reactions 4.3 and 4.4) in the H_2-to-H_2O_2 oxidation in the acidic medium containing Br promoter is, therefore, controlled mostly by the H_2O_2 hydrogenation.

4.4. Conclusions

The present studies on the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition (in the absence of H_2) and H_2O_2 hydrogenation reactions in an aqueous acidic (0.1 M H_3PO_4) medium containing Br promoter over Pd/Al_2O_3 (or C) catalyst thermally pretreated under different gas atmospheres at 500 º or 700 ºC led to the following important conclusions.

1) The pretreatment to Pd/Al_2O_3 in air at 500 ºC (followed by reduction with hydrazine) caused redispersion of Pd with a little change in the Pd particle size. However, it resulted in a decrease in the H_2O_2 formation and H_2O_2 decomposition activities but an increase in the H_2O_2 hydrogenation activity of the catalyst.
2) The pretreatment to Pd/Al_2O_3 in H_2 or N_2 at 500 ºC or 700 ºC caused a growth of Pd particles; creating bimodal Pd particle size distribution. It also caused an increase in the H_2O_2 formation (H_2O_2 yield). The pretreatment at 700 ºC in H_2 led to the best catalyst for the H_2-to-H_2O_2 oxidation (with 53.5 % H_2O_2 yield)
3) The pretreatment to Pd/C in H_2 at 700 ºC also caused a growth of Pd particles, but is resulted in a decrease in the H_2O_2 yield (without significantly affecting the H_2O_2 selectivity) and also a decrease in the H_2O_2 decomposition/hydrogenation activity of the catalyst.

4) The influence of thermal pretreatment to the supported Pd catalysts on their catalytic performance in the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition/hydrogenation reactions cannot be generalized; it depends upon the catalyst support. The Pd particle growth is beneficial for increasing the net H_2O_2 formation over Pd/Al_2O_3 but it is detrimental for the net H_2O_2 formation over Pd/C in the presence of Br promoter in the acidic medium. The support - Pd cluster interactions in the presence of catalyst promoter (adsorbed Br^- anions) seem to play important role in deciding the net H_2O_2 formation activity of the supported Pd catalysts.

4.5. References

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Chapter 5

Synergetic Effect of Two Halogen Promoters Present in the Reaction Medium or in the Catalyst on the H_2O_2 Formation and/or Destruction over Pd/C (or Al_2O_3) Catalyst

Chapter 5

Synergetic Effect of Two Halogen Promoters Present in the Reaction Medium or in the Catalyst on the H_2O_2 Formation and/or Destruction over Pd/C (or Al_2O_3) Catalyst

5.1. Background and Objective of the Present Work

Hydrogen peroxide is a versatile, environmentally clean oxidizing agent. Hence, its use, particularly in the production of bulk and fine/specialty chemicals by a number of organic oxidation reactions, has been increasing day-by-day [1,2]. Oxidation of H_2 by O_2 to H_2O_2 is an environmentally clean process and it involves direct formation of H_2O_2 from H_2. Hence it has a high potential to replace the currently practiced hydroquinone auto-oxidation process [3], which involves an indirect oxidation of hydrogen to H_2O_2 and also has several limitations. The direct H_2-to-H_2O_2 oxidation,

$$H_2 + O_2 \rightarrow H_2O_2 \quad (5.1)$$

is, therefore, of great practical importance. Unfortunately, this process also involves the following thermodynamically highly favored undesirable parallel and consecutive water-forming reactions [4,5].

$$H_2 + 0.5\ O_2 \rightarrow H_2O \text{ (parallel } H_2 \text{ combustion)} \quad (5.2)$$

$$H_2O_2 \rightarrow H_2O + 0.5\ O_2 \text{ (consecutive } H_2O_2 \text{ decomposition)} \quad (5.3)$$

$$H_2O_2 + H_2 \rightarrow 2\ H_2O \text{ (consecutive } H_2O_2 \text{ hydrogenation)} \quad (5.4)$$

Reactions 5.2 to 5.4 are responsible for the reduction in the net formation of H_2O_2. Although this process has been extensively patented, it has not yet commercialized; it is often considered as a “dream process”. Apart from its hazardous nature, a low H_2O_2 selectivity is a main problem associated with the process.

A use of halogen promoter, particularly bromide [5-8] or chloride [5,8-11] anions in acidic reaction medium [5,6,8,9,11] or in catalyst [7,10], has been reported earlier in a few recent studies for improving the H_2O_2 selectivity in the H_2-to-H_2O_2 oxidation over supported Pd catalysts. Among the halides (viz. F^-, Cl^-, Br^- and I^-), bromide and chloride anions were found to be highly effective halogen promoters for drastically increasing the H_2O_2 formation, while largely decreasing the H_2O_2 decomposition and hydrogenation activity of the supported Pd catalysts [5,7]. On the contrary, fluoride anions showed no promoting effect on the H_2O_2 formation but caused an increase in the undesirable H_2O_2 decomposition activity of the Pd catalysts with a little or no effect on their H_2O_2 hydrogenation activity. Whereas, iodide anions acted as strong inhibitor for all the reactions, causing catalyst deactivation due to poisoning. In the presence of fluoride or iodide anions in the catalyst [7] or acidic reaction medium [5], there was only a very little or no formation of H_2O_2 in the H_2-to-H_2O_2 oxidation over the supported Pd catalysts [5,7]. The earlier studies [5] also showed that the cations associated with the halide anions in the reaction medium have little or no influence on the H_2-to-H_2O_2 oxidation and H_2O_2 destruction reactions.

Because of their synergetic effect, the presence of two halogens differing widely in their electro negativity added in the acidic medium or in the Pd catalyst at their optimum concentrations is expected to cause a large enhancement in the H_2O_2 formation (in the H_2-to-H_2O_2 oxidation) and also a large retardation in the rate of H_2O_2 decomposition and hydrogenation. This, thus, provides a tremendous scope for developing a better and better process and/or halogenated catalyst by choosing two or more different halogen promoters and optimizing their concentrations to achieve highest possible H_2O_2 selectivity and yield in the process.

In this chapter, we have investigated and found a strong synergetic effect of two different halide anions (viz. F^- and I^-, Cl^- and I^-, Cl^- and Br^-, and F^- and Br^-) present in an acidic reaction medium or catalyst on the H_2-to-H_2O_2 oxidation, largely promoting the H_2O_2 formation through inhibiting the H_2O_2 decomposition and hydrogenation reactions, over the Pd/C, Pd/Al_2O_3 and halogenated Pd/Al_2O_3 catalysts. The results of this investigation revealed that the H_2O_2 formation with higher H_2O_2 yield/selectivity in the H_2-to-H_2O_2 oxidation can be accomplished by using two different halide anions (at optimum concentration) in the acidic reaction medium or in the halogenated catalyst than that can be achieved by using either of the two halides alone.

5.2. Catalysts and Brief Experimental Procedures

The Pd/C and Pd/Al_2O_3 catalysts (with 5 wt% Pd loading) in their reduced form were obtained from Lancaster, UK. All the catalysts were in fine powder form. The halogenated (F or Br or I) Pd/Al_2O_3 catalysts containing one halogen were prepared by impregnating the Pd/Al_2O_3 with NH_4F, NH_4Br and NH_4I, respectively, from their aqueous solutions by incipient wetness technique, which was followed by drying on water bath and calcining under O_2-free N_2 at 400 ºC for 2 h. The halogenated Pd/Al_2O_3 catalyst containing two different halogens were prepared by different methods (viz. simultaneous incorporation of two halogens, bromination followed by fluorination or vise-versa). Using simultaneous halogenations method, the F-I-Pd/Al_2O_3 and F-Br-Pd/Al_2O_3 catalysts were prepared by impregnating the Pd/Al_2O_3 catalyst with two ammonium halides (NH_4F - NH_4I and NH_4F - NH_4Br, respectively) simultaneously from their aqueous solutions by incipient wetness technique, which was followed by drying on water bath and calcining under O_2-free N_2 at 400 ºC for 2 h. Using step-by-step halogenations, the F-Br-Pd/Al_2O_3 catalysts with different concentrations of Br and F were prepared as follows: The F-Br-Pd/Al_2O_3 (Br loading = 0.13 mmol/g) catalysts with different fluorine concentrations (0 – 1.1 mmol/g) were prepared by impregnating the brominated Pd/Al_2O_3 with NH_4F by the above procedure. Similarly, the Br-F-Pd/Al_2O_3 (F loading = 0.53 mmol/g) catalysts with different Br concentrations (0 – 1.3 mmol/g) were prepared by impregnating the fluorinated Pd/Al_2O_3 with NH_4Br. All the impregnated catalysts were dried and then calcined under O_2-free N_2 at 400 ºC for 2 h.

The catalysts were characterized by XRD (using a Holland Phillips PW/1730 X-ray generator with CuKα radiation) for their bulk Pd species (Pd^o or PdO), by XPS (using a VG-Scientific ESCA-3MK II electron spectrometer and assuming the binding energy of C_{1s} as 285 eV) for their relative surface composition, and also by TEM (using a JEOL model 1200 EX instrument) for their Pd particle size; the sample for the TEM studies was prepared by placing a drop of an acetone suspension of the catalyst on a carbon coated copper grid.

The detailed experimental procedures for the direct oxidation of H_2 to H_2O_2 by O_2 and destruction of H_2O_2 in absence H_2 (i.e. in presence of air) and presence of H_2 over the Pd catalysts have already been described in sections 2.5.1, 2.5.2 and 2.5.3. All the reactions over the Pd catalysts were carried out at atmospheric pressure (95 kPa) in a jacketed magnetically stirred glass reactor (capacity 100 cm^3) containing 0.1 g catalyst in a fine power form and an aqueous acidic (0.1 M H_3PO_4) solution (50 cm^3) as a reaction medium with or without containing varying concentrations of different halides. The direct catalytic H_2-to-H_2O_2 oxidation was carried out by continuously passing H_2 and O_2 through the medium at the following reaction conditions: H_2 flow rate = 180 cm^3/h, O_2 flow rate = 180 cm^3/h, temperature = 27 ºC and reaction period = 1.0 h. The conversion of H_2, H_2O_2 yield and selectivity was calculated by following the equation described in section 2.5.1.

5.3. Catalysts Characterization

XRD spectra and TEM photographs of the Pd/Al_2O_3 and Pd/C catalysts are presented in Figures 5.1 and 5.2, respectively. Bulk and surface characterization data for the catalysts, obtained from their XRD, TEM and XPS, are given in Table 5.1.

For the Pd/Al_2O_3 catalyst, the bulk Al_2O_3 phase is γ-Al_2O_3 (major) and θ-Al_2O_3 (minor) (Figure 5.1) and for the Pd/C catalyst, C is in the graphite form. For both the catalysts, the bulk palladium is in the metallic form (Figure 5.1). The particle size of Pd in the Pd/Al_2O_3 and Pd/C catalysts are found to be in the range of 5 - 7 nm and 6 - 8 nm, respectively (Figure 5.2).

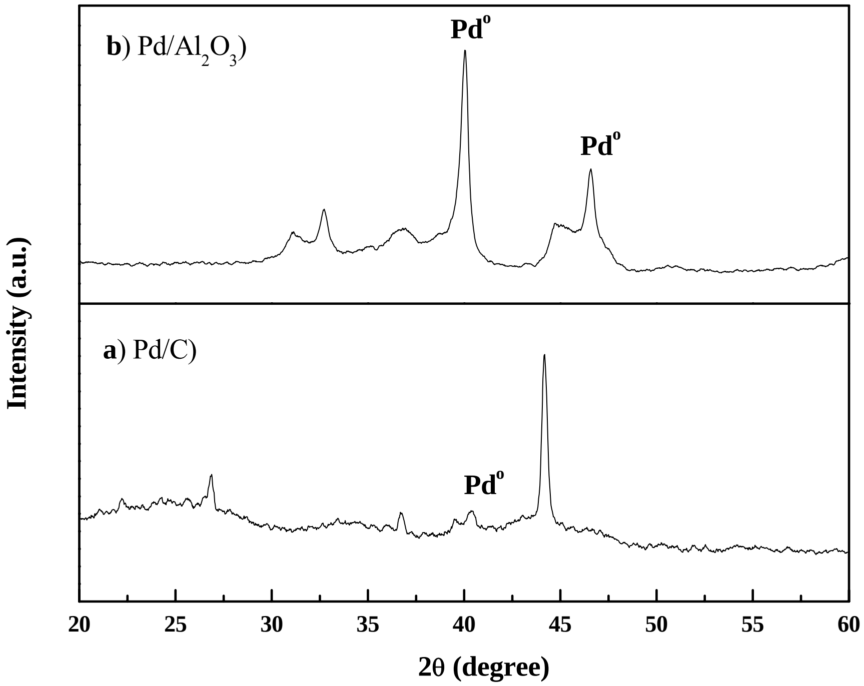


Figure 5.1: XRD spectra of a) Pd/C and b) Pd/Al_2O_3 catalysts.

The surface analysis of the catalysts (obtained from its XRD, XPS), before and after its use in the H_2-to-H_2O_2 oxidation in the aqueous acidic (0.1 M H_3PO_4) medium containing KBr (1.0 $mmol/dm^3$) is presented in Table 5.1.

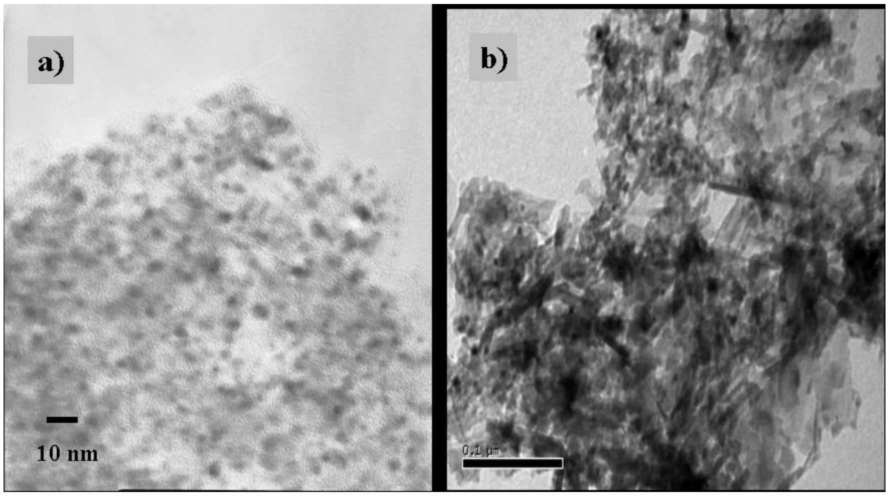


Figure 5.2: TEM photograph of a) Pd/C and b) Pd/Al_2O_3 catalysts.

Table 5.1: Bulk and surface properties of Pd/C and Pd/Al_2O_3 before and after their use in the H_2-to-H_2O_2 oxidation in presence of KBr (1.0 mmol/dm^3) in aqueous 0.1 M H_3PO_4 medium (n.d.= not determined).

Catalyst	Bulk phase (Pd^o/PdO)	XPS data				
		BE for $Pd_{3d3/2}$ (eV)	BE for $Pd_{3d5/2}$ (eV)	Δ BE (eV)	BE for halogen (eV)	Pd(II)[c] / Pd(0)
Pd/C						
Fresh	Pd^o	340.7 & 342.6	335.3 & 337.0	5.4[a] 5.6[b]	n.d.	1.1
Used	Pd^o	340.1& 342.6	335.2& 337.3	4.9[a] 5.3[b]	68.6 ($Br_{3d3/2}$)	5.2
Pd/Al_2O_3						
Fresh	Pd^o	340.1	334.9	5.2[a]	n.d.	0.0
Used	Pd^o	340.2 & 343.1	335.1	5.1[a]	191.2 ($Br_{3p1/2}$)	0.24

[a,b] Difference between the BE of $Pd_{3d3/2}$ and $Pd_{3d5/2}$ for Pd(0) and Pd(II), respectively. [c]The relative surface concentration of Pd(II) to Pd(0) for the $Pd_{3d3/2}$ peak.

For the Pd/C catalyst, both before and after its use in the reaction, the surface Pd is in both the metallic and oxidized forms [Pd(0) and Pd(II), respectively] (Table 5.1). For the Pd/Al_2O_3 catalyst, before the reaction, the surface Pd is in the metallic form but after its use in the reaction, both metallic and oxidized forms are found on the catalyst surface. The relative surface concentration of Pd(II) to Pd(0) is increased after the reaction due to the surface/subsurface oxidation of Pd by O_2 or H_2O_2 [12] formed in the reaction. After its use in the reaction, the catalyst was found to contain the bromide anion added to the reaction medium (as shown by the XPS analysis). These observations clearly indicate the adsorption of halide anions from the reaction medium on the catalyst during the reaction. However, the increase in the K/Pd ratio is relatively very small. It is interesting to note that, after the use of the catalyst, the difference in the electron binding energy for $Pd_{3d3/2}$ and $Pd_{3d5/2}$ (Δ BE) is reduced significantly, indicating a change in the electronic properties of the Pd of the catalyst due to the adsorption of halide anions.

5.4. Influence of the Presence of Single Halogen in Reaction Medium

Results showing the influence of different halide anions (viz. F^-, Cl^-, Br^- or I^-, with the concentration of 1.0 mmol/dm^3) present in the aqueous acidic (0.1 M H_3PO_4) reaction medium on the performance of the reduced Pd/C (or Al_2O_3) catalyst in the H_2-to-H_2O_2 oxidation (with 50 % H_2 in O_2) and H_2O_2 decomposition/hydrogenation reactions are presented in Table 5.2 and Figure 5.3.

From the results the following important observations can be made for both the Pd/C and Pd/Al_2O_3 catalysts.

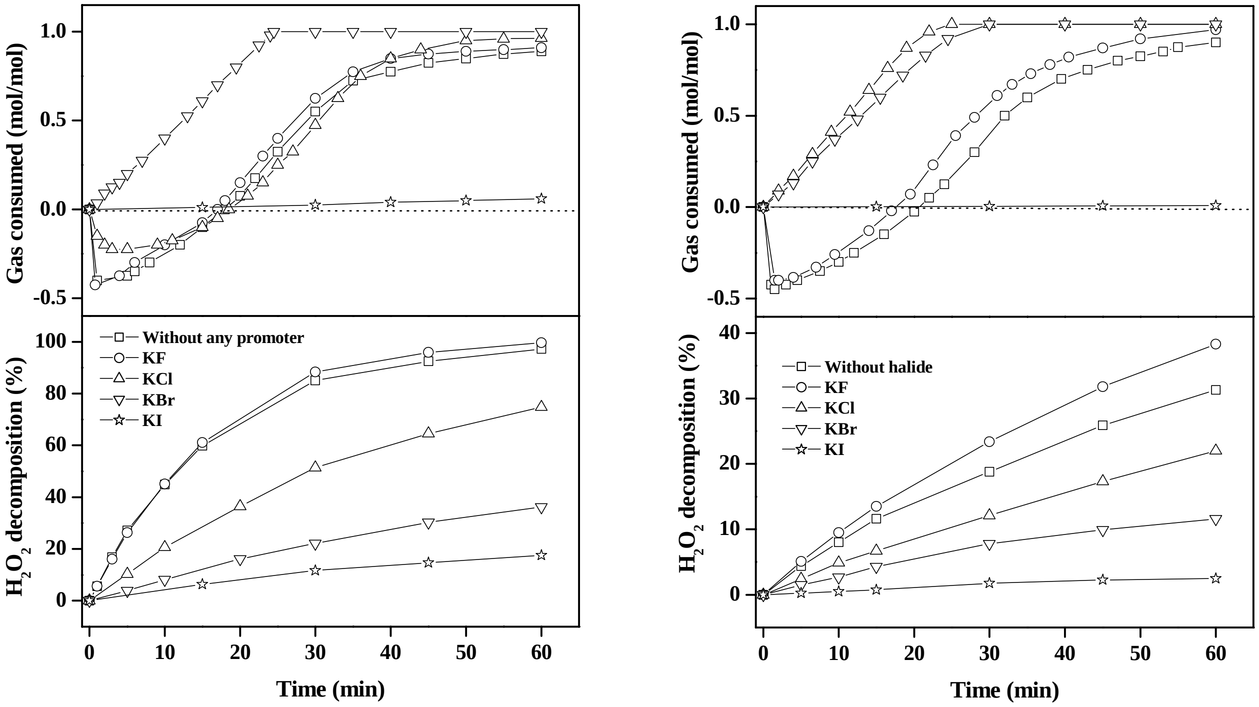
- In the presence of bromide or chloride anions in the acidic reaction medium, the H_2O_2 yield and selectivity in the H_2-to-H_2O_2 oxidation drastically increased, whereas the H_2O_2 decomposition/hydrogenation activity of the catalysts reduced markedly.
- The presence of fluoride anions showed no promoting effect on the H_2O_2 formation but caused an increase in the undesirable H_2O_2 decomposition activity of the Pd catalysts with a little or no effect on their H_2O_2 hydrogenation activity.
- The presence of iodide anions caused almost a complete catalyst deactivation for all the reactions due to the catalyst poisoning.

Table 5.2: Results of the direct oxidation of H_2 to H_2O_2 and H_2O_2 conversion in presence of air and H_2 over Pd/C or Pd/Al_2O_3 catalyst in the aqueous acidic reaction medium containing different halide anions (1.0 mmol/dm^3) [where X_{H2} = conversion of H_2, Y_{H2O2} = yield of H_2O_2 and S_{H2O2} = selectivity of H_2O_2].

Alkali halide present in the reaction medium (mmol/dm^3)	H_2-to-H_2O_2 oxidation			Time for half H_2O_2 conversion (min)	
	X_{H2} (%)	Y_{H2O2} (%)	S_{H2O2} (%)	In air	In H_2
Catalyst: Pd/C					
Nil	100	0.0	0.0	10.5	<0.5
KF	100	0.0	0.0	11.0	<0.5
KCl	98.5	6.5	6.6	30	2.5
KBr	96.3	38.5	40.0	Large[30][a]	14
KI	15.2	1.4	9.2	V.large[17][a]	V.large[b]
Catalyst: Pd/Al_2O_3					
Nil	100	0.2	0.2	Large[30][a]	<1.0
KF	100	0.5	0.5	Large[38][a]	<1.0
KCl	100	9.5	9.5	Large[22][a]	11.4
KBr	95.0	50.8	53	Large[12][a]	15.0
KI	7.0	0.3	4.2	V.large[2.5][a]	V.large[c]

[a] Values in the square bracket are the H_2O_2 conversion in 1 h. [b and c] 6.0 and 1.0 % H_2O_2 conversion in 1 h, respectively.

Poor H_2O_2 selectivity/yield in the direct H_2-to-H_2O_2 oxidation over Pd catalysts is a serious problem for the commercial exploitation of this environ-friendly process. The Pd catalyst, which promotes the H_2O_2 formation in the reaction between H_2 and O_2, is also active for H_2 combustion to water (reaction 5.2) and decomposition/hydrogenation of H_2O_2 to water (reactions 5.3 and 5.4, respectively) and all these reactions are thermodynamically favourable in a wide range of temperature. In order to obtain good selectivity for H_2O_2 in the H_2-to-H_2O_2 oxidation, the non-selective/undesired H_2-to-water oxidation (reaction 5.2) and H_2O_2 decomposition (reaction 5.3) and hydrogenation (reaction 5.4) reactions should, therefore, be minimized simultaneously.



(a) **(b)**

Figure 5.3: Influence of the presence of different halides (1.0 mmol.dm^{-3}) in the acidic reaction medium (0.1 M H_3PO_4) on the H_2O_2 decomposition in static air and gas consumption on the H_2O_2 hydrogenation under static H_2 over the Pd/C (a) and Pd/Al_2O_3 (b) catalyst (at 27 ºC).

The halide anions present in the reaction medium promote the net formation of H_2O_2 in the H_2-to-H_2O_2 oxidation by two ways - first, by directing the H_2 oxidation reaction to H_2O_2 rather than directly to water and second, by reducing the H_2O_2 decomposition/hydrogenation activity of the catalyst (except for F^-). Thus, the electronegativity of the halogens plays a very important role in all the reactions (reactions 5.1 – 5.4). It shows that halogen with intermediate electronegativity (chloride or bromide) plays better role in the H_2O_2 yield/selectivity. In the next sections, the presence of two halogens differing widely in their electro negativity (the net effect will be the intermediate one) in the aqueous acidic medium or in the catalyst is investigated for all the reactions (reactions 5.1 – 5.4).

5.5. Influence of the Presence of Two Different Halogens in the Aqueous Acidic (0.1 M H_3PO_4) Reaction Medium

Results in Tables 5.3 and 5.4 and Figures 5.4 - 5.11 reveal a strong synergetic effect of two different halide anions in the reaction medium on the formation of H_2O_2 in the H_2-to-H_2O_2 oxidation and also on the H_2O_2 decomposition and hydrogenation reactions over the Pd/C and Pd/Al_2O_3 catalysts in an acidic (0.1 M H_3PO_4) aqueous medium. Because of the presence of second halide, the net rate of H_2O_2 formation increased, whereas the H_2O_2 decomposition and hydrogenation rates decreased, depending upon the nature of the two different halide anions and their concentration in the reaction medium, as follows.

5.5.1. Synergetic Effect of I^- and F^- Anions

Results showing the influence of presence of KF and KI in aqueous acidic (0.1 M H_3PO_4) reaction medium on the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition/hydrogenation

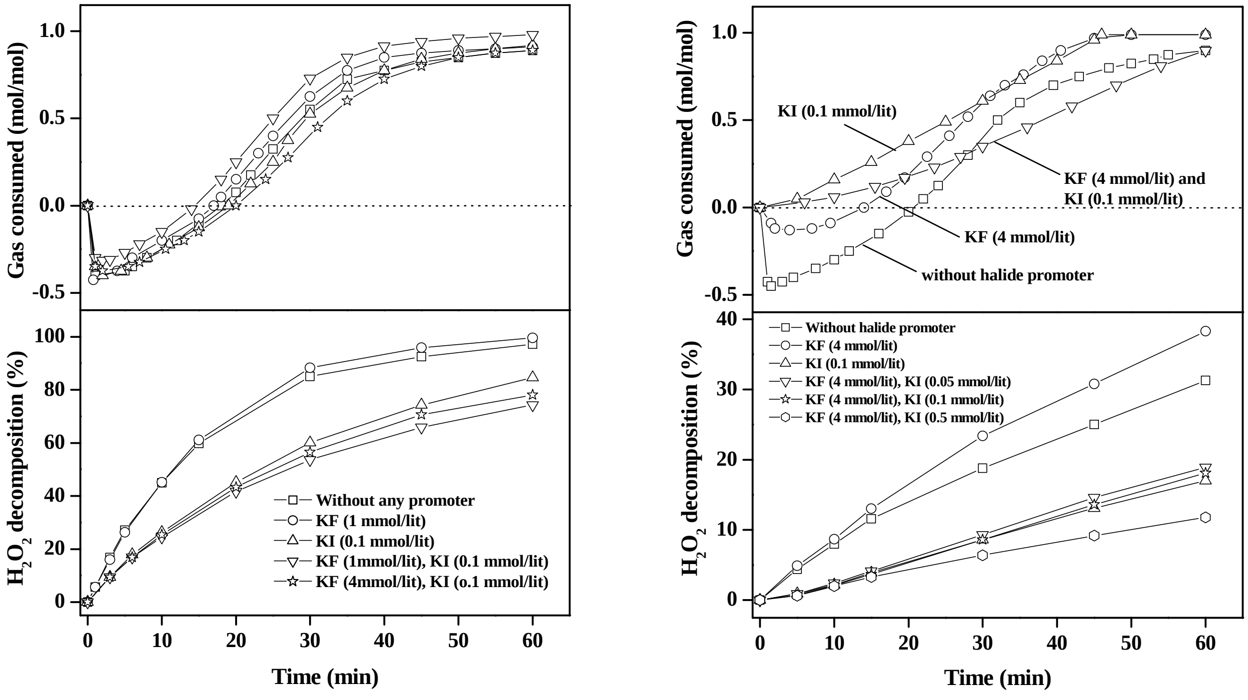
Table 5.3: Results of the H_2-to-H_2O_2 oxidation and H_2O_2 conversion in the presence and absence of H_2 over the Pd/C and Pd/Al_2O_3 catalyst in the acidic medium containing KF and KI with different concentrations. [where X_{H2} = conversion of H_2, Y_{H2O2} = yield of H_2O_2 and S_{H2O2} = selectivity of H_2O_2].

Halide in medium (mmol/dm^3)		H_2-to-H_2O_2 oxidation			Time for half H_2O_2 conversion (min)	
KF	KI	X_{H2} (%)	Y_{H2O2} (%)	S_{H2O2} (%)	In air	In H_2
Catalyst: Pd/C						
1.0/4.0	0.0	100	0.0	0.0	10.6	<1.0
0.0	0.1	90.9	3.0	3.3	23.3	<1.0
1.0	0.1	86.0	4.9	5.7	25.1	≈ 1.0
4.0	0.1	82.4	5.5	6.7	26.3	≈ 1.0
Catalyst: Pd/Al_2O_3						
4.0	0.0	100	0.0	0.0	Large[38][c]	<1.0
0.0	0.1	94.4	4.2	4.5	Large[17][c]	25.4
4.0	0.1	68.8	17.2	25.0	Large[18][c]	37.4

[a]Values in the square bracket are the H_2O_2 conversion in 1 h.

over the Pd/C (or Pd/Al_2O_3) catalyst are presented in Table 5.3 and Figures 5.4 – 5.6.

In the presence of fluoride anions in the reaction medium (4.0 mmol F^-/dm^3), the H_2 conversion in the H_2 oxidation over all the catalysts was complete (100 %) but without any formation of H_2O_2, most probably due to the very high rates of both the consecutive H_2O_2 decomposition and hydrogenation reactions (Table 5.3 and Figure 5.4). Also, when iodide alone was present in the medium (0.1 mmol I^-/dm^3), both the H_2O_2 yield and selectivity in the H_2-to-H_2O_2 oxidation were very poor. However, for all the catalysts (Pd/C or Pd/Al_2O_3), the rate of net H_2O_2 formation in the H_2-to-H_2O_2 oxidation increased very markedly, while that of the H_2O_2 decomposition and hydrogenation decreased appreciably, when both the fluoride and iodide anions were present in the medium (Table 5.3 and Figure 5.4).



(a) (b)

Figure 5.4: Influence of the presence of KF and KI in the aqueous acidic (0.01 M H_3PO_4) reaction medium on the H_2O_2 decomposition in static air and gas consumption on the H_2O_2 hydrogenation under static H_2 over the Pd/C (a) and Pd/Al_2O_3 (b) catalyst (at 27 ºC).

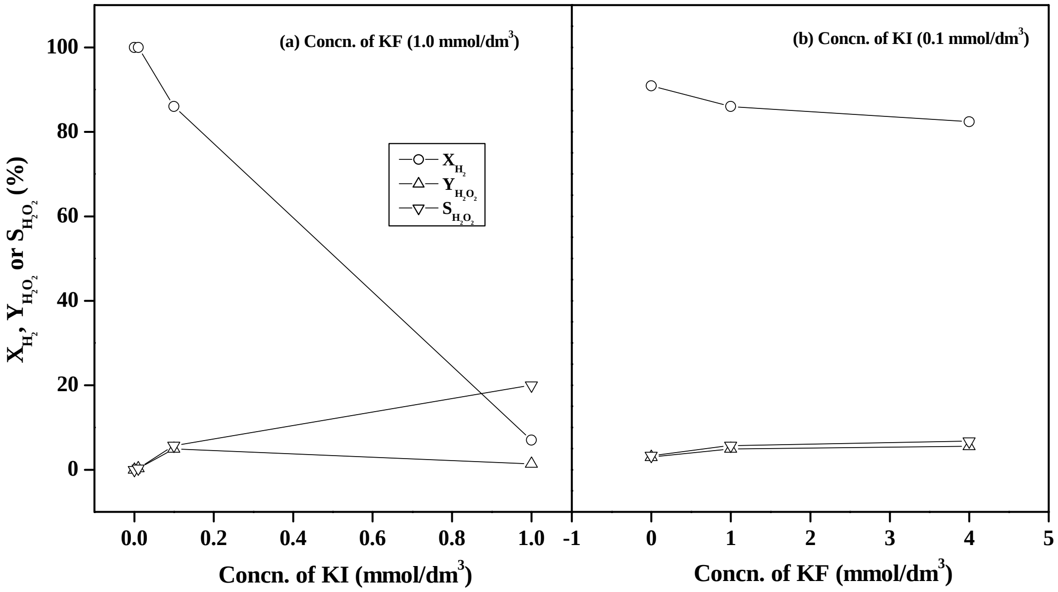


Figure 5.5: Effect of the concentration of KI [containing KF (1.0 mmol/dm^3)] (a) and the concentration of KF [containing KI (0.1 mmol/dm^3)] added to the acidic medium (0.1 M H_3PO_4) on the H_2 conversion (X_{H2}), H_2O_2 yield (Y_{H2O2}) and selectivity (S_{H2O2}) in the H_2-to-H_2O_2 oxidation over the Pd/C catalysts.

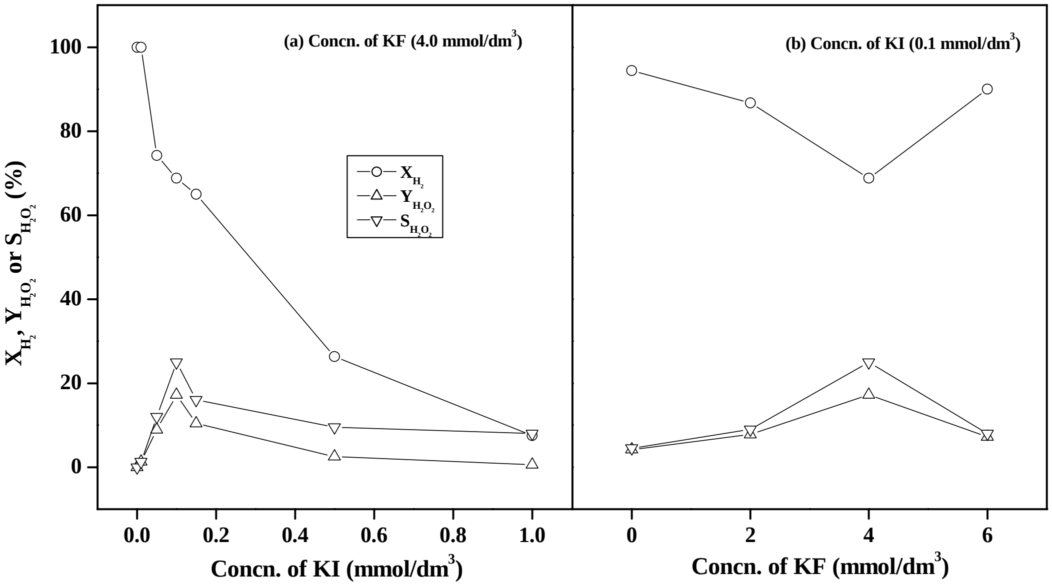


Figure 5.6: Effect of the concentration of KI [containing KF (4.0 mmol/dm^3)] (a) and the concentration of KF [containing KI (0.1 mmol/dm^3)] added to the acidic medium (0.1 M H_3PO_4) on the H_2 conversion (X_{H2}), H_2O_2 yield (Y_{H2O2}) and selectivity (S_{H2O2}) in the H_2-to-H_2O_2 oxidation over the Pd/Al_2O_3 catalysts.

For the Pd/C catalyst, with increasing the concentration of iodide [in the presence of fluoride (1.0 mmol/dm^3)] (Figure 5.5a) or fluoride [in the presence of iodide (0.1 mmol/dm^3)] (Figure 5.5b), both the H_2O_2 yield and selectivity increased while the H_2 conversion decreased. However, in the case of the Pd/Al_2O_3 catalyst, both the H_2O_2 yield and selectivity first rapidly increased and then passed through a maximum with increasing the iodide [in the presence of fluoride (4.0 mmol/dm^3)] (Figure 5.6a) or fluoride [in the presence of iodide (0.1 mmol/dm^3)] (Figure 5.6b) concentration in the medium. This indicates that an optimum concentration of halides is necessary for achieving the best results (highest H_2O_2 yield and/or selectivity).

5.5.2. Synergetic Effect of I^- and Cl^- Anions

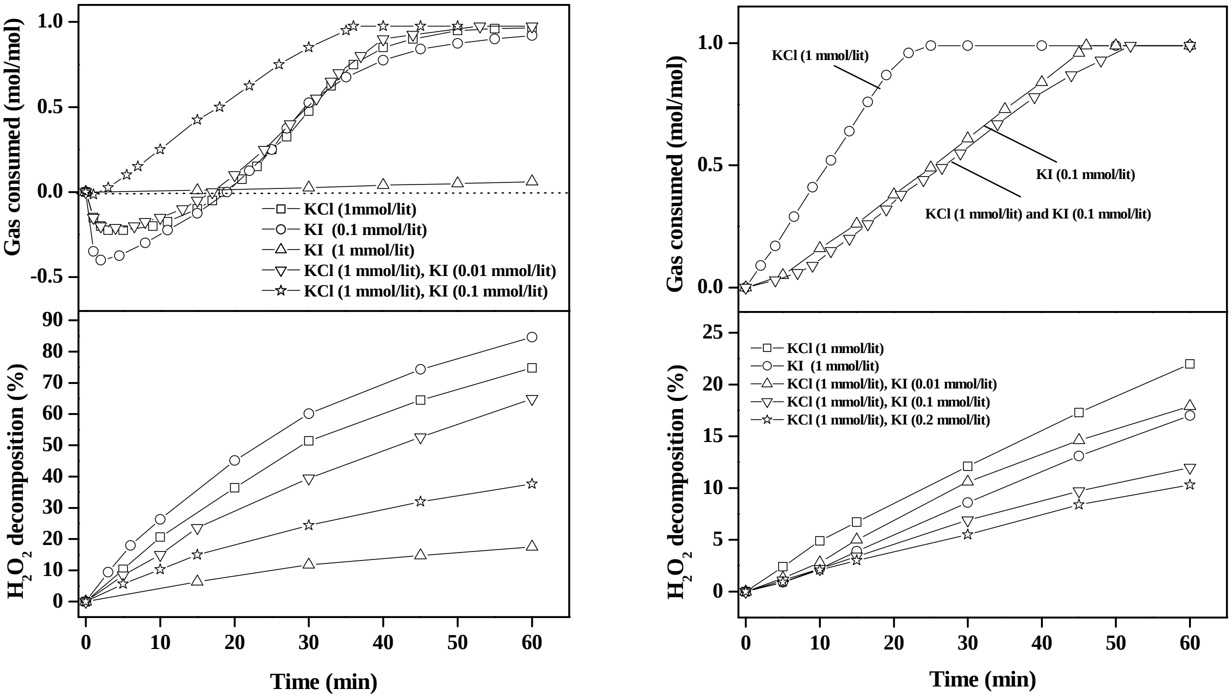
Results showing the influence of presence of KCl and KI in aqueous acidic (0.1 M H_3PO_4) reaction medium on the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition/hydrogenation over the Pd/C (or Pd/Al_2O_3) catalyst are presented in Table 5.4 and Figures 5.7.

Table 5.4: Results of the H_2-to-H_2O_2 oxidation and H_2O_2 conversion in the presence and absence of H_2 over the Pd/C and Pd/Al_2O_3 catalyst in the acidic medium containing KCl and KI (or KBr) with different concentrations. [where X_{H2} = conversion of H_2, Y_{H2O2} = yield of H_2O_2 and S_{H2O2} = selectivity of H_2O_2].

Halide in medium (mmol/dm^3)		H_2-to-H_2O_2 oxidation			Time for half H_2O_2 conversion (min)	
I	II	X_{H2} (%)	Y_{H2O2} (%)	S_{H2O2} (%)	In air	In H_2
Catalyst: Pd/C						
KCl (1.0)	Nil	97.7	6.5	6.7	29.8	3.0
KCl (1.0)	KI (0.1)	78.6	22.0	28.0	Large[38]^c	18.5
KBr (0.1)	Nil	91.7	22.5	30.0	56.4	<1.0
KBr (0.1)	KCl (1.0)	86.6	36.8	42.5	Large[32]^c	12.0
Catalyst: Pd/Al_2O_3						
KCl (1.0)	Nil	99.7	9.5	9.5	Large[22]^c	11.4
KCl (1.0)	KI (0.1)	80.7	24.6	30.5	Large[12]^c	26.5

[a] Values in the square bracket are the H_2O_2 conversion in 1 h.

For both the Pd/C and Pd/Al_2O_3 catalysts, in the presence of chloride (1.0 mmol/dm^3) in the medium, the H_2 conversion in the H_2-to-H_2O_2 oxidation was high (≥ 98 %) but both the H_2O_2 yield and selectivity were poor (Table 5.4). However, when iodide (0.1 mmol/dm^3) was added to the medium, both the H_2O_2 yield and selectivity increased markedly and also the rate of both the H_2O_2 decomposition and hydrogenation reactions reduced appreciably (Table 5.4 and Figure 5.7).



(a) (b)

Figure 5.7: Influence of the presence of KCl and KI in the aqueous acidic (0.01 M H_3PO_4) reaction medium on the H_2O_2 decomposition in static air and gas consumption on the H_2O_2 hydrogenation under static H_2 over the Pd/C (a) and Pd/Al_2O_3 (b) catalyst (at 27 ºC).

With increasing the concentration of iodide [in the presence of chloride (1.0 mmol/dm^3)] both H_2O_2 yield and selectivity in the H_2-to-H_2O_2 oxidation over the Pd/C and Pd/Al_2O_3 catalysts first increased and then passed through a maximum; the H_2 conversion, however, decreased continuously and very markedly (Figures 5.8a and 5.9). A similar trend was also observed when the chloride concentration in the medium [in the presence of iodide (0.1 mmol/dm^3)] was increased (Figure 5.8b); the decrease in the H_2 conversion was, however, much smaller. These observations also indicate the requirement of an optimum concentration of

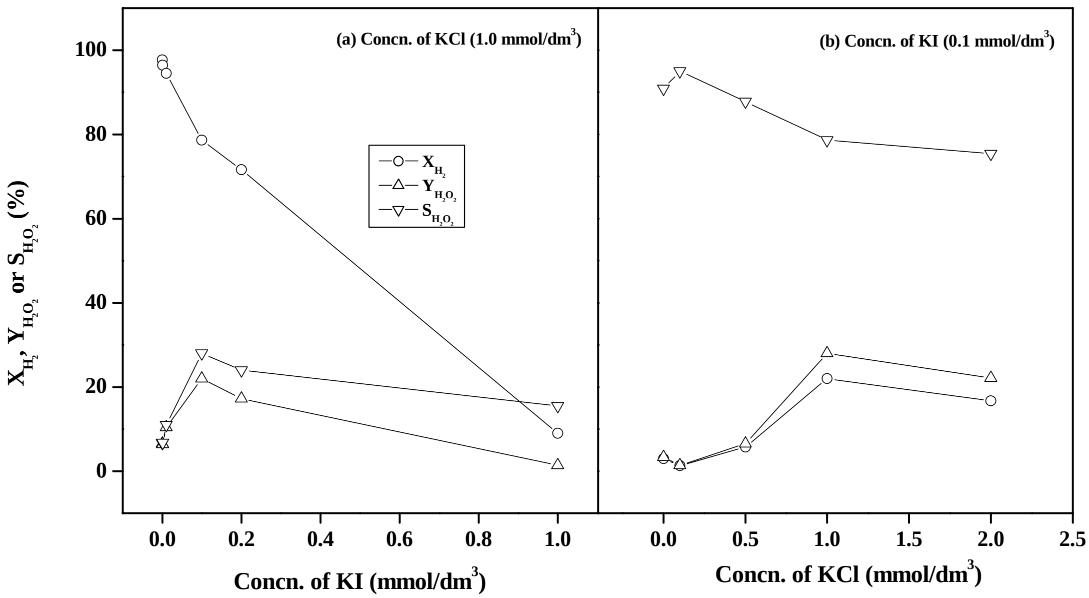


Figure 5.8: Effect of the concentration of KI [containing KCl (1.0 mmol/dm^3)] (a) and the concentration of KCl [containing KI (0.1 mmol/dm^3)] added to the acidic medium (0.1 M H_3PO_4) on the H_2 conversion (X_{H2}), H_2O_2 yield (Y_{H2O2}) and selectivity (S_{H2O2}) in the H_2-to-H_2O_2 oxidation over the Pd/C catalysts.

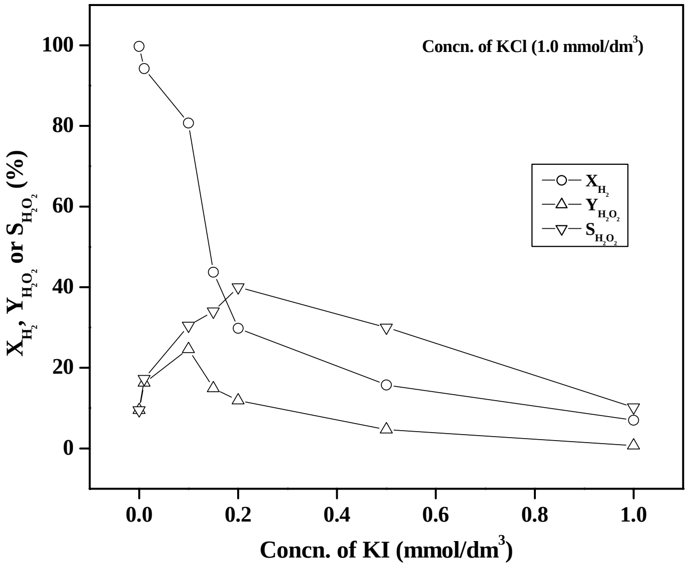


Figure 5.9: Effect of the concentration of KI [containing KCl (1.0 mmol/dm^3)] added to the acidic medium (0.1 M H_3PO_4) on the H_2 conversion (X_{H2}), H_2O_2 yield (Y_{H2O2}) and selectivity (S_{H2O2}) in the H_2-to-H_2O_2 oxidation over the Pd/Al_2O_3 catalysts.

the halides for achieving the best results in the H_2-to-H_2O_2 oxidation. The observed decrease in the H_2 conversion shows the catalyst deactivation due to poisoning of the catalytically active sites by the iodide or chloride anions; iodide, however, is the most effective for catalyst poisoning.

5.5.3. Synergetic Effect of Cl^- and Br^- Anions

The results in Table 5.4 and earlier studies [5,7] show that, among the different halide promoters, bromide is the best halide promoter for the H_2-to-H_2O_2 oxidation over the Pd catalysts. The presence of bromide also drastically reduces the rates of H_2O_2 decomposition and hydrogenation reactions over the Pd catalysts [5,7]. However, the addition of chloride (1.0 mmol/dm^3) to the reaction medium containing bromide (0.1 mmol/dm^3) caused an appreciable increase in both the H_2O_2 yield and selectivity, while causing a large decrease in the rates of both the H_2O_2 decomposition and hydrogenation reactions over the Pd/C catalyst (Table 5.4 and Figure 5.10).

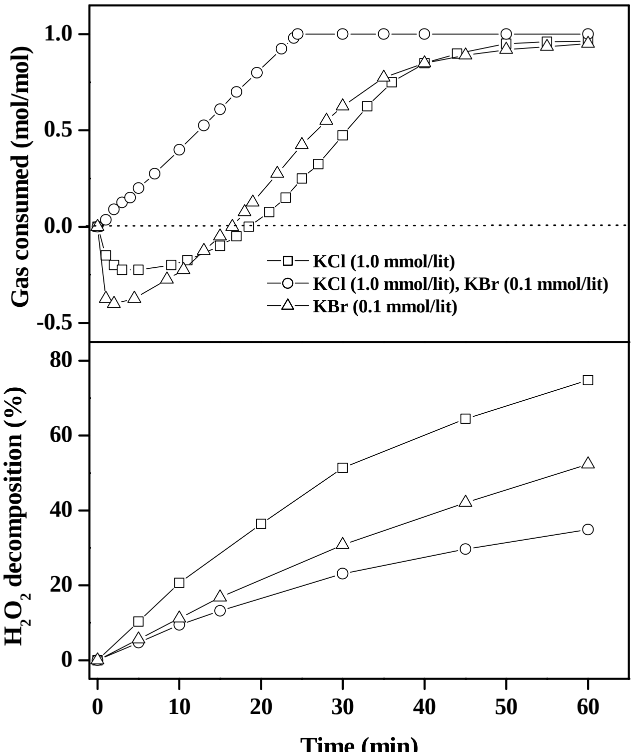


Figure 5.10: Influence of the presence of KCl and KBr in the aqueous acidic (0.01 M H_3PO_4) reaction medium on the H_2O_2 decomposition in static air and gas consumption on the H_2O_2 hydrogenation under static H_2 over the Pd/C catalyst (at 27 ºC).

Results in Figure 5.11 reveal that with increasing the concentration of chloride [in the presence of bromide (0.1 mmol/dm^3)] both H_2O_2 yield and selectivity in the H_2-to-H_2O_2 oxidation over the Pd/C catalyst first increased and then passed through a maximum; the H_2 conversion, however, decreased very slowly. The observed decrease in the H_2 conversion shows catalyst deactivation due to poisoning of the catalytically active sites by chloride anions, which is attributed at higher concentration.

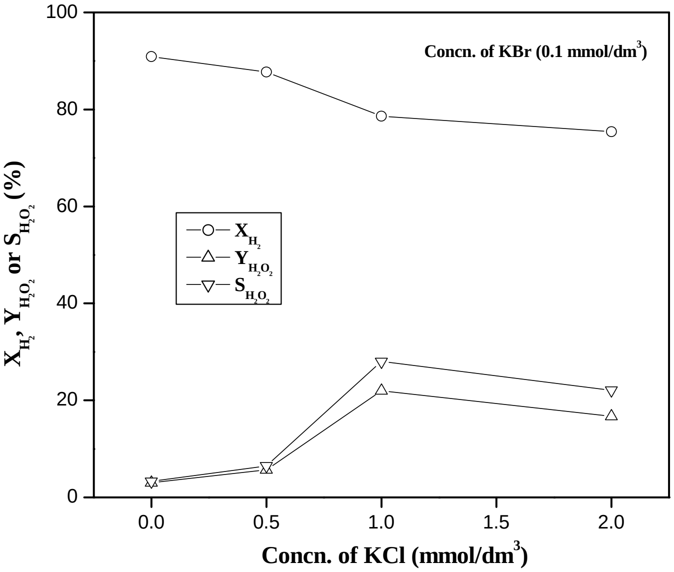


Figure 5.11: Effect of the concentration of KCl added to the acidic medium containing KBr (0.1 mmol/dm^3) on the H_2 conversion (X_{H2}), H_2O_2 yield (Y_{H2O2}) and selectivity (S_{H2O2}) in the H_2-to-H_2O_2 oxidation over Pd/C catalyst.

5.6. Influence of the Presence of Two Different Halogens in the Catalyst on the Performance of Halogenated Pd/Al_2O_3 Catalyst

The use of halogen promoters added into the acidic aqueous reaction medium for the H_2-to-H_2O_2 oxidation [5,6,8,11,13-15] is undesirable because of their highly corrosive nature. This serious problem could be avoided by incorporating the halogen promoters directly in the solid catalyst by its halogenation [7]. It is, therefore, very interesting to study the synergetic effect of two halogens in the catalyst on its H_2O_2 formation and destruction activities.

5.6.1. Synergetic Effect of I and F

Results in Table 5.5 and Figure 5.12 show a strong influence of the presence of F and I (or Br) in the catalyst on the formation of H_2O_2 in the H_2-to-H_2O_2 oxidation and also on the H_2O_2 decomposition and hydrogenation reactions over the halogenated Pd/Al_2O_3 catalysts in an acidic (0.1 M H_3PO_4) aqueous reaction medium.

Table 5.5: Results of the H_2-to-H_2O_2 oxidation and H_2O_2 conversion in the presence and absence of H_2 over the halogenated Pd/Al_2O_3 catalyst in the acidic medium containing F and I (or Br) in the catalyst. [where X_{H2} = conversion of H_2, Y_{H2O2} = yield of H_2O_2 and S_{H2O2} = selectivity of H_2O_2].

Halogen in the catalyst (mmol/g)		H_2-to-H_2O_2 oxidation			Time for half H_2O_2 conversion (min)	
I	II	X_{H2} (%)	Y_{H2O2} (%)	S_{H2O2} (%)	In air	In H_2
F (2.63)	Nil	100	0.0	0.0	1.0	<1.0
I (0.08)	Nil	27.7	5.7	20.5	V.large[1][a]	V.large[b]
F (2.63)	I (0.08)	40.8	13.3	32.5	V.large[1][a]	V.large[c]
Br (0.13)	Nil	93.4	51.4	55.0	V.large[3][a]	12.0
Br (0.13)	F (0.53)	98.0	58.8	60.0	V.large[3][a]	13.0
Br (0.13)	F (2.63)	99.4	56.7	57.0	V.large[2][a]	14.5

[a]Values in the square bracket are the H_2O_2 conversion in 1 h. [b and c]10.5 and 19.8 % H_2O_2 conversion, respectively in 1 h.

The H_2 conversion in the H_2 oxidation over the fluorinated Pd/Al_2O_3 (F loading = 2.63 mmol/g) catalyst was complete (100 %) without any formation of H_2O_2 (Table 5.5) due to the very high rates of both the consecutive H_2O_2 decomposition and hydrogenation reactions (Table 5.4 and Figure 5.12). On the other hand, for the iodinated Pd/Al_2O_3 (I loading = 0.08 mmol/g) catalyst, both the H_2O_2 yield and selectivity in the H_2-to-H_2O_2 oxidation were very poor (Table 5.5) but the H_2O_2 destruction (decomposition/hydrogenation) reactions decreased drastically (Table 5.5 and Figure 5.12). However, their combine effect i.e. when both the fluoride and iodide anions were present in the catalyst, the rate of net H_2O_2 formation in the H_2-to-H_2O_2 oxidation increased very markedly, (Table 5.5). The observed decrease in the H_2 conversion and H_2O_2 destruction (decomposition and hydrogenation) reactions due to the addition of I in the catalyst shows catalyst deactivation; it indicates that the catalytically active sites of the catalyst is blocked by the iodide anions; resulting the catalyst poisoning.

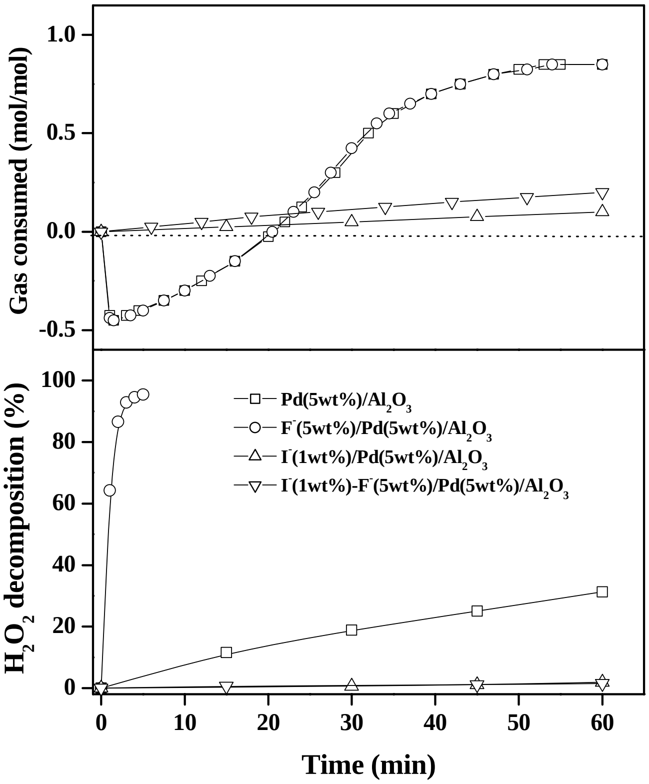


Figure 5.12: Influence of the presence of F and I in the catalyst on the performance of halogenated Pd/Al_2O_3 Catalyst in the H_2O_2 destruction (decomposition/hydrogenation) in the aqueous acidic (0.1 M H_3PO_4) reactions medium.

5.6.2. Synergetic Effect of F and Br

The incorporation of Br (0.13 mmol/g of Br) in the Pd/Al_2O_3 catalyst drastically reduced the rates of H_2O_2 decomposition and hydrogenation reactions (Table 5.5). The simultaneous incorporation of both fluorine (0.53 mmol/g) and bromine (0.13 mmol/g) in the Pd/Al_2O_3 resulted in an appreciable increase in both the H_2O_2 yield (from 51.4 % to 58.8 %)

and selectivity (from 55.0 % to 60.0 %) in the H_2-to-H_2O_2 oxidation (Table 5.5) while causing a small decrease in the rates of both the H_2O_2 decomposition and hydrogenation reactions (Table 5.5). Though the increase in H_2O_2 yield and selectivity and decrease in the H_2O_2 destruction reactions are small, it clearly shows a beneficial synergetic effect Br and F in halogenated Pd/Al_2O_3 catalyst on the H_2O_2 formation and destruction reactions for improving both the H_2O_2 yield and selectivity in the process. Therefore, the further study was undertaken to study the synergetic effect of F and Br at their different concentrations in the catalyst and also to study the way of incorporation of two halogens (Br and F) in the catalyst on its H_2O_2 formation and destruction activities.

5.6.2.1. Influence of the concentration of Br and F on H_2-to-H_2O_2 oxidation: Results showing a strong influence of the bromination of the pre-fluorinated Pd/Al_2O_3 (F loading = 0.53 mmol/g) catalyst on its performance in the H_2-to-H_2O_2 oxidation are presented in Figure 5.13. Since, the best catalyst performance was observed at the optimum bromine concentration of about 0.13 mmol/g, the influence of fluorination at different F concentrations (0 – 1.1 mmol/g) of the pre-brominated Pd/Al_2O_3 containing 0.13 mmol Br/g was also studied and the results are shown in Figure 5.14.

The results of the bromination of pre-fluorinated Pd/Al_2O_3 (Figure 5.13) reveal the following important information:

- The pre-fluorinated Pd/Al_2O_3 has very high H_2 conversion activity but a very little or no selectivity for the net H_2O_2 formation.
- The bromination of the catalyst caused a drastic increase in both the H_2O_2 selectivity and yield but an appreciable decrease in the H_2 conversion.
- With increasing the bromination (i.e. Br concentration in the catalyst), the H_2 conversion decreased continuously but both the H_2O_2 selectivity and yield first increased sharply up to the bromination concentration of 0.13 mmol/g and then decreased continuously, after passing through a maximum (at about 0.13 mmol Br/g).

However, the results for the fluorination of pre-brominated Pd/Al_2O_3 (Figure 5.14) are similar to that observed for the bromination of pre-fluorinated Pd/Al_2O_3 (Figure 5.13), except the following differences:

- The H_2 conversion activity of the pre-brominated Pd/Al_2O_3 passed through a maximum (at about 0.13 mmol F/g) with increasing the fluorination.

- Even in the absence of fluorine, the pre-brominated Pd/Al_2O_3 showed very good H_2O_2 selectivity and yield in the H_2-to-H_2O_2 oxidation.

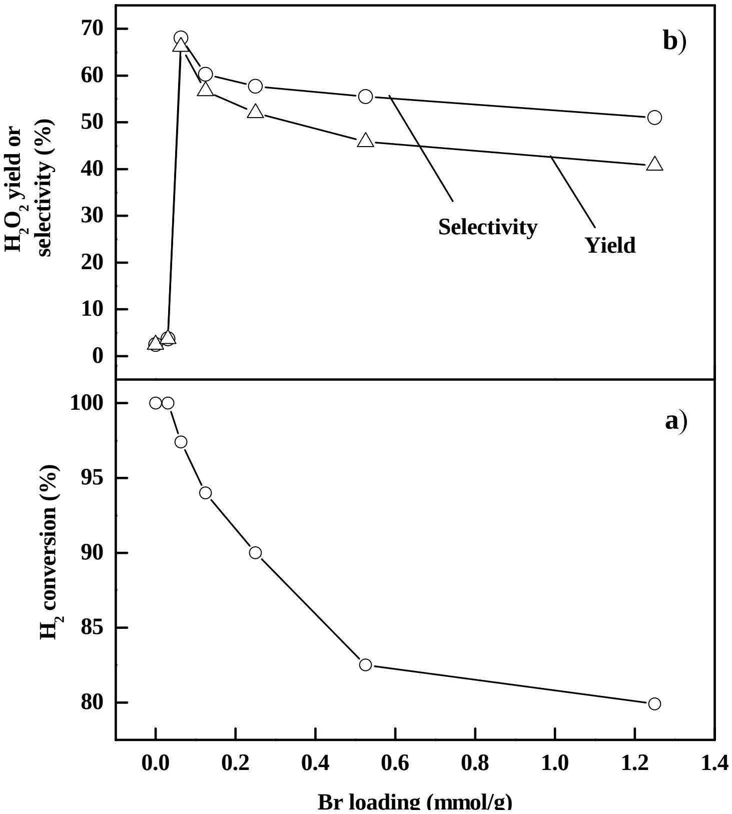


Figure 5.13: Influence of the bromination of pre-fluorinated Pd/Al_2O_3 (F loading = 0.53 mmol/g) catalyst on its performance in the H_2-to-H_2O_2 oxidation.

Nevertheless, in both the cases, the incorporation of second halogen (Br or F) in the pre-halogenated Pd/Al_2O_3 resulted in a large increase in the net H_2O_2 formation due to the synergetic effect of the two halogens (Br and F). The beneficial synergetic effect is, however, highest at the optimum concentration of the halogens present in the catalyst. It may, however, be noted that the optimum concentration of second halogen added to the pre-halogenated Pd/Al_2O_3 for the best catalyst performance is expected to depend upon the concentration of halogen present in the pre-halogenated Pd/Al_2O_3. Further work is necessary to optimize the concentration of two or more than two halogens in the catalyst for its best performance in the process.

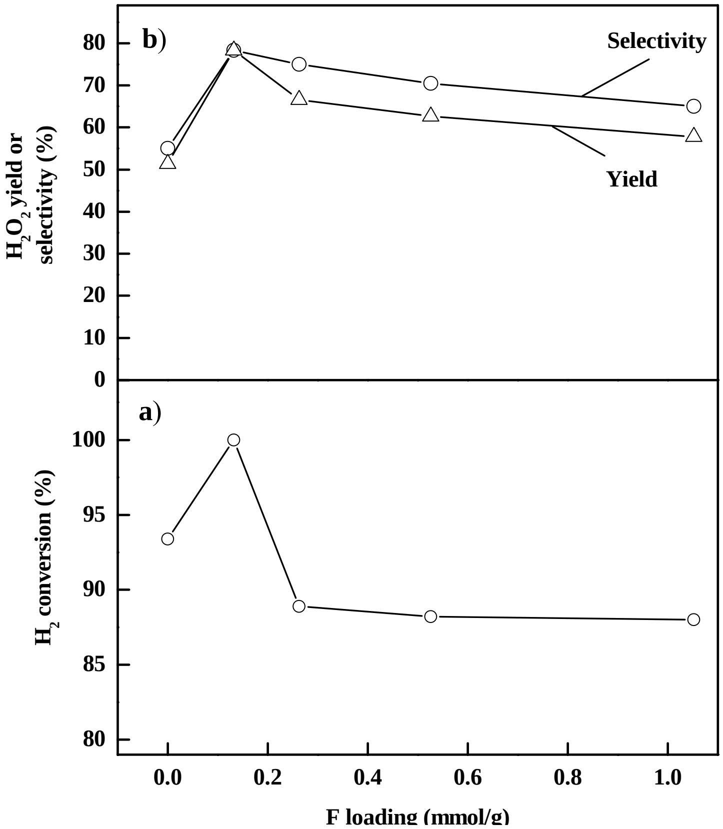


Figure 5.14: Influence of the fluorination of pre-brominated Pd/Al_2O_3 (Br loading = 0.13 mmol/g) catalyst on its performance in the H_2-to-H_2O_2 oxidation.

5.6.2.2. Influence of the concentration of Br and F on H_2O_2 decomposition: The influence of the bromination (of the pre-fluorinated catalyst) and fluorination (of the pre-brominated catalyst) at different Br and F, respectively, concentrations on the H_2O_2 destruction activity of the respective pre-halogenated catalyst in both the absence and presence of hydrogen was also investigated. The results of the H_2O_2 destruction in the absence of H_2 (i.e. the destruction of H_2O_2 by its decomposition alone) are presented in Figures 5.15 and 5.16.

The results in Figure 5.15 show that the addition of Br and increase in its concentration due to the bromination of pre-fluorinated Pd/Al_2O_3 caused a drastic decrease in the H_2O_2 decomposition activity of the catalyst, particularly at the lower Br concentrations. However, for the fluorination of pre-brominated Pd/Al_2O_3, the H_2O_2 decomposition passed through a minimum at the fluorine concentration of 0.13 mmol/g (Figure 5.16) with increasing the fluorine concentration. At the lower fluorine concentrations, the H_2O_2 decomposition decreased

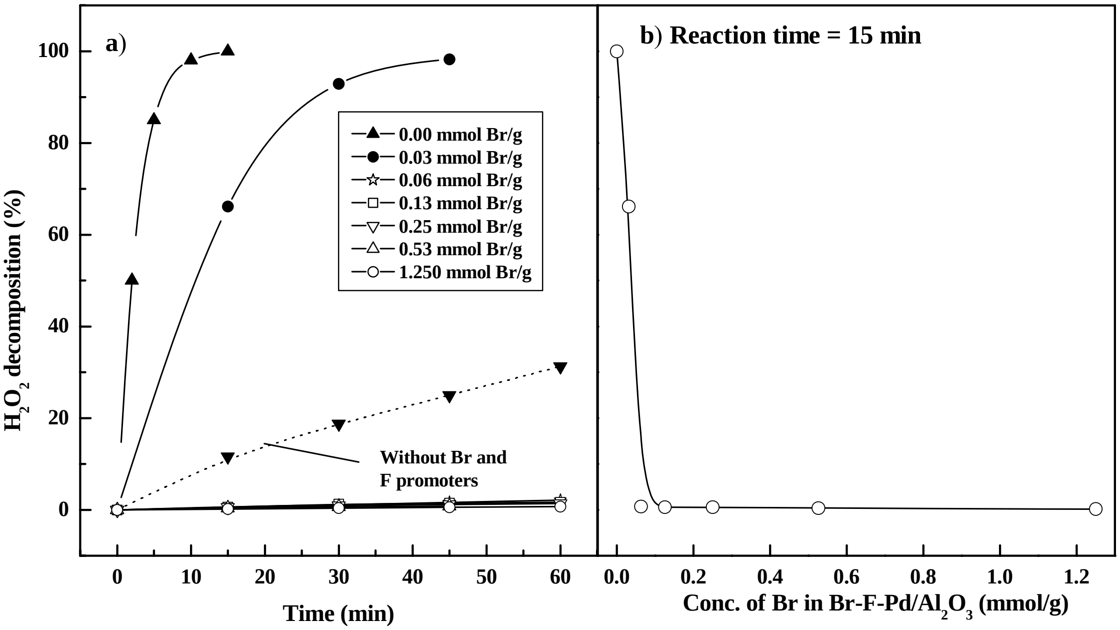


Figure 5.15: Influence of the concentration of bromine in the Br-F-Pd/Al_2O_3 (F loading = 0.53 mmol/g) catalyst on its performance in the H_2O_2 decomposition in the absence of H_2.

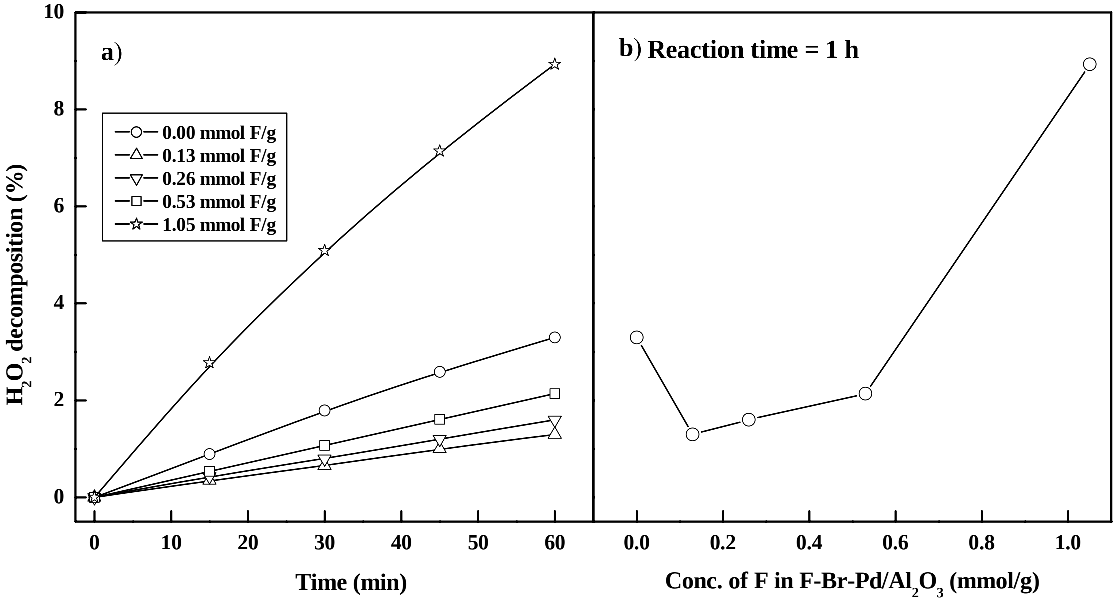


Figure 5.16: Influence of the concentration of fluorine in the F-Br-Pd/Al_2O_3 (Br loading = 0.13 mmol/g) catalyst on its performance in the H_2O_2 decomposition in the absence of H_2.

but, at the higher fluorine concentration (1 mmol/g), it was even higher than that in the absence of fluorine in the catalyst.

A comparison of the results in Figure 5.16b with that in Figure 5.14b clearly indicate that the effect of fluorine addition to the pre-brominated Pd/Al_2O_3 on the H_2O_2 decomposition (Figure 5.16b) is exactly opposite to that observed on the H_2O_2 formation (Figure 5.14b). Moreover, the synergetic effect of the presence of two halogens (Br and F) on the H_2O_2 decomposition was also highest at the fluorine concentration of 0.13 mmol/g, similar to that observed for the H_2O_2 formation in the H_2-to-H_2O_2 oxidation.

5.6.2.3. Influence of the concentration of Br and F on H_2O_2 destruction in the presence of H_2: The results of the H_2O_2 destruction in the presence of H_2 (i.e. the destruction of H_2O_2 by its fast decomposition and/or slow hydrogenation) are given in Figure 5.17 and Table 5.6.

Table 5.6: Results of the H_2O_2 destruction over the Pd/Al_2O_3 with or without containing Br and/or F in the presence of H_2 at 27 ºC.

Halogen conc. (mmol/g)		Time for half H_2O_2 destruction, $t_{1/2}$ (min)	Mode of H_2O_2 destruction (decomposition/hydrogenation)
F	Br		
0.0	0.0	<1.0	Fast decomposition
0.13	0.0	<1.0	Fast decomposition
0.0	0.13	13.5	Slow hydrogenation
0.13	0.13	13.6	Slow hydrogenation
0.53	0.13	15.0	Slow hydrogenation

The results in Figure 5.17 show that, in the presence of Br in the catalyst, H_2 consumed linearly with the reaction time and the maximum consumption of H_2 in the reaction was 1 mole H_2 per mole of H_2O_2 initially present in the reaction. After the period of 30 min, no H_2O_2 was present in the reaction mixture. These observations indicate that, in this case, the H_2O_2 destruction is due to the hydrogenation (reaction 5.4) independent of the H_2O_2 concentration (i.e. zero order with respect to H_2O_2). The rate of hydrogenation, however, decreased with increasing the concentration of F in the catalyst.

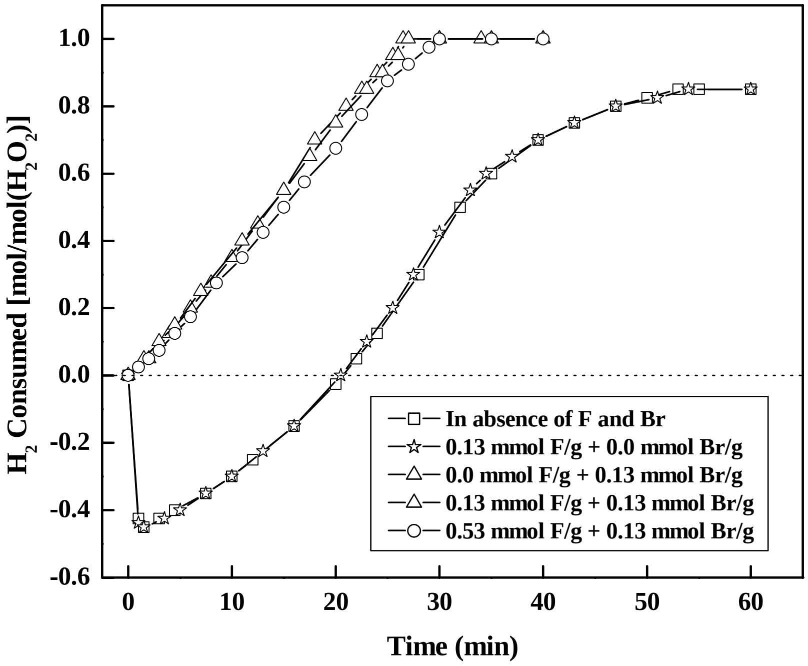


Figure 5.17: Effect of the concentration of F and/or Br in the F-Br-Pd/Al_2O_3 catalyst on its performance in the hydrogenation and/or decomposition of H_2O_2 in the presence of H_2.

In the absence of both F and Br or in the presence of F alone, the H_2 consumption in the initial period of about 20 min was negative, indicating the evolution of gas rather than the consumption of H_2. This is expected because of the H_2O_2 decomposition reaction (reaction 5.3) prevailing over the H_2O_2 hydrogenation (reaction 5.4). The initial evolution of gas (O_2) and later consumption of H_2, as shown in Figure 5.17 show a fast decomposition of H_2O_2 followed by the oxidation of H_2 by the O_2 evolved in the initial decomposition. The amount of gas evolved in about 1.0 min [4.5 mol(O_2)/mol(H_2O_2)] showed that at least 90 % of the H_2O_2 destruction is by the fast H_2O_2 decomposition.

The results of the H_2O_2 destruction in the presence of H_2 over the catalyst containing F and Br at different concentrations are compared in Table 5.6.

The observed beneficial effect on the formation in the H_2-to-H_2O_2 oxidation (Figures 5.13b and 5.14b) is attributed to the synergetic effect of the two halogens in the catalyst. The observed decrease in the H_2 conversion at the higher halogen concentrations (Figures 5.13a and

5.14a) is, however, due to the catalyst deactivation resulting from the poisoning of the catalyst active sites and/or their further surface modification through their interaction with the excess amount of halogen in the catalyst. The observed decrease in the H_2O_2 selectivity may particularly be attributed to the further modification of the catalytic sites responsible for the H_2O_2 formation and destruction reactions at the higher halogen concentration. A decrease in the H_2O_2 selectivity at a higher halide anion concentration in the acidic medium for the H_2-to-H_2O_2 oxidation over Pd/C [14], Pd/ZrO_2 [15] and Pd/Al_2O_3 [16] catalyst has also been observed earlier.

5.6.3. Influence of Catalyst Halogenation Method

The results in Table 5.7 show a strong influence of the halogenation methods, such as

- first bromination of Pd/Al_2O_3 and then fluorination of the pre-brominated Pd/Al_2O_3 (method -A)
- first fluorination of Pd/Al_2O_3 and then bromination of the pre-fluorinated Pd/Al_2O_3 (method -B), and
- simultaneous bromination and fluorination of Pd/Al_2O_3 (method -C),

used for incorporating the two halogens in the catalyst on its performance in the H_2-to-H_2O_2 oxidation.

Table 5.7: Results of the H_2-to-H_2O_2 oxidation over the F-Br-Pd/Al_2O_3 catalyst prepared by different halogenation methods [viz. bromination followed by fluorination (method -A), fluorination followed by bromination (method -B) and simultaneous bromination and fluorination (method -C)].

Conc. of halogen in catalyst (mmol/g)		Halogenation method used	H_2-to-H_2O_2 oxidation			Net rate of H_2O_2 formation [mmol/g(cat)/h]
F	Br		X_{H2} (%)	S_{H2O2} (%)	Y_{H2O2} (%)	
0.53	0.13	Method -B	88	71	63	44
0.53	0.13	Method -A	97	69	68	47
0.53	0.13	Method -C	98	60	59	41
0.13	0.13	Method -A	100	78	78	54

A comparison of the results (Table 5.7) reveal that the simultaneous incorporation of Br and F in the catalyst is least effective for improving the net rate of H_2O_2 formation. This is quite consistent with our observation that, when fluorine was added to the acidic reaction medium containing bromide, the observed synergetic effect of the two halide anions (Br^- and F^-) on the net H_2O_2 formation over Pd/C and Pd/Al_2O_3 catalysts was very small. Whereas, the incorporation of Br followed by that of F in the catalyst is most effective for enhancing the net rate of H_2O_2 formation. These observations point to the fact that the distribution and/or location (on Pd, close to Pd or away from Pd) of F and Br on the catalyst surface (which is expected to control the synergetic effect produced by the two halogens) depends upon the halogenation methods (method -A, method -B or method -C) used for incorporating the two halogens in the catalyst. Further studies are necessary to know how and why the distribution and/or location of the two halogens are influenced by the halogenation method.

The synergetic effect is expected to arise from the modification of the electronic properties of the Pd catalyst through the interactions of the two halogen anions (which differ appreciably in their electronegativity and electron affinity) with the Pd clusters in the catalyst (the electronegativity and electron affinity of halogens are in the order F>Cl>Br>I and Cl>F>Br>I, respectively). The combined effect of the two halides on the electronic properties of the Pd clusters seems to retard the rate of O-O bond cleavage of O_2 ($O_2 + 2\ Pd \rightarrow 2\ Pd.O$) and H_2O_2 ($2\ Pd + H_2O_2 \rightarrow 2\ Pd.OH$), thereby reducing the rates of the H_2 combustion [5,6,11,17] and H_2O_2 decomposition and hydrogenation [5,11] reactions. However, the decrease in the H_2O_2 selectivity at the higher halide concentration (Figures 5.5,5.6,5.8,5.9, 5.11,5.13 and 5.14) indicates that the favorable modification of the electronic properties of catalyst occurs only in a particular range of halide concentrations, probably depending upon the relative concentration and nature of the halides anions. Further thorough studies are necessary for better understanding the very complex issues of the synergetic effects and the decrease of H_2O_2 selectivity at the higher halide concentrations.

Fluorine is highly electronegative halogens and hence fluorination of the Pd catalysts may also cause modification of the support properties, particularly the acidity of the support (alumina or carbon) of the Pd catalysts. For example, alumina contains only Lewis acid sites, but after fluorination protonic acid sites are created [18]. It should be noted that, apart from the halide promoter, the presence of protons is also required for the selective formation of H_2O_2 [5]. The increase in the H_2O_2 yield and selectivity after the addition of fluorine in the brominated Pd/Al_2O_3 catalyst may at least partly be attributed to the creation of protonic acidity due to fluorination of the alumina support.

The synergetic effect depends upon the concentration of the two halides, it is more pronounced when the two halogen promoters differ greatly in their electronegativity and/or electron affinity (viz. Br and F). More than two halides are also expected to produce a synergetic effect on the H_2O_2 formation in the H_2-to-H_2O_2 oxidation. Hence, further work can be done for greatly improving the H_2O_2 formation in the H_2-to-H_2O_2 oxidation through an optimization of the concentrations of two or more halides in the medium or in the Pd catalyst.

5.7. Conclusions

The present studies on the direct H_2-to-H_2O_2 oxidation and H_2O_2 destruction reactions in acidic aqueous medium under ambient conditions lead to the following important conclusions.

1. H_2O_2 formation with a much higher selectivity/yield in the direct oxidation of H_2 by O_2 to H_2O_2 over supported Pd catalysts in an acidic medium can be accomplished by using two halogens (viz. F^- and I^-, Cl^- and I^-, Cl^- and Br^-, and F^- and Br^-) as catalyst promoter at their optimum concentrations in the medium or in the catalyst, instead of using either of the two halogens alone. The two halogen promoters have a synergetic effect. They promote the H_2O_2 formation by inhibiting the H_2O_2 decomposition and hydrogenation reactions. Fluorinated and brominated Pd/Al_2O_3 is a highly promising catalyst for the selective H_2-to-H_2O_2 oxidation with high yields.
2. Both the H_2 conversion and H_2O_2 selectivity/yield in the H_2-to-H_2O_2 oxidation are strongly influenced by the extent of bromination of the pre-fluorinated Pd/Al_2O_3 and also influenced by the extent of fluorination of the pre-brominated Pd/Al_2O_3. The largest enhancement in the H_2O_2 yield/selectivity is observed at the optimum concentration of F (0.13 mmol/g) in the F^-Br-Pd/Al_2O_3 (Br loading = 0.13 mmol/g) catalyst or that of Br (0.13 mmol/g) in the Br-F-Pd/Al_2O_3 (F loading = 0.53 mmol/g) catalyst.

3. The H_2O_2 decomposition (in the absence of H_2) activity of the halogenated Pd/Al_2O_3 catalyst decreases sharply with increasing the Br concentration in the Br-F (0.13 mmol/g)-Pd/Al_2O_3 but it passed through a minimum with increasing the concentration of F in the F-Br-(0.13 mmol/g)-Pd/Al_2O_3.
4. The H_2O_2 destruction (in the presence of H_2) over the halogenated Pd/Al_2O_3 catalyst, containing Br (0.13 mmol/g) with or without F, is only by the slow hydrogenation of H_2O_2.
5. The method of Pd/Al_2O_3 halogenation (viz. simultaneous bromination and fluorination, bromination followed by fluorination or fluorination followed by bromination) pay important role in controlling the synergetic effect produced by the two halogens (Br and F) incorporated in the catalyst. The best catalyst performance (i.e. highest net rate of H_2O_2 formation) is achieved when the Pd/Al_2O_3 was first brominetad (0.13 mmol/g) and then fluorinated (0.13 mmol/g); the halogenated catalyst showed complete H_2 conversion (100 %) with very high H_2O_2 selectivity/yield.

There is a further scope for developing a better catalyst for the H_2-to-H_2O_2 oxidation by optimizing the concentration of Br and F in the halogenated Pd/Al_2O_3 or different supported Pd catalysts.

5.8. References

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Chapter 6

H_2-to-H_2O_2 Oxidation over Highly Active/Selective Bromine and Fluorine Promoted Pd/Al_2O_3 Catalyst: Influence of Halogen Promoter Concentration and Process Parameter

Chapter 6

H_2-to-H_2O_2 Oxidation over Highly Active/Selective Bromine and Fluorine Promoted Pd/Al_2O_3 Catalyst: Influence of Halogen Promoter Concentration and Process Parameter

6.1. Background and Objective of the Present Work

Direct catalytic H_2-to-H_2O_2 oxidation is of great practical importance for replacing the presently practiced hydroquinone auto-oxidation process for the commercial production of hydrogen peroxide, a versatile/environmentally clean oxidizing agent. The later process is based on the indirect oxidation of H_2, involving a number of complicated steps and, moreover, it is economical only when operated for a large scale production of H_2O_2 [1]. Since, the storage, handling and transport of H_2O_2 are hazardous, there is an immediate need to develop the direct H_2O_2 synthesis process based on the H_2-to-H_2O_2 oxidation, which can be operated even at a small scale. The direct oxidation process has been extensively investigated, leading to a large number of publications in the last few years [2-23]. It has also be patented extensively but it is not yet commercialized. However, recently, Degussa [24] reported the start of a demonstration plant for this process.

Apart from the process safety, the main problem for exploiting the direct oxidation process is a low H_2O_2 formation activity of the catalysts used in the process, due to the undesirable parallel and consecutive water forming reactions occurring simultaneously with the H_2O_2 forming reaction in the process over the same catalyst [13,25]; as follows.

Parallel reactions:

$H_2 + O_2 \rightarrow H_2O_2$ (H_2O_2 forming reaction) (6.1)

$H_2 + 0.5\ O_2 \rightarrow H_2O$ (direct water forming reaction) (6.2)

Consecutive reactions:

$H_2O_2 \rightarrow H_2O + 0.5\ O_2$ (H_2O_2 decomposition reaction) (6.3)

$H_2O_2 + H_2 \rightarrow 2\ H_2O$ (H_2O_2 hydrogenation reaction) (6.4)

The net H_2O_2 formation is, therefore, controlled by the parallel water forming reaction (reaction 6.2) and consecutive H_2O_2 destruction to water (reactions 6.3 and 6.4).

In order to improve the net H_2O_2 formation in the process, efforts have been made for drastically increasing the H_2O_2 selectivity and yield by surface/sub-surface or bulk oxidation of Pd from the different supported Pd catalysts [3-6], by adding halide catalyst promoter, particularly chloride or bromide, in the aqueous acidic or non-aqueous reaction medium [8,9,13,14,20,21,22] and also by directly incorporating bromide promoters in supported Pd catalysts [10,22]. Recently, we have observed a large synergetic effect of two halide promoters, added in the acidic reaction medium or in the catalyst showing an appreciable improvement in both the H_2O_2 selectivity and yield over Pd/Al_2O_3 or Pd/C catalyst. The incorporation of both the bromide and fluoride in the Pd/Al_2O_3 catalyst showed an appreciable improvement in the H_2O_2 formation activity of the catalyst. Since, the halide promoters are directly incorporated in the catalyst, the acidic reaction medium is free from the halides; it is, therefore, is less corrosive than that containing Br^- and F^- anions.

There is also a scope for a further improvement in the H_2O_2 formation in the process through properly choosing the process conditions. The information available on the influence of various process conditions on the H_2O_2 formation is, however, scarce.

The present study was undertaken for thoroughly investigating the influence of different reaction conditions (viz. O_2/H_2 mole ratio in gaseous feed, initial concentration of H_2O_2, reaction temperature and period, concentration of acid in the reaction medium, space velocity of H_2 andO_2, etc) on the H_2O_2 formation in the H_2-to-H_2O_2 oxidation over a highly active/selective Br-F-Pd/Al_2O_3 catalyst in an aqueous acidic (H_3PO_4) medium for achieving further improvement in the net H_2O_2 formation in the process. The H_2O_2 decomposition (in air) and hydrogenation (in static H_2) over the catalyst in the acidic medium at different temperatures and acid concentrations (in the medium) have been studied. The H_2O_2 destruction during the H_2-to-H_2O_2 oxidation with different O_2/H_2 gas feed ratios and the net H_2O_2 formation in the oxidation at different initial concentrations of H_2O_2 have also been investigated.

6.2. Catalysts and Brief Experimental Procedures

Br(1.0 wt%)-F(1.0 wt%)-Pd(5.0 wt%)/Al_2O_3 catalyst was prepared by impregnating ammonium bromide and fluoride from their aqueous solution on Pd(5.0 wt%)/Al_2O_3 (obtained from Lancaster, UK), in powdered form, by the incipient wetness impregnation technique (described in the section 2.2.2), followed by drying on a water bath and decomposing the catalyst mass at 400 ºC for 2 h in a flow of O_2-free nitrogen.

The catalyst was characterized by XRD [using a Holland Philips, PW/1730 X-ray generator with CuK_α radiation (λ = 1.5406 Å)] and also by XPS (using a VG-Scientific ESCA-3MK II electron spectrometer). The XRD spectra of the catalyst showed a sharp peak at 2θ = 40º (Appendix 6.1), indicating the presence of palladium in its metallic form in the catalyst. The XPS of the catalyst showed that the Br/Pd and F/Pd atomic ratios at the catalyst surface are 0.73 and 3.4, respectively. The particle size and morphology of Pd in the catalyst were determined by HRTEM (using a JEOL JEM-1200EX transmission electron microscope operating at 100 kV) of the catalyst. The HRTEM photograph of the catalyst along with that of the Pd/Al_2O_3 catalyst is given in Figure 6.1. After the fluorination and bromination, the Pd particle size is increased very appreciably from 5 - 7 nm to 20 - 30 nm.

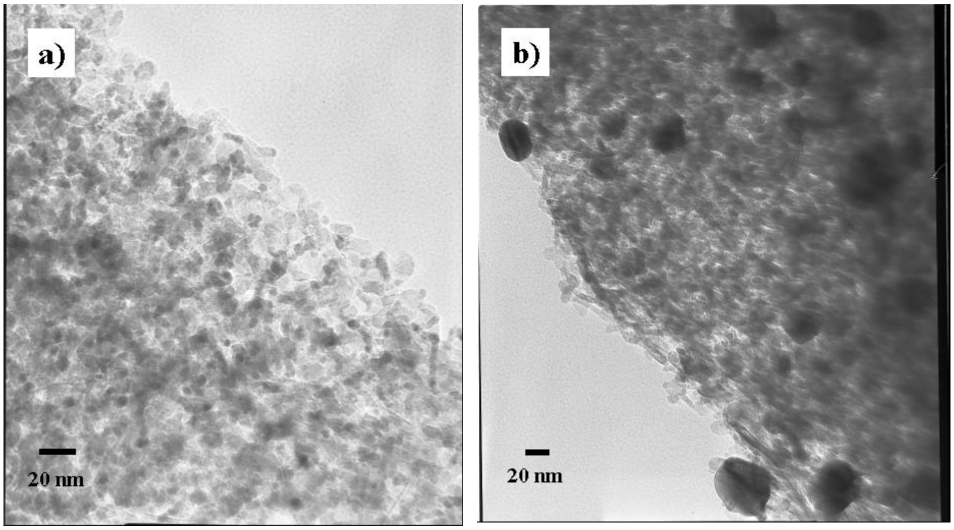

Figure 6.1: TEM photograph of a) Pd/Al_2O_3 and b) Br-F-Pd/Al_2O_3 (loading of Br or F = 1.0 wt%) catalysts.

The experimental procedure for the direct oxidation of H_2 to H_2O_2 by O_2 and destruction of H_2O_2 in absence H_2 (i.e. in presence of air) and presence of H_2 over the Pd catalysts have already been described in section 2.5.1, 2.5.2 and 2.5.3, respectively. The H_2-to-H_2O_2 oxidation reaction over the catalysts was carried out in a magnetically stirred glass reactor (capacity: 100 cm^3), containing 0.1 g catalyst and an aqueous acidic (H_3PO_4) reaction medium (50 cm^3), under vigorous stirring at the following reaction conditions: concentration of acid (H_3PO_4) = 0 – 5 mol/dm^3, O_2/H_2 ratio = 0.25 – 2.0, gas (H_2 and O_2) hourly space velocity (GHSV) = 5.8 – 23.4 h^{-1}, reaction period = 0.0 – 8.0 h, temperature = 5º - 50 ºC and pressure = atmospheric (95 kPa). The H_2O_2 formed was determined by the iodometric titration. The GHSV is defined as the volume of the two gases (H_2 and O_2) passed through per unit volume of the liquid reaction medium per hour. The product gases were collected, using a constant pressure gas collector [26]. The H_2 conversion, H_2O_2 yield and H_2O_2 selectivity was calculated by using the equations given in the section 2.5.1.

The H_2O_2 decomposition (in the absence of H_2) and hydrogenation (in the presence of H_2) reactions over the catalyst were carried out in the same reactor described above, in the presence of static air and static H_2, respectively, by injecting 1.0 cm^3 of aqueous 30 wt% H_2O_2 through a rubber septum in the acidic reaction medium (50 cm^3), containing 0.1 g catalyst, under vigorous stirring and following the reactions as a function of time.

The H_2O_2 destruction during the H_2-to-H_2O_2 oxidation with different O_2/H_2 feed gas ratios in the acidic medium was studied by injecting at the reaction start a 4.0 mmol of H_2O_2 in the acidic (0.1 M H_3PO_4) reaction medium and determining the H_2O_2 consumed during the oxidation for 1 h (at 27 ºC). The influence of initial concentration of H_2O_2 on the net H_2O_2 formation in the H_2-to-H_2O_2 oxidation (for O_2/H_2 = 1.0) was studied by injecting different amounts of H_2O_2 in the acidic reaction medium and determining in each case the H_2O_2 in the reaction mixture after the reaction period of 1 h.

6.3. Heterogeneity Test of the H_2-to-H_2O_2 Oxidation over the Br-F-Pd/Al_2O_3 catalyst

In order to confirm the fact that the H_2-to-H_2O_2 oxidation over the Br-F-Pd/Al_2O_3 catalyst is heterogeneously catalyzed process, the reaction was carried out as a function time, as indicated in Figure 6.2.

In the presence of the catalyst, the H_2O_2 formation in the oxidation reaction increased almost linearly with the reaction time (Figure 6.2a). However, when the catalyst from the reaction mixture was removed after the reaction period of 0.25 h, there was no further increase in the H_2O_2 formation in the reaction (Figure 6.2b). Also, when the reaction was carried out without the catalyst in the reaction medium (which was contacted with the catalyst under vigorous stirring at 27 ºC before using the medium for the reaction), no H2O2 formation was detected (Figure 6.2c). These results clearly show that the H_2-to-H_2O_2 oxidation over the catalyst is a heterogeneously catalyzed reaction.

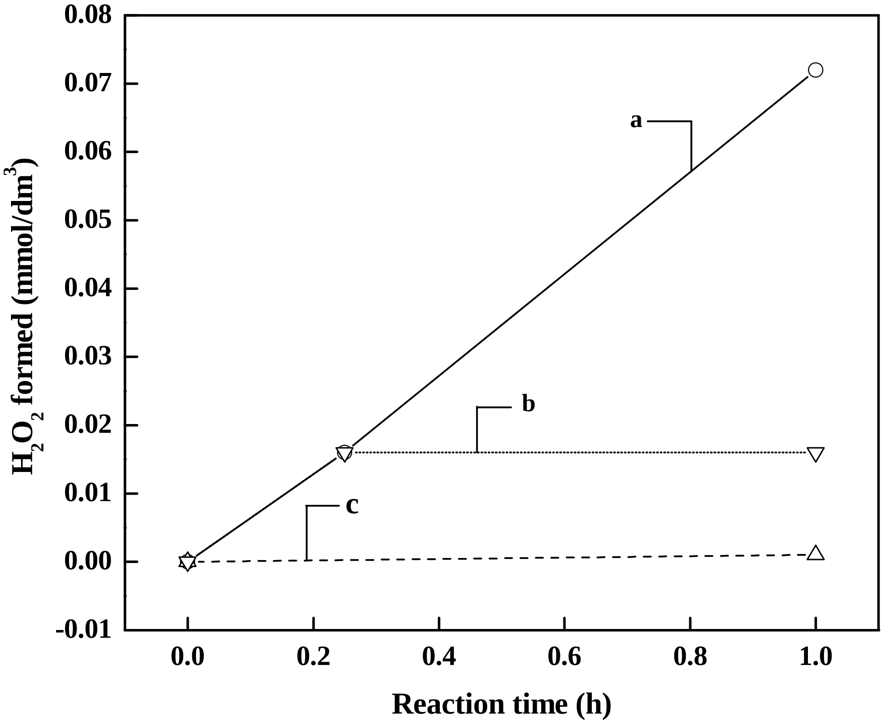

Figure 6.2: Heterogeneity test for the H_2-to-H_2O_2 oxidation reaction (H_2/O_2) over the Br-F-Pd/Al_2O_3 catalyst in the acidic (0.1 M H_3PO_4) reaction medium at 27 ºC [a) for the reaction without catalyst removal during the entire reaction period, b) for the reaction when the catalyst was removed from the reaction mixture after the reaction period of 0.25 f and c) for the reaction without the catalyst in the acidic medium, which was contacted with the catalyst (0.1 g) under vigorous stirring at 27 ºC for 0.5 h before the reaction]

6.4. Influence of the Different Process Parameters on the H_2-to-H_2O_2 Oxidation over the Br-F-Pd/Al_2O_3 Catalyst

Effects of the various process conditions (viz. concentration of phosphoric acid in the reaction medium, reaction temperature, space velocity of H_2 and O_2 feed gases, O_2/H_2 mole ratio in the feed gases, initial concentration of H_2O_2, and reaction period) on the net formation of H_2O_2 in the H_2-to-H_2O_2 oxidation and also on the H_2O_2 decomposition and hydrogenation reactions in the aqueous acidic reaction medium (at atmospheric pressure) have been investigated, as discussed below.

6.4.1. Influence of the Acid Concentration

Results showing a very strong influence of the concentration of phosphoric acid in the reaction medium on the H_2O_2 formation in the H_2-to-H_2O_2 oxidation and also on the H_2O_2 decomposition (in the absence of H_2) and hydrogenation (in H_2) reactions (at 27 ºC) have been presented on Figures 6.3 and 6.4, respectively.

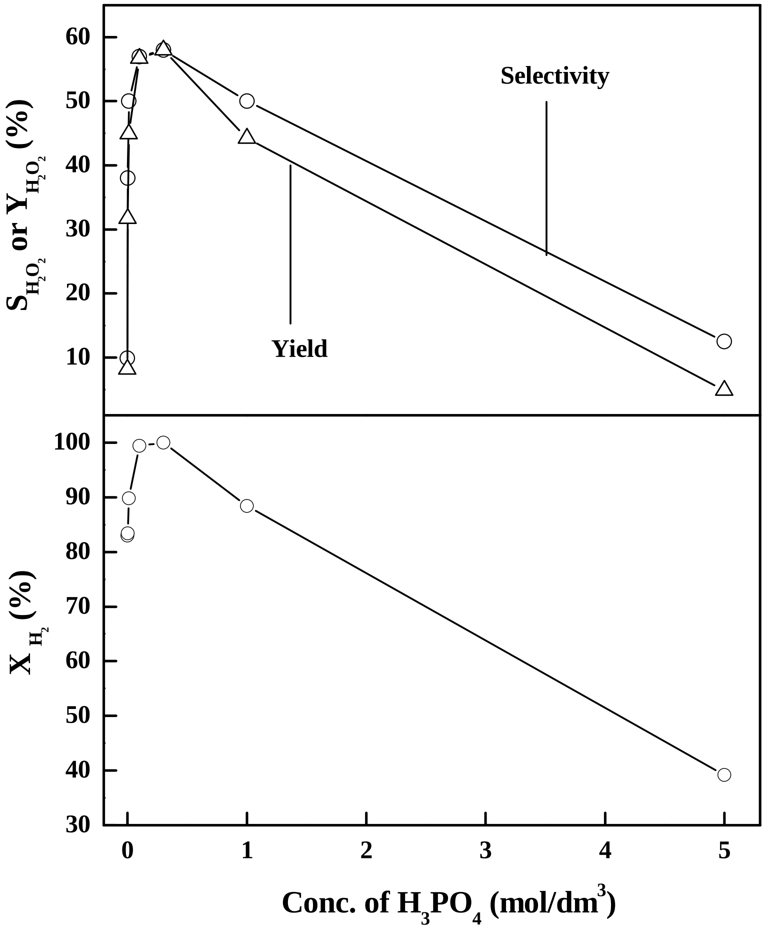

Figure 6.3: Effect of the concentration of H_3PO_4 in aqueous reaction medium on the H_2 conversion (X_{H2}) and H_2O_2 selectivity (S_{H2O2}) and yield (Y_{H2O2}) in the H_2-to-H_2O_2 oxidation over the Br-F-Pd/Al_2O_3 catalyst [O_2/H_2 feed ratio = 1.0, GHSV = 5.8 h^{-1}, reaction temperature = 27 ºC, reaction period = 1.0 h].

The Results (Figure 6.3) show that, with increasing the acid concentration, the H_2 conversion, H_2O_2 selectivity and H_2O_2 yield are first increased sharply at the lower acid concentrations up to 0.3 mol/dm^3) and then decreased at the higher acid concentration. At the optimum acid concentration (0.1 – 0.3 mol/dm^3), the H_2 conversion is complete (100 %) with a high H_2O_2 selectivity/yield (58 %). At the very low acid concentration (< 0.02 mol/dm^3), the catalyst yet shows good H_2 conversion activity but very poor activity for the H_2O_2 formation. Whereas, at the very high acid concentration (5.0 mol/dm^3), the catalyst showed poor H_2 conversion activity and H_2O_2 formation selectivity in the process.

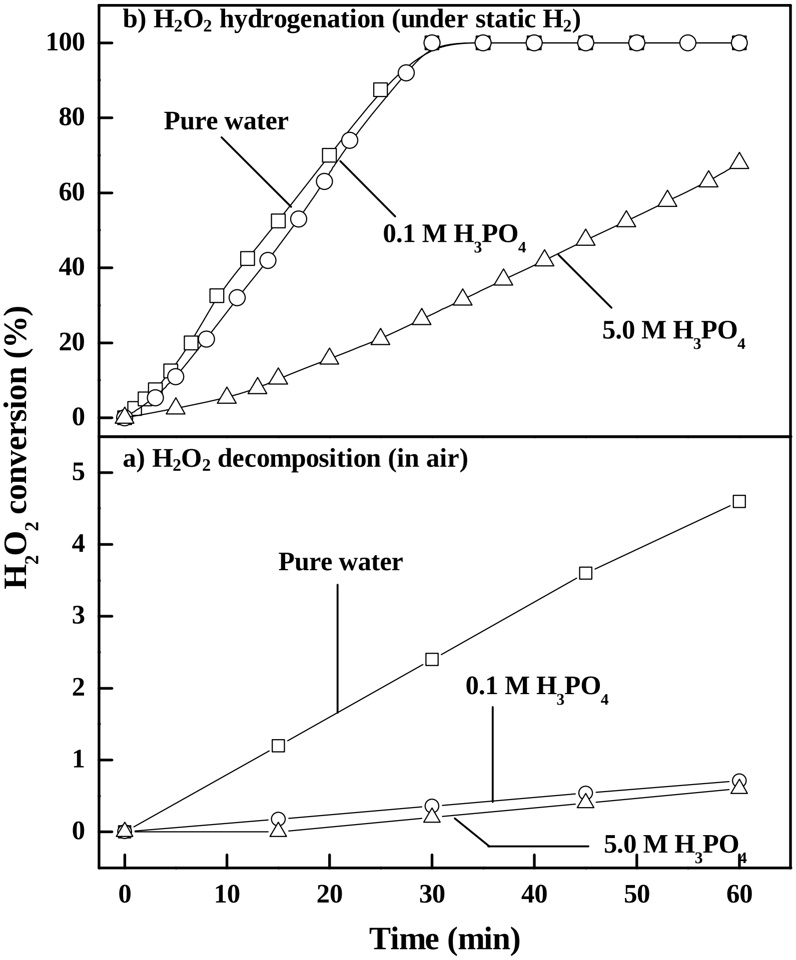

Figure 6.4: Effect of the acid (H_3PO_4) concentration in reaction medium on the H_2O_2 decomposition (in air) (a) and hydrogenation (under static H_2) (b) over the Br-F-Pd/Al_2O_3 catalyst in aqueous medium at 27 ºC.

The results in Figure 6.4 reveal that, at the lower acid concentrations (0 – 0.1 mol/dm^3), both the H_2O_2 decomposition and hydrogenation activities of the catalyst are decreased appreciably with increasing the acid concentration. The observed increased in the H_2O_2 formation at the lower acid concentrations (≤ 0.3 mol/dm^3) is, therefore, quite consistent with this. However, the H_2O_2 destruction activities are also further decreased with increasing the acid concentration from 0.1 to 5.0 mol/dm^3. Hence, the H_2O_2 formation is expected to increase with increasing the acid concentration, even above the acid concentration of 0.3 mol/dm^3. But this is not the case (Figure 6.3).

The observed poor catalyst performance for the H_2O_2 formation (both the H_2O_2 selectivity and yield) at the higher acid concentrations is expected mostly because of both the poor activity and selectivity of the catalyst in the presence of high acid concentration. No Pd leaching from the catalyst was observed in the reaction for the period of 1.0 h, when the acid concentration in the medium was low (≤ 0.3 mol/dm^3). But, at the higher acid concentrations (≥ 1.0 mol/dm^3), an appreciable leaching of Pd was observed. Moreover, the rate of dissolution of the catalyst support (Al_2O_3) is also expected to be faster at the higher acid concentrations. The leaching of both the active catalyst component(s) and support, which destabilizes the catalyst, seems to be mostly responsible for the poor catalyst performance at the higher acid concentrations. A change in the solubility of reactant gases (H_2 and O_2) at the high acid concentration may also affect the H_2 conversion and/or the H_2O_2 selectivity.

The results, however, reveal the importance of the presence of acid at its optimum concentration for achieving the high net H_2O_2 formation over the Br-F-Pd/Al_2O_3 catalyst. This is consistent with our earlier studies [13,21], which showed that the presence (in the reaction medium) of not only chloride or bromide promoter but also that of protons is essential for drastically increasing the H_2O_2 formation in the H_2-to-H_2O_2 oxidation over Pd/Al_2O_3 and Pd/C catalysts.

6.4.2. Influence of the Reaction Temperature

Results showing the effects of reaction temperature on the H_2O_2 formation and H_2O_2 destruction reactions over the catalyst in the acidic (0.1 M H_3PO_4) reaction medium are presented in Figures 6.5 and 6.6, respectively.

At the lower temperatures (5º - 27 ºC), the H_2 conversion is markedly increased and then leveled off (after 27 ºC) with increasing the reaction temperature (Figure 6.5a). The H_2O_2

selectivity is, however, continuously decreased appreciably and the H_2O_2 yield is passed through a maximum (at 27 ºC) with increasing the temperature (Figure 6.5b). Both the H_2O_2 decomposition and hydrogenation rates over the catalyst in the acidic reaction medium are decreased markedly with increasing the temperature (Figure 6.6). The decrease in the H_2O_2 selectivity (Figure 6.5b) in the H_2-to-H_2O_2 oxidation is consistent with the increase in both the H_2O_2 decomposition and hydrogenation activities of the catalyst (Figure 6.6).

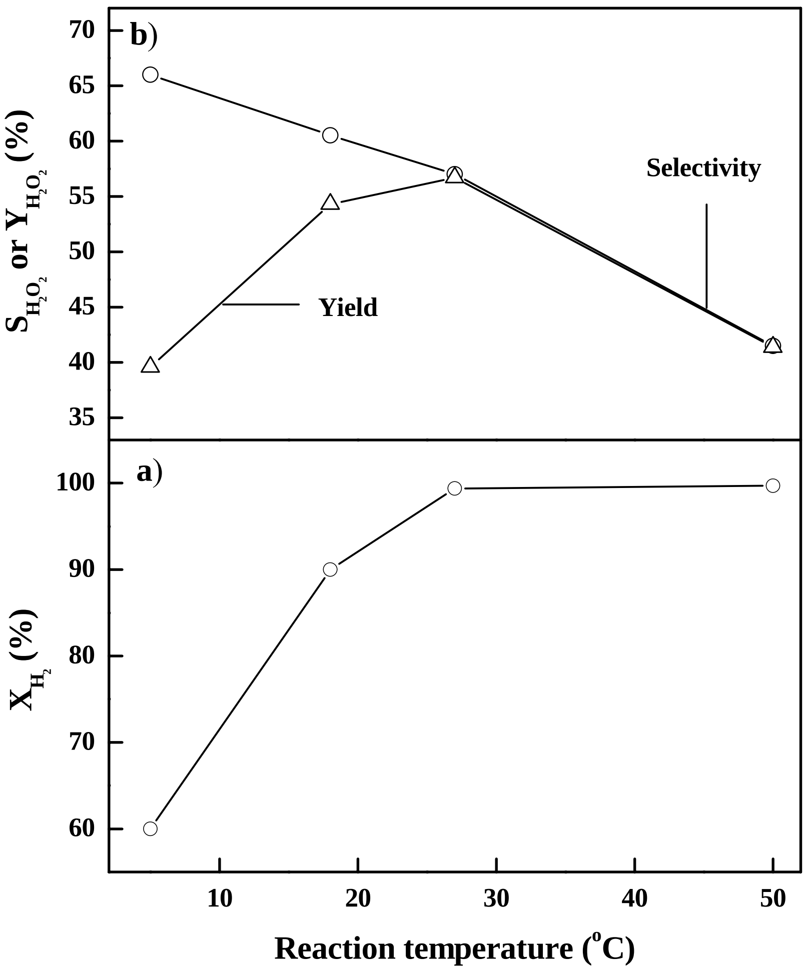

Figure 6.5: Effect of the reaction temperature on the H_2 conversion (X_{H2}) and H_2O_2 selectivity (S_{H2O2}) and yield (Y_{H2O2}) in the H_2-to-H_2O_2 oxidation over the Br-F-Pd/Al_2O_3 catalyst [O_2/H_2 feed ratio = 1.0, reaction medium = 0.1 M H_3PO_4, GHSV = 5.8 h^{-1}, reaction period = 1.0 h].

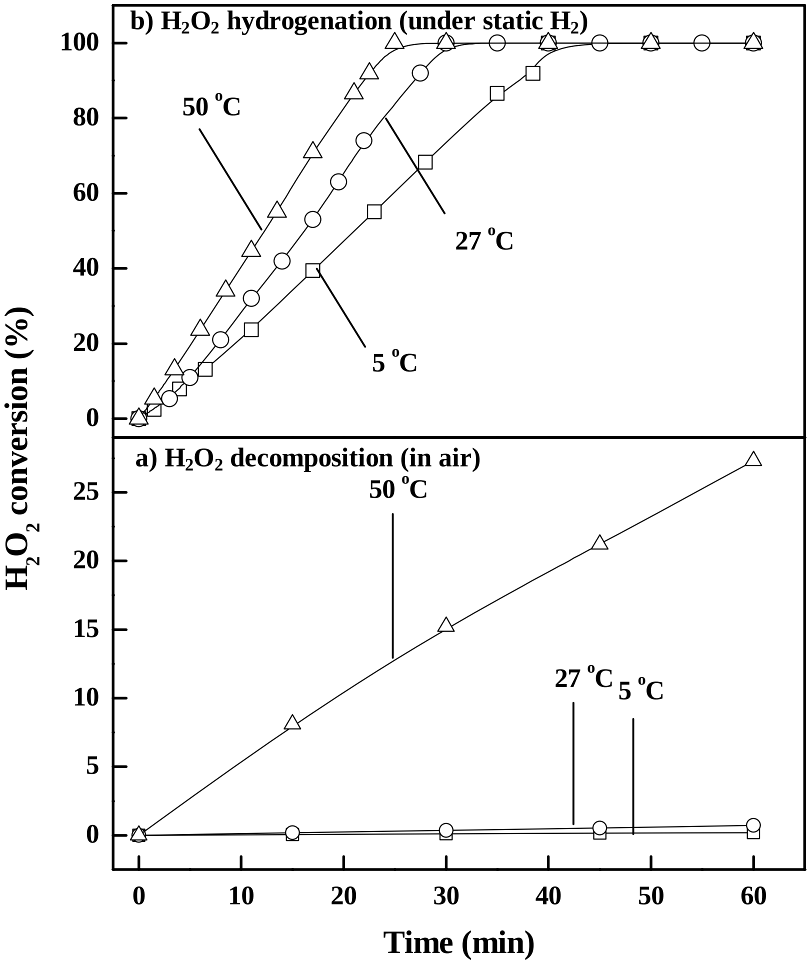

Figure 6.6: Effect of the reaction temperature on the H_2O_2 decomposition (in air) (a) and hydrogenation (under static H_2) (b) over the Br-F-Pd/Al_2O_3 catalyst in acidic (0.1 M H_3PO_4) medium at 27 ºC.

Under the reaction conditions, the H_2O_2 hydrogenation activity of the catalyst is much larger than its H_2O_2 decomposition activity (Figures 6.4 and 6.6). The effect of temperature on the H_2O_2 hydrogenation is, however, smaller than that on the H_2O_2 decomposition; the increase in the rate of H_2O_2 decomposition with increasing the temperature from 27 ºC to 50 ºC is quite large (Figure 6.6). The lower H_2O_2 selectivity at the higher temperature is, therefore, attributed to the increased rate of both the H_2O_2 destruction reactions at the higher temperature. However, at the lower temperatures (5 º and 27 ºC) the H_2O_2 hydrogenation is mainly responsible for controlling the H_2O_2 selectivity.

6.4.3. Influence of the GHSV

Results in Figure 6.7 show a strong influence of the GHSV (gas hourly space velocity, which is defined as the volume of H_2 and O_2 (1:1) gases passed thorough the reactor per unit volume of the liquid reaction medium per hour) on the H_2 conversion and H_2O_2 selectivity/yield in the H_2-to-H_2O_2 oxidation in the acidic (0.1 M H_3PO_4) medium.

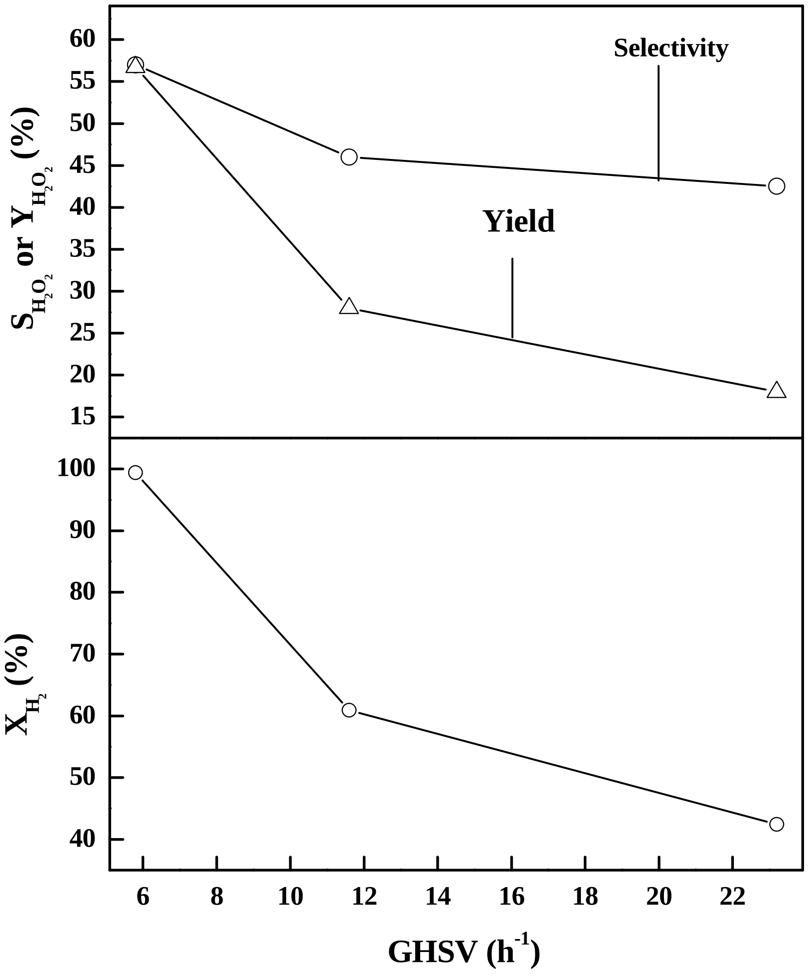

Figure 6.7: Effect of the gas hourly space velocity (GHSV) of H_2 and O_2 feed on the H_2 conversion (X_{H2}) and H_2O_2 selectivity (S_{H2O2}) and yield (Y_{H2O2}) in the H_2-to-H_2O_2 oxidation over the Br-F-Pd/Al_2O_3 catalyst [O_2/H_2 feed ratio = 1.0, reaction medium = 0.1 M H_3PO_4, reaction temperature = 27 ºC, reaction period = 1.0 h].

Both the H_2 conversion and H_2O_2 selectivity (and consequently the H_2O_2 yield) are decreased with the gas space velocity. The H_2 conversion is decreased because of the decrease in the contact time of the gaseous reactants in the reaction medium. However, the decrease of the H_2O_2 selectivity with the gas space velocity is unexpected. The decrease in the selectivity may be due to the surface/sub-surface oxidation of Pd of the catalyst to a large extent by the larger amount of H_2O_2 accumulated in the liquid reaction mixture at the larger gas space velocity, discussed later.

6.4.4. Influence of the O_2/H_2 Ratio

Results showing a very strong influence of the O_2/H_2 mole ratio in feed on the H_2 conversion and H_2O_2 formation in the H_2-to-H_2O_2 oxidation over the catalyst in the acidic (0.1 M H_3PO_4) medium are presented in Figure 6.8.

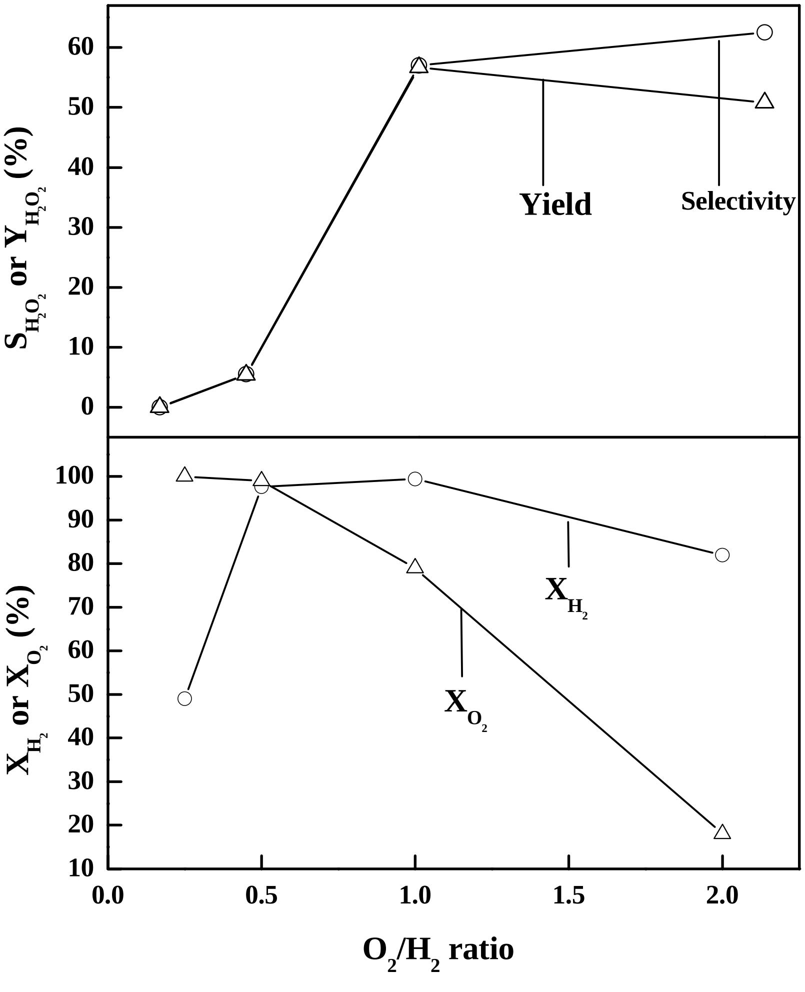

Figure 6.8: Effect of the O_2/ H_2 feed ratio on the H_2 conversion (X_{H2}) and H_2O_2 selectivity (S_{H2O2}) and yield (Y_{H2O2}) in the H_2-to-H_2O_2 oxidation over the Br-F-Pd/Al_2O_3 catalyst [reaction medium = 0.1 M H_3PO_4, GHSV = 5.8 h^{-1}, reaction temperature = 27 ºC, reaction period = 1.0 h].

With increasing the O_2/H_2 ratio from 0.25 to 2.0 (or decreasing the H_2/O_2 ratio from 4.0 to 0.5), the H_2 conversion and H_2O_2 yield increased very appreciably up to the O_2/H_2 ratio of 1.0 but decreased after passing through a maximum (at O_2/H_2 = 1.0). The O_2 conversion decreased continuously from 100 to 18%. The H_2O_2 selectivity, however, increased drastically almost from zero (for O_2/H_2 = 0.25 or H_2/O_2 = 4.0) to above 60 % (for O_2/H_2 = 2.0 or H_2/O_2 = 0.5), the increase was, however, exponential up to the O_2/H_2 ratio of 1.0. The results reveal that the optimum O_2/H_2 ratio for the highest H_2O_2 formation in the direct oxidation process is 1.0.

The observed very strong influence of the O_2/H_2 ratio on the H_2 conversion and H_2O_2 selectivity/yield is attributed mostly to a change in both the oxidation state of Pd at the catalyst surface and the H_2O_2 hydrogenation rate, depending upon the concentration of H_2 (C_{H2}) relative to that of O_2 (C_{O2}) in the feed, as follows.

For $C_{H2} > C_{O2}$ (i.e. $O_2/H_2 < 1.0$), mostly Pd^o is expected to be present on the catalyst surface due to the reduction of surface PdO to Pd^o by H_2. Hence, the catalyst showed high activity for the O_2 conversion (100 %) and also for the H_2O_2 hydrogenation. High H_2O_2 hydrogenation rates over the reduced catalyst are also expected because of the higher H_2 concentration. It may be noted that the observed low H_2 conversion (50 %) at the O_2/H_2 ratio of 0.25 is because of the presence of limited O_2 (which was completely converted in the process).

For $C_{O2} > C_{H2}$ (i.e. $O_2/H_2 > 1.0$) at least part of the surface Pd is oxidized to PdO. The catalyst with its Pd surface particularly covered with oxygen is expected to show lower H_2 conversion and H_2O_2 hydrogenation activities [5]. Also, at the lower H_2 concentrations, lower H_2O_2 hydrogenation rates are expected, leading to the higher selectivity for H_2O_2.

In order to confirm the increase in the H_2O_2 hydrogenation activity of the catalyst at the higher H_2 concentration relative to the concentration of O_2, the H_2-to-H_2O_2 oxidation over the catalyst was carried out in the presence of H_2O_2 added to the acidic reaction medium, before starting the reaction, at the different O_2/H_2 ratios. The interesting results are displayed in Figure 6.9.

With increasing the O_2/H_2 ratio the H_2O_2 conversion/destruction (by reaction 6.3 and/or 6.4) during the H_2-to-H_2O_2 oxidation is decreased up to the O_2/H_2 ratio of 1.0 and, after passing through a minimum (at O_2/H_2 = 1.0), it is increased. This clearly shows that the H_2O_2 destruction activity of the catalyst during the H_2-to-H_2O_2 oxidation depends strongly upon the O_2/H_2 ratio; it is lowest at the optimum O_2/H_2 ratio of 1.0 found for the H_2-to-H_2O_2 oxidation.

The observed very high H_2O_2 conversion for the O_2/H_2 ratio of 0.0 and 0.25 is due to the high rates of H_2O_2 hydrogenation at the higher H_2 concentrations ($C_{H2} >> C_{O2}$). The rate of H_2O_2 hydrogenation is reduced with decreasing the relative H_2 concentration up to the O_2/H_2 ratio of 1.0. However, the observed in the H_2O_2 destruction at the higher O_2/H_2 ratio (2.0) might have resulted from a large decrease in the H_2O_2 formation in the H_2-to-H_2O_2 oxidation due to the decreased H_2O_2 formation activity of the catalyst because of its oxidation (surface Pd to PdO) at the higher O_2 concentration and also due to the lower H_2 input to the reactor. Our earlier studies [5] also indicated that the catalytic activity of reduced supported Pd catalysts in the H_2-to-H_2O_2 oxidation is decreased appreciably after their oxidation.

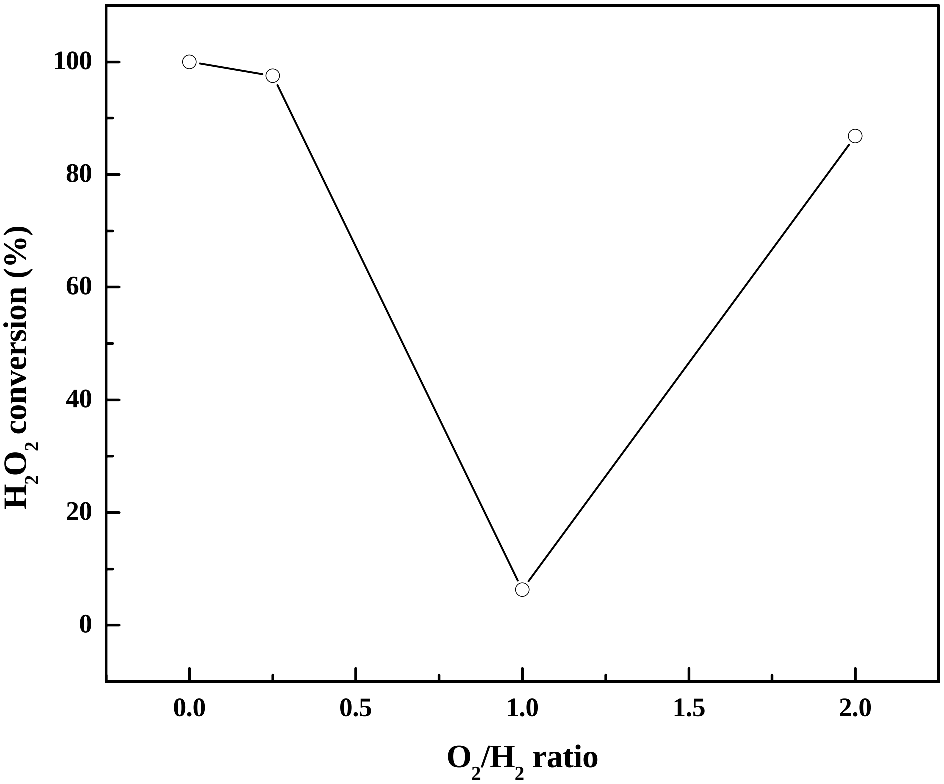

Figure 6.9: Effect of the O_2/H_2 gas feed ratio on the conversion of the H_2O_2, initially added in the reaction medium, during the H_2-to-H_2O_2 oxidation over the Br-F-Pd/Al_2O_3 catalyst [reaction medium = 0.1 M H_3PO_4, GHSV = 5.8 h^{-1}, initial concentration of H_2O_2 in the medium = 80 mmol/dm^3, reaction temperature = 27 °C, reaction period = 1.0 h].

6.4.5. Influence of the Initial Concentration of H_2O_2

Results showing the effect of the amount of H_2O_2 initially present in the reaction medium on the net H_2O_2 formed in the H_2-toH_2O_2 oxidation are presented in Figure 6.10.

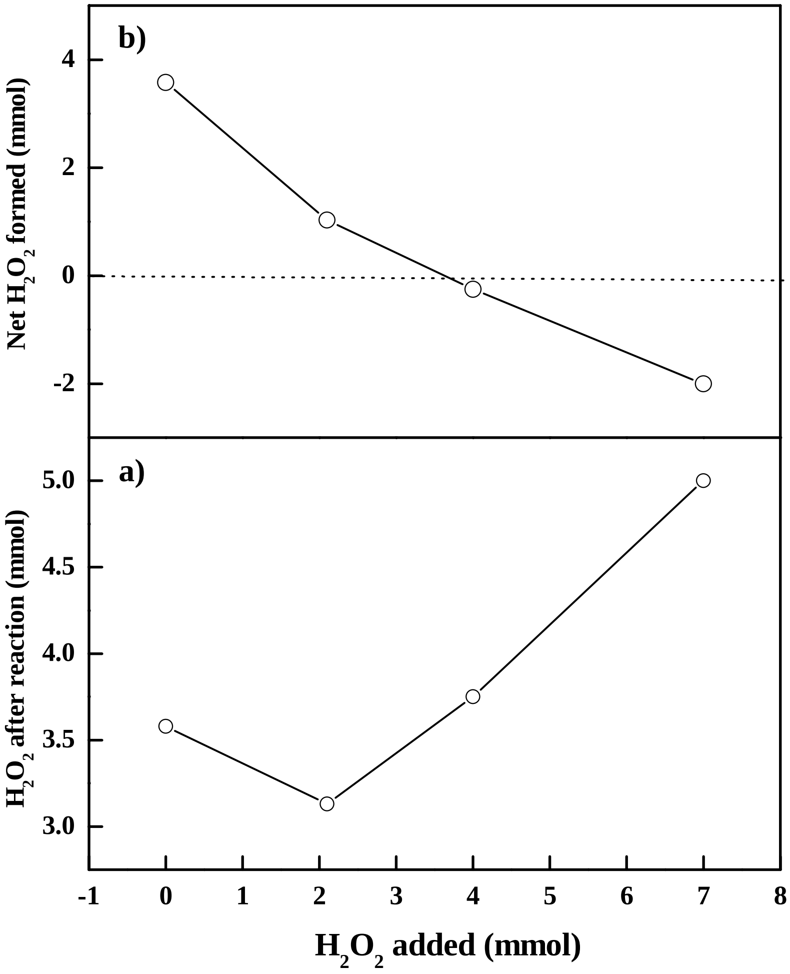

Figure 6.10: Effect of the amount of H_2O_2 initially added to the acidic (0.1 M H_3PO_4) reaction medium on the H_2O_2 present after the reaction (a) and net formation of H_2O_2 (b) in the H_2-to-H_2O_2 oxidation over the Br-F-Pd/Al_2O_3 catalyst [O_2/H_2 feed ratio = 1.0, reaction medium = 0.1 M H_3PO_4, GHSV = 5.8 h^{-1}, reaction temperature = 27 ºC, reaction period = 1.0 h].

The net formation of H_2O_2 is decreased sharply with increasing the initial amount of H_2O_2 present in the reaction medium (Figure 6.10). The observed negative net H_2O_2 formation indicates that the rate of H_2O_2 destruction is higher than the rate of H_2O_2 formation in the H_2-

to-H_2O_2 oxidation. The results clearly indicate that the presence of larger amount of H_2O_2 ultimately results in a drastic decrease in the net H_2O_2 formation in the H_2-to-H_2O_2 oxidation. The surface/sub-surface oxidation of Pd by the H_2O_2 [4] added at a start of the H_2-to-H_2O_2 oxidation may very likely be responsible for the observed decrease in the net H_2O_2 formation.

The H_2O_2 formation activity/selectivity of the catalyst in the H_2-to-H_2O_2 oxidation is controlled through the modification of surface properties (viz. oxidation state of Pd) of the catalyst by its environment (reducing or oxidizing) during the process.

6.4.6. Influence of the Reaction Period

Results showing the influence of reaction period on the H_2 conversion and also on both the H_2O_2 selectivity and yield in the H_2-to-H_2O_2 oxidation (with H_2:O_2 = 1:1) over the catalyst (at 27 ºC) in the acidic (0.1 M H_3PO_4) reaction medium are presented in Figure 6.11. Data for the concentration of H_2O_2 at the different reaction periods are also included in Figure 6.11.

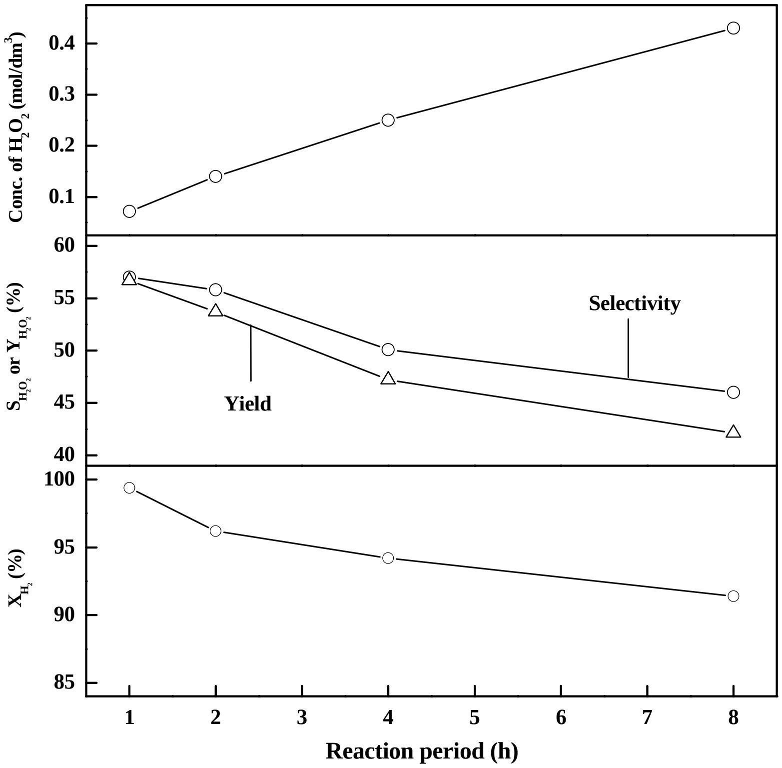

Figure 6.11: Effect of the reaction period on the H_2 conversion (X_{H2}) and H_2O_2 selectivity (S_{H2O2}) and yield (Y_{H2O2}) in the H_2-to-H_2O_2 oxidation over the Br-F-Pd/Al_2O_3 catalyst [O_2/H_2 feed ratio = 1.0, reaction medium = 0.1 M H_3PO_4, GHSV = 5.8 h^{-1}, reaction temperature = 27 ºC].

The results reveal that, not only the H_2 conversion and H_2O_2 yield but also the H_2O_2 selectivity are decreased appreciably with increasing the reaction period. Earlier Edward et. al. [16] have also observed a large decrease in the H_2O_2 productivity with increasing the reaction time in the H_2-to-H_2O_2 oxidation over Au-Pd/TiO_2 catalyst.

The decrease in both the catalytic activity and selectivity may be attributed mostly to the continuous deactivation of the catalyst due to the surface/sub-surface oxidation of Pd by the H_2O_2 produced and accumulated during the process. This is consistent with the earlier studies showing the effect of the initially present H_2O_2 in the reaction mixture (Figure 6.10).

It is also interesting to note from the results that the catalyst showed very high activity and selectivity in the initial short reaction period. We observed that, in the initial period of about 5 min, no unconverted gas was collected, indicating a complete consumption of both the H_2 and O_2 gases (1:1) from the gaseous feed with almost a complete (100 %) conversion of H_2 to H_2O_2, according to the H_2-to-H_2O_2 oxidation (reaction 6.1) stoichiometry. However, after the initial short period a gradual increase in the volume of unconverted H_2 and O_2 gases with the reaction period was observed. A similar observation was also made by us in case of the H_2-to-H_2O_2 oxidation (at 27 ºC) over Pd/Al_2O_3 catalyst in the acidic (0.1 M H_3PO_4) medium, containing bromide anions (1.0 mmol/dm^3) as the catalyst promoter, under the similar reaction conditions. After the reaction period of 0.13, 0.25, 0.5 and 1.0 h, the H_2 conversion was 100, 100, 100 and 95 %, respectively, and the H_2O_2 selectivity was 79, 71, 61 and 53 %, respectively.

The above observations point to the fact that the parallel direct H_2 combustion to water (reaction 6.2) is likely to be almost totally inhibited due to the Br catalyst promoter during the initial short period. The H_2O_2 decomposition (in absence of H_2) is also drastically inhibited by the bromide promoter [13,21,23,27]. The H_2O_2 selectivity is, therefore, controlled essentially by the H_2O_2 hydrogenation (which is not strongly inhibited by the promoter [13,21,23]), depending upon the concentration of H_2 relative to that of O_2, in the presence of Br promoter (which, in the presence of H_2, very strongly inhibits the fast H_2O_2 decomposition, while promoting the relatively slower H_2O_2 hydrogenation [13,21,23]). However, the H_2O_2 hydrogenation over the catalyst is zero order with respect to H_2O_2 (Figures 6.4b and 6.6b), and the same is true also for the hydrogenation over the other supported Pd catalysts [13,21,23]. Hence, the observed appreciable decrease in the H_2O_2 selectivity with the reaction time may be due to the increase in the rate of H_2O_2 decomposition (which was found to be a first order reaction with respect to H_2O_2 for the different supported Pd catalysts [4,5,13,21,27]) and/or because of a promotion of the parallel direct water forming reaction (reaction 6.2) after the surface/sub-surface Pd oxidation by the accumulated H_2O_2.

6.5. Conclusions

The H_2 conversion and H_2O_2 selectivity (or the net H_2O_2 formation) in the direct H_2-to-H_2O_2 oxidation over the Br-F-Pd/Al_2O_3 catalyst in the aqueous acidic (H_3PO_4) reaction medium are strongly influenced by the different process conditions, leading to the following conclusions:

1) Both the conversion and selectivity are sharply increased, passed through a maximum at the optimum acid concentration (between 0.1 and 0.3 mol/dm^3) and then decreased very appreciably with increasing the acid concentration in the reaction medium. The H_2O_2 decomposition and hydrogenation activities of the catalyst, however, decreased with the acid concentration.
2) The H_2 conversion is increased but the selectivity is decreased with increasing the reaction temperature; the highest H_2O_2 yield is observed at the optimum temperature of 27 ºC. The decrease in the selectivity is due to the increase in both the H_2O_2 decomposition and hydrogenation activities of the catalyst.
3) Not only the conversion but also the selectivity is decreased with increasing the GHSV of the H_2 and O_2 feed.
4) The selectivity is increased continuously but the conversion and H_2O_2 yield are passed through a maximum (at the optimum O_2/H_2 feed gas ratio of 1.0) with increasing the O_2/H_2 ratio. The highest H_2O_2 formation is achieved when the relative concentration of H_2 and O_2 is 1:1. At the higher concentration of H_2 relative to that of O_2, both the selectivity and yield are very much lower because of the high rates of H_2O_2 hydrogenation during the H_2-to-H_2O_2 oxidation.
5) The net H_2O_2 formation in the H_2-to-H_2O_2 oxidation is reduced because of the presence of H_2O_2 in the reaction medium at the reaction start; it is decreased continuously and ultimately became –ve with increasing the initial concentration of H_2O_2.

6) The conversion is decreased continuously with increasing the reaction period, mostly due to the catalyst deactivation resulting from the surface/sub-surface oxidation of Pd to PdO by the H_2O_2 formed and accumulated during the reaction. The selectivity is also decreased with the reaction period mostly due to the increase in the H_2O_2 decomposition rate with increasing the H_2O_2 concentration and/or promotion of the parallel direct H_2-to-H_2O_2 oxidation on the oxidized catalyst. The fresh catalyst showed almost 100 % H_2O_2 selectivity and yield in the initial short reaction period of about 5 min, indicating the Br and F catalyst promoters almost totally inhibit the direct H_2-to-H_2O_2 oxidation over the Br-F-Pd/Al_2O_3 catalyst.
7) The H_2O_2 formation activity/selectivity of the catalyst in the H_2-to-H_2O_2 oxidation is controlled through the modification of surface properties (viz. oxidation state of Pd) of the catalyst by its environment (reducing or oxidizing) during the process.

6.6. References

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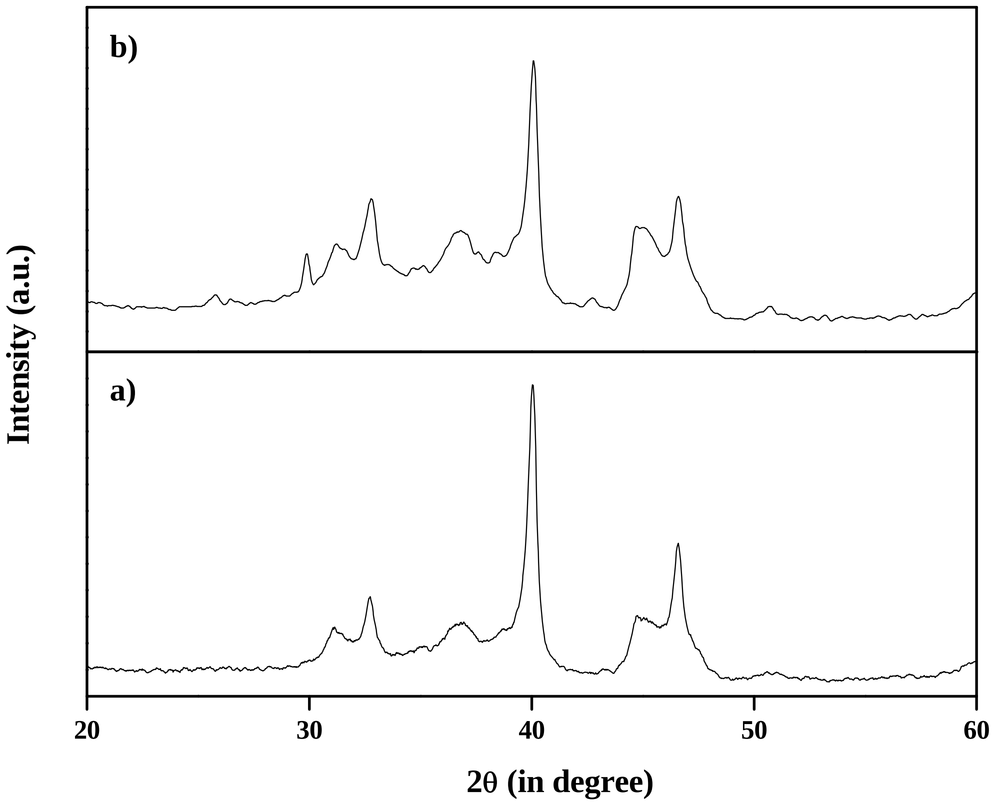
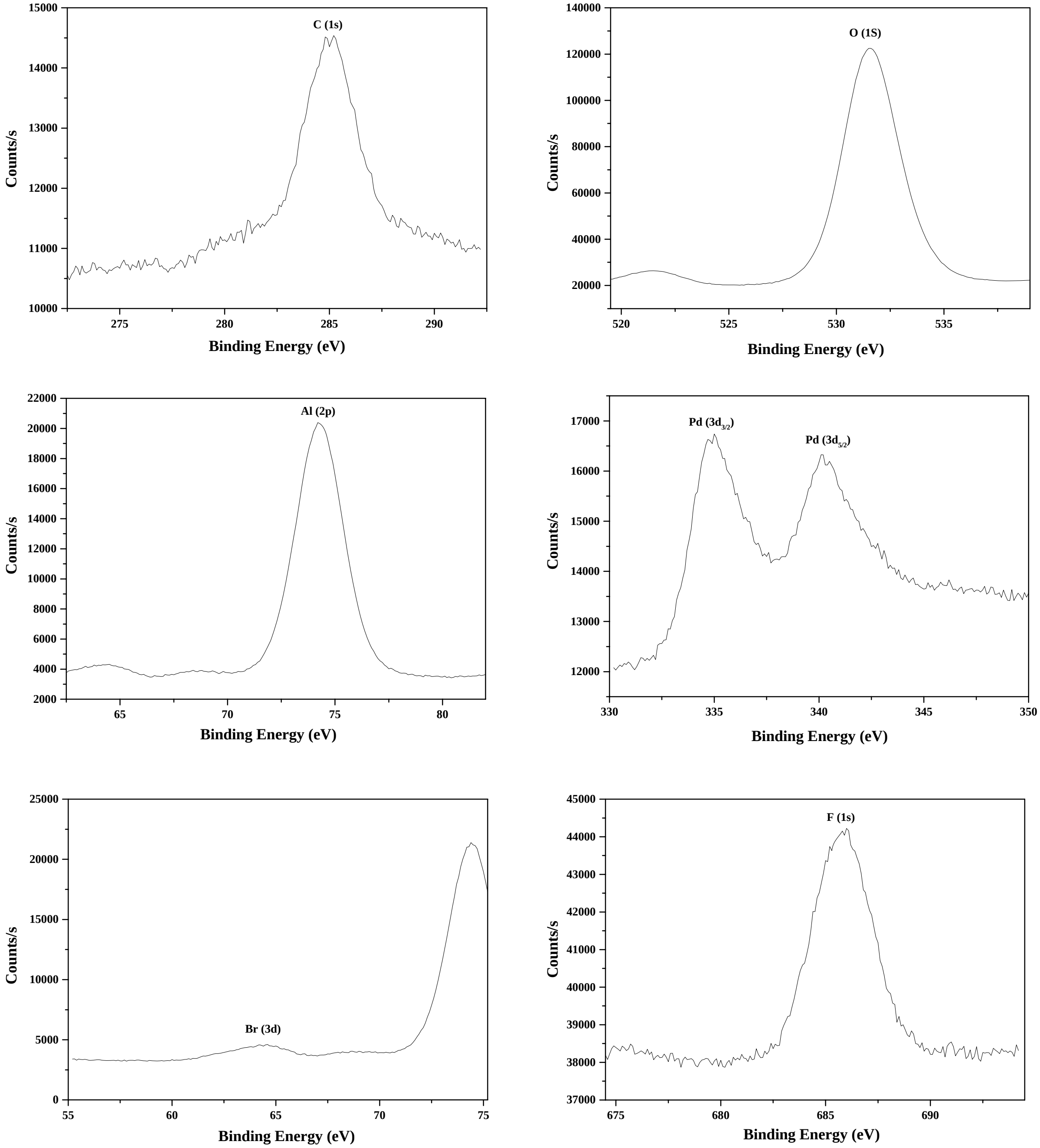
Appendix



Appendix 6.1: XRD of a) Pd/Al_2O_3 and b) Br-F-PdAl_2O_3 (loading of Br and F = 1.0 wt%) catalysts.



Appendix 6.2: XPS spectra of Br(1 wt%) – F(1 wt%) – Pd/Al_2O_3 catalyst before its use in the reaction.

Chapter 7

Factors Strongly Influencing H_2O_2 Decomposition and/or Hydrogenation over Pd/Al_2O_3 Catalysts in the Presence of H_2

Chapter 7

Factors Strongly Influencing H_2O_2 Decomposition and/or Hydrogenation over Pd/Al_2O_3 Catalysts in the Presence of H_2

7.1. Background and Objective of the present work

Direct oxidation of H_2 by O_2 to H_2O_2 (a clean, versatile oxidizing agent) is a green process of great practical importance for meeting the ever increasing demand of H_2O_2 for the paper/pulp manufacture, water purification/disinfection, waste-water treatment and organic oxidations. It is covered in a number of patents but not yet commercialized. One of the important reasons for the low net formation of H_2O_2 in the H_2-to-H_2O_2 oxidation is due to the parallel and consecutive H_2O_2 destruction reactions ($H_2O_2 \rightarrow H_2O + 0.5\ O_2$ and $H_2O_2 + H_2 \rightarrow 2\ H_2O$) over the same catalyst, along with the H_2-to-H_2O_2 oxidation. Both the H_2O_2 destruction reactions are highly favored thermodynamically.

In the recent years, the H_2-to-H_2O_2 oxidation process has attracted attention of many researchers and a number of studies have been reported for improving the process performance, using different supported Pd catalysts [1-14]. The catalyst performance for the H_2O_2 formation was drastically improved by the oxidation of Pd to PdO [2,4,6,13] or by the addition of chloride or bromide anions in the acidic reaction medium [9,11,12] and also by the incorporation of halogen (viz. bromide anions) in the catalyst [10].

The H_2O_2 decomposition activity of supported Pd catalysts was found to decrease drastically due to their oxidation [2,4,6,13] and also because of the addition of different halide anions (Cl^-, Br^- or I^-) in the catalyst [10] or in the acidic reaction medium [11,12]. A number of recent studies have been reported on the H_2O_2 decomposition over different supported Pd catalysts [2,4,6,7,10,11,13] for correlating their H_2O_2 formation (in the H_2-to-H_2O_2 oxidation) with H_2O_2 decomposition activity and also on the kinetics of H_2O_2 decomposition over Pd/C [15]. Very recently, Choudhary et. al. have investigated in details the factors strongly influencing the H_2O_2 decomposition activity of Pd/C and other supported Pd catalysts [16]. However, the investigations on the hydrogenation of H_2O_2 over Pd catalysts are scarce [9,11,12].

Recently, Choudhary et. al. [11] showed that, in the presence of chloride or bromide anions and protons in the reaction medium, the net formation of H_2O_2 in the H_2-to-H_2O_2 oxidation over Pd/Al_2O_3 (or C) is controlled by the hydrogenation of H_2O_2 rather than its decomposition.

It is, therefore, of great practical interest to study in details the H_2O_2 hydrogenation and/or decomposition in the presence of hydrogen over the supported Pd catalyst used in the H_2-to-H_2O_2 oxidation. The work in this chapter was undertaken for this purpose. In this investigation, kinetics of the H_2O_2 destruction (by both the hydrogenation and decomposition reactions) in the presence of H_2 over the Pd/Al_2O_3 catalyst, used earlier in the H_2-to-H_2O_2 oxidation ([11] and chapters 5 and 6), have been thoroughly investigated, covering a wide range of different reaction conditions (viz. presence or absence of different halide anions and/or protons, concentration of acid (protons) and/or halide anions, reaction temperature, etc). The influence on the H_2O_2 destruction rates of the incorporation of different halogens in the catalyst and also of the bulk oxidation of Pd (from Pd/Al_2O_3) to PdO has been studied.

7.2. Catalysts and Brief Experimental Procedures

The Pd(5.0 wt%)/Al_2O_3 catalyst in its reduced form was obtained from Lancaster (UK). The catalyst in its oxidized form (PdO/Al_2O_3) was prepared from the Pd/Al_2O_3 by calcining it in air at 500 ºC for 4 h.

The presence of Pd in its reduced form (Pd^o) and oxidized form (PdO) in the catalyst was confirmed by XRD (using a Holland Phillips PW/1730 X-ray generator with CuKα radiation). The catalyst was also characterized by XPS (X-ray photoelectron spectroscopy), using a VG-Scientific ESCA-3MKII electron spectrometer and assuming the binding energy of C_{1s} as 285 eV, for its relative surface composition and also by TEM (transmission electron microscopy), using a JEOL Model 1200 EX instrument, for its Pd particle size.

The catalytic H_2O_2 destruction in aqueous reaction medium was carried out in the presence of static or dynamic hydrogen (i.e. H_2 flowing through the reaction medium) at atmospheric pressure, using a magnetically stirred glass reactor (capacity: 250 cm^3), containing 150 cm^3 of aqueous acidic (H_3PO_4) reaction medium with 0.1 g of catalyst. The reactor was kept in a constant temperature water bath. For the reaction under flowing H_2, the reactor was flushed with pure H_2 (30 cm^3/min) to replace the air in the reactor by H_2. After completely flushing the reactor by H_2, it was connected to a gas burette filled with pure H_2 over water and then 1 cm^3 of 30 % H_2O_2 was injected in the reactor under vigorous stirring. The gas consumed and evolved in the H_2O_2 hydrogenation and decomposition, respectively, was measured quantitatively at a constant (atmospheric) pressure, as a function of time.

The rate data for the destruction of H_2O_2 by its decomposition ($H_2O_2 \rightarrow H_2O + 0.5\ O_2$) and/or hydrogenation ($H_2O_2 + H_2 \rightarrow 2\ H_2O$) were obtained in the absence of any mass transfer effect. The intra-particle (or pore diffusional) mass transfer effect was eliminated or minimized by using the catalyst in a very fine powder form. The gas-liquid and liquid-solid mass transfer effects were eliminated by carrying out the reaction by varying the voltage applied to the magnetic stirrer from 100 – 200 V and observing no change in the H_2O_2 conversion or gas consumed in the reaction (at 300 K) above the applied voltage of 220 V. To be on a safer side, the runs were carried by applying a voltage of 240 V to the magnetic stirrer.

7.3. Catalyst Characterization

The surface and bulk properties of the reduced and oxidized Pd/Al_2O_3 catalysts are given in Table7.1.The bulk palladium species present in the reduced and oxidized Pd/Al_2O_3 catalyst were found to be Pd^o and PdO, respectively. The observed smaller surface area of the oxidized catalyst is expected because of sintering of the Pd/Al_2O_3 during its oxidation at 500 ºC. The XPS studies of the catalysts reveal that the surface palladium species present in the oxidized, reduced catalysts are Pd(II), Pd(0), respectively. The size of Pd metallic particles in the reduced Pd/Al_2O_3 catalyst is found to be in the range of 5-7 nm from the TEM photograph. The PdO particle size in the oxidized catalyst estimated from the XRD peak broadening method and it was found to be 14 nm.

Table 7.1: Surface and bulk properties of the Pd/Al_2O_3 catalyst in its reduced and oxidized form.

Form of Pd/Al_2O_3 (Oxidized/ reduced)	XRD phase (Pd^o or PdO)	Surface area (m^2/g)	Pd or PdO particle size (nm)	Binding energy (eV)			
				O (2s)	Pd ($3d_{3/2}$)	Pd ($3d_{5/2}$)	Al (2p)
Oxidized	PdO	173.5	5-7[a]	531.8	342.2	336.9	74.7
Reduced	Pd^o	198.0	14[b]	531.7	340.6	335.4	74.5

[a]From TEM photograph, [b]From XRD spectra.

7.4. H_2O_2 Hydrogenation/Decomposition in the Presence of H_2 over the Pd/Al_2O_3 Catalyst

Results showing a strong influence of the reaction and catalyst parameters, such as halide anions (viz. F^-, Cl^-, Br^- and I^-) and their concentration in presence and absence of protons in aqueous medium, concentration of phosphoric acid and oxidation state of Pd in the catalyst, on the initial rate of H_2O_2 destruction in the presence of H_2 are presented in Table 7.2. The initial rates of H_2O_2 destructions under different conditions in the presence of H_2 are compared with that in the absence of hydrogen in Table 7.2. The initial rates were obtained from the slope of fractional H_2O_2 conversion vs. time curves at the zero reaction time.

The –ve values of the gas consumed in the H_2O_2 destruction (in presence of H_2) shows a rapid decomposition of H_2O_2 to water and oxygen (reaction 7.1) in the initial short reaction period.

$H_2O_2 \rightarrow H_2O + 0.5\ O_2$ (7.1)

The +ve values of the gas consumed are due to the consumption of H_2 in the hydrogenation of H_2O_2 and/or in the reduction of O_2 evolved in the initial rapid H_2O_2 decomposition, according to the following reactions.

$H_2O_2 + H_2 \rightarrow 2\ H_2O$ (7.2)

$H_2 + 0.5\ O_2 \rightarrow H_2O$ (7.3)

$H_2 + O_2 \rightarrow H_2O_2$ (7.4)

Depending upon the reaction conditions, all the above four reactions are expected to occur during the destruction of H_2O_2 over the catalyst in the presence of H_2. The H_2O_2 destruction is thus a complex process; it is strongly influenced by the reaction and catalyst parameters, as follows.

7.4.1. Influence of the Presence of H_2

A comparison of the initial rate of H_2O_2 hydrogenation over Pd/Al_2O_3 in acidic or non-acidic medium with or without containing different halides in the presence of H_2 with that in the absence of H_2 (Table 7.2) clearly shows a very strong influence of the presence of H_2 during the H_2O_2 destruction. The H_2O_2 destruction rates in the presence of H_2 were much higher than that observed in the absence of H_2. The H_2O_2 decomposition over Pd/Al_2O_3 in the presence of flowing H_2 through the acidic medium was found to be instantaneous whereas that in the flowing N_2 or O_2 was very much slower [11]. This is expected because of the reduction of surface PdO present in the Pd/Al_2O_3 by hydrogen and thereby making available Pd^o (at the catalyst surface), which is more catalytically active, for the H_2O_2 destruction. This is consistent with our earlier observation that the pretreatment of supported Pd catalysts caused a large increase in the H_2O_2 decomposition activity of the catalysts [16].

Table 7.2: Influence of different halides in the reaction medium in the presence or absence of acid in the medium and oxidation state of bulk palladium (in the catalyst) on the initial rate of H_2O_2 destruction in presence and absence of halogen

Halide	Acid in medium	Oxidation state of bulk Pd	Initial rate of H_2O_2 destruction (h^{-1})
Nil	0.03 M H_3PO_4	Pd (0)	42.0
KF (2.7)[a]	0.03 M H_3PO_4	Pd (0)	39.0
KCl (2.7)	0.03 M H_3PO_4	Pd (0)	5.1
KBr (2.7)	0.03 M H_3PO_4	Pd (0)	3.1
KI (2.7)	0.03 M H_3PO_4	Pd (0)	0.04
MBr (2.7) (M = Na, NH_4 or H)	0.03 M H_3PO_4	Pd (0)	3.0 ± 0.2
KBr (0.9)	Nil	Pd (0)	4.2
KBr (5.4)	Nil	Pd (0)	4.1
KCl (0.9)	Nil	Pd (0)	54.0
KCl (5.4)	Nil	Pd (0)	45.0
Nil	0.1 M H_3PO_4	Pd (0)	28.2
Nil	0.1 M H_3PO_4	Pd (II)	16.3
KBr (1.0)	0.1 M H_3PO_4	Pd (0)	1.5
KBr (1.0)	0.1 M H_3PO_4	Pd (II)	0.6

[a] Values in round correspond the concentration of halide ($mmol/dm^3$) in the reaction medium

Our earlier studies on H_2O_2 decomposition over different supported Pd catalysts also showed that the H_2O_2 destruction rate is drastically reduced after the surface/sub-surface oxidation of Pd from the catalysts [2,4,6,13,16].

It may be noted that, in the absence of H_2, the H_2O_2 destruction occurs only by the H_2O_2 decomposition (reaction 1). Whereas, in the presence of H_2, the H_2O_2 destruction is expected to involve the H_2O_2 decomposition (reaction 7.1) and/or H_2O_2 hydrogenation (reaction 7.2) reactions. Since, hydrogen is present along with O_2 in the direct H_2-to-H_2O_2 oxidation, it is more interesting to study the factors strongly influencing the H_2O_2 destruction over the Pd(or PdO)/Al_2O_3 catalyst in the presence of hydrogen.

7.4.2. Influence of Different Halides in Reaction Medium

Results showing the influence of the different halide anions added in aqueous medium on the kinetics of H_2O_2 destruction in the presence of H_2 over Pd/Al_2O_3 are presented in Figure 7.1.

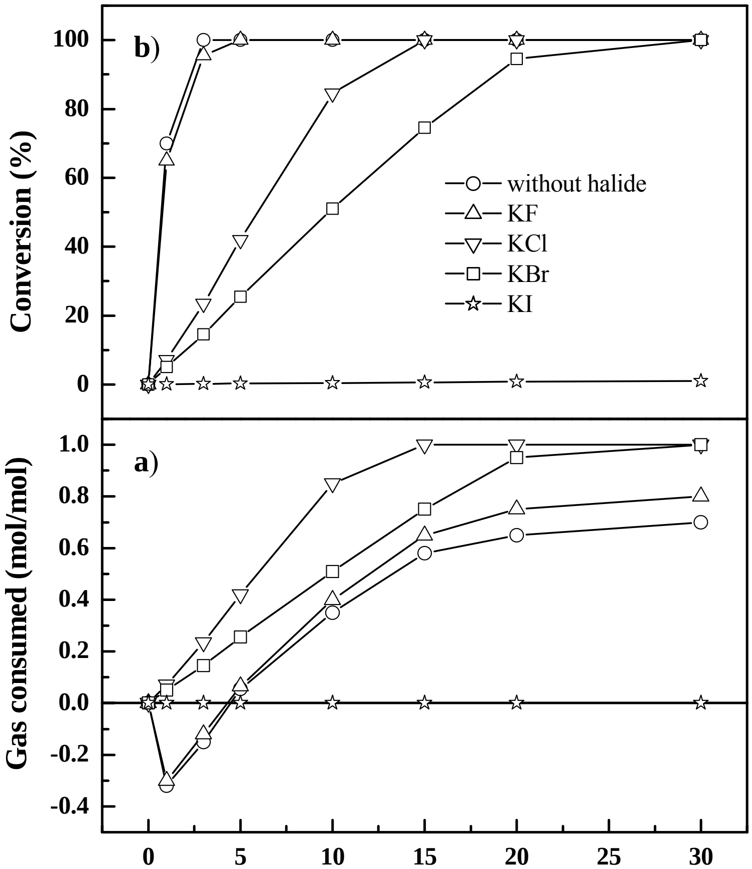


Figure 7.1: Influence of the presence of different halides (2.7 mmol.dm^{-3}) in the acidic reaction medium (0.03 M H_3PO_4) on the a) H_2 consumption and b) H_2O_2 conversion in the reaction of H_2O_2 over Pd/Al_2O_3 catalyst (at 27 ºC) under static H_2.

The H_2O_2 destruction over the Pd/Al_2O_3 catalyst in the presence of H_2 is strongly influenced by the nature of halide anions (F^-, Cl^-, Br^- or I^-) present in the aqueous reaction medium (Figure 7.1b). Moreover, the influence of a particular halide (KCl or KBr) shows strong dependence upon the presence of acid (i.e. protons) in the reaction medium and also upon the oxidation state of the Pd in the catalyst (Table 7.2). The influence of different halide anions in the presence and absence of protons can be summarized as follows.

In the presence of protons, the H_2O_2 destruction activity of Pd/Al_2O_3 was inhibited by the different halide anions (2.7 $mmol/dm^3$) in the following order $I^->>Br^->Cl^->F^-$. The fluoride anions had only a little effect on the H_2O_2 destruction and the iodide anions almost totally deactivated the catalyst by poisoning (Figure 7.1b). Whereas, the chloride or bromide anions moderately inhibited the H_2O_2 destruction. However, in the absence of protons, although the bromide anions (0.9 or 5.4 $mmol/dm^3$) inhibited the H_2O_2 destruction; the chloride anions promoted the H_2O_2 destruction (Table 7.2). The bromide anions were, however, also less effective in the absence of protons.

The results of H_2 consumption in the H_2O_2 destruction (Figure 7.1a), obtained in parallel to the H_2O_2 conversion data (Figure 7.1b), lead to the following interesting observations:

- In the absence of any halide or in the presence of fluoride anions, the H_2O_2 destruction was very fast; it completed within a period of 2-3 min. However, the H_2 consumption was –ve in the initial period of about 5 min and, after this period, there was gas consumption at a slow rate. The initial –ve gas consumption was expected because of the fast H_2O_2 decomposition with O_2 evolution (reaction 7.1) in a short reaction period of about 1.0 min, which was followed by the H_2 consumption reactions (reactions 7.2-7.4). The gas evolved [0.32 mol/mol (H_2O_2)] indicates that, in the absence of any halide or in the presence of fluoride anions, at least 64 % H_2O_2 destruction was due to the very fast H_2O_2 decomposition.
- In the presence of chloride or bromide anions, there was continuous consumption of H_2 throughout the reaction and the total amount of H_2 consumed was 1.0 mol(H_2)/mol(H_2O_2), as expected according to reaction 7.2. This clearly shows that, in this case, the H_2O_2 destruction was only due to the H_2O_2 hydrogenation (reaction 7.2).

A comparison of the initial rate of H_2O_2 destruction for the different bromides (Table 7.2) reveals that the cation (H^+, K^+, Na^+ or NH^+) associated with bromide anion present in the acidic medium has a little or no effect on the H_2O_2 destruction activity of the Pd/Al_2O_3 catalyst. Similar observation was made for the H_2O_2 decomposition (in absence of H_2) over Pd/Al_2O_3 in the presence of different bromides and also over Pd/C in the presence of different chlorides [11]. This reveals that the inhibition to H_2O_2 destruction is essentially caused by the halide anions and the cations associated with them do not play significant role in the process. This is also consistent with the earlier observations that the H_2O_2 formation in the H_2-to-H_2O_2 oxidation and H_2O_2 decomposition (in air) reactions over Pd/Al_2O_3 in the acidic medium are not strongly influenced by the cation associated with bromide anion promoter [11].

It may also be noted from the results in Table 7.2 that, at the same concentration of bromide anions (1.0 mmol/dm^3) and acid (0.1 M H_3PO_4) in the reaction medium, the H_2O_2 destruction rate was markedly reduced after the oxidation of Pd to PdO in the catalyst.

7.4.3. Influence of Halide Anion Concentration in Acidic and Non-acidic Mediums

Results showing the influence of the concentration of Br^- and Cl^- anions in the acidic reaction medium on the kinetics of H_2O_2 destruction are presented in Figures 7.2 and 7.3, respectively.

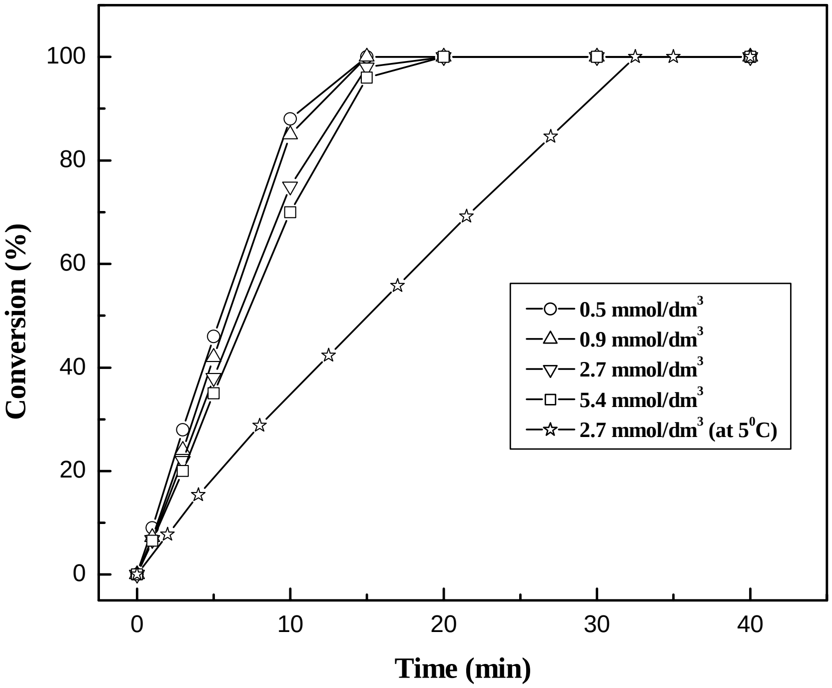


Figure 7.2: Effect of chloride anion concentration in aqueous medium (0.03 M H_3PO_4) on the H_2O_2 conversion in hydrogenation over Pd/Al_2O_3 catalyst (at 27 ºC) under static H_2.

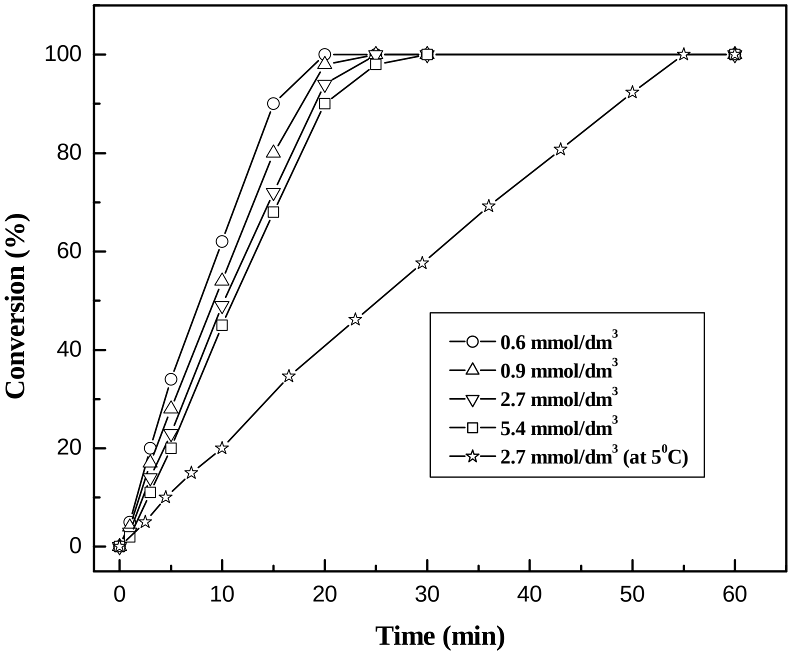


Figure 7.3: Effect of bromide anion concentration in aqueous medium (0.03 M H_3PO_4) on the H_2O_2 conversion in hydrogenation over Pd/Al_2O_3 catalyst (at 27 ºC) under static H_2.

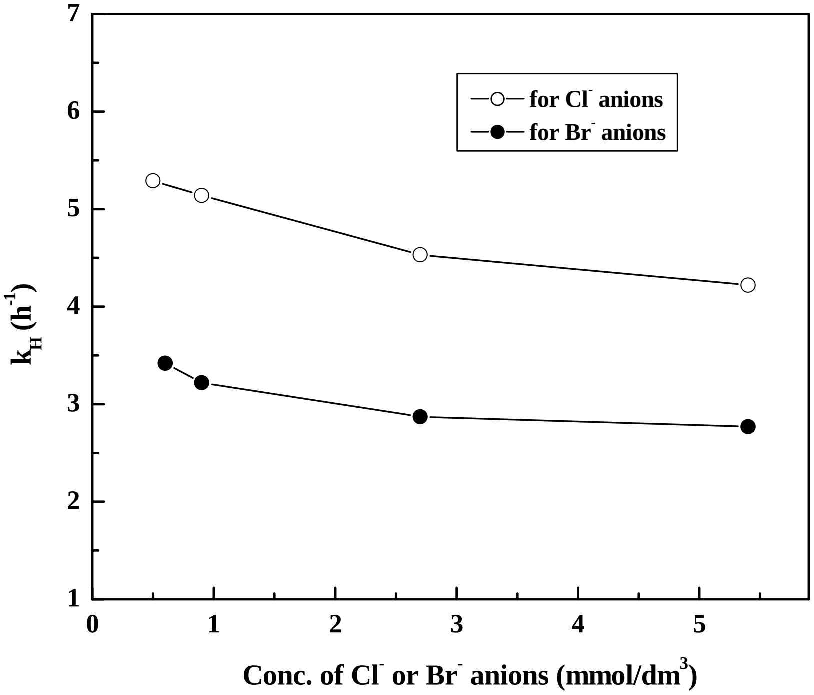


Figure 7.4: Influence of the concentration of Cl^- or Br^- anions (in 0.03 M H_3PO_4) on the H_2O_2 hydrogenation rate constant (k_H) at 27 ºC.

Results in Figures 7.2 and 7.3 show that, at all the concentration of chloride or bromide anions (0.5 – 5.4 mmol/dm^3) in the acidic medium, the H_2O_2 hydrogenation rate is almost independent of the reaction time and consequently independent of the H_2O_2 concentration. The H_2O_2 hydrogenation is thus a zero order reaction with respect to the H_2O_2 concentration. It is strongly influenced by the reaction temperature; as expected, the hydrogenation rate increased with increasing the temperature.

Variation of the H_2O_2 hydrogenation rate constant (k_H) with the concentration of chloride or bromide anions is shown in Figure 7.4. The H_2O_2 hydrogenation rate decreased appreciably with increasing the halide anion concentration. The bromide anions are more effective than the chloride anions for inhibiting the H_2O_2 hydrogenation.

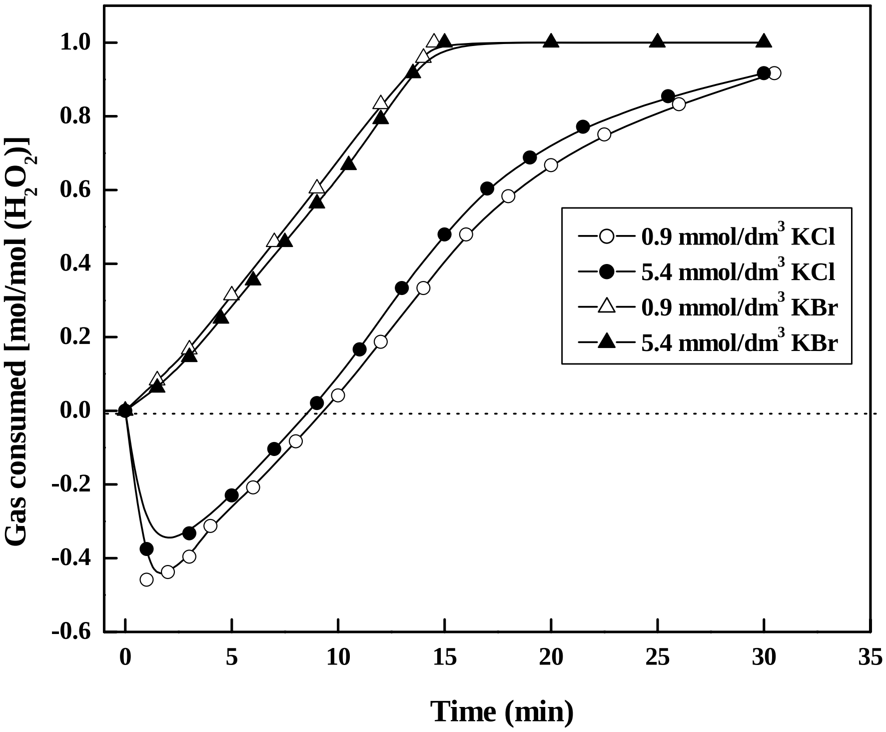


Figure 7.5: Effect of the concentration of chloride and bromide anions in non-acidic medium on the H_2O_2 destruction over Pd/Al_2O_3 catalyst (at 27 ºC) under static H_2.

The kinetic data for the H_2O_2 decomposition and/or hydrogenation in the presence of Cl^- or Br^- anions (0.9 and 5.4 mmol/dm^3) but in absence of protons in the medium are given in Figure 7.5. Results in Figure 7.5 show that, in the non-acidic medium, the presence of chloride anions (0.9 and 5.4 mmol/dm^3) led to a very fast H_2O_2 decomposition, resulting in the evolution of a large amount of O_2 in the initial short reaction period. The O_2 evolved [0.38 and 0.45 mol(O_2)/mol(H_2O_2) at the chloride concentration of 0.9 and 5.4 mmol/dm^3, respectively] suggests that at least 76 % and 90 % of the H_2O_2 was destroyed by a very fast H_2O_2 decomposition at the lower and higher chloride concentration, respectively. Thus, most of the H_2O_2 destruction is by the very fast decomposition of H_2O_2 rather than its hydrogenation. Whereas, in the presence of bromide anions (at the same concentration) in the non-acidic medium, the hydrogen was consumed continuously and almost linearly with the time. Moreover, the maximum amount of H_2 consumed was 1.0 mol per mole of H_2O_2, indicating that the H_2O_2 destruction in this case was only due to the H_2O_2 hydrogenation. However, the hydrogenation rate constant (k_H = 4.2 and 4.1 h^{-1} for the Br^- concentration of 0.9 and 5.4 mmol/dm^3, respectively) is higher than that (3.3 and 3.1 h^{-1} for the Br^- concentration of 0.9 and 5.4 mmol/dm^3, respectively) observed in the acidic medium (Figure 7.4).

In the absence of any halide in the acidic medium, the H_2O_2 destruction over Pd/Al_2O_3 under H_2 occurs mostly by the very fast H_2O_2 decomposition. However, the above results reveal that, in both the acidic and non-acidic mediums, the presence of bromide anions at a wide range of concentrations (0.5 – 5.4 mmol/dm^3) results in a drastic reduction in the rate of H_2O_2 destruction over Pd/Al_2O_3; the H_2O_2 destruction rate decreased with increasing the bromide concentration. Also, the H_2O_2 destruction is only due to the H_2O_2 hydrogenation rather than the fast H_2O_2 decomposition. On the contrary, the influence of chloride anions on the destruction of H_2O_2 (by its hydrogenation and/or decomposition) depends strongly on the presence or absence of acid (protons) in the medium; in the presence of acid, the H_2O_2 destruction occurs essentially by the H_2O_2 hydrogenation but, in the absence of acid, it occurs mostly by the very fast H_2O_2 decomposition.

7.4.4. Influence of Acid and Its Concentration in Reaction Medium

The initial rate of H_2O_2 destruction (in H_2) decreased after the addition of acid (0.03 M or 0.1 M H_3PO_4) in the reaction medium containing chloride or bromide; particularly for the chloride, the decrease was very large (Table 7.2). The H_2O_2 destruction over Pd catalysts even in the absence of H_2 (i.e. H_2O_2 decomposition) is inhibited due to the presence of acid in the medium [7,11,15,16]; the results on Pd/Al_2O_3 (Table 7.2) are consistent with this.

The results showing the influence of acid (H_3PO_4) concentration in the reaction medium containing bromide anions (0.9 mmol/dm^3) on the H_2O_2 conversion and hydrogenation rate/pseudo zero order hydrogenation rate constant (k_H) are given in Figures 7.6 and 7.7, respectively.

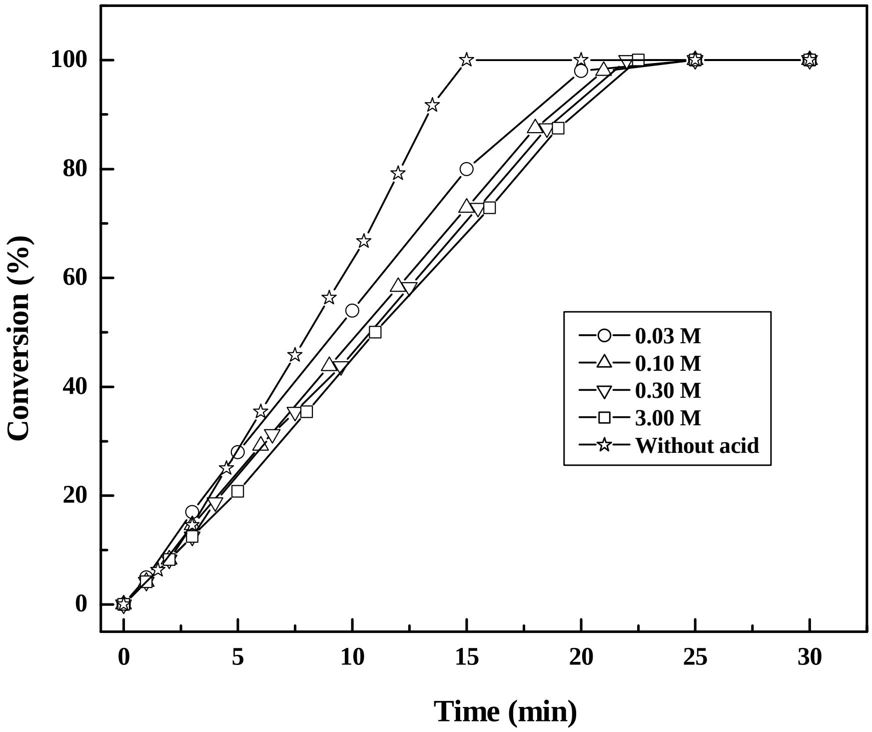


Figure 7.6: Effect of acid (H_3PO_4) concentration in the presence of KBr (0.9 mmol/dm^3) on the H_2O_2 conversion in hydrogenation over Pd/Al_2O_3 catalyst (at 27 °C) under static H_2.

The rate constant (k_H) decreased with increasing the acid concentration (Figure 7.7). The decrease was, however, sharp at the lower acid concentrations; above the acid concentration of 0.3 mol/dm^3, the decrease in the hydrogenation rate was very small.

As discussed earlier, after the addition of acid (0.03 M H_3PO_4) to the reaction medium containing chloride anions (0.9 or 5.4 mmol/dm^3), the H_2O_2 destruction over Pd/Al_2O_3 changed from the very fast H_2O_2 decomposition (Figure 7.5) to the much slower H_2O_2 hydrogenation (Figure 7.2), indicating a very strong influence of the presence of protons on the H_2O_2 destruction.

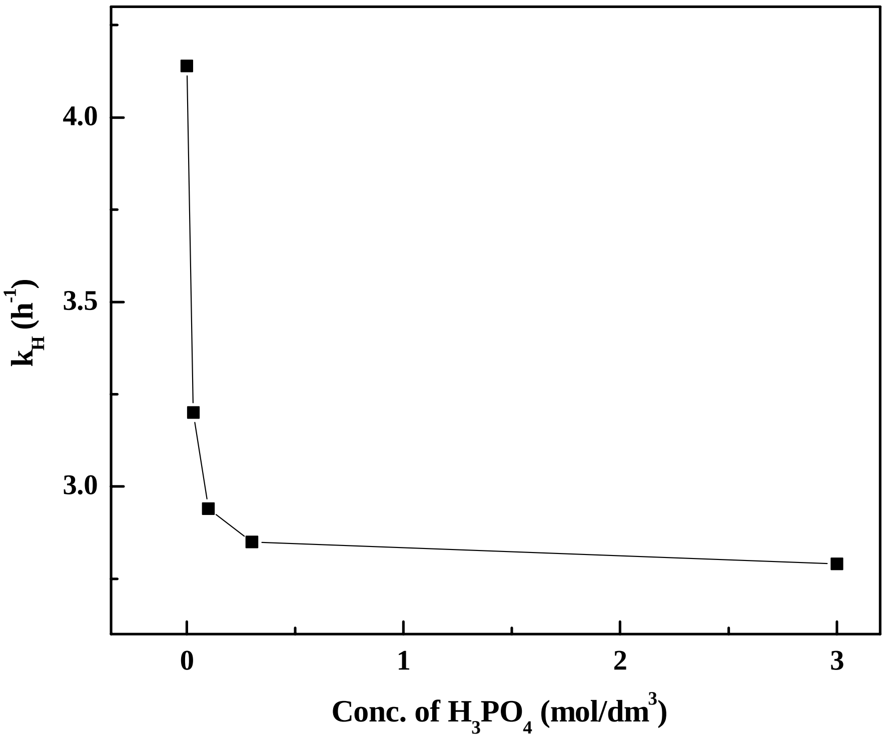


Figure 7.7: Influence of the concentration of acid (H_3PO_4) on the H_2O_2 hydrogenation rate constant (k_H) at 27 ºC.

As compared to other mineral acids, phosphoric acid was preferred in the aqueous reaction medium because of the fact that it is less corrosive and also phosphate ions act as H_2O_2 stabilizer. Moreover, a significant Pd leaching from the catalyst was observed only at the high concentration of phosphoric acid (>0.3 mol/dm^3), even in the presence of bromide anions [11].

7.4.5. Influence of the Pd Oxidation State

An influence of Pd oxidation state in the catalyst on the kinetics of H_2O_2 decomposition and/or hydrogenation in the acidic medium in the absence and presence of Br^- anions is presented in Figures 7.8 and 7.9, respectively.

In the absence of any halide in the acidic medium, the H_2O_2 destruction (in H_2) over both the Pd/Al_2O_3 and PdO/Al_2O_3 catalysts proceeded with the fast H_2O_2 decomposition, as indicated by the rapid evolution of gas in the initial short reaction period in both the cases (Figure 7.8). The rate of H_2O_2 destruction was, however, much slower for the oxidized catalyst (Table 7.2, Figure 7.8), indicating a strong influence of the oxidation state of Pd in the catalyst on the H_2O_2 destruction. The destruction of H_2O_2 by its decomposition alone during the reaction was at least 40 and 84 % over the PdO/Al_2O_3 and Pd/Al_2O_3, respectively.

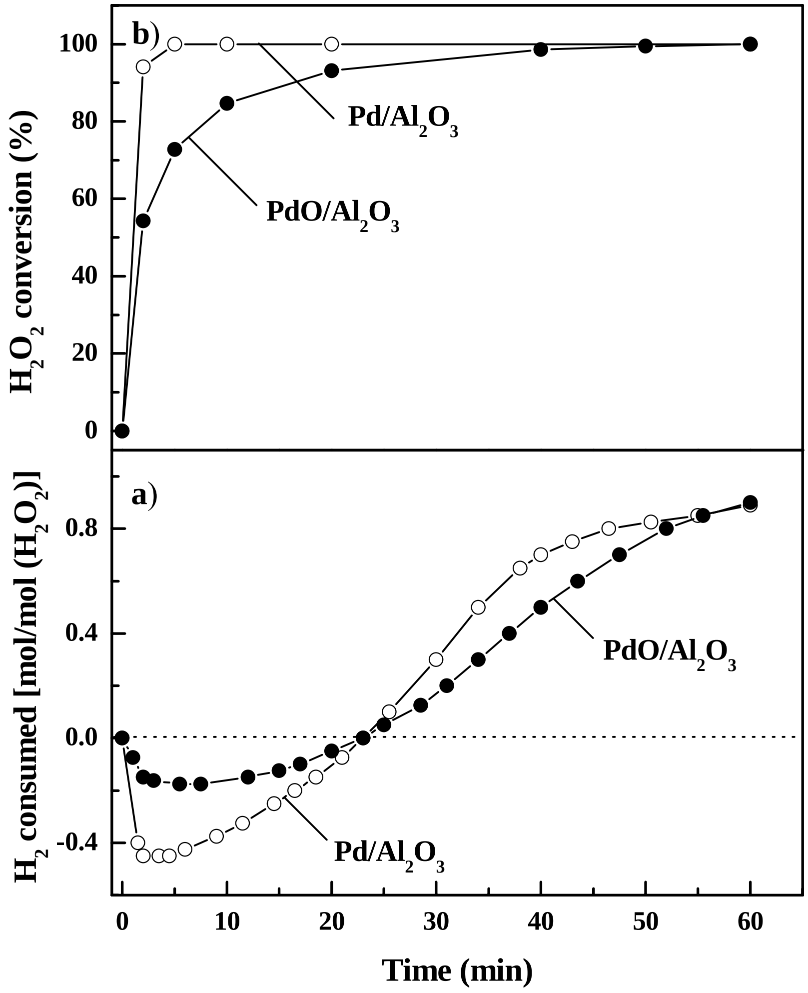


Figure 7.8: Influence of the Pd oxidation state of Pd/Al_2O_3 catalyst in the aqueous acidic medium (0.1 M H_3PO_4) on the H_2 consumption (a) and H_2O_2 conversion (b) in the reaction of H_2O_2 (at 27 ºC) under static H_2 in absence of any halide.

For both the catalysts, after the addition of bromide anions (0.9 mmol/dm^3) in the reaction medium, the fast H_2O_2 decomposition was changed to a much slower H_2O_2 hydrogenation (Figure 7.9 and Table 7.2), indicating a very strong influence of the bromide anions for inhibiting the H_2O_2 destruction. The H_2O_2 hydrogenation over the PdO/Al_2O_3 was, however, much slower than that over the Pd/Al_2O_3, indicating the strong influence of the Pd oxidation state, even in the presence of bromide anions.

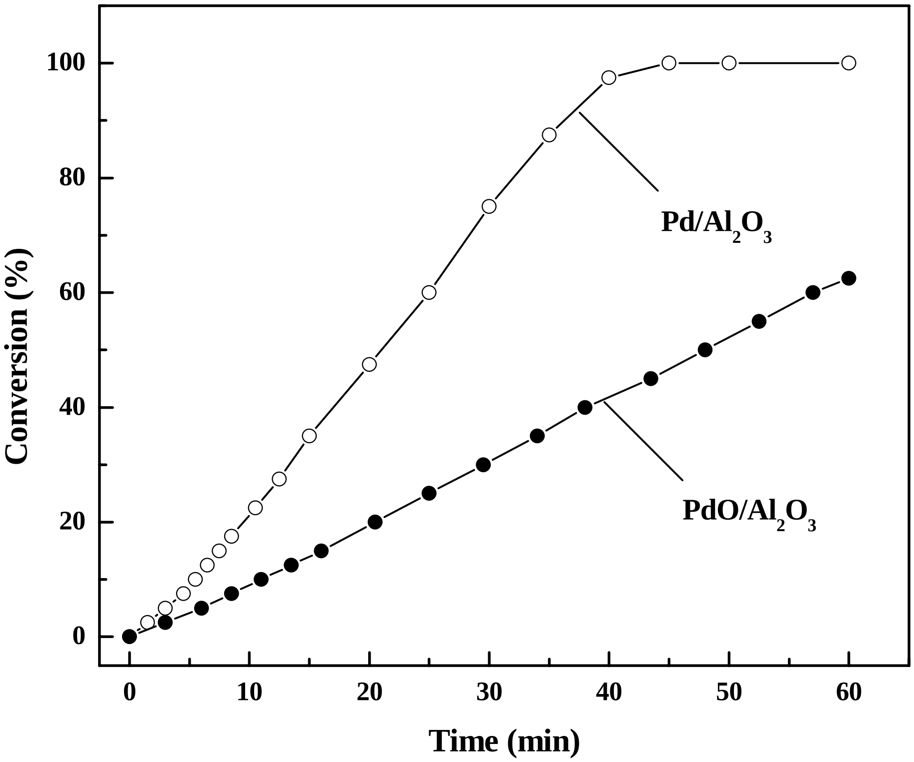


Figure 7.9: Influence of the Pd oxidation state of Pd/Al_2O_3 catalyst in presence of KBr (1 mmol/dm^3) in the acidic (0.1 M H_3PO_4) medium on the H_2O_2 conversion in hydrogenation (at 27 °C) under static H_2.

The surface Pd species for the PdO/Al_2O_3 catalyst are expected to be Pd^o due to the reduction of PdO at the catalyst surface by H_2 in the initial short reaction period. The observed very small induction period for the H_2O_2 hydrogenation (Figure 7.9) is expected because of the PdO-to-Pd^o reduction at the catalyst surface for the PdO/Al_2O_3 and due to the removal of chemisorbed oxygen by H_2 from the Pd/Al_2O_3. It may be noted that the kinetic plots are linear after the initial very short reaction period, indicating zero order reaction with respect to H_2O_2 concentration.

7.4.6. Influence of Different Halogens in Halogenated Pd/Al_2O_3 Catalysts

Results showing a strong influence of the nature of halogen incorporated in the catalyst by its pre-halogenation on the initial rate of H_2O_2 destruction, and on the gas consumption and H_2O_2 conversion in the presence of H_2 are presented in Table 7.3 and Figure 7.10, respectively. The influence of the fluorination, bromination and iodination of Pd/Al_2O_3 catalysts on its H_2O_2 destruction activity is more or less similar to that observed for the addition of fluoride, bromide and iodide anions, respectively, in the acidic reaction medium (Table 7.2). However, the chlorination of Pd/Al_2O_3 resulted into a very small inhibition to the H_2O_2 destruction as compared to that achieved by the bromination of Pd/Al_2O_3 or by the addition of chloride anions in the acidic reaction medium

Our earlier studies [10] revealed that the pre-bromination of Pd/Al_2O_3 leads to a drastic increase in the net H_2O_2 formation in the H_2-to-H_2O_2 oxidation in acidic medium. However, no H_2O_2 formation was observed due to the pre-fluorination, pre-chlorination or pre-iodination of the catalyst. The results of H_2O_2 destruction (in the presence of H_2) over the pre-halogenated Pd/Al_2O_3 catalysts in acidic medium (Figure 7.10) provide the answer for the above.

Table 7.3: Influence of different halogens pre-incorporated in the catalyst in the presence of acid (H_3PO_4) in the reaction medium on the initial rate of H_2O_2 destruction

Halogen	Acid in medium	Oxidation state of bulk Pd	Initial rate of H_2O_2 destruction (h^{-1})
Nil	0.03 M H_3PO_4	Pd (0)	42.0
F [1.0][a]	0.03 M H_3PO_4	Pd (0)	45.0
Cl [1.0]	0.03 M H_3PO_4	Pd (0)	40.8
Br [1.0]	0.03 M H_3PO_4	Pd (0)	4.2
I [1.0]	0.03 M H_3PO_4	Pd (0)	1.01

[a] Values square brackets correspond the concentration of halogen (wt %) in the halogenated catalyst.

The results obtained for the chlorinated Pd/Al_2O_3 are quite similar that observed for the addition of chloride anions in non-acidic medium (Figure 7.5). In both the cases, the interaction between Pd and Cl on the catalyst surface leading to the modification of the surface properties for inhibiting the H_2O_2 destruction seems to be avoided or drastically restricted probably due to the immobilization of chloride anions on the catalyst surface.

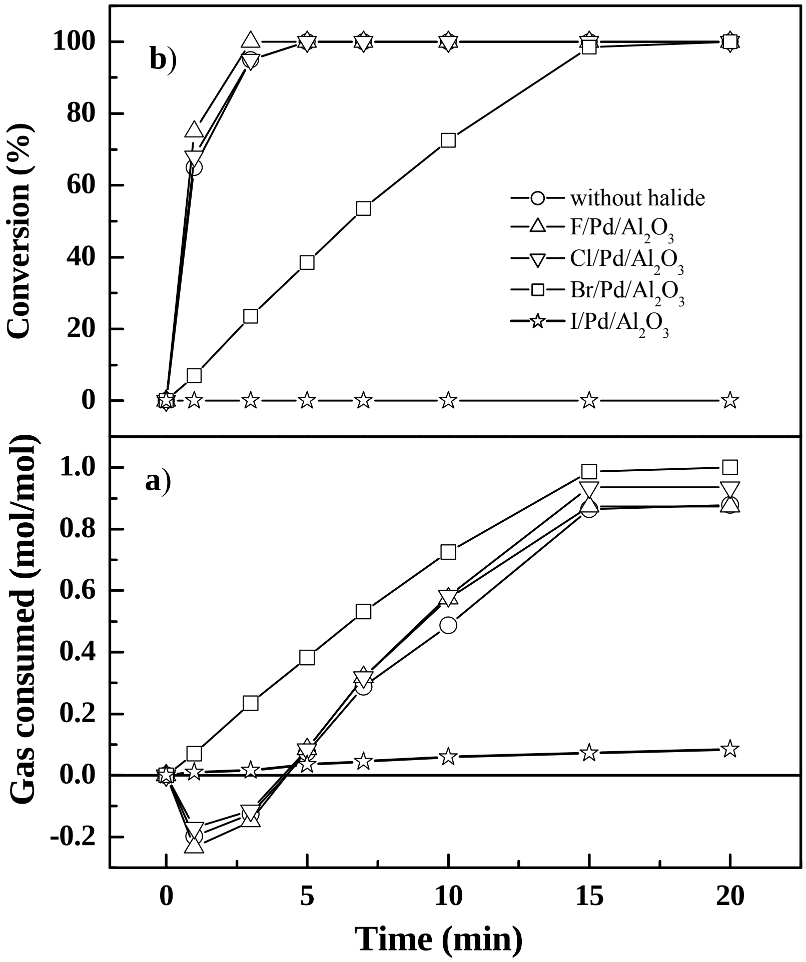
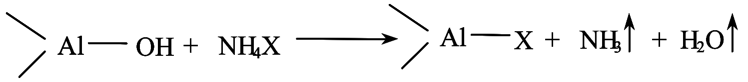


Figure 7.10: Influence of the different halogens (1 wt %) incorporated in the Pd/Al_2O_3 catalyst on the gas consumption (a) and H_2O_2 conversion (b) in the reaction of H_2O_2 (at 300 K) under static H_2 in the acidic (0.03 M H_3PO_4) medium.

It may be noted that the concentration of different halogens in the halogenated Pd/Al_2O_3 (halogen loading 1 wt%) was in the following order: F (0.53 mmol/g) > Cl (0.28 mmol/g) > Br

(0.13 mmol/g) > I (0.08 mmol/g). However, the order of halogens (in the catalyst) for their inhibiting action on the H_2O_2 destruction was found to be opposite (I>Br>>Cl≥F). This is expected because of the fact that the halide anions differ widely in their affinity to Pd and also for their mobility on the catalyst surface; their order for both the affinity to Pd and surface mobility is expected to be as follows: $I^- > Br^- > Cl^- > F^-$.

During the halogenation of Pd/Al_2O_3 catalyst, the halide anions are immobilized on the support surface through the reaction between surface hydroxyls and ammonium halide (at 400 ºC) as follows:



(7.5)

(X = F, Cl, Br or I)

Since, the electronegativity of halogens is in the following order: F>Cl>Br>I, the lesser electronegative halogen is expected to have higher mobility on the catalyst surface. In the case of chloride anions in the acidic medium, the mobility of adsorbed halide anions seems to be increased in the presence of acid (protons) in the medium, thereby increasing the effectiveness of chloride anions (added to the reaction medium) for inhibiting the fast H_2O_2 destruction on the Pd/Al_2O_3 (Figures 7.1 and 7.2).

7.5. Role of Protons and Cl or Br Inhibitor/Mechanism of H_2O_2 Destruction

Because of their intermediate affinity (or intermediate coordination ability) to Pd, the Cl^- and Br^- anions in the acidic reaction medium are more effective in interacting with Pd clusters on the catalyst surface and thereby drastically reduce the H_2O_2 destruction activity of the Pd clusters in presence of H_2 via changing the H_2O_2 destruction path from the rapid H_2O_2 decomposition to the slower H_2O_2 hydrogenation. However, because of their immobilization, the chloride anions in the pre-chlorinated catalyst showed only a little reduction in the fast H_2O_2 decomposition, even in the presence of protons in the medium; whereas, fluoride anions showed only a little or no influence on the rapid H_2O_2 decomposition. On the contrary, iodide anions have high affinity to Pd, which results in almost total catalyst deactivation due to poisoning for the H_2O_2 destruction.

The H_2O_2 destruction over the catalyst is expected to proceed with homolytic dissociation of H_2O_2 and H_2 on the Pd clusters, as follows.

$H_2O_2 + 2\ Pd^o \Leftrightarrow 2\ Pd^o.OH$ (7.6)

$H_2 + 2\ Pd^o \Leftrightarrow 2\ Pd^o.H$ (7.7)

Fast dissociative adsorption of H_2 on Pd is well known. Reaction 7.6 is the primary reaction responsible for the initiation of H_2O_2 destruction because the energy required for the cleavage of HO–OH bond (213 $kJ.mol^{-1}$) is appreciably lower than that (369 $kJ.mol^{-1}$) required for the cleavage of H–O_2H bond. The adsorbed H and OH free radicals are expected to under go further plausible elementary reactions, as follows.

$Pd^o.OH + Pd^o.H \rightarrow H_2O + 2\ Pd^o$ (7.8)

$2\ Pd^o.OH \rightarrow H_2O + Pd^o.O + Pd^o$ (7.9)

$Pd^o.O + 2\ Pd^o.H \rightarrow H_2O + 3\ Pd^o$ (7.10)

$2\ Pd^o.O \Leftrightarrow 2\ Pd^o + O_2\uparrow$ (7.11)

In the presence of bromide or chloride anions (in acidic medium), reaction 7.9 (forming $Pd^o.O$ i.e. atomically adsorbed oxygen) seems to be more strongly inhibited as compared to reaction 7.6 (forming OH radicals), which is some what similar to that proposed for the H_2-to-H_2O_2 oxidation over supported Pd catalysts [11,17]. This is consistent with the fact that the H_2O_2 destruction path is changed from the fast H_2O_2 decomposition to a much slower H_2O_2 hydrogenation 7.6-7.8; whereas the rapid H_2O_2 decomposition in the presence of fluoride anions or chloride anions (in the absence of protons) or in the absence of any halide is expected to involve reactions 7.6,7.7 and 7.9-7.11.

The role of acid (protons) is to facilitate the selective adsorption of halide anions from the aqueous reaction medium on the catalyst through lowering the pH of the reaction medium below the pH corresponding to the isoelectric point of the catalyst support. The adsorption of chloride or bromide anions from the acidic medium on Pd/Al_2O_3 was confirmed earlier by the XPS and EDAX studies of used catalysts [11]. The other important role of the protons seems to enhance the surface mobility of the adsorbed Cl^- or Br^- anions so that the adsorbed halide anions can freely interact with the Pd clusters from the catalyst and thereby modify its electronic properties. In the absence of acid, the presence of chloride anions in the reaction medium has only a little inhibiting effect on the fast H_2O_2 decomposition because of the immobilization of the adsorbed chloride anions on the catalyst support away from the Pd clusters.

7.6. Conclusions

This investigation revealed a strong influence of a number of factors [such as presence of H_2, nature of halide anions (F^-, Cl^-, Br^- or I^-) and their concentration in the reaction medium or in the catalyst, presence of acid (H_3PO_4) and its concentration in the reaction medium, oxidation state of Pd in the catalyst] on the rate of H_2O_2 destruction by H_2O_2 decomposition and/or hydrogenation over Pd/Al_2O_3 catalyst under ambient conditions, as follows.

1) The H_2O_2 destruction activity of Pd/Al_2O_3 and PdO/Al_2O_3 catalysts in both the presence and absence of different halide anions is drastically increased in the presence of H_2 during the reaction because of the removal of chemisorbed O_2 and due to the reduction of surface PdO to Pd^o, respectively, by the H_2.
2) The fast H_2O_2 decomposition (in H_2) over the Pd/Al_2O_3 and PdO/Al_2O_3 catalysts is changed to a much slower H_2O_2 hydrogenation due to the addition of bromide anions in the acidic reaction medium or because of the pre-bromination of the Pd/Al_2O_3. The addition of chloride anions is less effective in reducing the H_2O_2 destruction. Moreover, the chloride addition (even at high concentration) in the case of non-acidic reaction medium has only a little effect on the fast H_2O_2 decomposition. In the acidic medium, the H_2O_2 hydrogenation rate is appreciably decreased with increasing the bromide or chloride concentration. The addition of fluoride anions in the acidic medium or the pre-fluorination or pre-chlorination of the Pd/Al_2O_3 has only a little effect on the fast H_2O_2 decomposition; whereas, iodide anions in the medium or catalyst act as a strong catalyst poison. Thus, the most effective halide promoter for the H_2O_2 formation in the H_2-to-H_2O_2 oxidation is bromide (Br^- anions). The cations associated bromide anions have little or no effect on the H_2O_2 destruction. The H_2O_2 hydrogenation in all the cases is zero order with respect to the H_2O_2 concentration.
3) Protons in the reaction medium also play important role in controlling the H_2O_2 destruction, even in the presence of bromide anions. The H_2O_2 hydrogenation rate is decreased sharply with increasing the acid (H_3PO_4) concentration from 0 to 0.3 mol/dm^3; the further increase in the acid concentration up to 3.0 mol/dm^3, however, results in only a small decrease in the H_2O_2 hydrogenation rate.

4) The oxidation of Pd to PdO results in a large decrease in the H_2O_2 destruction activity of the catalyst in both the presence and absence of bromide anions in the acidic medium.
5) The role played by the bromide or chloride anions in controlling the H_2O_2 destruction activity of Pd/Al_2O_3 in presence of H_2 seems to inhibit both the formation and disproportionation of OH radicals ($H_2O_2 \rightarrow 2$ OH and 2 OH $\rightarrow H_2O + 0.5\ O_2$) and thereby to avoid the fast H_2O_2 decomposition. Whereas, the role of protons in the medium seems to facilitate the interaction of halide anions with the Pd clusters of the catalyst and thereby to change the electronic properties of Pd via. enhancing the adsorption of halide anions and their surface mobility on the catalyst.

7.7. References

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Chapter 8

Hydrogen Peroxide from Reduction of O_2 with Hydrogen Containing Compounds (viz. Hydrazine, Hydroxylamine or Their Salts) over Supported Pd or Nano-Gold Catalysts in Aqueous or Non-Aqueous Medium

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8.1. Background and Objective of the Present Work

Hydrogen peroxide is an environmentally clean oxidizing agent; the by-product of its use is only water (which is environmentally benign). Because of the increasing environmental concerns, the use of H_2O_2 in a number of organic oxidation processes (e.g. epoxidation of olefins, hydroxylation of aromatics/olefins, oxidation of benzylic –CH_2OH to –CHO or –COOH, etc.) for the synthesis of fine/specialty chemicals is increasing widespread and growing day-by-day [1-3]. The presently practiced anthraquinone process is economical only for a very large production of H_2O_2 (> 40,000 tpa). Hence, since the transport, storage and handling of H_2O_2 is quite hazardous, the use of *in situ* generated H_2O_2 (as soon as it is produced) in the organic oxidations is not only of scientific interest but also of great practical importance. However, the progress made in this hot topic is rather slow [3,4-6], mostly because of the lack of an efficient method for the *in situ* H_2O_2 generation in an environmentally friendly manner, particularly at mild conditions for avoiding or minimizing the mismatch between the optimal condition required for the *in situ* H_2O_2 generation and the consecutive step of consumption of the generated H_2O_2 in the oxidation of organic substrates.

Conventionally, H_2O_2 can be generated *in situ* by the oxidation of hydroanthraquinone (hydroanthraquinone + O_2 → anthraquinone + H_2O_2) [3,7]. However, the use of this method for the *in-situ* H_2O_2 generation is limited because of the use of a complex solvent system and also due to the difficulties in separation of the solvent, unconverted hydroquinone and product of the reaction (anthraquinone) from the product(s) of organic oxidations. Direct oxidation of H_2 to H_2O_2 is a clean but highly hazardous process and hence its use for the *in situ* H_2O_2 generation is very dangerous [8]. Very recently Choudhary and coworkers suggested a new method based on selective reduction of O_2 by hydrazine or its salts, using easily separable and reusable supported Pd catalyst in aqueous medium (at ambient conditions), for *in situ* H_2O_2 generation [9,10]. However, in this method, the presence of both mineral acid and bromide promoters is a must, both create corrosion problems for commonly used stainless-steel reactor in the organic oxidations. Earlier Sheriff and coworkers [11-13] used Mn (II or III) complexes for the reduction of O_2 (at 3 bar) by hydroxylamine to H_2O_2 in an aqueous medium; the Mn-complexes as homogeneous catalysts are, however, difficult to separate from the reaction mixture. Hence, there is an urgent need for developing a new non-hazardous, more cleaner route for *in situ* generation of H_2O_2 in the synthesis of fine/bulk chemicals in organic oxidation reactions.

An ideal method for the *in situ* H_2O_2 generation should involve the conditions (viz. solvent, temperature, pressure) which are same as or close to that used in the organic oxidation requiring the *in situ* generated H_2O_2; most of the organic oxidation reactions rarely use aqueous solvent and pressure above atmospheric pressure. Moreover, the catalyst should be heterogeneous (easily separable) and reusable.

In this chapter, we have investigated a more environ-friendly/greener method for the *in situ* H_2O_2 generation in high yields from the reduction of O_2 by hydrogen containing compounds (viz. hydrazine, hydroxylamine or their salts) with the formation of environmentally benign by-products (viz. N_2 and water) in aqueous (viz. water) or non-aqueous (viz. methanol or ethanol) medium in the absence of acid and/or halide promoter, even at ambient conditions, using a heterogeneous nano-gold (viz. nano-size Au particles supported on Gd_2O_3, La_2O_3, MgO,) and/or supported palladium catalysts. Influence of the concentration of bromide (KBr) promoter, reaction period, temperature, catalyst loading and initial concentration of hydroxylammonium sulfate on the formation of H_2O_2 in O_2 reduction by hydroxylamine over Pd(1 wt%)/Al_2O_3 catalyst in a neutral aqueous medium at close to the ambient conditions has been investigated. Decomposition of hydrazine or hydroxylamine (from their salt) and their reaction with H_2O_2 and also the destruction of H_2O_2 under similar reaction conditions (in the absence of O_2) have also been studied.

8.2. Catalysts and Brief Experimental Procedures

Gold was deposited on different metal oxides by homogeneous deposition–precipitation (HDP) method, described in the section 2.2.4. The Pd/Al_2O_3 catalyst (Pd loading = 1 wt% or 5 wt%) in their reduced form was obtained from Lancaster, UK. The halogenated Pd(5 wt%)/Al_2O_3 was prepared by the method described in the section 2.2.3. All the catalysts were in fine powder form.

All the catalysts were characterized by XRD (using a Holland Phillips PW/1730 X-ray generator with CuKα radiation) for their bulk species, by XPS (using a VG-Scientific ESCA-3MK II electron spectrometer and assuming the binding energy of C_{1s} as 285 eV) for their relative surface composition, by ICP-AES (using Perkin–Elmer Analyser) for Au loading on the catalyst and also by TEM (using a JEOL model 1200 EX instrument) for their Au or Pd particle size.

The catalytic reduction of O_2 by hydrazine/hydrazine salt (or hydroxylammonium salt/hydroxylamine) to H_2O_2 over the supported nano-gold or Pd catalysts in aqueous or non-aqueous medium was carried out in a magnetically stirred jacketed glass reactor (capacity 100 cm^3) by passing continuously pure O_2 (99.5 %) through the reaction mixture at the following general reaction conditions: volume of the reaction medium = 50 cm^3, amount of catalyst = 0.1 – 0.5 g, amount of reducing agent = 2.0 mmol - 5.0 mmol, O_2 flow rate = 5 - 10 cm^3/min, temperature = 10-70 ºC, pressure = atmospheric (0.95 atm) and reaction time = 1 - 8 h. In case of hydroxylammonium salt, before adding the catalyst, the solution of hydroxylammonium salt in water (which was acidic with a pH of about 4.0) was neutralized (to a pH of 7.0) by the addition of sodium hydroxide to the solution; in the absence of such neutralization, there was no formation of H_2O_2 in case of hydroxylamine. The H_2O_2 from the reaction mixture (after separating the catalyst by filtration) and unconverted hydrazine or hydroxylamine were determined by iodometric titration method, described in the section 2.4.1., 2.4.3. and 2.4.4., respectively. Only nitrogen and water were formed as by-products. The H_2O_2 yield is determined by considering the following reaction stoichiometry:

$2\ NH_2OH + O_2 \rightarrow N_2 + 2\ H_2O + H_2O_2$

[H_2O_2 yield (%) = (moles of H_2O_2 formed ÷ moles of NH_2OH in feed) x 2 x 100].

The catalytic destruction of H_2O_2 in presence/absence of hydrazine or its salt and/or hydroxylamine or its salt was carried out in the same reactor by injecting through the rubber septum 1.0 ml of 30% aqueous H_2O_2 solution in the reactor under vigorous stirring at 27 ºC and atmospheric pressure. The gas evolved (O_2), in the destruction of H_2O_2, was measured as a function of time, using a constant pressure gas collector [14], for a period of 1h. Thermal decomposition (in absence of catalyst) was found to be insignificant for the duration of the reaction. Independent analysis of unconverted H_2O_2 (via iodometric titration) was undertaken for selected experiments, which confirmed that the O_2 evolved provided a true measure of H_2O_2 decomposition. The destruction reaction of NH_2OH in presence of N_2 was also carried out in absence/presence of catalyst using the same reactor and the gas evolved was measured as a function of time, using a constant pressure gas collector, for a period of 1h. The unconverted N_2H_4 and/or NH_2OH was also measured by iodometric titration described in section 2.4.3 and 2.4.4., respectively.

8.3. Catalyst Characterization

8.3.1. For Gold Catalysts

Data for the gold loading (measured by ICP-AES method) in the different metal oxide supported catalysts are given in Table 8.1. Although the same amount of gold was available for the different metal oxides for gold deposition on them by deposition method, the gold loading varies from catalyst to catalyst, depending upon the metal oxide.

Table 8.1: Gold loading and gold particle size of the different supported gold catalysts

Catalyst	Au loading (wt%)	Au particle size (nm)
Au/MgO	7.5	8.9 ± 0.7
Au/MgO[a]	7.5	35 ± 3.2
Au/CaO	4.7	9.6 ± 1.2
Au/La_2O_3	6.5	8.6 ± 1.4
Au/CeO_2-ZrO_2[b]	6.6	4.3 ± 1.4
Au/Gd_2O_3	6.4	17.4 ± 2.1
Au/Tb_2O_3	6.7	11.6 ± 2.4
Au/Yb_2O_3	6.6	10.8 ± 0.5
Au/Yb_2O_3[a]	6.6	23 ± 3.0
Au/Al_2O_3	6.4	3.6 ± 1.1
Au/Ga_2O_3	6.4	6.6 ± 3.7
Au/ZrO_2	3.0	4.5 ± 1.2

[a] Calcined at 800 ºC for 2h. [b] Ce/Zr mole ratio = 1.0.

From the metal oxide supported gold catalysts, a few catalysts (viz. Au supported on MgO, CaO, ZrO_2, CeO_2-ZrO_2, Al_2O_3, Ga_2O_3 and La_2O_3) were characterized for their bulk phase species in the catalyst. The presence of gold particles on different support was confirmed by XRD measurements between 35-80° at a scan rate of 2°/min and is shown in Figure 8.1. The occurrence of intense peaks in all the spectra at (111), (200) and (220) Bragg's reflection are the characteristic of face centered cubic structure of gold crystal [15].

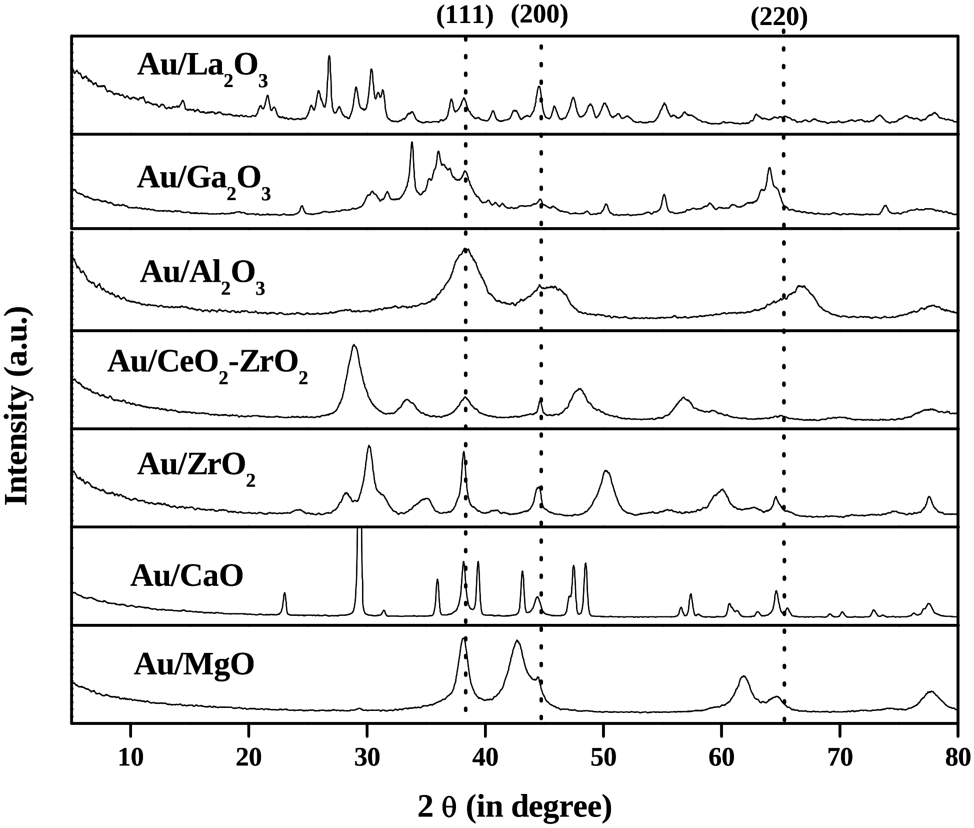

Figure 8.1: XRD spectra of the different supported Au catalysts.

Most of the supported gold catalysts were characterized for their gold particle size and gold particle shape by TEM, as shown in Figures 8.2 and 8.3. The gold particles sizes in these catalysts are listed in the Table 8.1 and in these catalysts, the gold particles are near spherical or hemi-spherical in shape. These observations indicate a strong influence of support on the Au particle size of the metal oxide supported gold catalysts prepared by the same method and the spherical and hemispherical shape of the gold particle shows a close contact of the Au particle with the support. When Au/MgO and Au/Yb_2O_3 catalysts were calcined at higher temperature

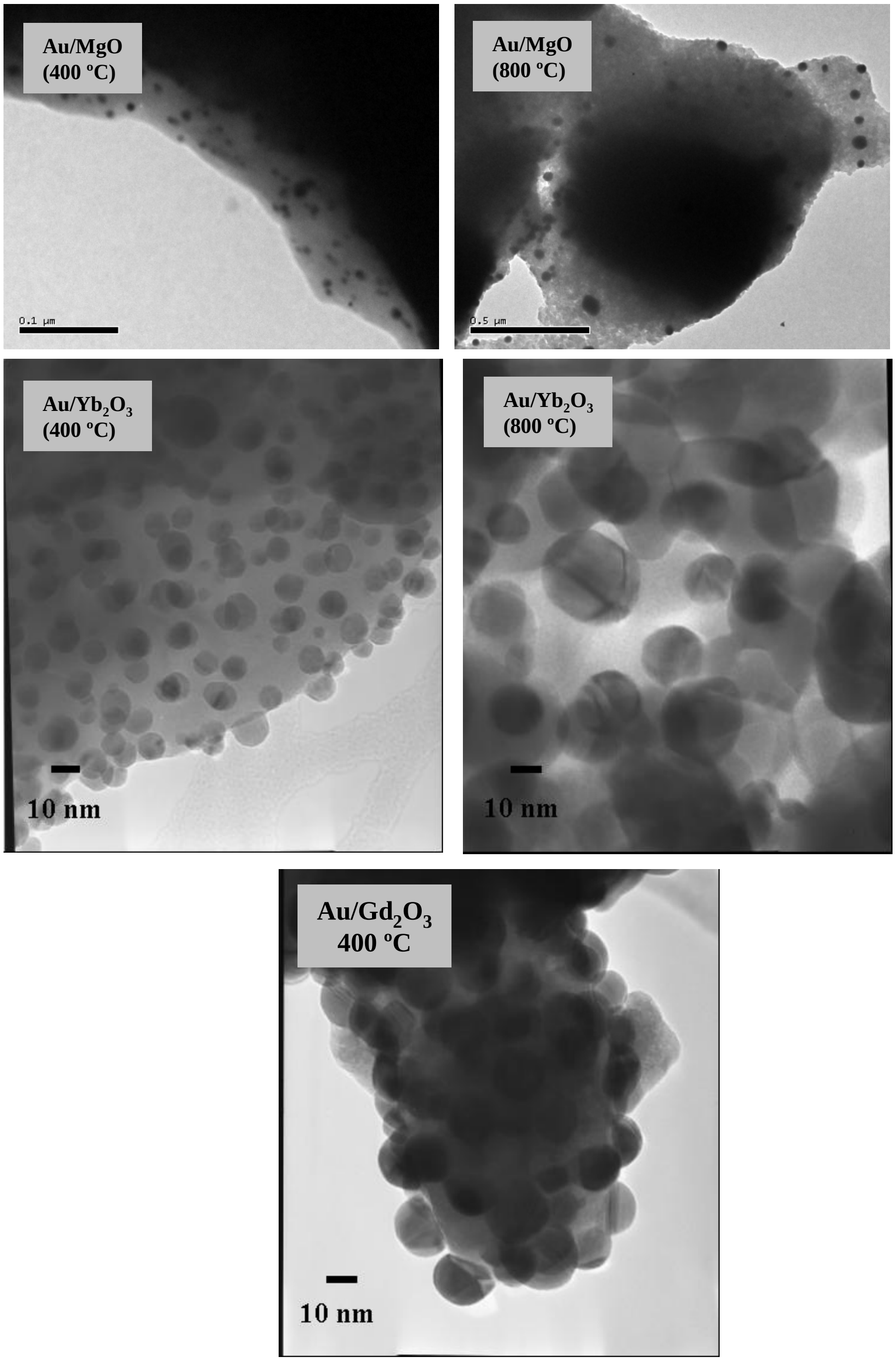

Figure 8.2: TEM photograph of the Au/MgO (calcined at 400ºC and 800ºC), Au/Yb_2O_3 (calcined at 400ºC and 800ºC) and Au/Gd_2O_3 (calcined at 400ºC) catalysts.

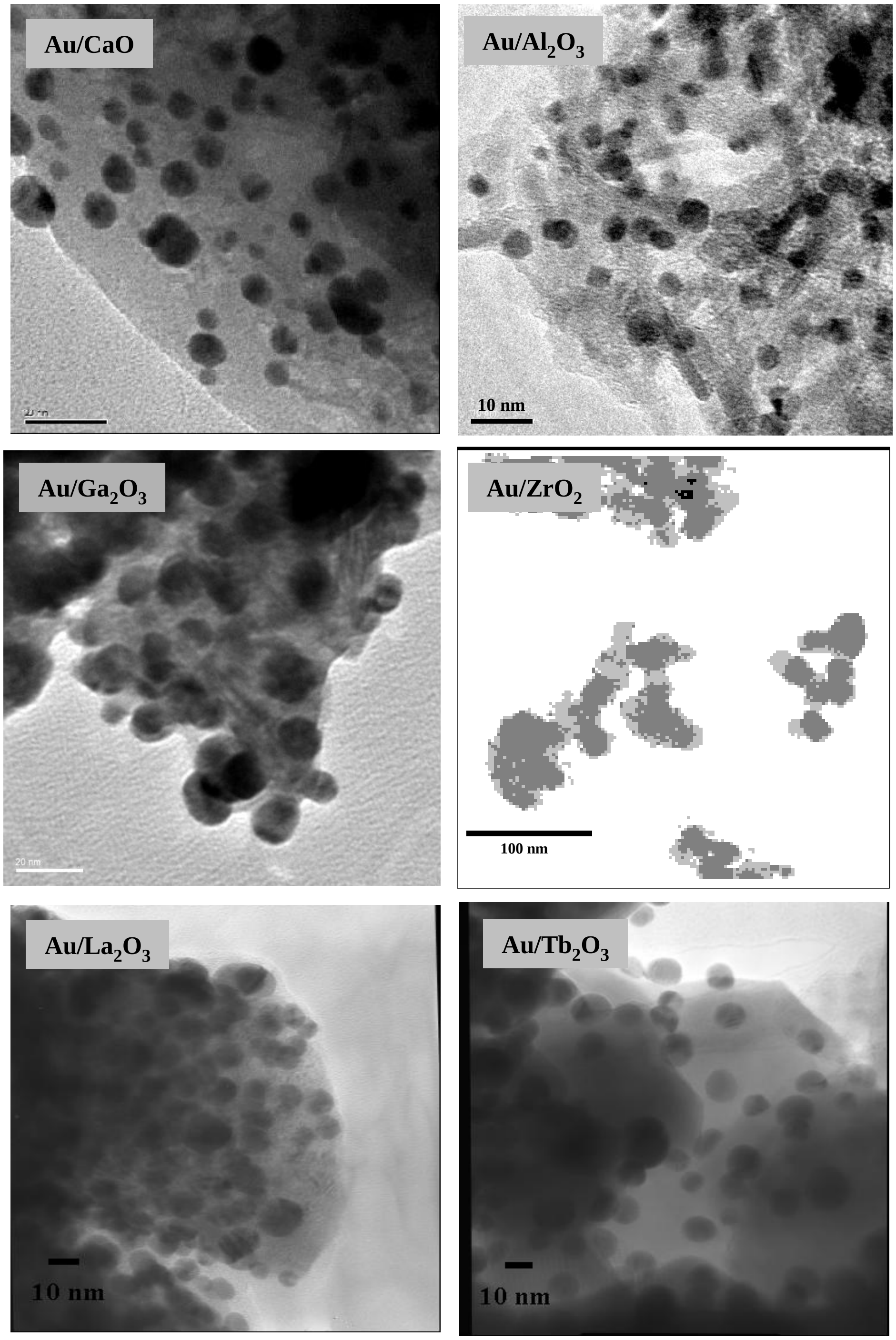

Figure 8.3: TEM photograph of the Au/CaO, Au/Al_2O_3, Au/Ga_2O_3, Au/ZrO_2, Au/La_2O_3 and Au/Tb_2O_3 (calcined at 400ºC) catalysts.

(800 ºC), there was an appreciable increase in the Au particle size (Figure 8.2). The increase in Au particle size with temperature is due to agglomeration of the gold particles.

8.3.2. For Pd/Al_2O_3 Catalyst

XRD spectra and TEM photographs of the Pd/Al_2O_3 (Pd loading = 1 wt%) catalyst are presented in Figure 8.4a and 8.4b, respectively. For the Pd/Al_2O_3 catalyst, the bulk Al_2O_3 phase is purely γ-Al_2O_3 (Figure 8.4a) and the palladium loading (1 wt% of Pd) is so small that it is not detected in the XRD spectra. The particle size of Pd in the Pd/Al_2O_3 is found to be in the range of 5 - 7 nm (Figure 8.4b).

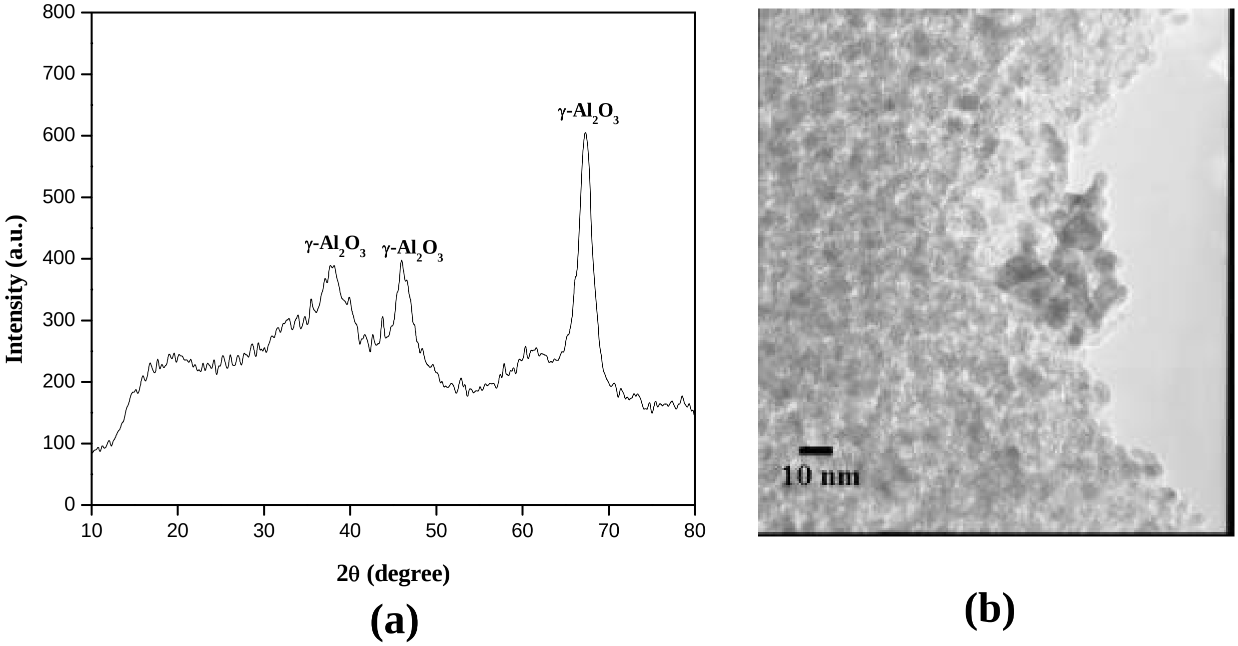

Figure 8.4: a) XRD spectra and b) TEM photograph of Pd/Al_2O_3 (Pd loading = 1 wt%) catalyst.

The surface analysis of the catalyst (obtained from XPS), before its use in the O_2 reduction by hydroxylamine, is presented in the Figure 8.5 (C1s with binding energy 285.0 eV was as an internal standard). The O1s peak at ~532.8 eV arise from the contribution of oxygen from the support (Al_2O_3) and the Al2p core level shows a characteristic peak of alumina of the support around ~74.2 eV. It is seen that the surface Pd is in the metallic form (i.e. Pd^o).

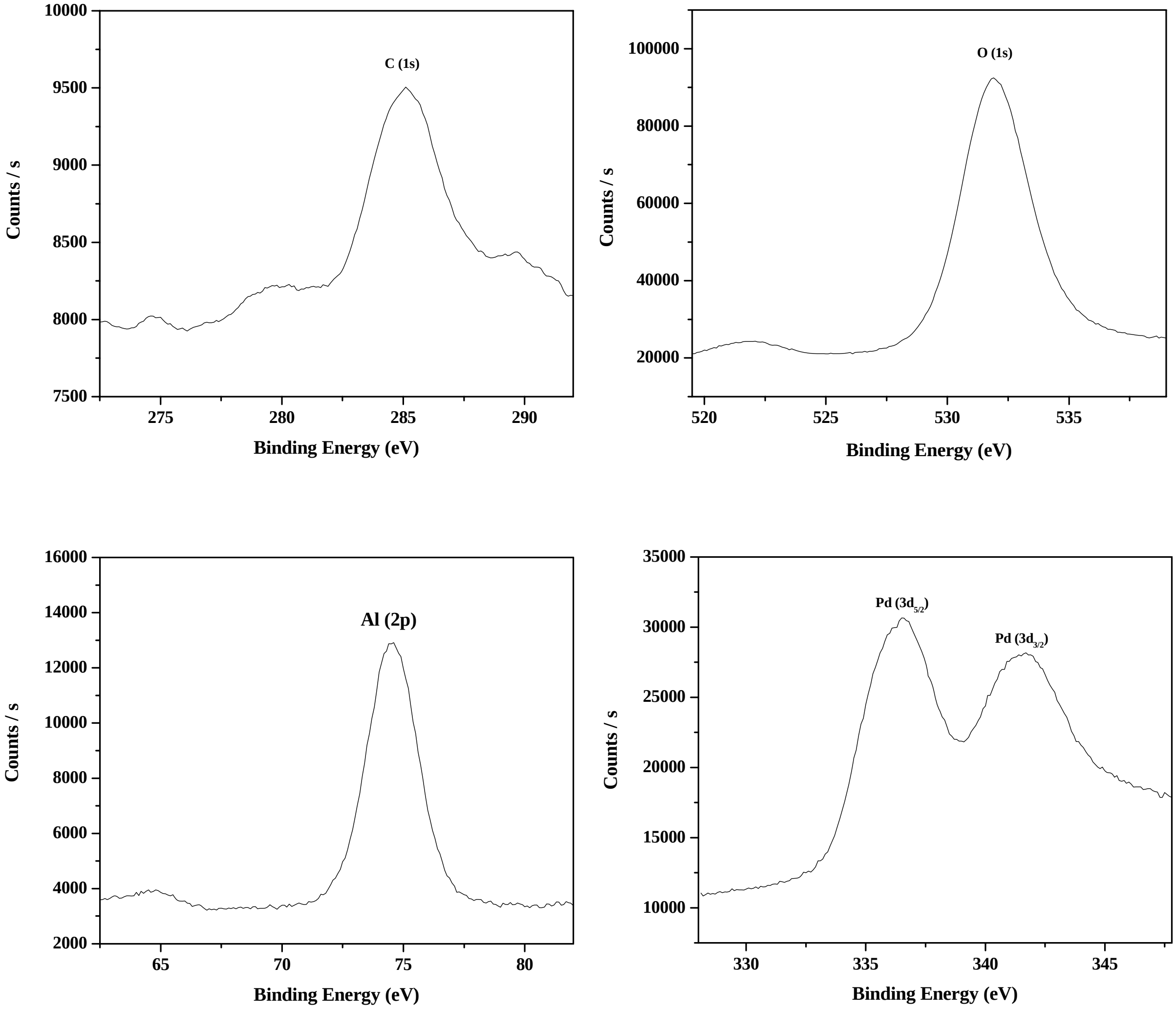

Figure 8.5: XPS spectra of Pd/Al_2O_3 (Pd loading = 1 wt%) catalyst before its use in the reaction.

8.4. O_2-to-H_2O_2 Reduction by Hydrazine or Its Salt over Brominated Pd (5wt%)/Al_2O_3 (1 wt% of Br) Catalyst

In our previous work [9,10], we have throughly invetigated the H_2O_2 generation via the selective reduction of O_2 by hydrazine ($N_2H_4 + 2\ O_2 \rightarrow 2\ H_2O_2 + N_2$) over highly active/selective supported Pd catalyst in an acidic aqueous medium in the presence of Br promoter at ambient conditions. High H_2O_2 yields were obtained at 100 % N_2H_4 conversion by this process. It was observed that the reduction of O_2 by hydrazine (from hydrazine salt or hydrate) leads to the H_2O_2 formation with high yields only in the presence of Br^- anions and protons (mineral acid) [9,10]. In their absence or in the presence of other halides and acid, only water without even traces of H_2O_2 was formed in the reaction. It was also observed that the associated cation with the bromide anions has no beneficial effect on the H_2O_2 formation. The formation of H_2O_2 was found to drastically increase with increasing the concentration of Br promoter in the acidic reaction medium particularly at low concentrations of Br (0 – 1.0 $mmol/dm^3$ in the reaction medium). The modification of the Pd/Al_2O_3 catalyst through a change in the electronic environment on its surface due to the bromide anions adsorbed on or close to Pd seems to be responsible for the observed promoting effect of the bromide anions on the H_2O_2 formation. The adsorption of bromide anions on the catalyst surface during the reaction was confirmed from the XPS of the used catalyst [16]. At a very high concentration of Br^- anions, the catalyst is at least partially deactivated due to poisoning of its active sites by Br^- anions.

8.4.1. Influence of the Presence of Different Acids in Aqueous Medium

Since, the presence of bromide anions (which are essential for the selective O_2-to-H_2O_2 reduction by hydrazine sulfate) in the acidic aqueous reaction medium is highly corrosive for commonly used stainless steel reactors, it will be more convenient if bromide ions are incorporated in the catalyst itself. Therefore, in this section we have studied the O_2-to-H_2O_2 reduction by hydrazine sulfate over the brominated Pd/Al_2O_3 (1wt% Br) catalyst.

Results showing the influence of the presence of different acids on the formation of H_2O_2 in the oxidation of hydrazine hydrate by O_2 (at 25 ºC) over brominated Pd (5wt%)/Al_2O_3 (1wt% Br) catalyst in aqueous medium are presented in Table 8.2. The results in this table reveal that in absence of any acid, there was no formation of H_2O_2 but hydrazine was completely converted to water. This also indicates that both the presence of protons and bromide promoter is essential for the H_2O_2 formation in the O_2-to-H_2O_2 reduction. It was observed that with increasing the acid/hydrazine mole ratio, the H_2O_2 yield/selectivity increased appreciably. But with the same acid/hydrazine mole ratio for the two different initial concentrations of hydrazine, the higher one showed lower yield/selectivity for the H_2O_2 formation. The observed decrease in the H_2O_2 yield/selectivity with increasing the initial concentration of hydrazine sulfate may be due to the conversion of H_2O_2 (after its formation) by its reaction with the unconverted hydrazine. In the presence of HBr in the reaction medium, the N_2H_4 conversion decreased drastically and consequently, the H_2O_2 yield; indicating the deactivation of the brominated Pd/Al_2O_3 catalyst due to poisoning of its active sites by the adsorption excess Br^- anions from the reaction medium. Among the mineral acids, sulfuric and hydrochloric acids are more preferable acids for the selective reduction of O_2 to H_2O_2.

Table 8.2: Influence of the presence of different acids on the formation of H_2O_2 in the oxidation of hydrazine hydrate by O_2 (at 25 ºC) over brominated Pd(5wt%)/Al_2O_3 (1wt% Br) catalyst in aqueous medium [reaction conditions: amount of catalyst = 0.1 g, Initial concentration of hydrazine hydrate = 42 mmol/dm^3, O_2 flow rate = 10 cm^3/min and reaction period = 0.5 h].

Acid in the medium	Concentration of acid (mol/dm^3)	Acid/N_2H_4 mole ratio	Conversion of N_2H_4 (%)	Selectivity for H_2O_2 (%)	H_2O_2 yield (%)
Nil	0.0	0.0	100	0.0	0.0
H_2SO_4	0.04	1.0	100	57.9	57.9
H_2SO_4[a]	0.08	1.0	64.5	29.8	19.2
H_2SO_4	0.02	0.5	87.7	43.4	38.1
H_2SO_4[a]	0.04	0.5	87.3	21.3	18.6
HCl	0.08	2.0	100	53.3	53.3
HBr	0.08	2.0	39.5	34.9	13.8
H_3PO_4	0.04	1.0	100	32.7	32.7
H_3PO_4[a]	0.08	1.0	87.2	26.5	23.1

[a] Initial concentration of hydrazine hydrate was 84 mmol/dm^3.

8.4.2. Influence of the H_3PO_4/N_2H_4 mole Ratio

The further investigation for studying the influence of the acid/N_2H_4 mole ratio was carried out with phosphoric acid instead of sulfuric or hydrochloric acid in the reaction medium. This is because of the fact that the phosphoric acid is less corrosive and the phosphate anions act as H_2O_2 stabilizer. Results showing the influence of the H_3PO_4/N_2H_4 mole ratio on the hydrazine conversion and H_2O_2 yield/selectivity in the reduction of O_2 by hydrazine over the brominated Pd/Al_2O_3 (1 wt% Br) catalyst are presented in Figure 8.6.

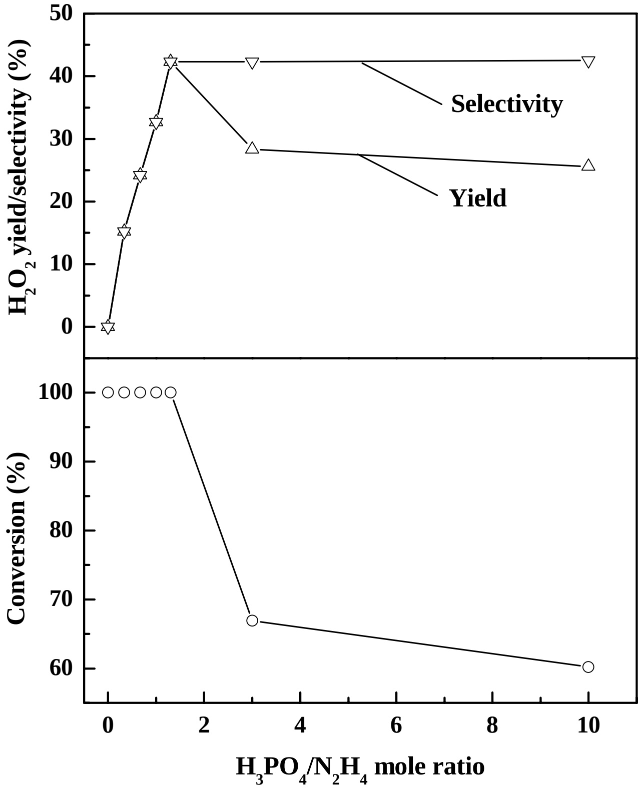

Figure 8.6: Influence of the H_3PO_4/N_2H_4 mole ratio on the hydrazine conversion and H_2O_2 yield/selectivity in the reduction of O_2 by hydrazine over the brominated Pd/Al_2O_3 (1 wt% Br) catalyst [reaction conditions: amount of catalyst = 0.1 g, volume of reaction medium = 50 cm^3, Initial concentration of hydrazine hydrate = 42 $mmol/dm^3$, O_2 flow rate = 10 cm^3/min and reaction period = 0.5 h].

The H_2O_2 yield was found to increase first and then passed through a maximum with increasing the H_3PO_4/N_2H_4 mole ratio from 0 – 10, whereas the H_2O_2 selectivity first increased up to about 1.3 H_3PO_4/N_2H_4 mole ratio and then leveled off (Figure 8.6). This indicates that an optimum acid/N_2H_4 mole ratio is necessary for achieving the best results in the O_2-to-H_2O_2 reduction by hydrazine.

8.5. Reaction between N_2H_4 and H_2O_2 in Aqueous Medium Containing Bromide Promoter in the Presence or Absence of Pd(5 wt%)/Al_2O_3 Catalyst

Our earlier study [10] showed that the H_2O_2 yield in the reaction passed through a maximum with increasing the reaction time and/or the temperature, it increased with increasing the concentration of H_3PO_4 added to the reaction mixture but it decreased with increasing the concentration of hydrazine in the reaction mixture. This reveals that H_2O_2 is an intermediate product, which may be further converted to water by its decomposition ($H_2O_2 \rightarrow H_2O + 0.5\ O_2$) and reaction with hydrazine ($2\ H_2O_2 + N_2H_4 \rightarrow N_2 + 4\ H_2O$) in consecutive reactions. Therefore, the decomposition of H_2O_2 and the reaction between N_2H_4 (from $N_2H_4.H_2SO_4$) and H_2O_2 under similar reaction conditions (in the absence of O_2) have also been studied, which are presented in Tables 8.3.

Table 8.3: Results of the reaction between N_2H_4 from hydrazine sulfate and H_2O_2 in aqueous medium containing bromide promoter in the presence and absence of Pd catalyst [reaction mixture = 4.0 mmol $N_2H_4.H_2SO_4$ + 8.2 mmol H_2O_2 + KBr (1.0 mmol/dm^3) + 50 cm^3 distilled water with or without Pd catalyst (0.1 g), temperature = 27 ºC, reaction time = 0.5 h, pH of the reaction mixture < 2.0].

Catalyst	Conversion (%)	
	N_2H_4	H_2O_2
Nil	2.2	2.3
Pd/Al_2O_3	50.3^e	49.8
Pd/Al_2O_3^{a}	--	5.1
Pd/Al_2O_3^{b}	--	100
Pd/Al_2O_3^{c}	99.6^f	96.1
Pd/Al_2O_3^{d}	100^g	100

[a] In the absence of $N_2H_4.H_2SO_4$ but in the presence of H_2SO_4 (4.0 mmol), [b] In the absence of $N_2H_4H_2SO_4$, any mineral acid and bromide anions. [c] When the reaction medium was neutralized to a pH of 7.0 with alkali. [d] In the absence of bromide anions. [e] Amount of gas evolved was 2.0 mmol. [f, g] Amount of gas evolved was ≅ 4.0 mmol.

Results of the reaction between H_2O_2 and N_2H_4 (Table 8.3) show that, in the absence of the Pd/Al_2O_3 catalyst, the reaction between H_2O_2 and N_2H_4 was very slow but it proceeded with a considerable rate in the presence of the catalyst. However, the H_2O_2 conversion in the absence of the reducing agent (i.e. the H_2O_2 decomposition alone in the presence of bromide anions and H_2SO_4) was quite small. The conversion of N_2H_4 (50.3 %) and H_2O_2 (49.8 %) and gas evolved (2.0 mmol) in the reaction confirm the reaction stoichiometry (i.e. $N_2H_4 + 2\ H_2O_2$

→ $N_2 + 4\ H_2O$). The observed decrease in the H_2O_2 yield/selectivity with increasing the initial concentration of hydrazine sulfate is consistent with the conversion of H_2O_2 (after its formation) by its reaction with the unconverted hydrazine. When the aqueous solution of hydrazine sulfate was neutralized by alkali to a pH of about 7.0, the reaction between the hydrazine and H_2O_2 was much faster (Table 8.3) than in the absence of the neutralization (i.e. in the presence of protons). In the absence of bromide anions, the reaction was found to be very fast; it was completed within a period of just 2.0 min. These observations clearly reveal that the reaction is very strongly influenced by the presence of both protons and bromide anions; it is drastically retarded in the presence of acid (protons) and/or bromide anions. Thus the role of protons and bromide anions in the O_2 reduction by hydrazine sulfate seems to enhance the net H_2O_2 formation by drastically inhibiting/retarding the consecutive reactions, H_2O_2 decomposition and reaction between H_2O_2 and unconverted N_2H_4.

8.6. Decomposition of N_2H_4 (from Hydrazine Sulfate) over the Pd(5 wt%)/Al_2O_3 Catalyst in Aqueous Medium under Different Conditions in the Absence of O_2

Moreover, although the hydrazine is completely converted, the observed H_2O_2 yield is less than 100 % and with increasing temperature H_2O_2 yield also decreased [10]. This indicates that the decomposition of N_2H_4 ($N_2H_4 \rightarrow N_2 + 2H_2$) and water formation can also occur via the direct oxidation of N_2H_4 in a parallel reaction ($N_2H_4 + O_2 \rightarrow N_2 + 2\ H_2O$). Therefore, the deco-

Table 8.4: Results of the decomposition of N_2H_4 from hydrazine sulfate over the Pd/Al_2O_3 catalyst in aqueous medium under different conditions in the absence of O_2 [reaction mixture = 4.0 mmol $N_2H_4.H_2SO_4$ + 50 cm^3 distilled water (with or without KBr), catalyst wt. = 0.1 g and reaction time 0.5 h].

Temperature (ºC)	Concentration of KBr (mmol/dm^3)	Conversion of N_2H_4 (%)
27	00	0.0
27	1.0	0.0
50	1.0	11.0

mposition of N_2H_4 (in the absence of O_2) over the Pd/Al_2O_3 catalyst (at 27º and 50º C) in the presence or absence of bromide anions in aqueous medium has also been studied. The results are presented Table 8.4.

At a temperature of 27 ºC, there was very little or no decomposition of N_2H_4 in the presence or absence of bromide anions (Table 8.4). However, at the higher temperature (50 ºC), the decomposition of N_2H_4 was appreciable (11 %) even in the presence of bromide anions (Table 8.4). Therefore, the decrease of H_2O_2 yield with 100% conversion of N_2H_4 is due to the water forming direct oxidation of N_2H_4 and at higher temperature the decomposition of N_2H_4 also plays some role in the decrease of the H_2O_2 yield.

8.7. O_2-to-H_2O_2 Reduction by Hydroxylamine or Its Salts over Au-catalysts

Until the pioneering work of Haruta et.al. on nano-gold catalysts [17,18], gold was believed to be catalytically inactive metal in both the oxidation and reduction reactions [19]. In the last 1 - 2 decades, gold catalysts have attracted attention of many researchers. Highly active nano-gold catalysts have been extensively used for a number of practically important oxidation reactions. It is, therefore, interesting to explore a possibility of using supported nano-gold catalysts for the reduction of oxygen by reducing agent such as hydrazine, hydroxylamine or their salts, to hydrogen peroxide.

8.7.1. Influence of Different Metal Oxide Supported Nano-gold Catalysts on O_2-Reduction in Aqueous Medium

Results of the O_2 reduction by hydroxylammonium salts or hydroxylamine to H_2O_2 over different metal oxide (viz. MgO, CaO, Al_2O_3, Ga_2O_3, ZrO_2, La_2O_3, CeO_2-ZrO_2, Gd_2O_3, Yb_2O_3 and Tb_2O_3) supported nano-gold catalysts in aqueous medium at a pH of 7.0 are presented in Tables 8.5. Under the conditions similar to that used in this study, H_2O_2 even in trace amounts was not generated in the reduction of O_2 by hydrazine or its salt over the gold catalysts.

Among the nano-gold catalysts (Table 8.5), the Au/Gd_2O_3, Au/MgO and Au/La_2O_3 catalysts showed very good performance in the H_2O_2 formation in aqueous medium from the O_2 reduction by hydroxylammonium sulfate; the order of catalyst performance is Au/Gd_2O_3 (H_2O_2 yield = 83.5 %) > Au/MgO (81.5 %) > Au/La_2O_3 (72.0 %). However, based on the Au loading, the Au/La_2O_3 showed better performance than that of the Au/MgO. Both the Au/MgO

Table 8.5: Reduction of O_2 by hydroxylammonium sulfate to H_2O_2 over different supported nano-gold catalysts (calcined at 400 ºC for 2h) in aqueous medium [reaction conditions: hydroxylammonium sulfate = 40 mmol/dm^3, catalyst wt. = 0.1 g, O_2 flow = 5 cm^3/min, temperature = 27 ºC and reaction period = 1.0 h].

Catalyst	Rate of H_2O_2 formation (mmol/ $g_{(Au)}$/ h)	H_2O_2 yield (%)
Au/MgO	217.3	81.5
Au/MgO[a]	158.7	59.5
Au/CaO	159.6	37.5
Au/La_2O_3	221.5	72.0
Au/CeO_2-ZrO_2[b]	145.5	48.0
Au/Gd_2O_3	264.1	83.5
Au/Tb_2O_3	19.4	6.5
Au/Yb_2O_3	121.7	36.5
Au/Yb_2O_3[a]	88.3	26.5
Au/Al_2O_3	31.3	10.0
Au/Ga_2O_3	148.4	47.5
Au/ZrO_2	43.3	6.5

[a] Calcined at 800 ºC for 2h. [b] Ce/Zr mole ratio = 1.0.

and Au/CaO catalysts were found to be partly dissolved in the aqueous medium, even though the aqueous solution of hydroxylammonium sulfate was neutralized by alkali before the reaction. However, this was not the case for the other catalysts. Hence, the Au/Gd_2O_3 and Au/La_2O_3 catalysts are recommended for the *in situ* H_2O_2 generation in an aqueous medium.

When the Au/MgO and Au/Yb_2O_3 catalysts were calcined at higher temperature (800 ºC), there was an appreciable decrease in the H_2O_2 yield for both the catalysts (Table 8.5). In this case the decrease in the catalyst performance is expected because of the increase in the Au particle size (Figure 8.2) and may also be due to sintering of the support. It may be noted that the Au particle size for the Au/Al_2O_3, Au/ZrO_2 and Au/CeO_2-ZrO_2 catalysts is smaller than that for the Au/Gd_2O_3, Au/La_2O_3, Au/MgO (calcined at 400 ºC or 800 ºC) and Au/Ga_2O_3, but the later ones showed better catalytic performance. Even for the promising catalysts (Au/Gd_2O_3, Au/La_2O_3 and Au/MgO), their catalytic performance showed no direct dependence upon their Au particle size. The Au/Gd_2O_3 having larger Au particle size showed better performance than the Au/La_2O_3 and Au/MgO (calcined at 400 ºC) (Tables 8.5). However, the Au/MgO calcined at 800 ºC, having much larger Au particle size, showed poorer performance than that of the Au/MgO calcined at 400 ºC, Au/Gd_2O_3 and Au/La_2O_3 catalysts. In this catalytic process, the factors other than Au particle size or dispersion, such as the shape of Au particle (e.g. hemispherical shape observed for the Au/Gd_2O_3), which controls the contacting between the Au particle and support surface and consequently Au-support interactions, Au-Au coordination number and also the oxidation state of Au (Au^o, Au^{+1} or Au^{+3}) at the catalyst surface, seem to play more important role in deciding the performance of the gold catalysts. The observed high activity of the Au/Gd_2O_3 with Au particle size of 17.4 nm is in contrast to that observed for the low temperature CO oxidation over gold catalysts [20]. For the CO oxidation, the catalytic activity is drastically reduced with increasing the Au particle size.

8.7.2. Influence of Different Metal Oxide Supported Nano-gold Catalysts on O_2 Reduction in Non-Aqueous Medium

Results of the O_2 reduction by hydroxylammonium salts or hydroxylamine to H_2O_2 over different metal oxide (viz. MgO, La_2O_3, CeO_2-ZrO_2, and Gd_2O_3) supported nano-gold catalysts in non-aqueous medium (viz. methanol, ethanol or acetonitrile) are presented in Table 8.6.

Among the non-aqueous solvents (viz. methanol, ethanol and acetonitrile), methanol provides the best results for the reduction of O_2 by hydroxylamine to H_2O_2 over the Au/Gd_2O_3 catalyst; acetonitrile is the least preferred one (Table 8.6). In case of the use of non-aqueous solvent, hydroxylamine should be preferred over hydroxylammonium salt, as the reducing agent; the later has also lower solubility in non-aqueous solvent. The yield of H_2O_2 in the O_2 reduction by hydroxylammonium chloride in methanol medium, even after neutralizing the hydroxylammonium salt by NaOH, is much lower (15.5 %) than that (48.0 %) obtained using hydroxylamine; however, in the absence of alkali neutralization, there was no formation of H_2O_2 (Table 8.6).

Table 8.6: Reduction of O_2 by hydroxylammonium chloride or hydroxylamine over supported nano-gold catalysts in non-aqueous medium [reaction conditions: catalyst wt. = 0.1 g, O_2 flow = 5 cm^3/min, temperature = 27 ºC and reaction period = 1.0 h].

Catalyst	Reaction medium	Reducing agent used (4 mmol)	Rate of H_2O_2 formation (mmol/ $g_{(Au)}$/ h)	Yield of H_2O_2 (%)
Au/MgO	CH_3OH	$NH_2OH.HCl$	0.0	0.0
Au/MgO	CH_3OH	NH_2OH	128.0	48.0
Au/La_2O_3	CH_3OH	NH_2OH	278.5	90.5
Au/Gd_2O_3	CH_3OH	NH_2OH	312.0	99.8
Au/Gd_2O_3	C_2H_5OH	NH_2OH	165.6	53.0
Au/Gd_2O_3	CH_3CN	NH_2OH	103.6	33.0
Au/CeO_2-ZrO_2	CH_3OH	NH_2OH	189.4	32.5
Au/MgO[a]	CH_3OH	$NH_2OH.HCl$	41.3	15.5

[a] with the addition of equimolar amount of NaOH.

Interestingly, the Au/Gd_2O_3 and Au/La_2O_3 catalysts also showed excellent performance (99.8 and 90.5 % H_2O_2 yield, respectively) in non-aqueous (methanol) medium for the reduction of O_2 by hydroxylamine (Table 8.6). Both the catalysts could be reused several times without an appreciable loss in their catalytic activity. Apart from these two catalysts, the Au/MgO, although less active than the former ones, is also a promising catalyst for the *in situ* H_2O_2 generation in non-aqueous medium.

8.7.3. Influence of the Reaction Temperature and Time over the Au/MgO Catalyst on O_2-Reduction in Aqueous or Non-aqueous Medium

Results showing the influence of the reaction temperature in aqueous medium and reaction time in methanol medium on the H_2O_2 formation by the reduction of O_2 by hydroxylammonium sulfate over the Au/MgO catalyst are presented in Figures 8.7 and 8.8, respectively.

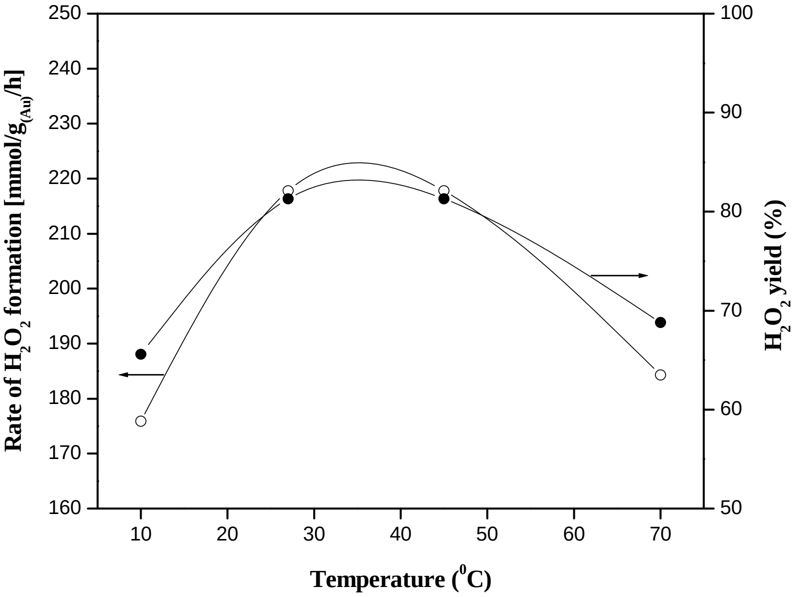

Figure 8.7: Influence of temperature on the H_2O_2 formation by the reduction of O_2 by hydroxylammonium sulfate over the Au/MgO catalyst in the aqueous medium [reaction conditions: hydroxylammonium sulfate = 40 mmol/dm^3, catalyst wt. = 0.1 g, O_2 flow = 5 cm^3/min and reaction period = 1.0 h].

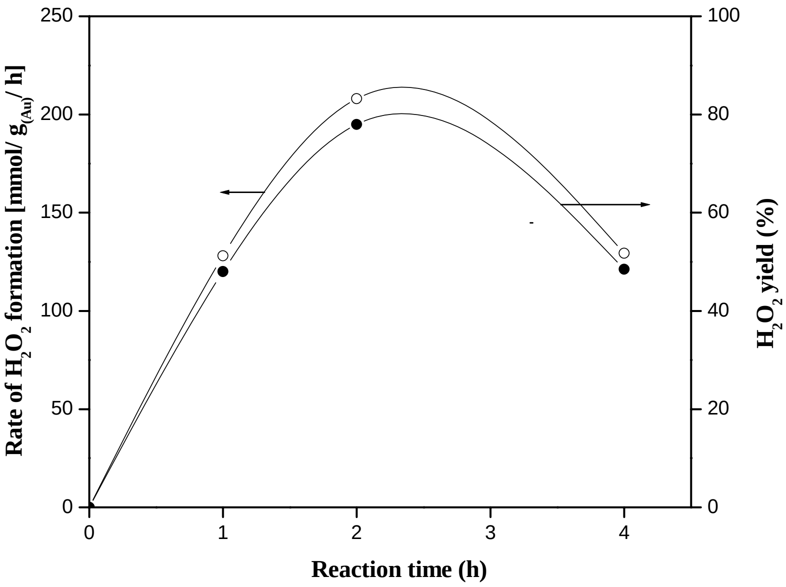

Figure 8.8: Influence of the reaction time on the H_2O_2 formation by the reduction of O_2 by hydroxylamine over the Au/MgO catalyst in methanol medium [reaction conditions: hydroxylamine = 80 mmol/dm^3, catalyst wt = 0.1 g, O_2 flow = 5 cm^3/min and temperature = 27 ºC].

The H_2O_2 formation rate and H_2O_2 yield passed through a maximum with increasing the reaction temperature and/or time (Figures 8.7 and 8.8, respectively), indicating that both the optimum temperature and time are required for achieving maximum H_2O_2 yield/formation rate in the O_2 reduction. The decrease in the H_2O_2 yield at the higher temperature is attributed to the loss of more and more H_2O_2 after its formation due to a larger increase in the rate of H_2O_2 decomposition ($H_2O_2 \rightarrow H_2O + 0.5\ O_2$), as compared to the increase in the rate of H_2O_2 formation, with increasing the temperature. The decrease in the H_2O_2 yield at the longer reaction periods clearly shows that H_2O_2 is an intermediate product of the consecutive reaction. Our preliminary study also showed that the nano-gold catalysts also catalyze the decomposition of H_2O_2.

8.8. O_2-to-H_2O_2 Reduction by Hydroxylamine or Its Salts over Pd/Al_2O_3 Catalyst

8.8.1. Influence of Hydroxylammonium Salt, Reaction medium (Aqueous or Non-Aqueous) and Pd Loading

Results of the reaction of O_2 with hydroxylammonium salt over the Pd/Al_2O_3 catalyst showing the influence of hydroxylammonium salt, reaction medium (aqueous or non-aqueous) and Pd loading on the conversion of NH_2OH (from the hydroxylammonium salt) and H_2O_2 generated per mole of hydroxylamine initially present are presented in Table 8.7.

A comperison of the results for the two different hydroxylamine salts (Table 8.7) shows that, as compared to hydroxylammonium chloride, hydroxylammonium sulfate is a better choice as compared for the H_2O_2 generation in the aqueous medium. However, in the non-aqueous medium (viz. methanol), the choice is reversed because $(NH_2OH)_2.H_2SO_4$ has a much lower solubility in methanol than $NH_2OH.HCl$. Interestingly, the generation of H_2O_2 in methanol medium was possible only when the salt was pretreated with equimolar amounts of alkali. However, when the salt was replaced by hydroxylamine (i.e. in the absence of any acid), the H_2O_2 formed in the reaction in methanol medium was 0.61 mol/mol(NH_2OH).

A comparison of the results for the Pd (1wt%)/Al_2O_3 and Pd (5 wt%)/Al_2O_3 (Table 8.7) indicates that the catalyst with higher Pd loading showed an inferior performance (i.e. a much lower TOF for the H_2O_2 generation). For the Pd (5 wt%)/Al_2O_3 catalyst, the conversion was higher but the H_2O_2 formed, and consequently H_2O_2 yield/selectivity was lower. Hence, all the further studies were carried out using Pd(1 wt%)/Al_2O_3 catalyst.

Table 8.7: Results of the reaction between O_2 and NH_2OH (from hydroxylammonium salt) over the Pd (1 wt%)/Al_2O_3 catalyst in neutral aqueous (pH = 7.0) or non-aqueous medium [reaction conditions: $(NH_2OH)_2.H_2SO_4$ (or $NH_2OH.HCl$) = 40 (or 80) mmol/dm^3, catalyst wt. = 0.1 g, O_2 flow = 5 cm^3/min, temperature = 27 ºC and reaction period = 1.0 h].

Hydroxylammonium salt used	Reaction medium	Partial pressure of O_2 (atm)	Conversion of NH_2OH (%)	H_2O_2 formed[d]	TOF (h^{-1})
$NH_2OH.HCl$	Water	1.0	51	0.33	70
$(NH_2OH)_2.H_2SO_4$	Water	1.0	72	0.47	200
$(NH_2OH)_2.H_2SO_4$[a]	Water	1.0	71	0.46	196
$(NH_2OH)_2.H_2SO_4$	Water	0.2	66	0.22	94
$NH_2OH.HCl$	Methanol	1.0	--	0.0	0
$NH_2OH.HCl$[b]	Methanol	1.0	--	0.34	71
$(NH_2OH)_2.H_2SO_4$[c]	Water	1.0	84	0.19	16

[a] Fourth reuse of the catalyst. [b] When the salt was treated with the equimolar amounts of NaOH before the reaction. [c] For the Pd (5 wt%)/Al_2O_3 catalyst. [d] Moles of H_2O_2 formed per mole of NH_2OH initially present.

The catalyst from the reaction mixture can be easily separated, simply by filtration, and it can be reused/recycled without a significant loss of its activity (Table 8.7). It may also be noted that the TOF of H_2O_2 generation over the Pd (1wt%)/Al_2O_3 catalyst (Tables 8.5 and 8.6) are very much higher than that (TOF = 33.2) observed for the supported Au-catalyst.

8.8.2. Influence of pH of the Medium

The neutralization of the aqueous solution of hydroxylammonium salt was must by the addition of an alkali to the solution in the hydroxylamine-to-H_2O_2 oxidation. In the absence of such neutralization, there was no formation of H_2O_2. Even in the methanol medium, the H_2O_2 generation was possible only when the salt was pretreated with equimolar amount of alkali. Therefore, pH of the medium plays a important role in the hydroxylamine-to-H_2O_2 oxidation process. Results of the reaction of O_2 with the hydroxylamine from hydroxylammonium salt over the Pd (1 wt%)/Al_2O_3 catalyst showing pH of the aqueous hydroxylammonium salt solution on the conversion of NH_2OH (from the hydroxylammonium salt) and H_2O_2 generated per mole of hydroxylamine initially present are presented in Figure 8.9.

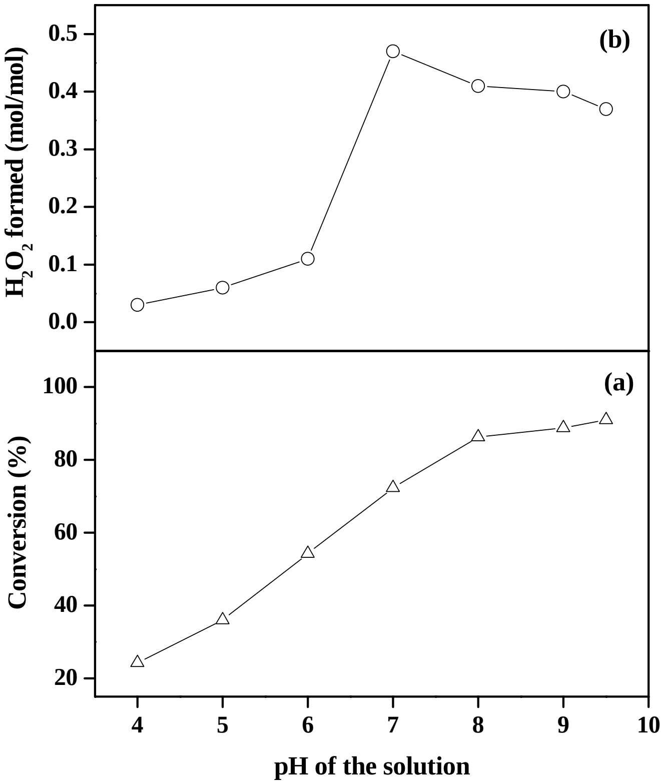

Figure 8.9: Effects of pH of the aqueous solution of $(NH_2OH)_2.H_2SO_4$ on the conversion of NH_2OH [from $(NH_2OH)_2.H_2SO_4$] over the Pd (1 wt%)/Al_2O_3 catalyst and H_2O_2 formed per mole of NH_2OH initially present in the reaction medium [reaction conditions: $(NH_2OH)_2.H_2SO_4$ = 40 mmol/dm^3, catalyst wt. = 0.1 g, O_2 flow = 5 cm^3/min, temperature = 27 ºC and reaction period = 1.0 h].

The influence of the pH of aqueous hydroxylammonium salt solution on the H_2O_2 formation is very strong (Figure 8.9). The H_2O_2 formation first increased sharply and then decreased after passing through a maximum (at the pH of 7.0). At the lower pH (below 6.0), there was only a little or no generation of H_2O_2. At the pH of 7.0 (i.e. in the absence of acid); the formation of H_2O_2 was appreciable even in the absence of any halide (e.g. bromide) promoter. This is contradictory to that observed in the H_2O_2 generation by the reaction of O_2 with hydrazine or its salt in aqueous medium over Pd/Al_2O_3 [9]. The NH_2OH conversion, however, increased continuously with increasing the pH. The pH of reaction mixture was found to decrease with increasing the reaction time. This is expected because of the consumption of NH_2OH in the reaction. The decrease in the H_2O_2 formation at the higher pH (> 7.0) is expected due to an increase in the rate of H_2O_2 decomposition; a base acts as a catalyst for the H_2O_2 decomposition [7]. Decomposition of H_2O_2 under the similar reaction condition was investigated by varying the pH of the reaction medium from 4.0 to 9.0; it was found to increase from 12% to 100% with increasing the pH from 4 to 9, discussed later. In the neutral or basic medium (i.e. at pH ≥ 7.0), the reacting species in the reaction mixture is NH_2OH, which is released from the hydroxylammonium salt. However, in the acidic medium, there is no release of NH_2OH; the cationic species $(NH_3OH)^+$ existing at pH < 7.0 are unreactive or less reactive than NH_2OH for reducing oxygen to H_2O_2. Hence, the H_2O_2 generation is decreased drastically with decreasing the pH of medium below 7.0.

8.8.3. Influence of Reaction Temperature

Results showing the influence of reaction temperature in the reaction of O_2 with the hydroxylamine from hydroxylammonium salt over the Pd (1 wt%)/Al_2O_3 catalyst in aqueous solution on the conversion of NH_2OH (from the hydroxylammonium salt) and H_2O_2 generated per mole of hydroxylamine initially present are presented in Figure 8.10.

The results in Figure 8.10 show that the NH_2OH conversion increased as expected, but the H_2O_2 formation decreased with increasing the reaction temperature. The decrease in H_2O_2 generation, particularly at the higher temperature (50 ºC) is very large. This is expected mostly because of an increase in the rate of NH_2OH decomsition; the NH_2OH decomposition increased from 8% to 30% by varying the reaction temperature from 27 ºC to 50 ºC and also due to the H_2O_2 decomposition at higher temperature. Decomposition of H_2O_2 under the similar reaction condition (intail pH of the reaction medium 7.0) was investigated by varying the reaction temperature from 27 ºC to 50 ºC; it was found to increase from 81% to 100% (in 30 min).

8.8.4. Influence of Reaction Time

Results showing the influence of reaction time in the reaction of O_2 with the hydroxylamine from hydroxylammonium salt over the Pd (1 wt%)/Al_2O_3 catalyst in aqueous solution on the conversion of NH_2OH (from the hydroxylammonium salt) and H_2O_2 generated per mole of hydroxylamine initially present are presented in Figure 8.11.

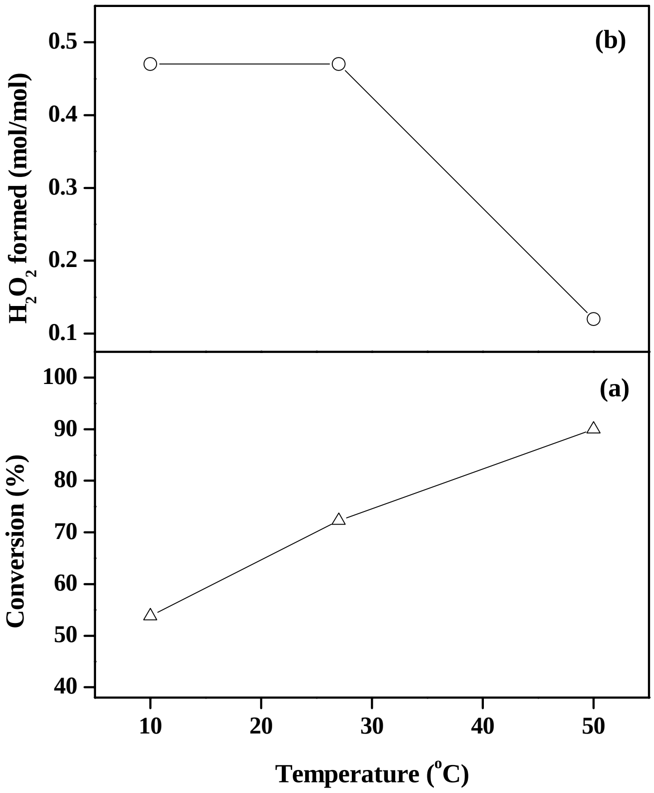

Figure 8.10: Effects of temperature on the conversion of NH_2OH [from $(NH_2OH)_2.H_2SO_4$] over the Pd (1 wt%)/Al_2O_3 catalyst and H_2O_2 formed per mole of NH_2OH initially present in the reaction medium [reaction conditions: $(NH_2OH)_2.H_2SO_4$ = 40 mmol/dm^3, catalyst wt. = 0.1 g, O_2 flow = 5 cm^3/min, pH = 7.0 and reaction period = 1.0 h].

The results in Figure 8.11 reveal that the NH_2OH conversion increased continuously as expected but the H_2O_2 formation passed through a maximum with increasing the reaction time. This indicates that H_2O_2 is an intermediate product of the reaction. At higher reaction periods, the net formation of H_2O_2 decreased because of the H_2O_2 decomposition,

$$H_2O_2 \rightarrow H_2O + 0.5\ O_2 \quad (8.1)$$

which is known to be catalyzed by Pd catalysts [8,16,21], and also due to the reaction of H_2O_2 with unconverted NH_2OH (reaction 8.2).

$$2\ NH_2OH + H_2O_2 \rightarrow N_2 + 4\ H_2O \quad (8.2)$$

Thus, the above consecutive reactions occur along with the following O_2 reduction reactions:

$$2\ NH_2OH + O_2 \rightarrow N_2 + 2\ H_2O + H_2O_2 \quad (8.3)$$

$$2\ NH_2OH + 2\ O_2 \rightarrow N_2 + 3\ H_2O_2 \quad (8.4)$$

$$2\ NH_2OH + 0.5\ O_2 \rightarrow N_2 + 3\ H_2O \quad (8.5).$$

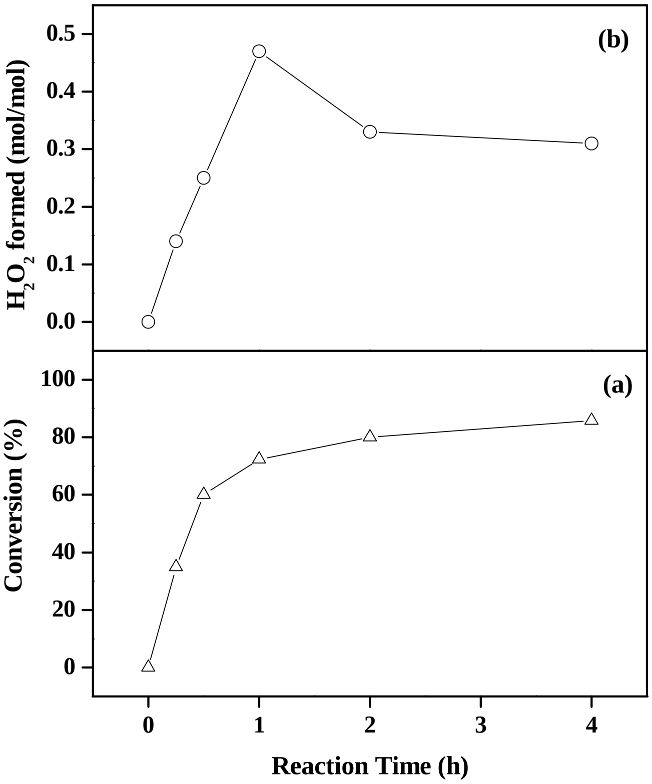

Figure 8.11: Effects of reaction time on the conversion of NH_2OH [from $(NH_2OH)_2.H_2SO_4$] over the Pd (1 wt%)/Al_2O_3 catalyst and H_2O_2 formed per mole of NH_2OH initially present in the reaction medium [reaction conditions: $(NH_2OH)_2.H_2SO_4$ = 40 mmol/dm^3, catalyst wt. = 0.1 g, O_2 flow = 5 cm^3/min, pH = 7.0 and temperature = 27 ºC].

8.8.5. Influence of Catalyst Loading

Results showing the influence of catalyst loading (i.e. catalyst concentration in the aqueous reaction medium) in the reaction of O_2 with the hydroxylamine from hydroxylammonium salt over the Pd (1 wt%)/Al_2O_3 catalyst in aqueous solution on the conversion of NH_2OH (from the hydroxylammonium sulfate) and H_2O_2 generated per mole of hydroxylamine initially present are presented in Figure 8.12.

The results in Figure 8.12 show that the NH_2OH conversion increased, as expected, with increasing the catalyst loading. The increase in conversion of NH_2OH was also reflected in the decrease of pH of reaction mixture with increasing the catalyst loading. But the H_2O_2 formation first increased up to the catalyst 2 g/dm^3 and then continuously decreased with increasing the catalyst loading, indicating the requirement of optimum catalyst loading for achieving the best results.

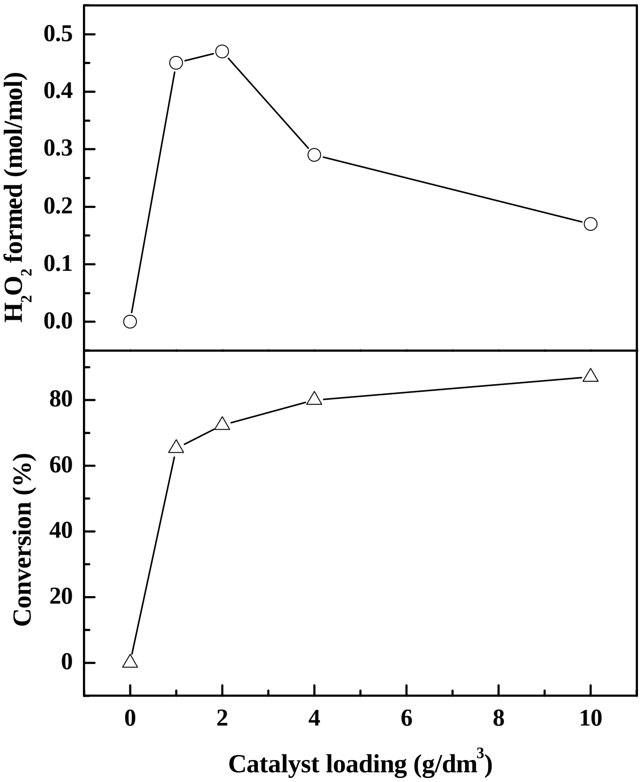

Figure 8.12: Effects of catalyst loading on the conversion of NH_2OH [from $(NH_2OH)_2.H_2SO_4$] over the Pd (1 wt%)/Al_2O_3 catalyst and H_2O_2 formed per mole of NH_2OH initially present in the reaction medium [reaction conditions: $(NH_2OH)_2.H_2SO_4$ = 40 mmol/dm^3, O_2 flow = 5 cm^3/min, pH = 7.0, temperature = 27 ºC and reaction time = 1.0 h].

At the lower catalyst loadings, the rate of H_2O_2 generation increased due to the increase in the rate of O_2 reduction. However, at the higher catalyst loadings (> 2.0 g/dm^3), the net H_2O_2 formation sharply decreased due to a large increase in the rate of decomposition of H_2O_2, formed in the O_2 reduction with complete conversion of the reducing agent in a shorter reaction period than that required at the lower catalyst loadings.

8.8.6. Influence of Initial Concentration of NH_2OH (from Hydroxylammonium Sulfate)

Results showing the influence of initial concentration of hydroxylammonium sulfate in the reaction of O_2 with the hydroxylamine from it over the Pd (1 wt%)/Al_2O_3 catalyst in aqueous solution on the H_2O_2 generated per mole of hydroxylamine initially present are presented in Figure 8.13.

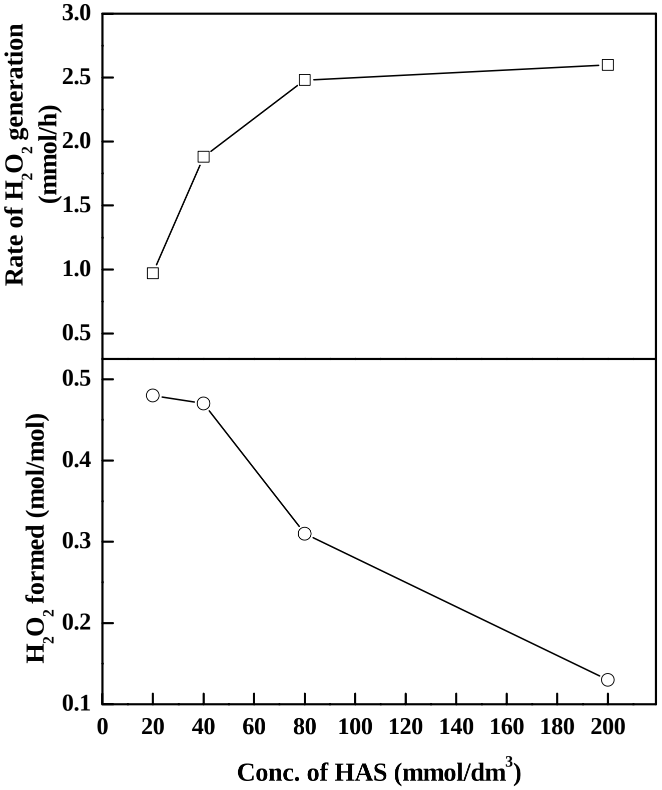

Figure 8.13: Effects of the initial concentration NH_2OH from $(NH_2OH)_2.H_2SO4$ (HAS) on the H_2O_2 formed per mole of NH_2OH initially present in the reaction medium over the Pd (1 wt%)/Al_2O_3 catalyst [reaction conditions: catalyst wt. = 0.1 g, O_2 flow = 5 cm^3/min, pH = 7.0, temperature = 27 °C and reaction time = 1.0 h].

Results in Figure 8.14 suggest that the rate of H_2O_2 generation increased with increasing the concentration of the reducing agent (hydroxylammonium sulfate). However, the moles of H_2O_2 formed per mole of the reducing agent decreased markedly. The decrease is expected most probably because of the consumption of H_2O_2 formed by its reaction with the hydroxylamine from the hydroxylammonium sulfate, leading to the formation of water and N_2, (reaction 8.2). The consumption of H_2O_2 in the reaction 8.2 was confirmed by carrying out the reaction between H_2O_2 and hydroxylamine in the absence of O_2, discussed later.

8.8.7. Influence of Halide Promoter Present in the Reaction Medium

Results in Table 8.8 show a benificial effect of the addition of KCl or KBr in the reaction medium on the H_2O_2 generation. The benificial effect is, however, more appreciable for the KBr addition. Whereas, the KI addition very strongly inhibited the reaction, most probably by catalyst poisoning; the catalyst was totally deactivated at the higher KI concentration. The NH_2OH conversion activity of the Pd (1wt%)/Al_2O_3 is inhibited by the addition of potassium chloride,

Table 8.8: Effect of halide added to the aqueous medium at 7.0 pH on the H_2O_2 formation in the reaction of O_2 with NH_2OH from hydroxylammonium sulfate over the Pd (1 wt%)/Al_2O_3 catalyst [reaction conditions: $(NH_2OH)_2.H_2SO_4$ = 40 mmol/dm^3, catalyst wt. = 0.1 g, O_2 flow = 5 cm^3/min and temperature = 27 ºC].

Halide added	Conn. of halide (mmol/dm^3)	Reaction period (h)	Conversion of NH_2OH (%)	H_2O_2 formed[a]	TOF (h^{-1})
Nil	0.0	1.0	72	0.47	200
KF	0.05	1.0	72	0.41	175
KCl	0.05	1.0	71	0.48	204
KBr	0.05	1.0	64	0.53	226
KI	0.05	1.0	21	0.03	13
Nil	0.0	2.0	80	0.33	70
KF	2.0	2.0	81	0.32	68
KCl	2.0	2.0	73	0.39	83
KBr	2.0	2.0	61	0.45	96
KI	2.0	2.0	<5	0.00	0

[a] Moles of H_2O_2 formed per mole of NH_2OH initially present.

bromide or iodide in the following order: KCl < KBr << KI. Like in the H_2-to-H_2O_2 oxidation [16] and also in the O_2 reduction by hydrazine or its salt [9], the bromide or chloride anions present in the aqueous medium act as a catalyst promoter for the H_2O_2 formation. The increase in the H_2O_2 formation due to the KCl or KBr addition may also be partly attributed to a decrease in the rates of H_2O_2 destruction reactions (reactions 8.1 and 8.2). The strong inhibiting action of Br^- or Cl^- anions on the H_2O_2 decomposition over Pd catalyst is well known [16].

8.8.8. Influence of Bromide Concentration at Different Reaction Temperatures and Reaction Periods on H_2O_2 Generation

Results showing a strong influence of the concentration of bromide in the neutral aqueous reaction medium on the rate of H_2O_2 generation over the catalyst at different reaction periods and temperatures are presented in Figures 8.14 - 8.16.

In all the cases, the H_2O_2 generation rate passes through a maximum with increasing the bromide concentration. This reveals that for achieving the highest H_2O_2 generation rate, an optimum concentration of bromide in the reaction medium is necessary. Moreover, the optimum bromide concentration depends upon both the reaction period and temperature; it is increased with increasing the reaction period and/or temperature (Figure 8.14).

The sharp increase in the H_2O_2 generation rate at the lower bromide concentration is expected mostly because of the fact that the destruction of H_2O_2 (formed by the reduction of O_2 with hydroxylamine) by its decomposition (reaction 8.1) over the Pd/Al_2O_3 catalyst is reduced markedly due to the interaction of bromide anions with the Pd clusters of the catalyst [16].

The influence of bromide anions on the H_2O_2 decomposition was further confirmed by carrying out separately the decomposition of H_2O_2 over the catalyst under the similar reaction conditions, discussed later. However, the slow decrease in the H_2O_2 generation rate at the higher bromide concentrations (Figure 8.14) is expected due to poisoning of the H_2O_2 generation active sites of the catalyst with the bromide anions. These observations are quite consistent with that observed for the direct oxidation of H_2 to H_2O_2, in the presence of bromide anions in aqueous medium, over Pd/Al_2O_3 [16] and Pd/C [22].

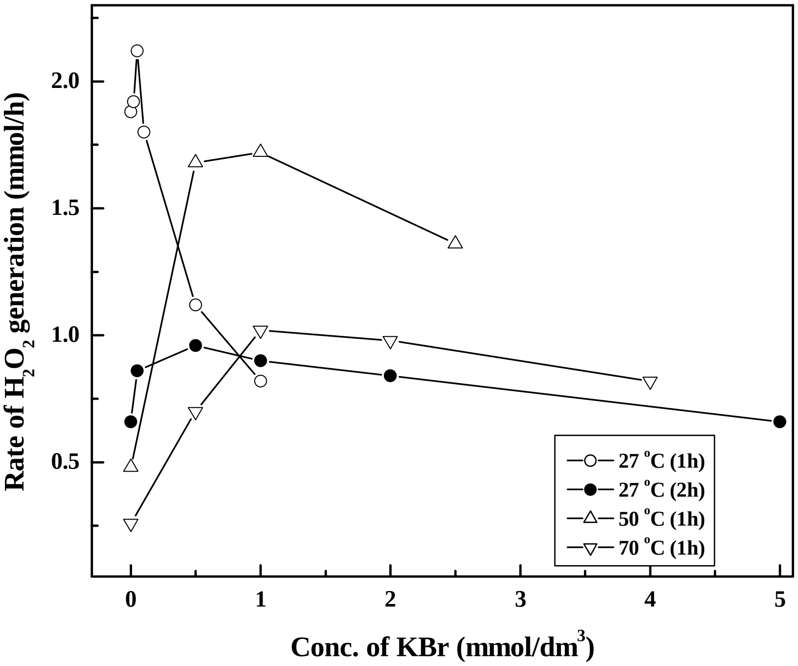

Figure 8.14: Influence of the concentration of KBr in aqueous medium (initial pH = 7.0) on the rate of H_2O_2 generation from the reaction of O_2 with hydroxylamine from hydroxylammonium sulfate (HAS) over the Pd/Al_2O_3 catalyst at different temperatures and reaction period [reaction conditions: $(NH_2OH)_2.H_2SO_4$ = 40 mmol/dm^3, catalyst wt. = 0.1 g, O_2 flow = 5 cm^3/min].

When the cation associated with the bromide anions was changed from K^+ to H^+, NH_4^+ or Na^+, similar to that observed in the H_2-to-H_2O_2 oxidation over Pd/Al_2O_3 [16], almost no change was observed in the H_2O_2 generation. Hence, the observed effect on the H_2O_2 generation due to the addition of KBr in the medium is essentially attributed to the bromide anions alone; the associated cation (K^+) plays little or no role in enhancing the H_2O_2 generation rate.

The role of bromide anions in the reaction medium is to inhibit the decomposition of H_2O_2 formed in the reduction of O_2 by hydroxylamine and thereby the net H_2O_2 formation is increased. The bromide anions may also cause inhibition to the dissociative adsorption of O_2 ($O_2 + 2\ Pd \Leftrightarrow 2\ Pd.O$) [23], which is expected to result in a complete oxidation of hydroxylamine to water and N_2 (reaction 8.5).

Results in Figure 8.15 show that, both in the presence and absence of bromide in the neutral aqueous medium, the H_2O_2 generation passes through a maximum with increasing the reaction period. Also the decrease in the H_2O_2 formation after reaching its maximum value is slower at the higher concentration of bromide.

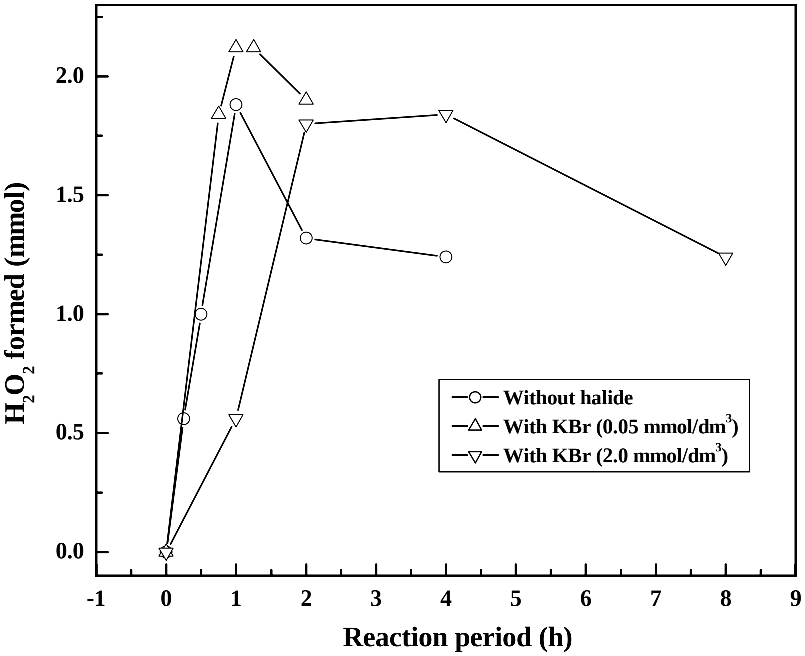

Figure 8.15: Influence of the reaction period on the net H_2O_2 formation from the reaction of O_2 with hydroxylamine from hydroxylammonium sulfate (HAS) over the Pd/Al_2O_3 catalyst at different KBr concentrations in the aqueous medium (initial pH = 7.0) [reaction conditions: $(NH_2OH)_2.H_2SO_4$ = 40 mmol/dm^3, catalyst wt. = 0.1 g, O_2 flow = 5 cm^3/min and temperature = 27 ºC].

The above results clearly show that H_2O_2 is an intermediate product in the reduction of O_2 by hydroxylamine and the decrease in the net H_2O_2 formation at the higher reaction periods are attributed to the destruction of H_2O_2 after its formation in the O_2 reduction. The observed slower decrease in the H_2O_2 formation at the higher reaction periods is consistent with the fact that the H_2O_2 decomposition is more inhibited at the higher bromide concentration [16].

It is also interesting to note from the results (Figure 8.15) that the H_2O_2 generation rate is increased due to the addition of 0.05 mmol/dm^3 of bromide but it is decreased markedly due to the addition of 2.0 mmol/dm^3 of bromide. This shows that the influence of bromide on the H_2O_2 generation is complex.

Results showing the influence of temperature on the H_2O_2 generation in the presence and absence of bromide in the neutral medium are presented in Figure 8.16. In the absence of bromide, the H_2O_2 generation rate is decreased continuously with increasing the temperature. Whereas, in the presence of bromide (0.5 or 1.0 mmol/dm^3), it is passed through a maximum.

The decrease in the H_2O_2 generation rate can be attributed to the increase in the rate of H_2O_2 destruction at the higher temperatures. However, the increase of the H_2O_2 generation at the lower temperatures in the presence of bromide is expected because of the increase in the rate of H_2O_2 formation with increasing the temperature from 27 to 50 ºC. However, this is not the case in the absence of bromide. This shows that in the absence of bromide above 27 ºC or in the presence of bromide (0.5 or 1.0 mmol/dm^3) above 50 ºC, the increase in the rate of H_2O_2 destruction is larger than that in the rate of H_2O_2 formation.

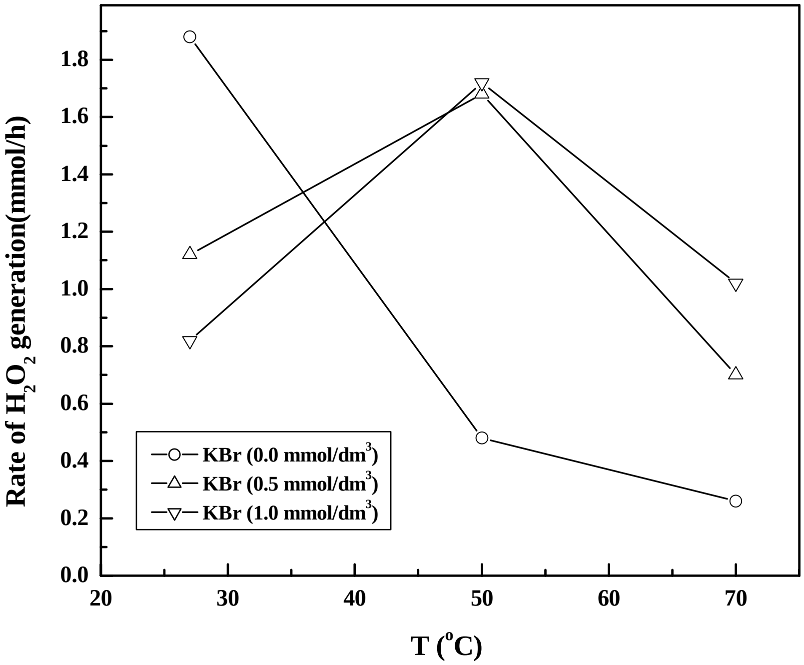

Figure 8.16: Influence of the reaction temperature on the rate of H_2O_2 formation from the reaction of O_2 with hydroxylamine from hydroxylammonium sulfate (HAS) over the Pd/Al_2O_3 catalyst in aqueous medium (initial pH = 7.0) containing KBr at different concentrations [reaction conditions: $(NH_2OH)_2.H_2SO_4$ = 40 mmol/dm^3, catalyst wt. = 0.1 g, O_2 flow = 5 cm^3/min and reaction time = 1.0 h].

The above results (Figures 8.14-8.16) also lead to the conclusion that the influence of bromide on the H_2O_2 generation is quite complex; it depends not only on the bromide concentration but also on the reaction temperature and/or period. In general, for the generation of H_2O_2 at lower temperatures and/or shorter reaction periods, bromide promoter at lower concentration is more beneficial. However, for the generation of H_2O_2 at higher temperatures and/or longer reaction periods, bromide promoter at higher concentration is more preferable.

8.8.9. Influence of pH and Bromide Promoter on the Conversion of Hydroxylamine (in Absence of O_2) over the Catalyst

The results in Figure 8.17 indicate that the conversion of hydroxylamine (in N_2) increases with increasing the pH of the aqueous reaction medium; the increase is large above the pH of 7.0. The presence of bromide promoter, however, caused a decrease in the conversion.

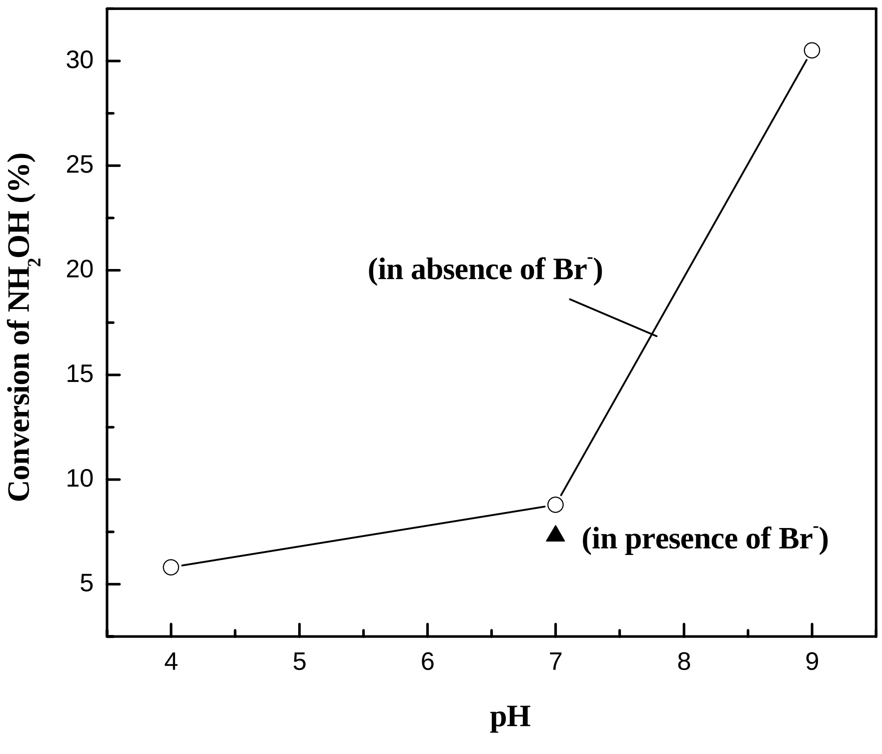

Figure 8.17: Effect of pH and Br promoter (1.0 mmol/dm^3) on the conversion of hydroxylamine (at 27 ºC) over the Pd/Al_2O_3 catalyst in aqueous medium under N_2 atmosphere [reaction conditions: NH_2OH = 80 mmol/dm^3, catalyst wt. = 0.1 g, temperature = 27 ºC and reaction time = 1.0 h].

The conversion of hydroxylamine at the pH of 7.0 (i.e. in the neutral medium) is, however, small (< 10 %), even in the absence of bromide promoter. In the presence of O_2, the hydroxylamine conversion is therefore, expected mostly by the reaction between O_2 and hydroxylamine. The results (Figure 8.17) reveal the beneficial effect of the use of neutral medium (pH = 7.0) by eliminating or decreasing the destruction of hydroxylamine by its decomposition.

8.8.10. Influence of pH and Bromide in Medium and Temperature on H_2O_2 Decomposition over the Catalyst

The results showing the strong influence of pH of the aqueous medium on the H_2O_2 conversion at different reaction periods and also on the initial rate of H_2O_2 decomposition over the catalyst in the absence of hydroxylamine are presented in Figure 8.18. Both the conversion and rate of H_2O_2 decomposition are increased with increasing the pH.

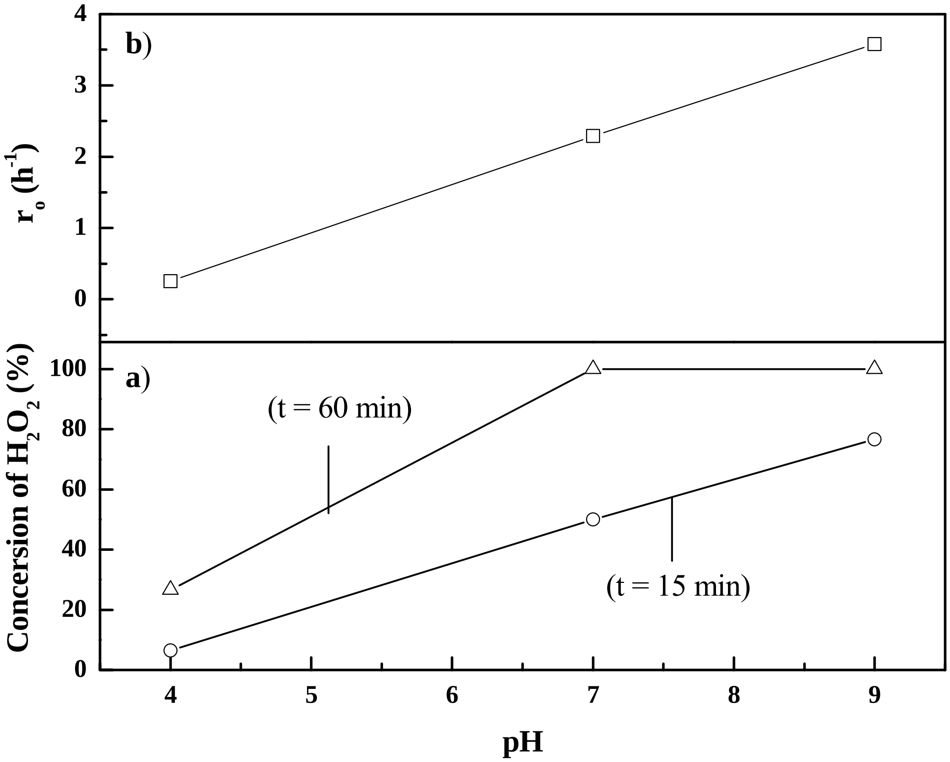

Figure 8.18: Effect of pH on the conversion of H_2O_2 at two different reaction periods (t = 15 and 60 min) and the initial reaction rate (r_o) in the H_2O_2 decomposition over the Pd/Al_2O_3 catalyst in aqueous medium (in absence of NH_2OH or its salt) [reaction conditions: catalyst wt. = 0.1 g and temperature = 27 ºC].

The influence of temperature on the H_2O_2 decomposition in both the presence and absence of bromide promoter in the medium is shown in Figure 8.19. The H_2O_2 conversion and initial rate of H_2O_2 formation are higher in the absence of bromide. At the higher temperatures (above 27 ºC), both are increased very appreciably.

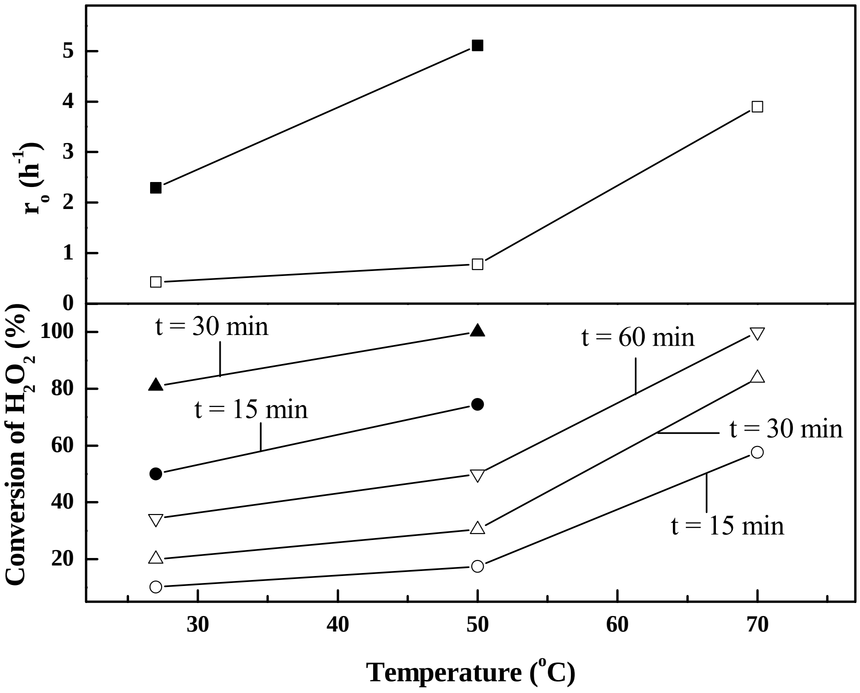

Figure 8.19: Effect of temperature on the conversion of H_2O_2 at different reaction period (t) and the initial reaction rate (r_o) in the H_2O_2 decomposition over the Pd/Al_2O_3 catalyst in absence of KBr (solid symbols) and in presence of 1.0 mmol/dm^3 KBr (open symbols) in aqueous medium (initial pH = 7.0) [reaction conditions: catalyst wt. = 0.1 g and temperature = 27 ºC].

The above results confirm the earlier observations indicating the decrease in the H_2O_2 generation rate in the O_2 reduction with increasing the pH above 7.0 (Figure 8.9) and/or reaction temperature in the absence of bromide promoter (Figures 8.12 and 8.16). The decrease in the H_2O_2 decomposition rate due to the presence of bromide is responsible for the increased H_2O_2 generation rate in the presence of bromide promoter at the lower concentrations (Figure 8.14).

8.8.11. Influence of NH_2OH on the Destruction of H_2O_2

The results in Figure 8.20 show the strong influence of the concentration of NH_2OH (relative to that of H_2O_2) on the conversion of H_2O_2 over the catalyst in the absence of O_2. The fast conversion of H_2O_2 by its decomposition (reaction 8.1) in the absence of NH_2OH is reduced from 100 to about 50 % in the presence of NH_2OH with the NH_2OH/H_2O_2 mole ratio of about 0.6. However, above this ratio (i.e. at the higher NH_2OH concentration) the conversion of H_2O_2 was increased appreciably. Even at the NH_2OH/H_2O_2 mole ratio as high as 4.0, the H_2O_2 conversion is lower than that observed in the absence of NH_2OH.

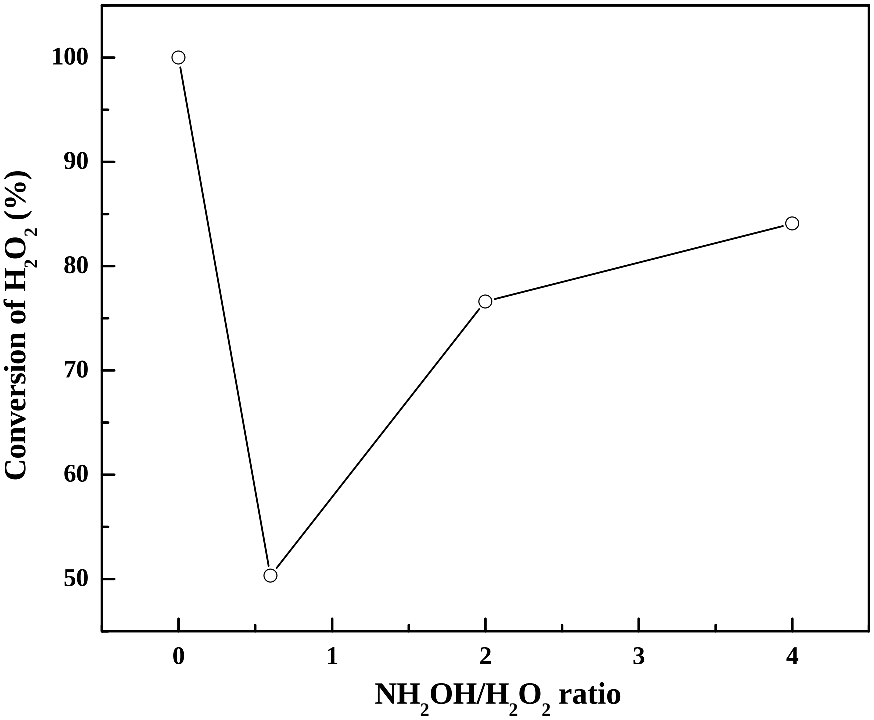

Figure 8.20: Influence of the NH_2OH/H_2O_2 mole ratio on the conversion of H_2O_2 in the presence of NH_2OH but absence of O_2 over the Pd/Al_2O_3 catalyst in aqueous medium [reaction conditions: catalyst wt. = 0.1 g, initial pH = 7.0, temperature = 27 ºC and reaction period = 1.0 h].

These results clearly show that the catalytic H_2O_2 conversion by its decomposition is reduced in the presence of NH_2OH, particularly at the lower NH_2OH/H_2O_2 ratios. This may be due to a strong acid-base interaction between H_2O_2 (acid) and NH_2OH (base), causing stabilization of the H_2O_2 against its decomposition. The increase in the H_2O_2 conversion at the higher NH_2OH/H_2O_2 ratios (> 0.6) is expected due to the consumption of H_2O_2 by its reaction with NH_2OH (reaction 8.2).

The influence of pH of the reaction medium on the catalytic (heterogeneous) and non-catalytic (i.e. homogeneous) conversion of H_2O_2 in the presence of hydroxylamine sulfate [NH_2OH from (HAS)/H_2O_2 = 0.6] is shown in Figure 8.21. Both the catalytic and non-catalytic conversions of H_2O_2 are increased markedly with increasing the pH. Also, because of the presence of bromide promoter, the catalytic H_2O_2 conversion is decreased appreciably.

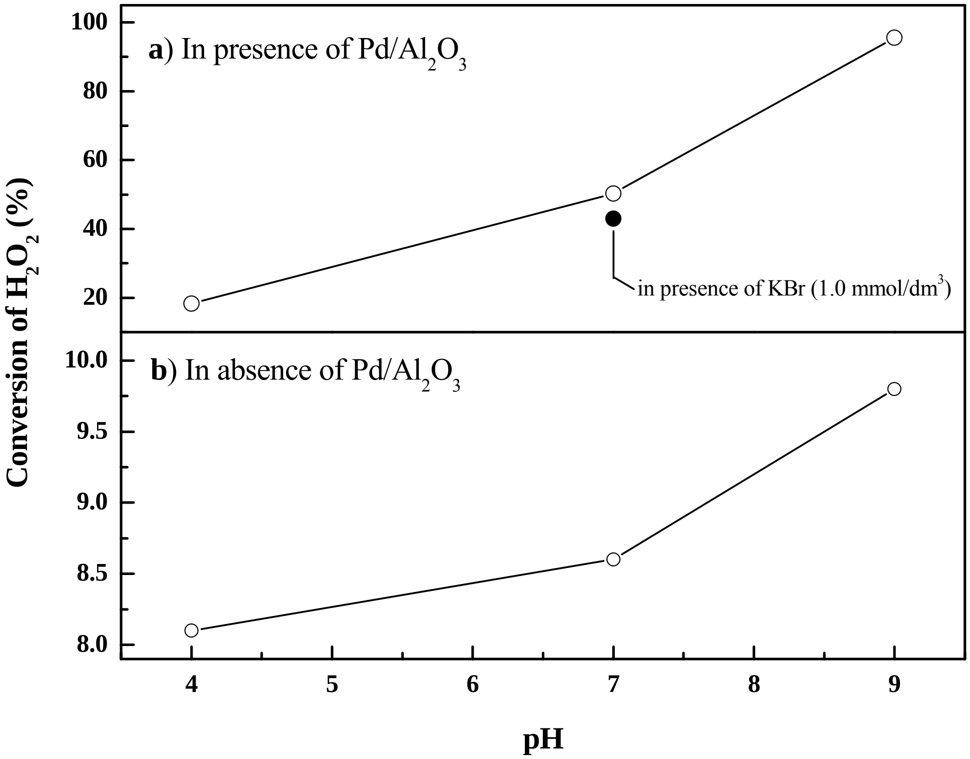

Figure 8.21: Effect of the pH and presence of Br promoter and/or Pd/Al_2O_3 catalyst on the conversion of H_2O_2 in the presence of hydroxylammonium sulfate (NH_2OH/H_2O_2 mole ratio = 0.6) [reaction conditions: catalyst wt. = 0.1 g, temperature = 27 ºC and reaction period = 1.0 h].

A comparison of the results in Figures 8.18a and 8.21a also show that the catalytic H_2O_2 conversion is much lower in the presence of hydroxylammonium sulfate. The catalytic H_2O_2

decomposition, even in the methanol medium, is also found to decrease very appreciably because of the presence of NH_2OH (Figure 8.22).

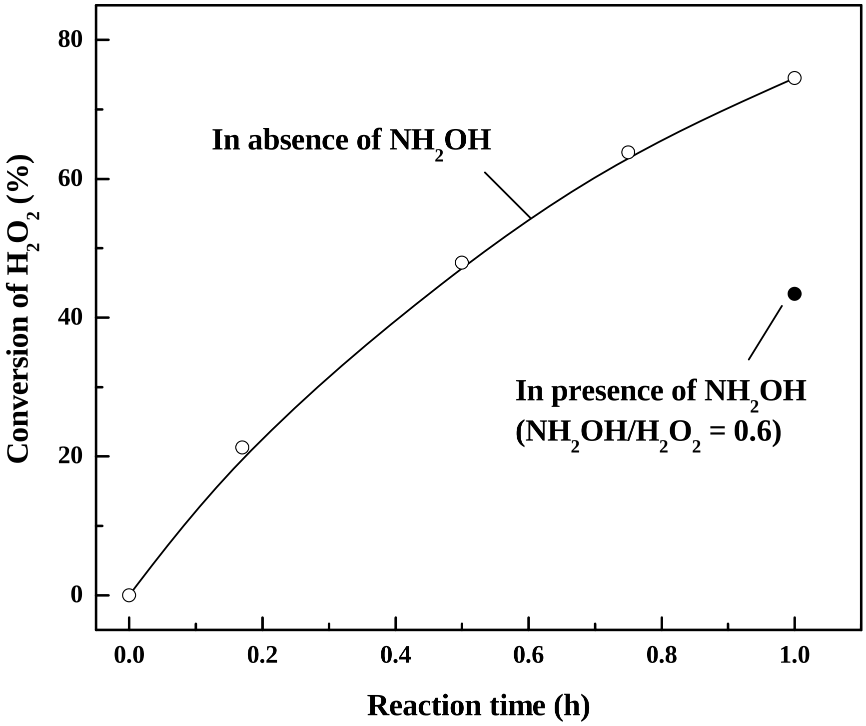

Figure 8.22: H_2O_2 destruction by its decomposition over the Pd/Al_2O_3 catalyst in methanol medium in the presence and absence of NH_2OH [reaction conditions: catalyst wt. = 0.1 g and temperature = 27 ºC].

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8.8.12. Reaction Path/Mechanism

Based on the above results, the reactions involved in the catalytic process for the *in situ* regeneration of H_2O_2 by the reduction of O_2 with hydroxylamine are the parallel H_2O_2 formation (reactions 8.3 and 8.4), and direct water forming (reaction 8.5) reactions and the consecutive H_2O_2 destruction and/or consumption reactions (reactions 8.1 and 8.2). The reaction path for the catalytic is shown in Figure 8.23.

Reactions 8.3 and 8.4 are favored in a neutral aqueous or non-aqueous medium (pH = 7.0), particularly in the presence of bromide promoter at its optimum concentration. Reactions 8.1 and 8.2 are inhibited at lower pH (≤ 7.0) and also in the presence of bromide promoter, depending upon its concentration. Reaction 8.5 may also be inhibited in the presence of bromide promoter. Thus all the undesirable reactions are inhibited by the bromide promoter.

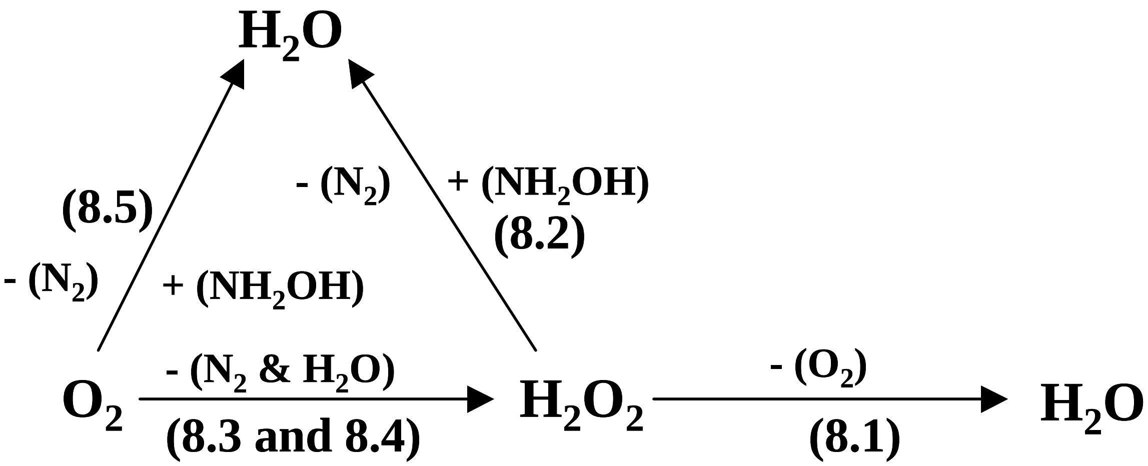

Figure 8.23: Reaction path for the catalytic process for *in situ* generation of H_2O_2 by the O_2 reduction with hydroxylamine.

If the *in situ* generated H_2O_2 is utilized in the simultaneously occurring organic oxidation reaction; the net formation of H_2O_2 would be much more than that in the absence of any organic oxidation. For the low temperature and/or fast organic oxidations, the *in situ* H_2O_2 generation in neutral medium may be carried out in the presence bromide promoter at low concentration. However, for the higher temperature and/or slow organic oxidations, it may be carried out in the presence of bromide promoter at high concentration.

Following free radical mechanism is proposed for the generation of H_2O_2 in the neutral aqueous or non-aqueous medium. The O_2 reduction is expected to proceed with both the molecular and dissociative adsorption of O_2 and also by the cleavage of $H_2N—OH$ bond on the Pd sites.

$Pd + O_2 \Leftrightarrow Pd.O_2$ (8.6)

$2\ Pd + O_2 \Leftrightarrow 2\ Pd.O$ (8.7)

$NH_2OH + 2\ Pd \Leftrightarrow Pd.NH_2 + Pd.OH$ (8.8)

The interaction of between the adsorbed species then leads to the formation of H_2O_2, N_2 and water, as follows.

$Pd.NH_2 + Pd.O_2 \rightarrow H_2O_2 + 2\ Pd + 0.5\ N_2$ (8.9)

$Pd.NH_2 + Pd.O \rightarrow H_2O + 2\ Pd + 0.5\ N_2$ (8.10)

$2\ Pd.OH \Leftrightarrow H_2O_2 + 2\ Pd$ (8.11)

$2\ Pd.OH \rightarrow H_2O + Pd.O + Pd$ (8.12)

$Pd.NH_2 + 2\ Pd.OH \rightarrow 2\ H_2O + 3\ Pd + 0.5\ N_2$ (8.13)

In the presence of acid (pH < 7.0), the hydroxylamine is protonated,

$NH_2OH + H^+ \rightarrow (NH_3OH)^+$ (8.14)

forming the less reactive cationic species $(NH_3OH)^+$, inhibiting the dissociation of NH_2OH (reaction 8.8) and thereby inhibiting the rate of O_2 reduction at the lower pH (< 7.0). Whereas, in the presence of bromide promoter, the dissociative adsorption of O_2 (reaction 8.7) is inhibited [23] and consequently water forming reactions (reaction 8.10) is also inhibited. Since, the bromide promoter strongly inhibit the H_2O_2 decomposition, the reverse reaction 11 and subsequent water forming reactions (reaction 8.12 and 8.13) seem to be inhibited in the presence of bromide promoter. By the above mechanism, the O_2-to-H_2O_2 reduction (reactions 8.6,8.8,8.9 and 8.11), H_2O_2 destruction by H_2O_2 decomposition (reverse reaction 8.11 and reaction 8.12), destruction of H_2O_2 by its reaction with NH_2OH (reactions 8.8 and 8.13 and reverse reaction 8.11) and O_2-to-water reduction (reactions 8.7,8.8 and 8.10) over the catalyst in the presence and absence of bromide promoter could very well be explained.

8.9. Conclusions

This investigation leads to the following important observations.

1) The presence of both the protons and Br promoter is a must for the generation of H_2O_2 in the O_2 reduction by hydrazine. Whereas, a neutralization of the acidity of hydroxylammonium salt is a must for the generation of H_2O_2 in the O_2 reduction by hydroxylamine in both the aqueous and non-aqueous mediums in both presence or absence of bromide promoter. Only environmentally benign by-products (N_2 and water) are formed during the H_2O_2 generation in both the cases.

2) The H_2O_2 yield in the N_2H_4-to-H_2O_2 oxidation reaction is passed through a maximum with increasing the H_3PO_4/N_2H_4 mole ratio. This indicates that an optimum acid/N_2H_4 mole ratio is necessary for achieving the best result in H_2O_2 formation. This also indicates that H_2O_2 is an intermediate product of the reaction

and its net rate of formation is mainly controlled by the two consecutive reactions, H_2O_2 decomposition and the reaction between H_2O_2 and unconverted hydrazine; both the reactions are strongly inhibited in the presence of bromide promoter and/or protons. In the presence of protons and bromide promoter, the reaction with hydrazine occurs more predominantly than the H_2O_2 decomposition.

3) Among the different supported nano-gold catalysts (viz. nano-gold supported on MgO, CaO, La_2O_3, CeO_2-ZrO_2, Gd_2O_3, Tb_2O_3, Yb_2O_3, Al_2O_3, Ga_2O_3 or ZrO_2), the Au/Gd_2O_3, Au/La_2O_3 and Au/MgO are promising environ-friendly catalysts for the H_2O_2 generation under ambient conditions from the O_2 reduction by hydroxylammonium salt or hydroxylamine. The Au/MgO is, however, partially dissolved in aqueous medium, and hence, it may be used only in non-aqueous medium. The H_2O_2 yield or rate of the H_2O_2 generation is passed through a maximum with increasing the temperature and reaction time over the Au/MgO catalyst, indicating H_2O_2 is an intermediate product in the reaction.

4) The beneficial influence of bromide promoter in neutral medium on the *in-situ* generation of H_2O_2 in the O_2 reduction by hydroxylamine from the hydroxylammonium sulfate over Pd/Al_2O_3 catalyst is quite complex. It depends not only upon the bromide concentration but also on the reaction conditions (viz. reaction period and temperature). The best H_2O_2 generation performance is achieved at the optimum concentration of bromide promoter, depending upon the reaction conditions and/or at the optimum reaction period or temperature, depending upon the bromide concentration. The H_2O_2 generation is also strongly influenced by the catalyst loading and also by the concentration of O_2 reducing agent. An optimum catalyst loading is required for achieving the highest H_2O_2 generation.

5) The decomposition of NH_2OH at the neutral pH (7.0) is found to be small; it is decreased further due to the presence of bromide promoter.

6) H_2O_2 is an intermediate product of the O_2-to-H_2O_2 reduction by the hydroxylamine. Its destruction by decomposition is strongly inhibited due to the presence of bromide promoter. The H_2O_2 decomposition is also strongly

influenced by the reaction conditions (viz. pH of medium and temperature). It is, however, decreased in the presence of NH_2OH, depending upon the NH_2OH/H_2O_2 mole ratio.

7) The O_2-to-H_2O_2 reduction by hydroxylamine over Pd/Al_2O_3 catalyst has a complex reaction path, involving parallel O_2-to-water and O_2-to-H_2O_2 reduction reactions and consecutive H_2O_2 destruction reactions, involving H_2O_2 decomposition and H_2O_2 consumption by its reaction with NH_2OH.

A plausible reaction mechanism for the catalytic O_2-to-H_2O_2 reduction by hydroxylamine, explaining all the above parallel and consecutive reactions, has been proposed. The beneficial effect of bromide promoter is attributed mostly to the inhibition caused to the formation of atomically adsorbed oxygen on Pd/Al_2O_3 catalyst by the adsorbed Br^- promoter; the atomically adsorbed oxygen is responsible for the undesirable water forming reactions over the catalyst.

8.10. References

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PUBLICATIONS AND PATENTS BASED ON WORK REPORTED IN THE THESIS

A. Papers (published/accepted/communicated/to be communicated):

1) “A novel route for in-situ generation from selective reduction of O_2 by hydrazine using heterogeneous Pd catalyst in an aqueous medium.”

   V. R. Choudhary, C. Samanta and **P. Jana**, *Chem. Comm., 2005, 5399-5401.*

2) “Reduction of oxygen by hydroxylammonium salt or hydroxylamine over supported Au nanoparticles for in situ generation of hydrogen peroxide in aqueous or non-aqueous medium”

   V. R. Choudhary, **P. Jana** and S. K. Bhargava, *Catal. Commun., 8 (2007) 811-816.*

3) “Generation of hydrogen peroxide via the selective reduction of oxygen by hydrazine sulfate over Br-promoted Pd/Al_2O_3 catalyst in an aqueous medium at ambient conditions”

   V. R. Choudhary, **P. Jana** and C. Samanta, *Appal. Catal. A: Gen., 323 (2007) 202-209*.

4) “Synergetic effect of two halogen promoters present in acidic reaction medium or catalyst on the H_2O_2 formation (in H_2-to-H_2O_2 oxidation) and destruction over Pd/C (or Al_2O_3) catalyst”

   V. R. Choudhary and **P. Jana**, *J. Catal., 246 (2007) 434-439.*

5) “In situ generation of hydrogen peroxide from reaction of O_2 with hydroxylamine from hydroxylammonium salt in neutral aqueous or non-aqueous medium using reusable Pd/Al_2O_3 catalyst”

   V. R. Choudhary and **P. Jana**, *Catal. Commun., 8 (2007) 1578-1582.*

6) “Decomposition and/or hydrogenation of hydrogen peroxide over Pd/Al_2O_3 catalyst in aqueous medium: Factors affecting the rate of H_2O_2 destruction in presence of hydrogen.”

   V. R. Choudhary, C. Samanta and **P. Jana**, *Appl. Catal. A: Gen., (communicated).*

7) “Factors influencing the *in situ* generation of hydrogen peroxide from the reduction of oxygen by hydroxylamine from hydroxylammonium sulfate over Pd/alumina.”

   V. R. Choudhary and **P. Jana**, *Appl. Catal. A: Gen., (communicated).*

8) “Direct oxidation of H_2 to H_2O_2 over Br and F-promoted Pd/Al_2O_3 in aqueous acidic medium: Influence of the concentration of Br and F and the method of incorporation of the two halogens in the catalyst on their beneficial synergetic effect on the net H_2O_2 formation.”

   V. R. Choudhary and **P. Jana**, *Appl. Catal. A: Gen., (communicated).*

9) “Direct oxidation of H_2 to H_2O_2 over different supported PdO Catalysts in aqueous acidic medium: Influence of the calcination temperature, reduction and support of the catalyst on its net H_2O_2 formation activity”

V. R. Choudhary and **P. Jana**, *J. Chem Sci., (communicated).*

10) “Direct oxidation of H_2 to H_2O_2 over PdO/Al_2O_3 catalysts in aqueous acidic medium: Influence on H_2O_2 formation of Pd loading, calcination temperature and reduction of catalyst and presence of halide anions”

V. R. Choudhary and **P. Jana**, *Appl. Catal. A: Gen., (communicated).*

11) “Direct H_2-to-H_2O_2 oxidation in aqueous acidic medium containing Br promoter over Pd/Al_2O_3 and Pd/C catalysts thermally pretreated under different conditions”

V. R. Choudhary, **P. Jana** and S. K. Bhargava, *J. Catal., (communicated).*

12) “Direct H_2-to-H_2O_2 oxidation over highly active/selective $Br\text{-}F\text{-}Pd/Al_2O_3$ catalyst in aqueous acidic medium: Influence of the O_2/H_2 ratio in feed and other reaction conditions on the H_2O_2 formation”

V. R. Choudhary and **P. Jana**, *J. Catal., (communicated).*

B. US Patents:

1) *US patent (**Pub. No. 20060120949**):* V. R. Choudhary, C. Samanta and **P. Jana**.
“ Method for drastically improving both the selectivity and yield of hydrogen peroxide in the direct oxidation of hydrogen to hydrogen peroxide over a solid catalyst comprising palladium.”

2) *US patent (Filed, April 2004):* V. R. Choudhary, C. Samanta and **P. Jana**.
“A novel process for the production of hydrogen peroxide from hydrazine hydrate or hydrazine salt.”

3) *US patent (Filed, March 2006):* V. R. Choudhary and **P. Jana**.
“A process for the *in-situ* generationof hydrogen peroxide from hydroxylamine or hydroxylammonium satls.”

PUBLICATIONS AND PATENTS OTHER THAN THESIS WORK
(carried out in collaboration with others in the group)

A. Papers (published/accepted/communicated/to be communicated):

1) “Epoxidation of styrene by anhydrous t–butyl hydroperoxide over reusable nano–gold supported on MgO and other alkaline earth oxides”

   Nilesh S. Patil, Balu S. Uphade, **Prabhas Jana**, Suresh K. Bharagava and Vasant R. Choudhary, *J. Catal., 223, 2004, 236-239.*

2) “Epoxidation of styrene by t–butyl hydroperoxide over gold supported on Yb_2O_3 and other rare earth oxides”

   Nilesh S. Patil, Balu S. Uphade, **Prabhas Jana**, Suresh K. Bharagava and Vasant R. Choudhary, *Chem. Lett., 33, 2004, 400-401.*

3) “Epoxidation of styrene by anhydrous TBHP over Au/TiO_2 catalysts”

   N.S. Patil, B.S. Uphade, **P. Jana**, R.S. Sonawane, S.K. Bhargava and V.R. Choudhary, *Catal. Lett., 94, 2004, 89-93.*

4) “A green process for chlorine-free benzaldehyde from the solvent-free oxidation of benzyl alcohol with molecular oxygen over supported nano-size gold catalyst.”

   V. R. Choudhary, A. Dhar, **P. Jana**, R. Jha and B. S. Uphade, *Green Chemistry, 7, 2005, 768-770.*

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12) “Nano-gold supported on Fe_2O_3: A highly active catalyst for low temperature oxidative destruction of methane green house gas from exhaust/waste gases”

V. R. Choudhary, V. P. Patil, **P. Jana** and B. S. Uphade, *Catal. Commun., (To be communicated).*

13) “Low temperature selective oxidation of carbon monoxide in hydrogen rich gas mixture over supported nano-gold catalyst to produce CO-free hydrogen for PEM Fuel Cell”

V. R. Choudhary, V. P. Patil, **P. Jana** and B. S. Uphade, *Catal. Commun., (To be communicated).*

B. US Patents:

1) *US patent 6,933,397 (August 2005):* V.R. Choudhary, B.S. Uphade, N.S. Patil and **P. Jana.**

“Liquid–phase epoxidation of olefinic compounds using solid catalysts comprising nano–gold.”

PRAPER PRESENTED IN SYMPOSIUMS/CONFERENCES

1) “Nano-Gold Supported on Fe_2O_3: A Highly Active Catalyst for Low Temperature Oxidative Destruction of Methane.”

Presented in the 17th National Symposium on Catalysis, CSMCRI, Bhavnagar, India, January 18-20, 2005.

2) “Low Temperature Selective Oxidation of Carbon Monoxide in Hydrogen Rich Gas Mixture Over Supported Nano-Gold Catalyst to Produce CO-free Hydrogen for PEM Fuel Cell.”

Presented in the National Workshop on Catalysis for Energy, Banaras Hindu University, Banaras, India, 23 25 February 2006.